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Structure in carbon/carbon fibre composites as studied by microscopy and etching with chromic acid

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Structure of the matrix carbon in two industrially prepared carbon/carbon fibre composites and in four composites prepared in the laboratory was studied using optical microscopy and SEM examination of surface topography after oxidation in chromic acid solution. In the industrial composites and in the laboratory composites prepared with PAN fibres, the orientation of the basal planes of the matrix carbon is parallel to the fibre length within ~ 5 μm of the fibre. The fibre-matrix interface is an area of weakness. Use of CVD coated carbon fibres, however, prevented this alignment; here the basal planes of the matrix carbon are randomly aligned relative to the surfaces of the fibres.

1. Introduction

Carbon fibre reinforced composites are of considerable interest in fields such as aeronautics and aerospace where resistance to high temperatures and thermal shock, coupled with high strength, is of importance. Factors influencing the properties of such composites, which consist of fibres in a carbon matrix, e.g. pitch coke, are bonding between the fibre surface and the matrix carbon as well as the orientation of the basal planes of the matrix carbon at the fibre interface.

Knowledge of the orientation of basal planes of the matrix carbon and extent of macrocrystallinity at the interface is central to an understanding of the thermal conductivity, electrical conductivity and mechanical strength of the composite [1–3]. The technique of polarized light optical microscopy of polished surfaces of carbon is a powerful tool in the elucidation of structure in the matrix carbon [4, 5].

The optical texture of anisotropic carbon seen under the optical microscope describes, to a first approximation, the "macrocrystallinity" of the carbon [5]. Reflection interference colours (RIC) produced from polished surfaces of carbon with polarized light microscopy are directly related to the orientation of the basal planes at the carbon surface [4] and may therefore be used to map out the structure at the surface of the carbon. However, the structure within each "macrocrystal" seen in the microscope as an isochromatic area of the optical texture is not necessarily homogeneous. A method is therefore needed to study structure within these isochromatic components of size ~0.5 to 300 μm within anistropic carbon. This paper describes the use of chromic acid solution as an etchant in association with microscopy to reveal structure in the matrix carbon of carbon/carbon fibre composites.

The technique of chromic acid oxidation was originally used in kinetic assessments of oxidation phenomena [6]. Recently, however, the technique has been reassessed and applied to investigations of structure in anistropic carbons [7–9]. Chromic acid oxidizes preferentially at sites within anisotropic carbon and appears to have little relative affinity towards isotropic carbon. The consequence of this selective removal within anisotropic carbon is the development of a surface topography which clearly shows the orientation of the stacked lamellar molecules which constitute structure within anisotropic carbon. It should be emphasized that the carbon remaining after etching does not

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represent individual lamellae but the general orientational trends of a large number of lamellae.

The objectives of this study are to investigate the structure of matrix carbon in a range of carbon composites made industrially and in the laboratory using techniques of optical microscopy and of scanning electron microscopy (SEM) after oxidation in chromic acid. Particular attention is given to the matrix carbon immediately adjacent to the carbon fibres and to regions where fibres or fibre bundles intersect. The effects of carbon vapour deposited (CVD) coatings used to stiffen fibres during composite manufacture, upon the orientation of the surrounding matrix carbon is also investigated.

2. Experimental procedures

2.1. Materials used

1. Felt based carbon fibre reinforced composite (CFRC BB-UHT).

2. Industrially prepared 3-dimensional reinforced carbon fibre composite.

3. Laboratory prepared composites: high tensile, surface untreated polyacrylonitrile fibre (HTU PAN fibres) and CVD coated PAN fibres in A240 petroleum pitch coke and Esso CP1510 petroleum pitch coke matrices.

2.2. Laboratory carbonization of composites

The HTU PAN fibres and CVD coated fibres were carbonized with A240 petroleum pitch and Esso CP1510 petroleum pitch in a Carbolite horizontal electrical tube furnace, to a heat treatment temperature (HTT) of 1173 K (900° C) at 3 K min^{-1} under nitrogen.

2.3. Examination of HTU and CVD coated fibres

The HTU PAN fibres and the CVD coated fibres were mounted on stubs, gold coated to prevent charging and examined by SEM to determine differences in terms of surface structure and topography.

2.4. Examination of composites

A polished surface of each composite was prepared, examined and characterized using a Vickers M41 polarized light microscope. The polished surface of each composite was first examined by SEM to characterize the surface and was then oxidized in chromic acid at 373 K (100° C) for times ranging from 1 to 7 h. The chromic acid was prepared using 10 g potassium dichromate in 50 cm^3 orthophosphoric acid, heated together in a water bath. The topography developed during oxidation was studied by SEM. The same area of carbon surface was examined before and after oxidation to correlate the surface topography seen by SEM with the optical texture of the carbon.

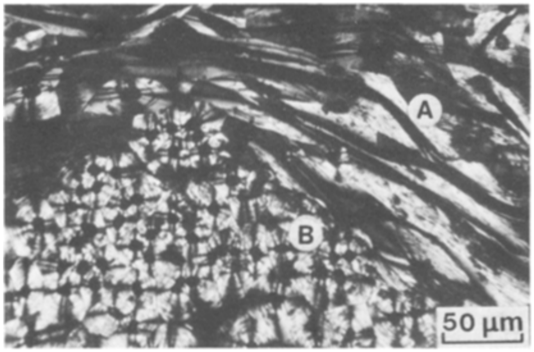

Figure 1 Optical micrograph of CFRC BB-UHT.

3. Results

3.1. Felt based CFRC BB-UHT

Optical examination of the unoxidized surface of this composite (Fig. 1) revealed a complex pattern of apparently isotropic fibres (Position A) surrounded by a region of pyrolytically deposited anisotropic carbon matrix typically 10 to 15 μm thick (Position B). This region consists of basal planes concentrically arranged around the central fibre (as deduced from RIC). Few fissures were present in the original polished surface; those which were present ran parallel to the basal planes of the material, i.e. were concentric with the fibre. After 4 h oxidation in chromic acid at 373 K, SEM examination (Fig. 2)

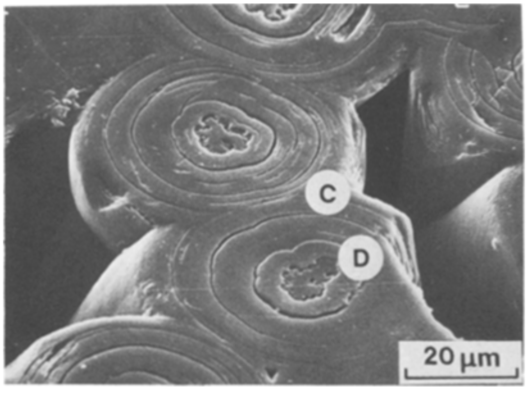

Figure 2 SEM micrograph of a polished surface of CFRC BB-UHT after 4 h oxidation in chromic acid.

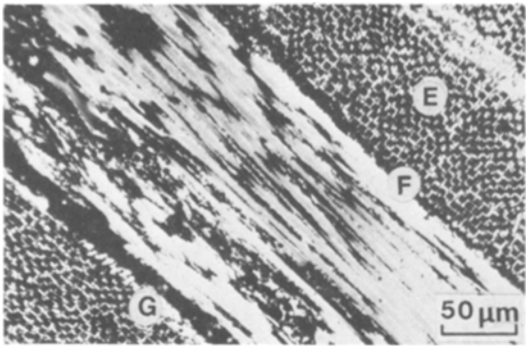

Figure 3 Optical micrograph of industrially prepared carbon composite.

showed the development of preferential oxidation fissures of typical width 1 μm, closely following the orientation of the basal planes (Position C). The carbon at the interface between the central fibre and surrounding anisotropic carbon is preferentially oxidized (Position D).

3.2. Industrially prepared carbon composite

Fig. 3 is an optical micrograph of the industrially prepared composite showing part of a cross-sectioned fibre bundle (Position E) and the surrounding matrix carbon. Examination of the polished surface of this composite reveals the following features.

1. Porosity of the composite is very low. The total number of pores is significantly less than normally found in anisotropic carbons.

2. Almost every fibre bundle is surrounded by a fissure of typical width ~ 2 to 5 μm (Position F).

3. The regions betwen fibre bundles are filled with matrix carbon and it is through these regions that the fissures propagate.

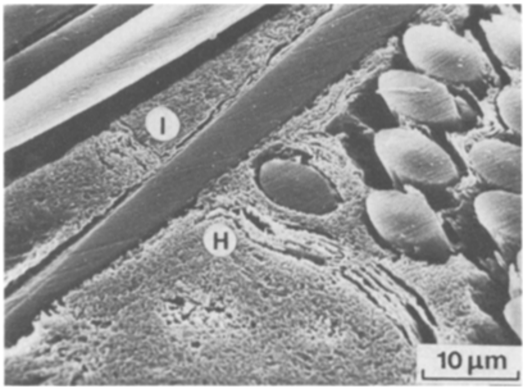

Figure 4 SEM micrograph of industrially prepared carbon composite after 2 h oxidation in chromic acid.

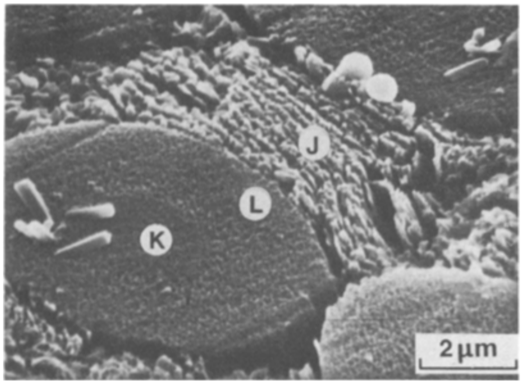

Figure 5 SEM micrograph of industrially prepared carbon composite after 2 h oxidation in chromic acid.

4. Alignment of the basal planes of the matrix carbon as deduced from RIC is parallel to the fibre length within each fibre bundle but undergoes a rapid change in orientation (over ~ 5 μm) in the region between fibre bundles. It is this region of rapid change in structural orientation which is particularly prone to fissuring (Position G). Oxidation of the surface using chromic acid (Figs. 4 and 5) clearly demonstrates the orientation of the matrix coke. The preferential oxidation fissures (Fig. 4, Position H) which follow basal plane orientation show the rapid change in orientation in the region between two fibre bundles sectioned longitudinally and in cross-section. The fibre/matrix interface is a region of preferential oxidation (Fig. 4, Position I), possibly because of weak bonding of the fibre to the matrix carbon or the existence of a microfissure at this point in the original surface which has been enlarged by oxidation to sizes typically 1 to 2 μm wide and up to ~ 100 μm in length.

The preferential oxidation fissuring seen in Fig. 5, Position J, shows the arrangement of the basal planes to be parallel to the fibre length between fibres in a bundle. Some structure can be seen in the fibres themselves; a central core of size ~ 1 μm is surrounded by a sheath of slightly pitted material of width ~ 2 μm (Positions K and L, respectively).

3.3. Composites prepared in the laboratory

The surface topographies of the HTU PAN fibres and CVD coated fibres are markedly different. The PAN fibres (Fig. 6) show smooth ridging parallel to the fibre length (Position M) while

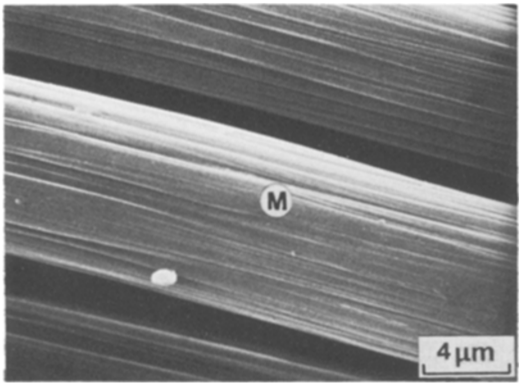

Figure 6 SEM micrograph of HTU PAN fibres.

the CVD coated fibres (Fig. 7) are characterized by a surface roughness caused by the coating. This appears as small "granules" of size ~ 0.1 μm covering the fibre surface (Position N).

Optical examination of the HTU PAN fibres in matrices of coke from A240 and Esso CP1510 pitches (e.g. Fig. 8) showed that alignment of the basal planes of the matrix carbon (as deduced from RIC) is predominantly parallel to the length of the fibre within about 5 μm of the fibre surface (Fig. 8, Position O). Oxidation of the composite surface in chromic acid for 7 h confirmed this. The selective removal of carbon indicated basal plane orientation to be along the fibre length (Fig. 9, Position P).

Optical examination of the CVD coated fibres in matrix carbon from A240 and Esso CP1510 pitches (Fig. 10) showed that the basal plane orientation of the matrix in the vicinity of the fibre was not predominantly parallel to the fibre length. The RIC indicated that over significant distances along the fibre length, basal plane orientation was perpendicular to the fibre surface (Fig. 10, Position Q).

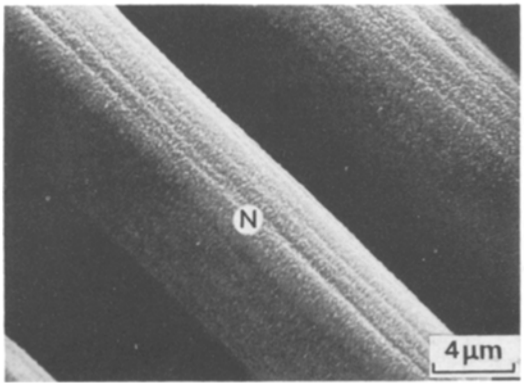

Figure 7 SEM micrograph of CVD coated PAN fibre.

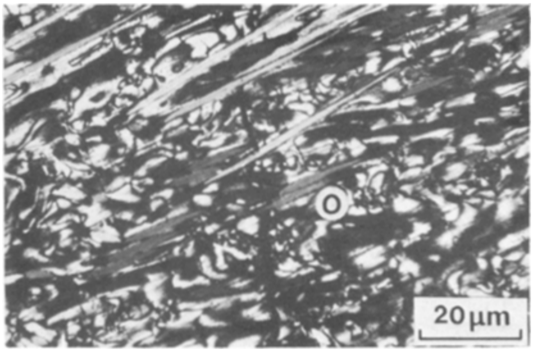

Figure 8 Optical micrograph of HTU fibres in an A240 matrix. HTT 1173 K, 3 K min^{-1}.

4. Discussion

4.1. Industrially prepared carbon composites

The two industrial composites examined were prepared in markedly different ways (by pyrolytic deposition of the matrix carbon and by impregnation of a 3-dimensional woven fibre cloth with fluid pitch under pressure) but both showed two important features in common. The basal plane alignment of the matrix carbon was parallel to the fibre length adjacent to the fibre. Also the matrix carbon at the matrix/fibre interface was preferentially oxidized. This preferential oxidation may be the result of residual stresses set up in the matrix adjacent to the fibre because of differential contraction of the matrix carbon during pyrolysis. Small fissures already present in the composite at these interfaces become enlarged by oxidation. This is an important factor in con-

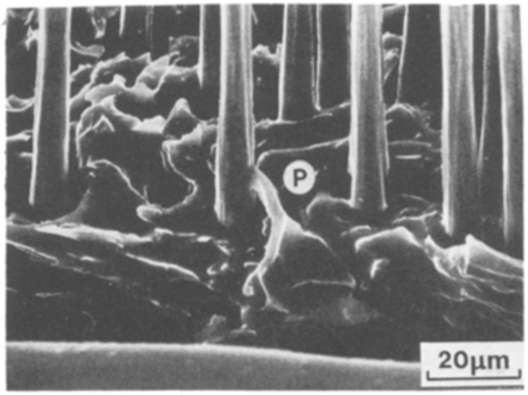

Figure 9 SEM micrograph of HTU fibres in an A240 matrix after 7 h oxidation in chromic acid.

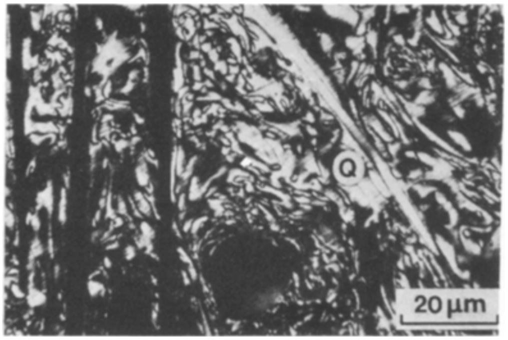

Figure 10 Optical micrograph of CVD coated fibres in an A240 matrix. HTT 1173 K, 3 K min^{-1}.

sideration of composite properties; a strong bond between the fibre and the matrix along the whole length of the fibre would lead to a brittle composite, while complete lack of bonding would easily facilitate pull-out of the fibres. A weak bond, or the presence of a small fissure, along some of the fibre length, is therefore desirable.

4.2. Composites prepared in the laboratory

In the laboratory prepared composites a marked difference exists in the structure of the matrix carbon at the matrix/carbon fibre interface when HTU PAN and CVD coated fibres are used. The HTU fibres formed a composite in which basal plane alignment of the matrix carbon adjacent to the fibre was parallel to the fibre length. When CVD coated fibres were used, this alignment was not present. The CVD fibres were also found to have a surface roughness on a scale of $\sim 0.1\,\mu\text{m}$, compared to the smooth surface of the HTU fibres.

It is felt that these differences in surface topography between the two types of fibre are the main reason for the differences seen in the orientation of the basal planes of the matrix carbon when these fibres are carbonized with a pitch to form a composite.

With the HTU and other PAN fibres the flow regime of the fluid mesophase [10] between fibres during the carbonization process will be similar to flow through a capillary tube, with zero fluid velocity at the tube walls (i.e. fibre surfaces) and with velocity increasing with distance from the walls. This type of velocity distribution produces shear forces in the fluid parallel to the capillary walls. For fibre "walls" with fluid mesophase consisting of plate-like molecules flowing between them, these shear conditions are most easily met if the molecules lie parallel to the fibre surface such that shear produces slip between the molecular surfaces. This then produces the alignment of basal planes parallel to the fibre length as seen in the industrial and laboratory composites examined here. With CVD coated fibres, the roughened fibre surface appears to prevent steady flow conditions at the "walls" (i.e. matrix/fibre interface) and to cause some degree of turbulent flow. This in turn will prevent any overall orientation of the basal plane of the fluid mesophase parallel to the fibre length, as seen in the composites prepared using the CVD coated fibres.

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