Direct Observations of the Internal Structure of Carbon Fibres

Carbon fibres are potentially useful as load-bearing constituents in composite materials. The strengths of present high modulus fibres are limited by structural degradation at heat-treatment temperatures above 1600° C, which restricts their range of application. Polyacrylonitrile-based carbon fibres have been prepared, in collaboration with Weapons Research Establishment, South Australia, in order to determine the nature of defects responsible for this reduction in ultimate tensile strength at high graphitising temperatures. This note presents a study of microstructural development during graphitisation using transmission electron microscopy with an improved method of specimen preparation.

Previous investigations of carbon fibre structure have utilised crushed fragments or microtomed slices [1, 2], which are liable to be mechanically damaged, or the peripheral regions of cellulose-based fibres having fluted cross-sections [3], which are unlikely to be reresentative of the internal structure. In the present study fibres were flame-polished in an alumina crucible using an oxygen-hydrogen mixture. This thinning procedure eliminated the major causes of accidental damage in the specimen. The fibre temperature was below 1000° C and the process occupied only a few seconds; microstructural changes during polishing were extremely unlikely since fibres were initially graphitised at temperatures above 1900° C for 10 min. Similar methods developed for bulk graphites have no effect on structural integrity during thinning [4, 5]. The technique also enables particular areas to be selected for examination.

Electron diffraction from polished fibres (fig. 1) indicated that, over the whole range of heat treatment temperatures, fibres consisted mainly of turbostratic graphite in which carbon atoms form two-dimensionally ordered basal layers randomly stacked along the *c*-axis. The degree of preferred orientation of these layers parallel to the fibre axis increased progressively with graphitising temperature, as shown by a reduction in the angular width of the (002) diffraction arc in fig. 1.

The microstructures of fibres after progressively higher graphitising temperatures are illustrated in fig. 2. After 10 min at 1900° C (fig. 2a), a high density of small reflecting areas is apparent; the slightly textured appearance is developed further at higher temperatures. The fibrillar structure previously observed in longitudinal microtomed sections [6] was not detected and such features were probably artefacts produced by mechanical damage.

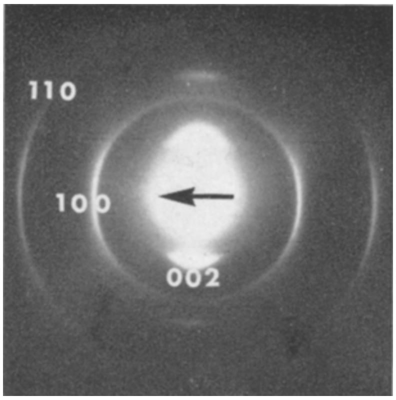
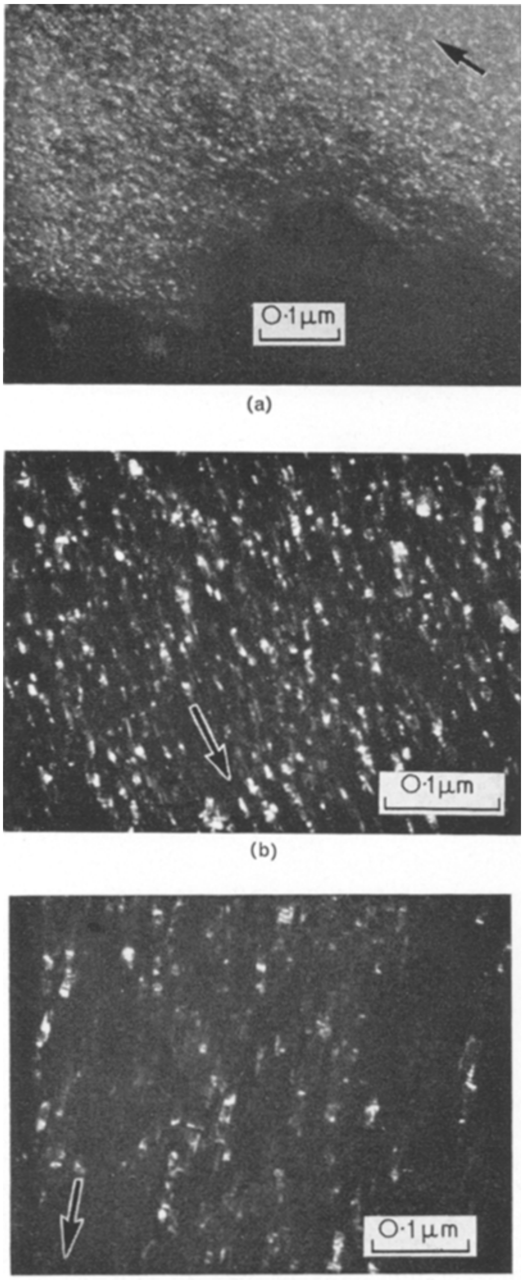


Figure 1 Electron diffraction pattern from a fibre graphitised at 2500° C for 10 min, showing (002), (110) and (100) reflections in relation to the direction of the fibre axis (shown arrowed). The absence of other reflections indicates random stacking of graphitic layers.

Figs. 2b and c show microstructures after isochronal heat treatments at 2500 and 3200° C respectively. Here diffraction contrast arises from groups of parallel graphitic basal layers, termed crystallites for convenience. At higher temperatures groups of crystallites form more distinct, parallel ribbons which enclose a network of extended pores. The observed dimensions of the pores, separating adjacent crystallite ribbons, are consistent with low-angle diffraction measurements [7]. The elongation of these microvoids with increasing graphitising temperature is attributed to a decrease in the density of branching points along each ribbon; the mean misalignment of ribbons (with respect to the fibre axis) also decreases until an almost linear configuration of crystallite ribbons with few branching points is formed at 3200° C.

Transverse tilt or bend plane boundaries between individual crystallites in each ribbon appear as distinct contrast fringes in electron micrographs. Larger crystallites result from higher graphitising temperatures; at the highest temperatures the average crystallite dimensions parallel to the layer planes were $L_a \sim 50$ Å and normal to the planes, $L_c \sim 150$ Å. The more rapid increase in the number of layers in each



(a)

(b)

(c)

Figure 2 Dark-field electron micrographs using the (002) reflection of carbon fibres graphitised for 10 min at (a) 1900° C. (b) 2500° C. (c) 3200° C. The direction of the fibre axis is arrowed.

crystallite than in the width of the stack, and the regularity in spacing of the contrast fringes associated with transverse tilt or bend plane boundaries, are considered in a further paper.

The use of flame-polishing facilitated the detection of a platelet phase dispersed internally in undoped fibres heat treated to high moduli; similar flakes have been observed in crushed fragments [2]. These platelets often occur in clusters and exhibit extinction fringes (fig. 3). Electron diffraction patterns from such areas show diffraction spots typical of ordered graphite as well as the normal turbostratic reflections. Segregated trace impurities probably catalyse the formation of this phase by the same mechanism as in deliberately doped fibres; it has been shown that specific impurity additions catalyse the growth of three-dimensionally ordered graphite platelets to larger than one micron in dimension, by the removal of obstacles to extended layer growth [8].

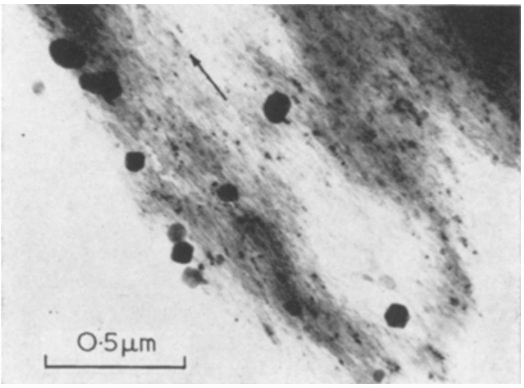


Figure 3 Bright-field electron micrograph of a cluster of platelets in an untreated fibre graphitised at 2500° C for 10 min.

Macroscopic internal voids and surface flaws occur in all fibres and were detected by scanning electron microscopy. Regions around these defects were examined by transmission electron microscopy after flame-polishing pre-selected areas. The peripheries of such lenticular voids show layer stacks of considerably larger dimensions than in the body of the fibre. In fig. 4 (at A and B) growth of layer stacks resulted in extended crystalline blocks. Three-dimensionally ordered platelets are likely to form preferentially at flaws, either because of impurity segregation, or as a result of a local enhancement in the preferred orientation of basal planes, parallel to a free surface, which provides favourable conditions for the formation of extended layer plane regions.

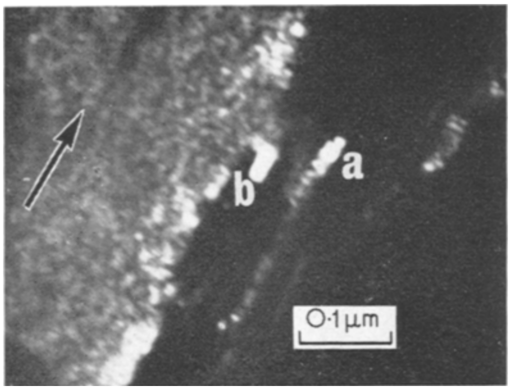


Figure 4 Dark-field electron micrograph using the (002) reflection of the peripheral region around an internal flaw in a fibre graphitised at 2100° C for 10 min.

Mechanical tests on recrystallised fibres show that the fracture strength is reduced in the presence of single crystal graphite platelets [8], possibly due to platelets oriented perpendicular to the fibre axis such that the weak bonding between basal layers is aligned along the stress axis.

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B. J. WICKS
Aeronautical Research Laboratories
Melbourne, Australia

A Note on the Stoichiometry Limits in NiO and Fe_2O_3

The oxygen rich stoichiometry limits in many oxide systems have not in general been well defined. The desirable gas-solid oxidation reaction path has the considerable experimental disadvantage that high oxygen pressures must be contained for long periods of time in pressure vessels operating at relatively high temperatures. Alternative reaction paths, for example the production of oxides in degradation reactions, often lead to uncertainty about the purity, and therefore, the stoichiometry of the oxide sample obtained.

The chemistry of the oxides of the later transition metals suffers particularly from this lack of definition. Here, we report on the oxygen-rich stoichiometry limits in the iron-oxygen and nickel-oxygen systems. In the iron-oxygen system, the oxides up to Fe_2O_3 are well established and preparable by direct oxidation. One higher oxide, FeO_2, has been reported to form in the thermal decomposition of $FeO(NO_3)$ [1], but no characterisation has been given. Contrary to this result, the maximum Fe^{+4} concentration at 500° C and 10 kbar in the ternary system Fe-Cr-O does not exceed 15% along the tie-line between sesquioxide and dioxide [2].

In the nickel-oxygen system similar discrepancies are to be found. Bogatsky [3-5] has reported that only three compositions (NiO, Ni_2O_3 and NiO_2) of some 25 nickel oxides reported to exist, can be positively identified as separate distinct phases. Ni_2O_3 was identified in the dehydration of nickel nitrate and NiO_2 in the dehydration of nickel oxide hydrate. Kuznetsov [6] has, however, suggested that all these higher oxides and oxide solid solutions are in fact merely partial hydroxide decomposition products. All workers agree that the direct oxidation reaction leads only to nickel monoxide at low gas pressures, but it has been reported [7] that the oxidation can proceed to $NiO_{1.07}$ in oxygen pressures of 300 bar. These data are to be compared with the very limited excess oxygen content reported at higher temperatures [8] and oxygen pressures [9].