Role of Interface on the Development of Microstructure in Carbon-Carbon Composites

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Abstract

Microstructure plays an important role in controlling the fracture behaviour of carbon-carbon composites and hence their mechanical properties. In the present study effort was made to understand how the different interfaces (fiber/matrix interactions) influence the development of microstructure of the matrix as well as that of carbon fibers as the heat treatment temperature of the carbon-carbon composites is raised. Three different grades of PAN based carbon fibres were selected to offer different surface characteristics. It is observed that in case of high-strength carbon fiber based carbon-carbon composites, not only the matrix microstructure is different but the texture of carbon fiber changes from isotropic to anisotropic after HTT to 2600°C. However, in case of intermediate and high modulus carbon fiber based carbon-carbon composites, the carbon fiber texture remains nearly isotropic at 2600°C because of relatively weak fiber-matrix interactions.

Keywords : Carbon fibers, Carbon-carbon composites, Interface, Microstructure

1. Introduction

Carbon-carbon composites are an important class of materials used for a number of demanding applications in the modern era of science and technology [1, 2]. The mechanical performance of these composites are controlled by the properties of individual components *i.e.* reinforcement, matrix and reinforcement-matrix interactions [3-7]. Fiber/matrix interactions further depends on the surface chemistry of reinforcement, the matrix precursor as well as on the heat treatment temperature. The development of matrix microstructure in these composites is influenced by surface characteristics of carbon fibers, matrix precursor and processing parameters. Different matrix local textures can develop during processing of these composites, specifically at fiber/matrix interphase. Using pitch as matrix precursor, c-axis radial, c-axis axial or c-axis tangential type of matrix orientation has been predicted depending on the surface energetics of carbon fibers used while an iostropic matrix orientation has been predicted with phenolic resin as matrix precursor [8]. The proposed microstructure have actually been observed and reported in the literature [3, 9-12]. The fiber/matrix interphase influences the fracture behaviour as well as the ultimate mechanical properties of carbon-carbon composites.

Carbonization of neat phenolic resin results in the formation of non graphitizable carbon with glass-like texture [13]. However, in carbon-carbon composites, matrix derived from phenolic resin is influenced by the surface chemistry/functional groups of the fibers and stresses generated at the fiber-matrix interface during the carbonization and graphitization process [14, 15]. Previous studies by the authors have reported the effect of carbon fiber surface functional groups on the development of interfaces and its influence on mechanical properties of carbon-carbon composites [5, 16, 17, 18] using phenolic resin as matrix and very interesting observations were made on the influence of the surface energetics of the carbon fibres on the development of microstructure of the matrix and the nature of the interface. However, these studies have remained scattered.

It was therefore thought interesting to carry out a systematic study on the development of microstructure of not only the matrix but also that of carbon fibres during the processing of carbon-carbon composites. Since the different grades of PAN based carbon fibres offer different surface characteristics three grades of commercially available carbon fibres, namely 'High strength', 'Intermediate modulus' and 'High modulus', were selected. Since the final heat treatment temperature of all these fibres is different these offer different surface characteristics and should therefore lead to different wetting behaviour with the phenolic resin matrix. Another interesting parameter which has been given attention in the present study is the development of the microstructure of the matrix and the fibres as it passes from carbonization to graphitization stages.

2. Experimental

Unidirectional composites were prepared using conventional match mold die technique [17] with 45±2% fiber volume fraction. These composites were prepared using three different type of PAN based carbon fibers and their respective composites were codified as follows:

A, High-strength carbon fiber carbon composites;
B, Intermediate-modulus carbon fiber carbon composites;
C, High-modulus carbon fiber carbon composites.

These composites were heat treated to different temperatures ranging from 1000°C to 2600°C under inert atmosphere. These composites were characterized for microstructural investigation by optical microscope having polarized light facility.

Pores and cracks were more easily distinguished from the surrounding material when observed with unfiltered white light. However, use of polarised light in case of carbon materials offered more detailed analysis of microstructure as it offered a means of identifying anisotropic components in the composite structure. The reflectance, dependent on the wavelength of light, in case of crystalline graphite, is different for the two principal directions showing black and white regions thus giving rise to patterns of extinction contours [19] when crossed polars are used in the reflectance microscope.

The patterns of extinction contours are used to map the structure of the lamelliformation (stacking of structural planes) as it varies within the material. The orientation of lamelli formation is observed through the generation of "reflectance interference colours" when 1 X_{red} retarder plate is used. Purple colouration (previously black without 1 X_{red} retarder plate) is observed at the surface of isotropic carbon or when the basal planes (002 planes) are parallel to the pol-

ished surface which remains unchanged on rotation of specimen stage of the microscope. Blue and yellow colours (previously white) are observed when prismatic edges are parallel to the polished surface. Rotation of specimen by 90° changes yellow colour into blue colour (through an intermediate purple) and blue colour to yellow colour. Thus changes in the orientation over the surface can be assessed by observing how the colour changed. Fig. 1 shows the positions of polarisr, analyser and lambda plate with respect to the orientation of the micrographs.

3. Results and Discussion

Figures (2-7) compare the microstructure change of matrix and reinforcement (CFs) in composites A, B and C after these were heat treated to temperatures 1000°C, 1400°C, 1800°C, 2200°C and 2600°C respectively. The texture of anisotropic carbon under the polarized light is known to show different reflection of interference colors produced from polished surface of carbon-carbon composites and is
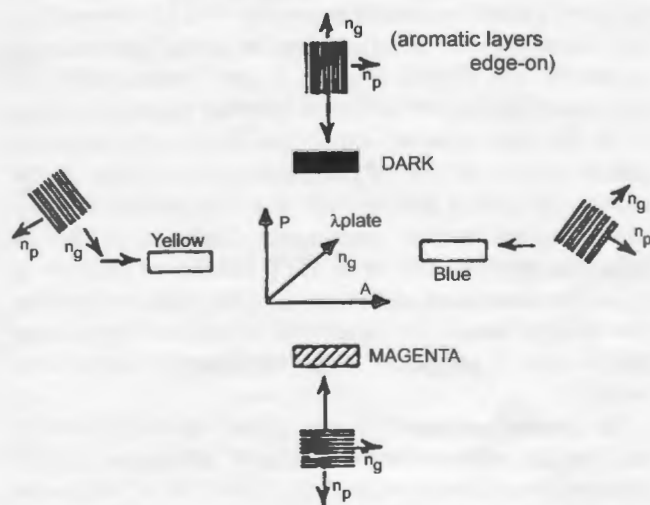

Fig. 1. Shows the positions of polariser, analyser and lambda plate with respect to the orientation of micrographs (reference 16).
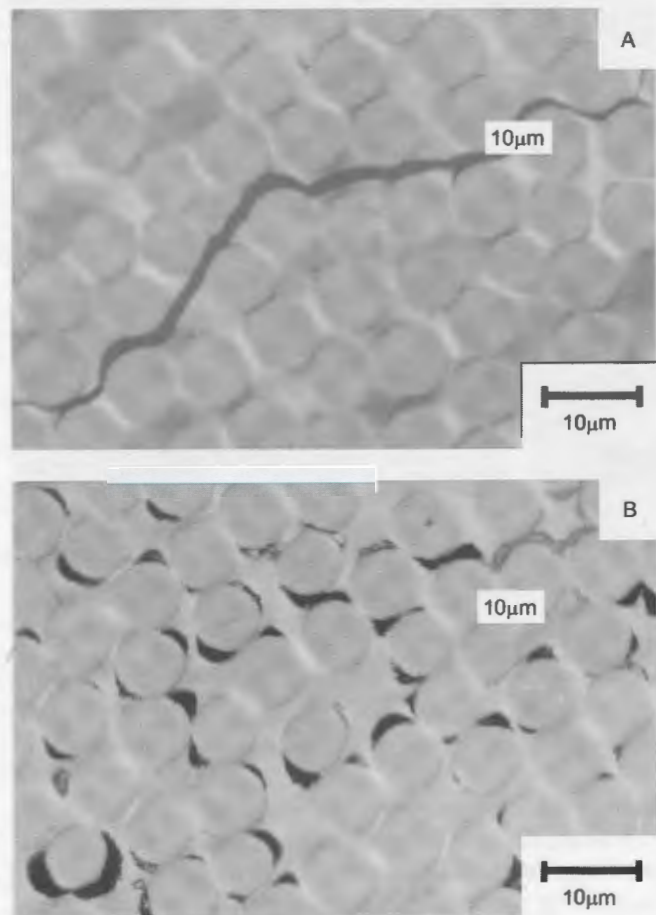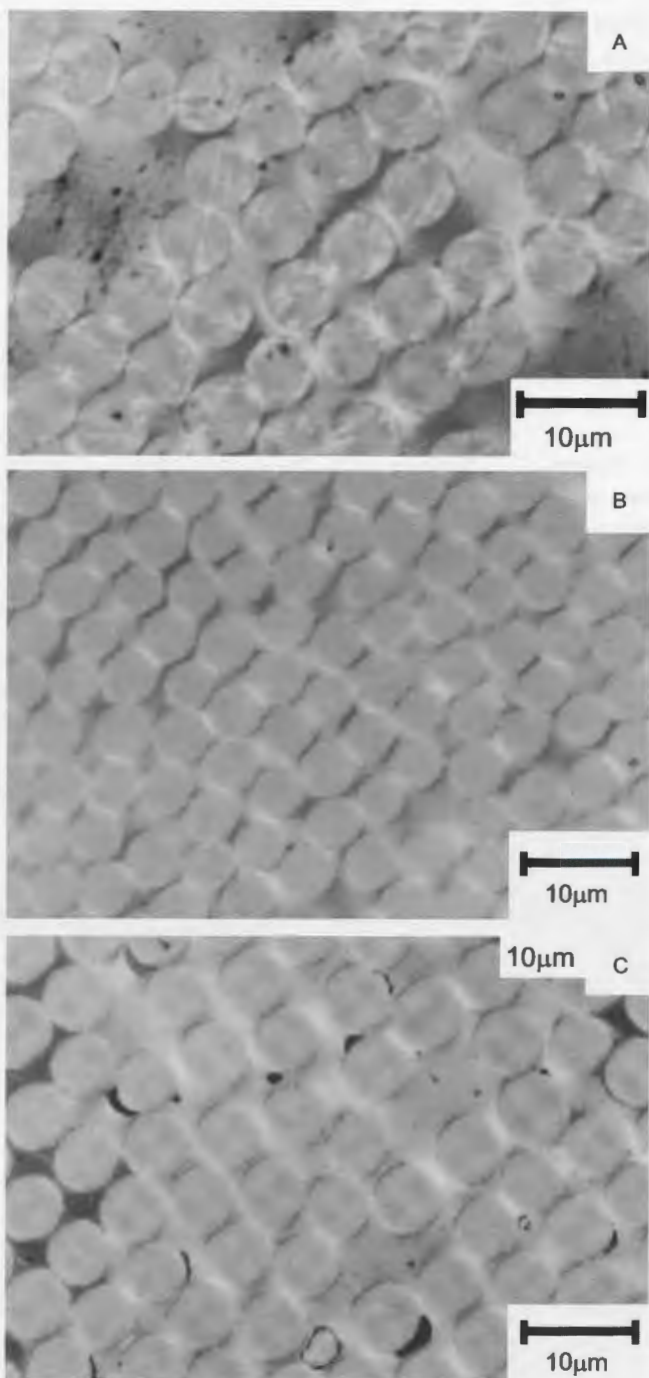

Fig. 2. Crack propagation in composite A perpendicular to fiber direction and annular gaps in composite C during heat treatment to different temperatures.

Fig. 3. Microstructure of Composites A, B and C, HTT 1000°C showing the development of anisotropy in the matrix.

directly related to orientation of the basal planes at surface [19] as explained in the experimental part. The carbon generated from thermosetting phenolic resin matrix is known to be isotropic in nature and its texture does not exhibit any graphitic structure even if heat treated to 3000°C under normal conditions [13]. In carbon-carbon composites, however, phenolic resin matrix in contact with the carbon fibre (co-car-

bonisation) exhibit optical anisotropy (basal plane orientation) near the interface even when heat treated at 1000°C (Figure 3). The composites heat treated to 2600°C, leads to oriented graphitised matrix showing well developed optical anisotropy on the fiber-matrix interface (Figure 7) [20].

The optical anisotropic regions are observed preferentially at the interface between carbon fiber and matrix due to orientation of basal planes on fiber-matrix interface. The graphene layers of matrix carbon are alligned as c-axis radial or tangential [8]. It is due to accumulation of thermal or shrinkage stresses during carbonization. The development of stresses depends upon severity of fiber-matrix interactions or bonding strength at the interface between the carbon fiber and resin matrix [21]. In case of composite A, fiber makes strong interactions with the resin matrix and during carbonization the composite as a whole will shrink in all directions including the fiber direction [22]. The strong fiber/matrix interactions between fiber surface and matrix precursor will not allow the matrix to shrink away from fiber, rather matrix will shrink on to the fiber. Such high degree of stresses generated through strong fiber-matrix interactions accumulate large compressive forces on the fibers. As the heat treatment temperature of composite progresses, these stresses become so severe that cracks are found to propagate through fiber-matrix interface perpendicular to fiber direction as shown in Figure 2(a), (composites A). In case of composite C, the fiber-matrix interactions are weak comparatively, therefore, the stresses generated on the fiber-matrix interface are also lower compared to composite A. The matrix is found to shrink away from the surface causing annular gaps [23] between fiber and matrix as shown in Figures 2(b).

As shown in Figure 3, the matrix tends to develop anisotropy even at 1000°C (basal plane start to develop at interface region oriented along the fiber direction) near fiber-matrix interface in all the three type of composites. Composite A, however, exhibit maximum anisotropy which is revealed by the relative intensity of reflections. On further heat treatment to 1400°C and 1800°C (Figures 4 and 5 respectively), the anisotropic regions at fiber-matrix interface gradually increase in all the three type of composites, though the maximum enhancement is in case of composite A, as revealed by the intensity of colours and the total area. The increase in anisotropic regions around fiber-matrix interface, is due to enhanced graphitisation with HTT leading to increase in crystallite dimensions and decrease in the interlayer spacing. But the total anisotropy developed shows maximum sharpness in case of composite A and minimum in case of composite C.

The amount and extent of anisotropic regions (intensity in the blue and yellow colour and area of anisotropic regions) becomes more prominent in all the three type of composites as the heat treatment temperature progresses to 2200°C as shown in Figure 6. At this temperature the two dimensional carbon-matrix starts to undergo structural rearrangement and
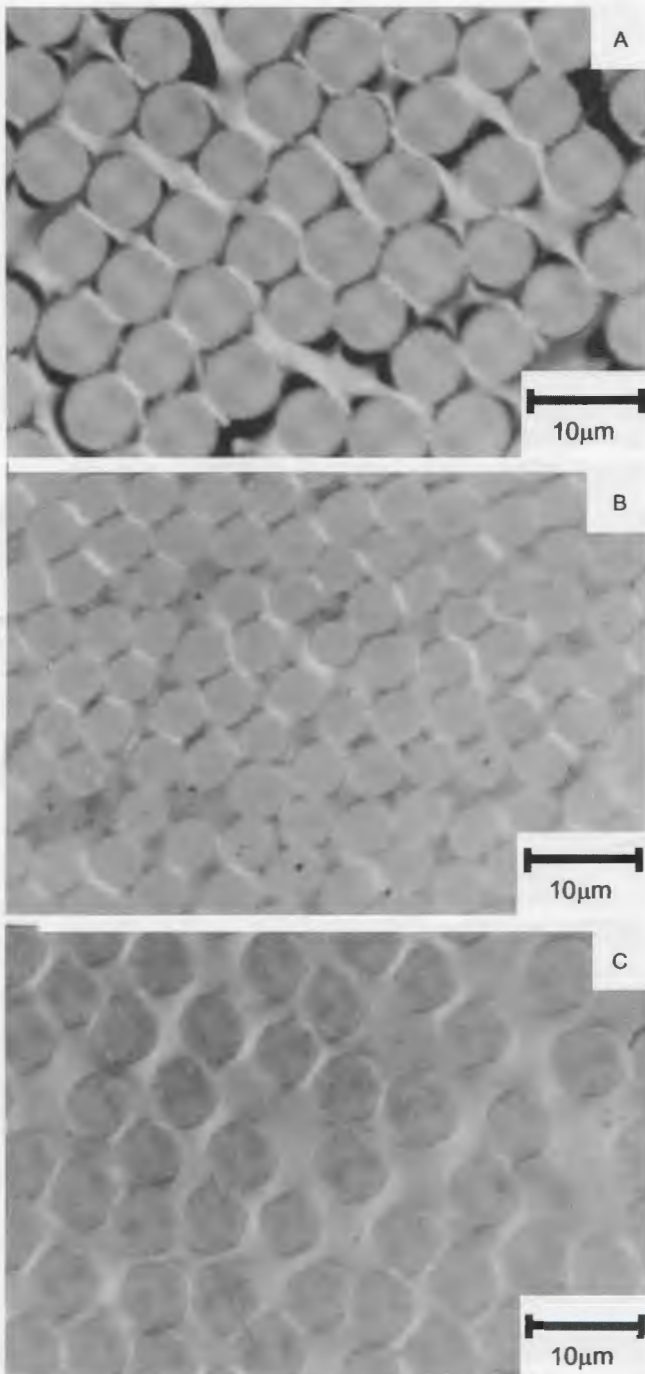
Fig. 4. Microstructure of Composites A, B and C, HTT 1400°C showing the increase in the degree of anisotropy of the matrix.

Fig. 5. Microstructure of Composites A, B and C HTT 1800°C showing intense reflections and an increase in the degree of anisotropy.

transform into three dimensional graphitic structure around the carbon fiber surface. In case of composite A, the matrix start to develop a laminar type texture with extinction lines or partially columnar type texture between the adjacent fibers. This texture is more prevalent at the interphase near the fiber surface compared to regions away from the fiber surface. This texture is not present throughout the cross sec-
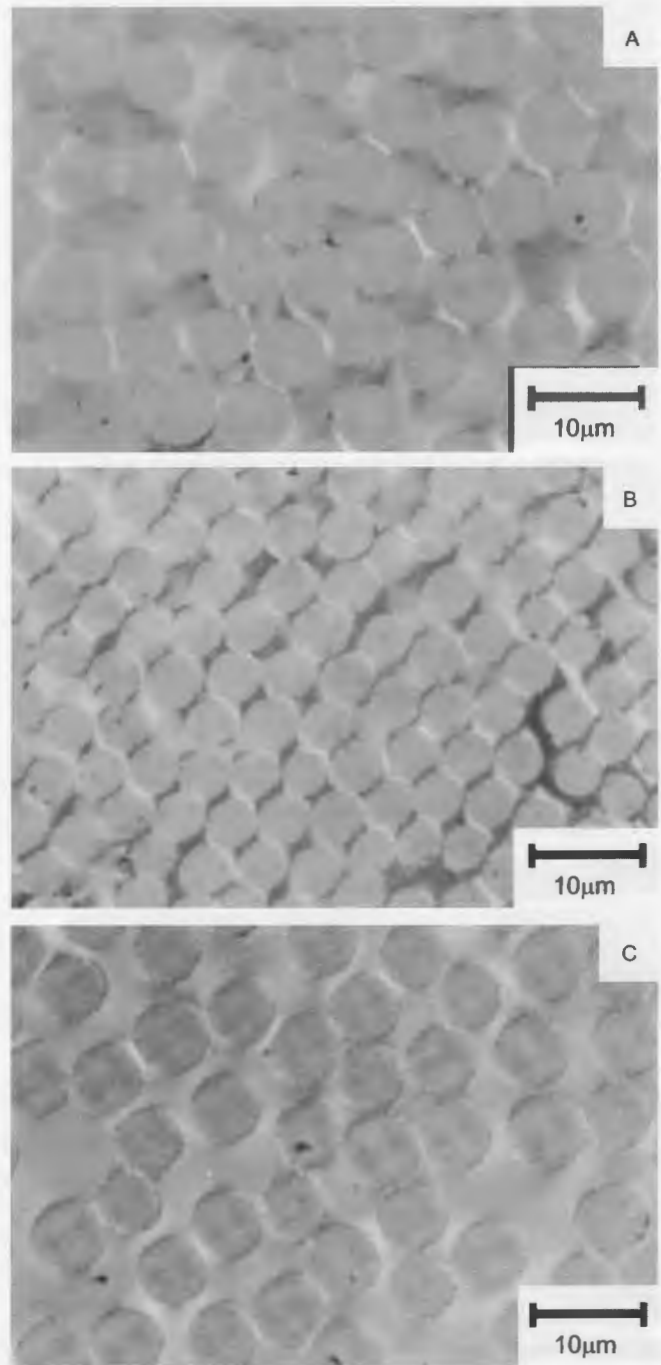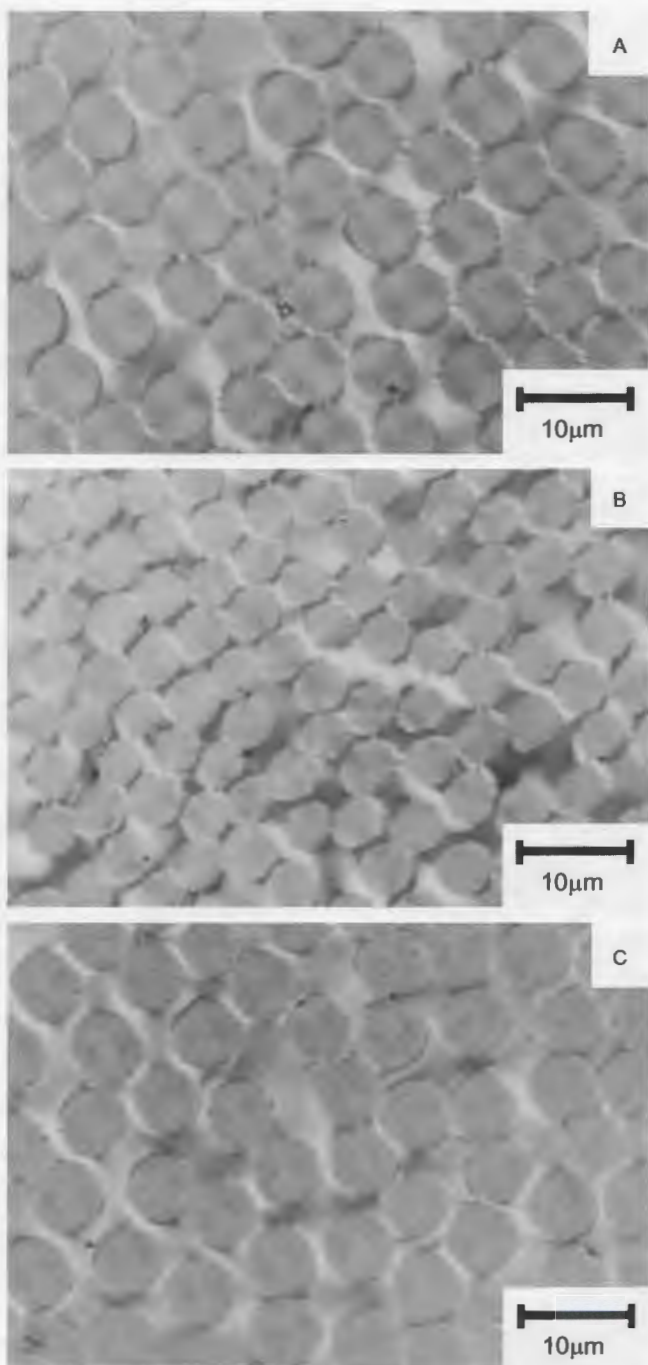
tion of the composite but is present only at selected portions where the distance between adjacent fibers is small. Since the fiber-matrix interactions gradually decreases in composites B and C respectively, the composite B shows mixed type of texture *i.e.* partially laminar plus columnar, while composite C shows more or less nearly laminar type texture.

Fig. 6. Microstructure of Composites A, B and C, HTT 2200°C showing the development of intense anisotropy in matrix and modification of texture of CF from isotropic to anisotropic (the feature decreasing from compsite A to C).

After heat treatment to 2600°C, as expected, the amount of matrix anisotropy increases to a large extent in all the composites as shown in Figure 7. In composite A, a well defined columnar type texture [21, 23] is observed on fiber-matrix interface. The columnar type texture is observed throughout the space between adjacent fibers. In case of composite B,
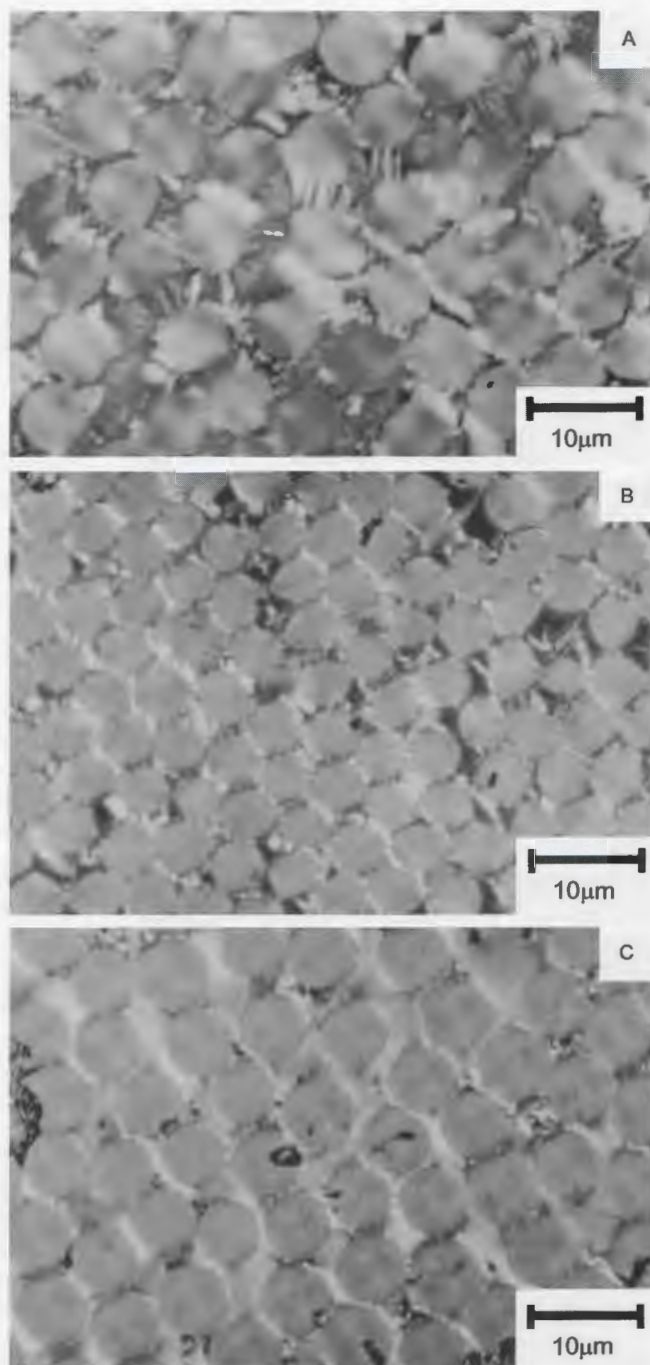
Fig. 7. Microstructure of Composites A, B and C, HTT 2600°C showing the development of columnar type microstructure in matrix and modification of texture of CF from isotropic to anisotropic (the feature decreasing from composite A to C).

the domain of laminar type texture with relatively lesser amount of extinction lines is observed while in composite C the texture is still largely laminar type due to weak fiber-matrix interactions [24, 25]. Due to strong fiber-matrix interactions in composite A, the microstructure of the carbon fiber itself transforms from isotropic to anisotropic during

co-carbonisation which has been observed for the first time in case of carbon fibers. This is evident by the yellow sectors in the fibre cross section suggestive of the development of partial radial texture from folded texture present in the original fibre. A similar observation was made by the authors [16] but this was in the case of PANEX FIBERS (c/c composites based on oxidised PAN fibres, where the surface energetics are entirely different) instead of carbon fibers. This effect is not so obvious in case of composites B and C.

4. Conclusions

The development of microstructure of the matrix in the carbon-carbon composites depends to a large extent on the fiber-matrix interactions, which themselves depend on surface energetics of the fiber and matrix precursor, established at polymer stage. When these interactions are strongest as in the case of composite A made from high-strength carbon fibers, not only columnar type of matrix texture is observed on HTT to 2600°C but even the texture of carbon fiber changes from isotropic to anisotropic due to stress graphitisation. The texture of intermediate and high-modulus carbon fibers in composites, on the other hand, remains unaffected to a large extent because of relatively weak fiber-matrix interactions.

Acknowledgement

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