

The Strength of Carbon Fibres

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The available information on the structure and properties of high strength carbon fibres is reviewed, and some new data are presented, showing the effects of boron doping and neutron irradiation on the properties of PAN—based carbon fibres.

Theories relating the Young's modulus of the fibre to its microstructure are examined, and it is concluded that their relationship is qualitatively understood. Variations in electrical resistivity with different treatments may also be explained satisfactorily, again, in qualitative terms.

The strength of carbon fibres is less well understood, however. It has been suggested that the fibre strength is governed by the presence or absence of stress-raising flaws, but while it is clear that such flaws can markedly reduce the strength, there is no clear estimate of the strength of an unflawed fibre.

In this paper, we examine an alternative failure mechanism, initiated by shearing of the graphite crystallites in the fibre, and we conclude that such a mechanism may control the strength of the more graphitic fibres. Increases in the strength of carbon fibres may thus be achieved, not only by reducing the number and severity of the flaws, but also by applying the principles of solid-solution or dispersion hardening, and by reducing the graphite crystallite size ("grain refining").

1. Introduction

As part of a broad programme of composite materials research at the National Physical Laboratory, an attempt is being made to understand the structure of carbon fibres and to find ways of improving their mechanical properties.

The relation of Young's modulus to the structure of the fibre has been considered by a number of workers [1, 2] and is reasonably well understood. In this paper, we wish to consider some recent work on the microstructure, and to propose a mechanism which accounts for the observed variation of fibre strength with different treatments.

2. Experimental Results

The RAE process for producing carbon fibres from polyacrylonitrile involves an oxidation of the fibre at about 220° C while it is prevented from shrinking [3]. It has been suggested that the oxidation involves some cross-linking of adjacent polymer chains, although doubt has recently been cast upon this theory [4], and it seems that

there may be negligible cross-linking until temperatures of 300 to 400° C are reached. Whatever the mechanics of the process, however, the oxidation stage "freezes" the highly oriented structure of the drawn polymer fibre, and this is preserved during subsequent heat-treatment. An additional advantage is that the carbon yield of the fibres is increased by oxidation. Pyrolysis involves numerous possible cross-linking reactions [4, 5] leading to the formation of six-membered rings. The rings link, and eventually form the hexagonal network of graphite layer planes which are more or less aligned parallel with the fibre axis. During pyrolysis, fibre strength and stiffness increase. At temperatures above about 1100° C, however, the stiffness increases more slowly (fig. 1) while the strength reaches a peak and then declines (fig. 2).

The addition of boron from the vapour phase [6, 7] increases the stiffness of PAN-based fibres (fig. 1) while the breaking stress appears to be unaffected (fig. 2). Irradiation with neutrons also affects the fibre properties. A dose of

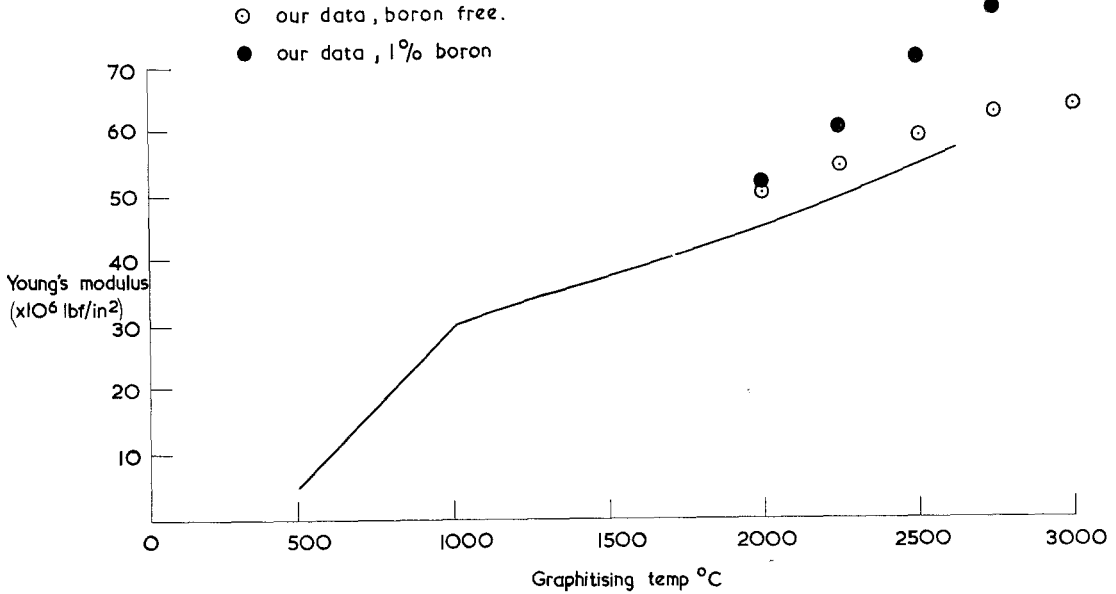


Figure 1 Typical variation of Young's modulus with heat-treatment temperature for PAN-based fibres [25, 28], ○ our data, boron free; ● our data, 1% boron present [6].

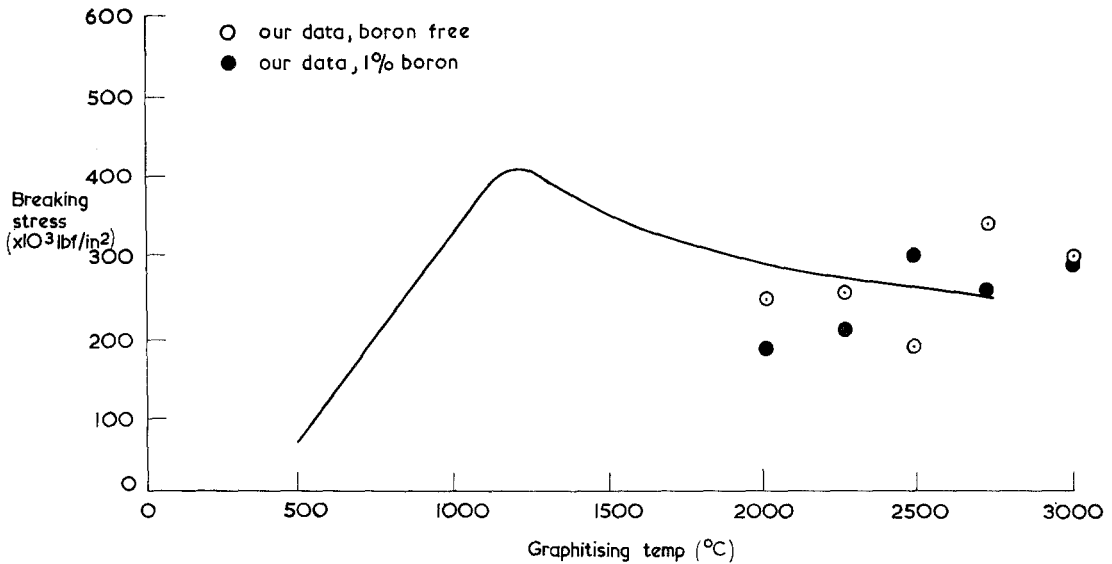


Figure 2 Typical variation of tensile strength with heat treatment temperature for PAN-based fibres [25, 28], ○ our data, boron free; ● our data, 1% boron present [6].

2×10^{17} n/cm² at pile temperature produces increases in both strength and stiffness of about 10% (fig. 3).

“Hot stretching” at temperatures greater than 2000° C also produces increases in both strength

and stiffness of PAN-based fibres [8] and forms an essential part of the Union Carbide process for making high quality carbon fibres from a rayon precursor [9, 10]. Bacon has shown that both the stiffness and strength of rayon-based fibres

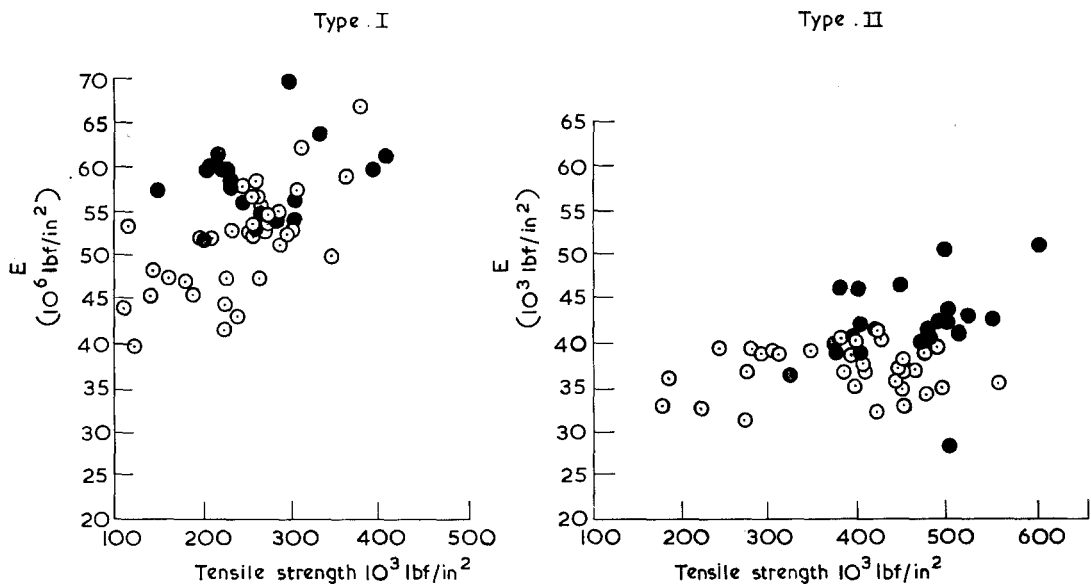


Figure 3 Changes in strength and Young's modulus of PAN-based carbon fibres on irradiation [19]. (Solid points irradiated results, open points unirradiated).

depend only on the degree of plastic deformation and are independent of applied load or temperature of deformation.

3. The Structure of Carbon Fibres

The detailed structure of carbon fibres is not fully known. X-ray investigations by Johnson and Tyson [11] and Perret *et al* [12] show the fibres to be composed of aligned crystallites of turbostratic graphite. The dimensions of the crystallites vary, being typically 10 Å in the *c*-direction (L_c) by 20 Å in the *a*-direction (L_a) for PAN-based fibres heat-treated to 1300° C (type II), and 100 Å (L_c) by 60 Å (L_a) after treatment at 2500° C (type I).

There are many voids present between the crystallites. These voids are elongated in the direction of the fibre-axis, and are of order 200 to 300 Å long by 10 Å wide. It is not possible to say whether the voids are needle or penny-shaped, but the latter would seem to be more likely if they are voids between stacks of graphite layer-planes.

Herinckx *et al* [13] have also reported that several graphite-potassium intercalation compounds have been observed in carbon fibres. The fibres can be fully saturated with potassium up to the theoretical maximum proportion without difficulty, and the potassium may be subsequently driven off to regenerate the original structure. The workers concluded from this evidence that

there were virtually no regions of three-dimensional (sp^3) bonding in the carbon fibres. In all probability, the stacks of graphite layer-planes were continuous over large distances along the length of the fibre, and the measured value of L_a was a reflection not so much of the size of the stacks, but of the distance between successive bends in the graphite-layer-planes. They also concluded that the bent stacks of layer-planes were probably not very wide and were attached to other stacks at their edges by a relatively small number of cross-linking atoms. This structure is similar to that proposed by Johnson, reproduced in fig. 4. Electron micrographs taken by Johnson [14] show that the voids are most easily seen when the thin foil contains crystallites which have their *c*-axes in the plane of the foil. Voids are not seen where the beam is parallel with the *c*-direction.

This observation reinforces the view that the voids are planar and lie between the graphite layer-planes. Synthesis of all these observations leads to a structure such as is sketched in fig. 5, in which the layer-planes are quite large, and can be followed for some distance through the structure, although they are kinked and distorted in such a way as to give the effect of a large number of smaller crystallites. This model has been largely confirmed by direct resolution of the graphite layer-planes in the electron microscope [7, 15, 29, 30], although changes in orientation of the

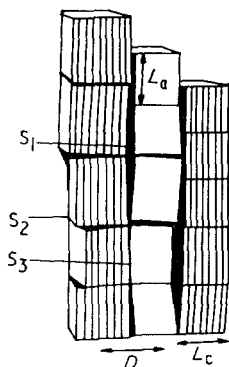


Figure 4 Model of the structure of a carbon fibre, after Johnson [11].

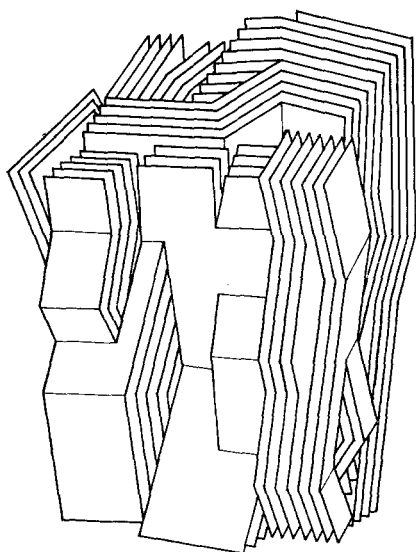


Figure 5 Schematic structure of a carbon fibre.

layer-planes usually occur by a gradual bending rather than at sharp kinks.

4. Discussion

Ruland, Watt, and others [1, 16] have shown that the Young's modulus of carbon fibres can be described by imagining the applied stress to be resolved into components parallel and perpendicular to the graphite layer-planes. The stiffness of the fibre is then a function of the crystallite orientation and moduli, notably in tension and in shear parallel with the layer-planes.

Since irradiation is known to increase the shear modulus of graphite, [17, 18] our results ([19] and fig. 3) would appear to form a direct confirmation of the theory, since the neutron dose employed was sufficient to displace only

one atom in ten thousand. Such a small dose can hardly have altered the orientation or size of the crystallites, although it is capable of making a large change in the shear modulus of a graphite single crystal [18]. The effects of boron doping are less clear-cut. Our measurements on the resistivity of boron-doped carbon fibres [19] showed that boron has the effect of decreasing the resistivity of the fibres, whereas Mayer [20] found that similar concentrations of boron in single crystal graphite caused increases in the resistivity. This, together with the X-ray evidence for increased perfection and alignment of the crystallites in boron-doped fibres [7] and the increases in their stiffness relative to undoped fibres (fig. 1) leads us to suppose that boron assists in the promotion of a recrystallisation process such as is sketched in fig. 6. This would

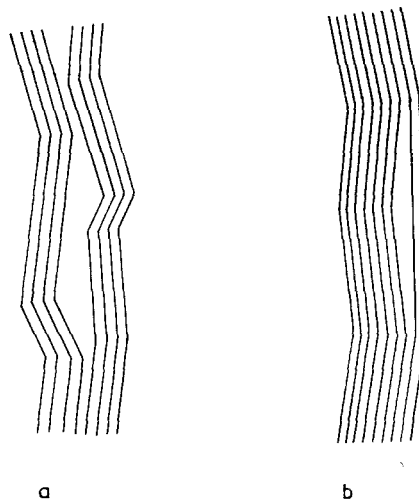


Figure 6 A possible recrystallisation process leading to increases in stiffness, but decreases in electrical resistivity.

adequately explain the observed decrease in the resistivity, since the reduction in scattering from crystallite boundaries would outweigh the effects of individual boron atoms. The hypothesis also explains the increases in stiffness which were observed, since not only is the preferred orientation increased, but also, boron is known to increase the shear stiffness of graphite [21].

Why the effects of irradiation and boron-doping are so relatively large is not clear. The experiments of Curtis, Milne, and Reynolds [22] showed that there is some non-Hookean behaviour in carbon fibres at low stress which disappears as the fibre is loaded. Simultaneously

the ultrasonic damping coefficient, which is initially large, decreases to a uniform value. The conclusion of these workers was that there are glissile dislocations of some sort, active in the graphite crystallites, and that these move under relatively low stress towards barriers such as crystallite boundaries. The effect of irradiation or boron doping would be expected to interfere with such dislocation motion, and to give increases in the measured modulus.

We expect the failure stress of the fibre to be affected in a similar way. If the crystallite size is sufficient for there to be significant dislocation motion, one can envisage a failure mechanism whereby, as the applied stress is increased, dislocations are generated in the crystallite and are driven towards the crystallite boundary. Pile-ups of dislocations produce an increasing stress at the boundary until the critical crack nucleation stress is reached and the fibre fails. Under such conditions, a relation of the Hall-Petch type [23] is expected to obtain. Data to check this supposition are scarce, but some measurements of breaking stress and crystallite size are available. Johnson and Marjoram [24] have measured values of L_a and breaking stress for a variety of fibres derived from the same precursor. Three data points corresponding to Type I, Type II and an ultra fine-grained fibre are shown plotted in log-log form in fig. 7. A gradient of -0.5 has been drawn over the data points, and while the data are not sufficient to be

definite, this line is as good as fit as any. A similar plot of fibre strength against the crystallite size when measured parallel with the c -axis (L_c) gives no such correlation. This adds further support to the idea that the failure process is associated with shear deformation parallel with the basal planes.

An experiment reported by Johnson [25] throws further light on this supposition. He took samples of carbon fibres derived from the same precursor but pyrolysed at different temperatures. Some of the fibres were tested "as made", while others were subjected to an etching procedure to remove surface defects. The fibres which were pyrolysed at temperatures up to about 1000°C were increased in strength by the etching treatment. Plots of strength against heat-treatment temperature gave two lines (fig. 8), the line corresponding to the etched fibres having the greater gradient.

Above about 900°C for the etched fibres, and about 1250°C for the unetched fibres, the strength began to decrease, data points for both fibres falling on the same curve. Johnson showed that for fibres treated at temperatures below 1000°C , the failure was essentially brittle and was governed by the presence of stress-raising defects, many of which were actually identified on fracture surfaces. The effect of etching was to remove some of these defects and to improve the strength of the fibre.

We suppose that the increase in fibre strength with heat-treatment temperature in this region is a reflection of the increasing close packing of strong carbon-carbon bonds as pyrolysis proceeds. Above 1250°C , the fibre strength is independent of whether the fibres were etched or not, indicating that defects other than surface flaws are governing the strength. We have suggested above that this may be due to shearing inside the crystallites causing stress concentrations and ultimately the formation of failure cracks. It is interesting to note, in support of this theory how the strength of the etched fibres in the region 1000 to 1300°C forms an extrapolation of the line from 2500 to 1300°C , and that the second failure mechanism apparently becomes operative for fibres annealed at or above the temperature when the crystallite size becomes a definable parameter of more than a few Ångstroms (say $> 20\text{Å}$), when it may become sensible to speak of "dislocations" and slip parallel with the increasingly definite basal planes.

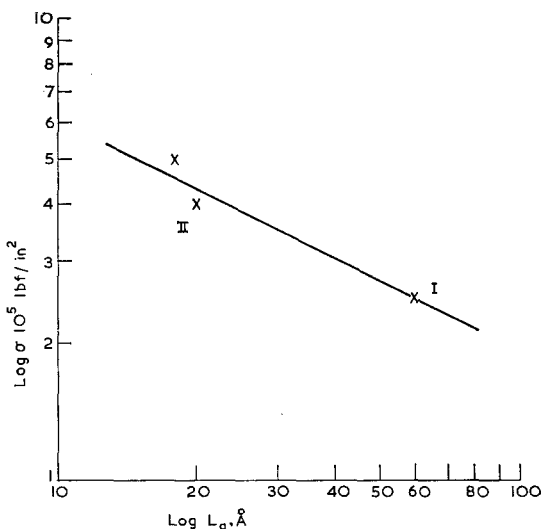


Figure 7 Correlation between fibre strength and crystallite dimension L_a . The line has gradient $-\frac{1}{2}$.

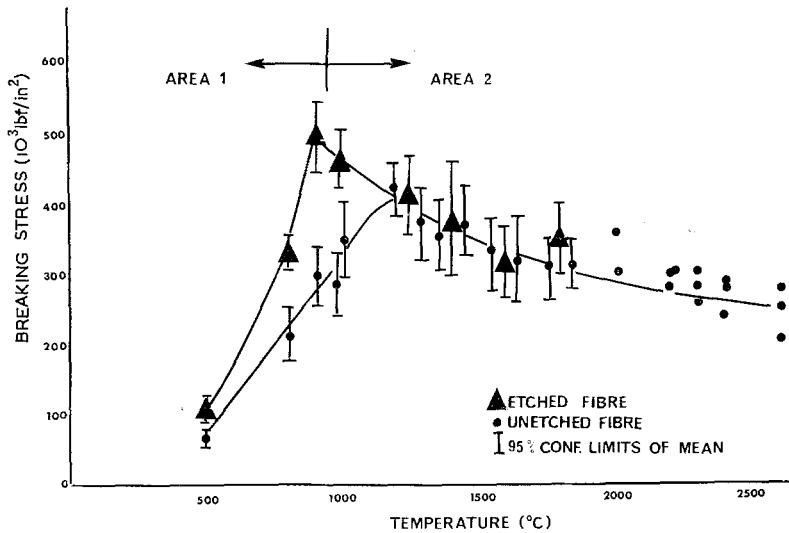


Figure 8 Showing the effect on strength of polishing carbon fibres, after Johnson [25].

The Hall-Petch relationship gives the shear stress at a barrier, τ_B , in terms of the shear stress on the slip-plane, $(\tau_a - \tau_0)$, and the number of dislocations, n , piled up against the barrier:

$$\tau_B = n(\tau_a - \tau_0), \quad (1)$$

where

$$n = \frac{\pi l(\tau_a - \tau_0)}{Gb} \quad (2)$$

in which G is the shear modulus of the crystallite, b the Burgers vector and l the length of slip plane (in our case being assumed equal to L_a). Rearranging equations 1 and 2:

$$\tau_a = \tau_0 + \left(\frac{\tau_B G b}{\pi} \right)^{\frac{1}{2}} L_a^{-\frac{1}{2}} \quad (3)$$

Treating carbon fibres in terms of this theory immediately raises the question of the relation of τ_a to σ , the stress applied to the fibre. Plotting fibre failure stress against $L_a^{-\frac{1}{2}}$ gives an intercept on the stress axis of ~ 15000 psi (the "friction stress") and from the gradient, assuming $\tau_a = \frac{1}{2}\sigma$, a value of τ_B of $1350 \text{ Kgm/mm}^2 (= 1925000 \text{ psi})$. We have assumed a value for the shear modulus of 0.398 Kgm/mm^2 , following Soule *et al* [26]. X-ray evidence, however, shows that the crystallites have a strong preferred orientation, $\bar{\phi}$ normally being less than 10° for fibres of high modulus. Assuming a trial value for crystallite orientation (and hence the orientation of the slip plane) of 10° , gives $\tau_a = \sigma \cdot \cos 10^\circ \sin 10^\circ$ and hence $\tau_B \sim 202000 \text{ psi}$.

Clearly, the orientation of the slip plane may

be chosen to give almost any value for τ_B , the strength of the barrier, which must therefore remain speculative until additional evidence is forthcoming, although the values estimated above would seem to be quite reasonable. It is worthwhile noting, however, that if the failure process is induced by slip, yet is independent of crystallite size, the usual decrease in $\bar{\phi}$ with increasing pyrolysis temperature would require the observed fibre failure stress to increase with increasing pyrolysis temperature – the opposite of what is actually found.

The effects of hot-stretching are also explicable in terms of our theory. In general, the effect of the plastic deformation is to rotate the graphite crystallites towards the fibre axis, and thereby to increase the modulus. The crystallite size is also increased, as would be expected, but this does not lead to a loss in strength. In our view, this is not only because a decrease in $\bar{\phi}$ leads to reduced shear stress parallel with the crystallite layer planes, but also because at these temperatures dislocations may be brought up to the crystallite boundaries, by stressing, and are there eliminated by a suitable diffusion-aided atomic rearrangement. On subsequent cooling and testing at room temperature, the fibres are found to be strong, because the dislocations which could have formed undesirable stress concentrations have been largely eliminated during the hot-stretching treatment.

Jackson and Marjoram [27] annealed nickel-coated carbon fibres for 24 h at 1100°C , and found a disastrous reduction in strength and

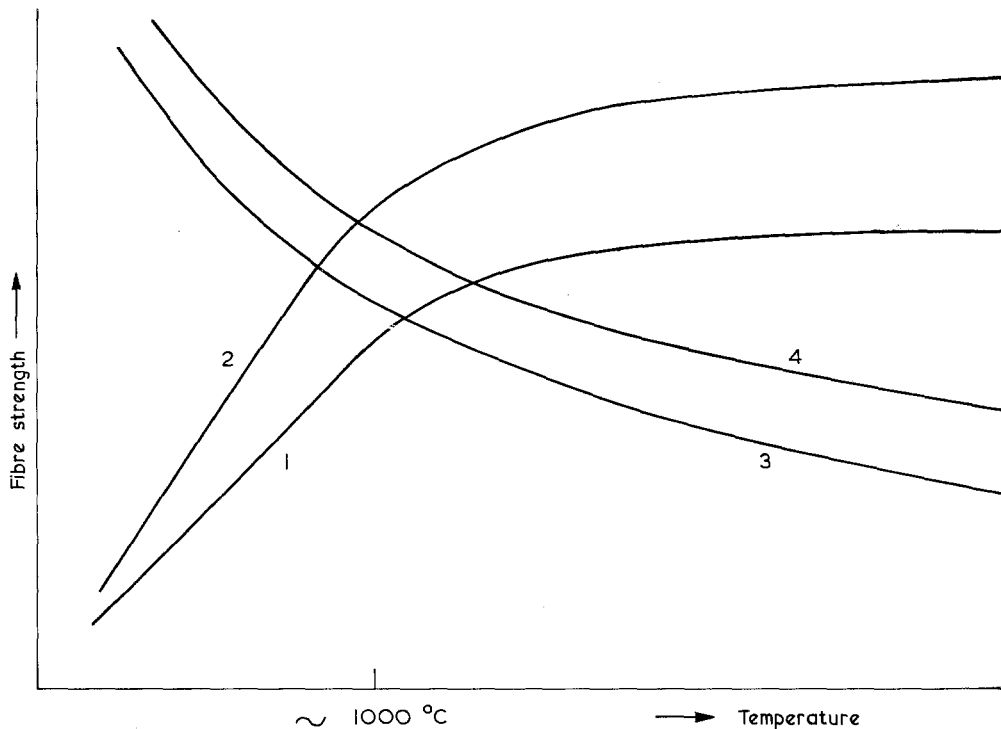


Figure 9 Possible variation of carbon fibre properties with heat-treatment temperature.

modulus, while X-ray powder photographs showed the presence of strong (hkl)-type reflections.

In one of our experiments where we found strong (hkl) reflections after boron doping, the strength and modulus were, however, not reduced. Two explanations for this difference may be suggested: either the degree of re-crystallisation was not so advanced in our fibres, or, following the theory advanced above, the boron was not only causing an increase in crystallinity, but was also acting as a solid solution hardening element in the graphite, preventing shear in the crystallites and hence maintaining the modulus and strength. We may also speculate that, since nickel dissolves carbon, the re-crystallisation was achieved by a process of solution and re-precipitation of carbon in the nickel. This may well have had the effect of destroying the preferred orientation since the re-precipitated graphite would probably be of random orientation. Boron would be less likely to have had this effect since no gross solution-and-re-precipitation process occurs.

4.1. A Tentative View of Fibre Strength Properties and Future Capability

The arguments advanced above lead to the following speculation on the form of the graph of fibre strength versus fibre heat-treatment temperature (see fig. 9).

Curve (1) represents the increasing strength of a purely elastic fibre with increasingly complete pyrolysis. As pyrolysis proceeds, hydrogen and nitrogen atoms are stripped from the polymer chains, and the carbon backbones of these chains pack closer together. Thus, as the fibre shrinks, if the carbon-carbon bonds in the polymer backbone are not disrupted, the failure stress of the fibre increases, although the failure load may well remain approximately constant. Curve (1) must decrease in gradient above 1000°C , and must be nearly parallel with the axis above 1300°C , when fibre density is only increasing slowly.

Curve (2) shows the effect on curve (1) of decreasing the number of defects in an elastic fibre by, for example, surface-etching.

Curve (3) shows the form of the strength curve for fibres whose strength is governed by a Hall-

Petch type relationship, and in which the crystallite size increases with increasing temperature.

Curve (4) shows fibres which fail by a similar mechanism to those shown in curve (3), but in which the crystallite size is smaller after any particular heat-treatment, or in which there is some form of hardening mechanism which reduces dislocation mobility. Failure of the fibre will occur by whichever mechanism predicts the lowest fracture stress.

If this interpretation is substantially correct, then future development should be directed towards two aims. The first aim should be to produce a fibre which is as free as possible from microscopic defects such as surface flaws, and defects derived from foreign particles, or bubbles in the spinning dope. The second aim should be to hinder dislocation motion in the finished carbon fibre. This could be achieved by a variety of means, including: (i) refining the crystallite size while maintaining a high fibre density, (ii) the use of hot-stretching to eliminate dislocations and (iii) the use of various micro-hardening mechanisms such as irradiation or solid-solution hardening to discourage dislocation motion.

If these means can be realised it should be possible to produce carbon fibres which are substantially stronger than those produced so far.

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