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Lattice images of carbon fibres treated with intercalating agents

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Carbon fibres were treated with nitrogen dioxide, bromine, and hydrazine to determine whether any changes in the arrangement of the carbon layer planes could be observed. A statistical analysis of lattice image photographs showed small increases in crystallite width (most notable with hydrazine) and also in the apparent length. This is consistent with previous suggestions that intercalation produces ordering by means of dislocation movement during changes in the graphite stacking mode.

1. Introduction

It is known from X-ray diffraction studies, and from the examination of lattice images obtained by high resolution electron microscopy, that the arrangement of the hexagonal carbon layers in carbon fibres becomes progressively more ordered as the heat treatment temperature (HTT) is raised. The possibility that increased order could be induced chemically at very much lower temperatures has also been considered. This is a possible explanation of the changes in fibre mechanical properties described by Hart and Pritchard [1], who subjected fibres to moist nitrogen dioxide under pressure, and by Warner *et al.* [2], who immersed filament bundles in bromine and in iodine monochloride. Vogl [3] gives the mechanism by which ordering occurs as follows. During intercalation with nitric acid, and probably with other intercalating agents, the normal graphite stacking of hexagonal planes ABAB . . . is changed to an AAA . . . sequence on either side of the intercalated layer; the stacking sequence is changed by the passage of a partial dislocation through the lattice. Other dislocations and crystal sub-boundaries are in turn also swept through, with a consequent increase in orientation and in elastic modulus. During de-intercalation, stacking sequences are returned to ABAB . . . with a further movement of partial dislocations and increased alignment of the planes.

The object of the present study is to present evidence from lattice image measurements showing whether certain chemical treatments produce detectable increases in crystallite size. The fibres were accordingly those produced by a relatively low HTT process, and originally showed only a very short-range order with no extensive aggregates of parallel layer planes.

2. Experimental procedure

The filaments were taken from a batch of Courtaulds Ltd. "Grafil" fibres having no surface treatment. The batch had been rejected from the "type 2" classification because the mechanical properties were inferior in some respects. Electron microscopic examination showed the fibres to be similar in appearance to those studied by Crawford [4] which had been prepared at HTT 600 to 700° C, although it is probable that they had actually been produced at a higher temperature. The mechanical properties were as in Table I.

Bundles of filaments were chemically treated in the following ways:

(a) Certain samples were immersed in 0.2 M solutions of bromine in carbon tetrachloride at 23° C for periods ranging from 3 days to several weeks. On removal of the sample, the solvent was left to evaporate, and debromination accomplished by heating in air at 125° C for 20 to 36 h.

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TABLE I Properties of control fibres

Diameter	8.2 μm
Tensile strength	2194 MPa
Elastic modulus	248 GPa
Ultimate elongation	0.85%

(b) Bundles containing approximately 2500 filaments were suspended in the same solution under 2 kg load for 72 h and then debrominated as before.

(c) Thin samples were mounted on glass formers in aluminium bombs and exposed to nitrogen dioxide. Two samples were heated at up to 250° C for 2 h at a pressure estimated as 2.5 to 4.0 MPa, while the third sample was exposed at little more than atmospheric pressure and at ambient temperature for two years. After removal from their bombs, the samples were heated in air for a few minutes to remove volatiles.

(d) Samples were immersed in hydrazine hydrate for three months at 23° C and, after removal, washed and dried in air at 125° C for 24 h.

Filaments were prepared for transmission electron microscopy by powdering with an agate mortar and pestle, suspending in AnalaR methanol using ultrasonic agitation, leaving for 24 h, and depositing drops of the liquid on to a grid coated with a "holey" carbon film. The examinaton was then carried out by means of a Phillips EM 301 instrument at 100 kV, with the aid of an anti-contaminator. Axial illumination was used with a 250 μm condenser and a 100 μm objective aperture. Crystalline fragments were located by their 0 0 2 lattice plane diffraction beams, taking care to avoid confusion with the carbon of the grid supporting film. Certain grids had to be rejected because preliminary examination showed their carbon supporting films to contain numerous regions of turbostratic graphite at the edges of holes, and flakes of three-dimensional graphite or carbon filaments coated with turbostratic graphite. Many of these features probably originated in the sparking or sputtering from the carbon arc used to prepare the films [5].

The lattice images were examined at 500 000 × magnification with a 10 × binocular viewer. They became visible as the objective lens was defocused, and remained visible over a small range of defocus which could be measured with the calibrated fine-focusing control of the microscope. Photographs were taken at 50 000 × magnification at the midpoint of this range of defocus, which was usually reached when the objective lens current was decreased to produce an increase in focal length ($\Delta f+$) of 160 nm. Magnification was calibrated using lattice images of potassium chloroplatinate and graphitized carbon black test samples, and in order to minimize the effect of hysteresis , the magnification was cycled from 1500 × to 500 000 × three times before focusing and photographing at 500 000 ×.

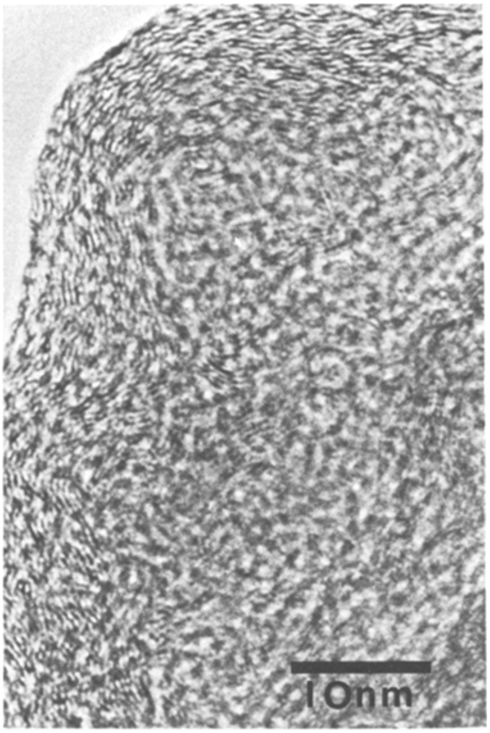

Figure 1 Control fibre (Δf + 168 nm).

Up to 14 fragments of fibre were examined for a given treatment process, with 30 or 40 photographs taken per fragment. Close examination of these photographs enabled representative regions to be found, and from these, several hundred crystallites or aggregates of fringes were measured.

3. Results

Electron diffraction patterns from the edges of intact fibres indicated that surface layers were oriented approximately parallel to the longitudinal axis of the fibres, but most fragments of powdered control fibres gave diffraction patterns of such low intensity that it was difficult to discern any preferred orientation.

The lattice images in the control fragments

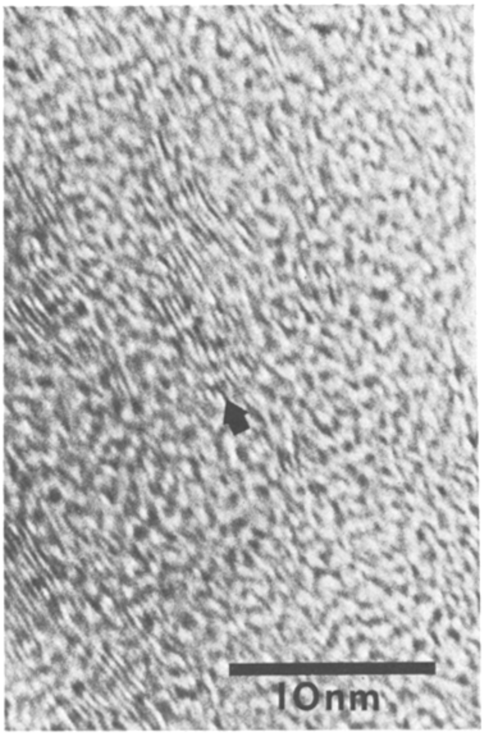

Figure 2 Isolated crystallites in a bromine-treated fibre ($\Delta f - 154$ nm).

Figure 3 Extensive lattices induced by bromine treatment ($\Delta f + 49$ nm).

show crystallites which are poorly demarcated from one another, as some fringes run continuously from one crystallite to another, or else change direction (Fig. 1). The images from chemically treated fragments were generally similar, but often included isolated crystallites surrounded by regions of apparently amorphous structure (Fig. 2). In just a few instances, there were atypical crystallites with remarkably extensive lattices. This was particularly noticeable after bromine treatment (Fig. 3). There was also some preferred orientation of the layer planes in treated samples (Fig. 4), and more intense diffraction patterns.

The lattice image, although commonly called a "crystallite", is not a true representation of the crystal structure but shows merely those areas of a crystallite in which the lattice layers are well-ordered and oriented so as to produce the Bragg reflections needed to give lattice images [6]. Deciding which lattice fringes form an aggregate and then measuring the latter's dimensions can yield rather subjective data. In the present study an aggregate was recognised as any group of three or more dark fringes lying parallel to each other. The width of an aggregate was taken as the maximum number of parallel dark fringes in the aggregate. To measure the length of an aggregate a magnifier fitted with a scale marked in 0.1 mm divisions was used to measure the length of each dark fringe in the aggregate, and the mean fringe length calculated and taken as the length of the aggregate. All measurements were carried out by one person using photographs without knowing from which sample they were taken. The widths of 3376 aggregates were investigated in the hope that large numbers might average out subjective errors. Measuring aggregate lengths was much more difficult and fewer aggregates were investigated. The data on aggregate width (Table II) and length (Table III) should be accepted, therefore, as being not absolutely quantitative but of value in comparing control and intercalated carbon fibres.

4. Discussion

Comparing the crystallite widths of control samples with those of hydrazine-treated samples, the Kolmogorov–Smirnov test [7] showed that the two populations were significantly different at the 0.1% level, and by the same criterion, the crystallite population in nitrogen dioxide-treated fibres differed from the control at between the

TABLE II Crystallite widths

Fibre	Average number of fringes per aggregate	Standard deviation	No. of aggregates measured
Control	4.74	1.70	702
Bromine-treated (no tension)	5.53	2.58	504
Bromine-treated (under tension)	4.78	1.68	701
Nitrogen dioxide-treated:			
first sample	4.50	2.06	424
second sample	5.70	2.26	487
third sample	4.60	1.57	96
Hydrazine-treated	5.99	2.64	462

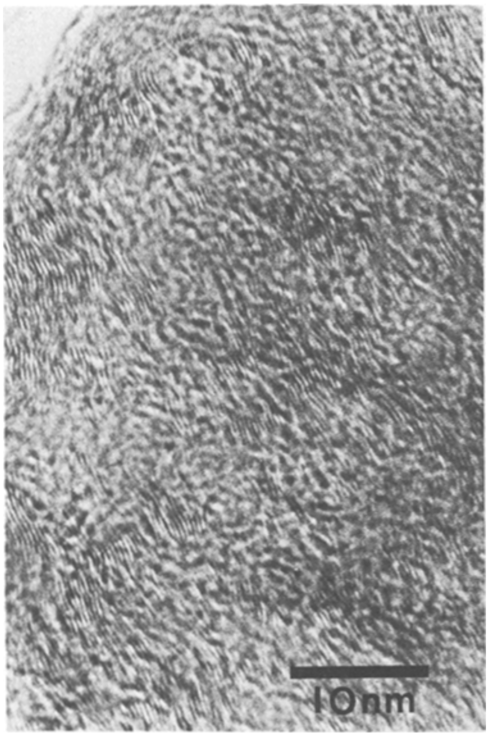

Figure 4 Preferred orientation in hydrazine-treated fibres ($\Delta f - 112$ nm).

0.5% and 0.1% levels. However, closer examination of three separate nitrogen dioxide-treated samples shows that the differences are accounted for by one group of fibres only, which had crystallite populations differing from the control pattern at less than 0.1% level, while the other two were not distinguishable from the controls. The reason for this may be the experimental problems encountered with the nitrogen dioxide method of treatment, which was known to produce variable and unpredictable changes in filament diameter and mechanical properties. Experimental problems may also be responsible for variable results when a bundle of filaments is tensioned in bromine; but the fact that untensioned bromine-treated fibres contained significantly larger crystallites (at 0.1% level) than the controls, while the tensioned bromine-treated fibres did not, could be seen as a predictable result; tensioning might reduce the extent of effective intercalation. Hydrazine, the most powerful intercalating agent, produced the largest average crystallite widths and differed significantly from the controls at the 0.1% level.

TABLE III Apparent lengths of crystallites

Fibre	Length (nm)	No. of dark fringes measured
Control	1.8 ± 0.9	282
One nitrogen dioxide-treated sample	1.9 ± 1.1	259*
Hydrazine-treated	2.2 ± 1.1	533

*Refers only to the second sample, in which significant differences were found.

Examination of the distribution of crystallite widths shows that of all the regions examined, no control contained more than 11 fringes, while the bromine-treated samples contained up to 26 fringes and the hydrazine-treated samples contained up to 20.

Table IV shows the distribution of crystallite widths, expressed as the number of fringes per aggregate, for the various treated samples compared with the controls. The larger crystallites found in the treated samples were rather uncommon. Less than 3% of those found in bromine-treated fibres and only 4% of those in hydrazine-treated samples were larger than any in the controls. Two of the three nitrogen dioxide-treated samples contained no aggregates exceeding 10 fringes, but the effect of intercalating agents was clearly to produce a small increase in average crystallite size.

TABLE IV Distribution of crystallite widths

x	Number of fringe aggregates with x fringes				Fraction of fringe aggregates with x or less fringes			
	Controls	Bromine-treated	Hydrazine-treated	Nitrogen dioxide-treated	Controls	Bromine-treated	Hydrazine-treated	Nitrogen dioxide-treated
	(Out of 702)	(Out of 504)	(Out of 462)	(Out of 1007)				
3	167	83	66	209	0.238	0.165	0.143	0.207
4	230	122	97	267	0.565	0.407	0.353	0.473
5	125	106	78	203	0.744	0.617	0.522	0.674
6	87	68	62	138	0.867	0.752	0.656	0.811
7	42	51	51	82	0.927	0.853	0.766	0.893
8	17	24	44	42	0.952	0.903	0.861	0.934
9	18	14	23	31	0.977	0.931	0.911	0.965
10	9	14	13	13	0.990	0.958	0.939	0.978
11	7	7	9	10	1.000	0.972	0.959	0.988
12	0	5	6	7	–	0.982	0.972	0.995
13	0	2	3	2	–	0.986	0.978	0.977
14	0	2	2	1	–	0.990	0.983	0.998
15	0	0	2	1	–	0.990	0.987	0.999
16	0	2	2	0	–	0.994	0.991	0.999
17	0	1	0	0	–	0.996	0.991	0.999
18	0	0	2	1	–	0.996	0.996	1.000
19	0	0	1	0	–	0.996	0.998	–
20	0	0	1	0	–	0.996	1.000	–
24	0	1	0	0	–	0.998	–	–
26	0	1	0	0	–	1.000	–	–

The measurements of uninterrupted parallel lattice lengths suggest that nitrogen dioxide-treated fibres do not differ significantly from the controls in this respect, but hydrazine treated samples have longer apparent lengths with populations differing at less than 0.1% significance.

5. Conclusions

Lattice image examination can give useful information not available from a simple analysis of X-ray diffraction data [8], but it suffers from the disadvantage that the images are derived from very small samples which may not be representative of the sample as a whole. Sample preparation by the method described also has the disadvantage of not indicating the original position of a fragment in a filament, but considerable practical difficulties would attend the sectioning of filaments and the subsequent exposure and examination of sections.

The findings show that some differences in the degree of order in hexagonal layer planes do result from treatment with chemical intercalating agents. Generally these changes are small, but in a few instances substantial increases in crystallite length have been seen. These observations illustrate the usefulness of high resolution electron microscopy for studying poorly ordered graphitic materials.

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