INFLUENCE OF PYROLYSIS PRESSURE ON MICROSTRUCTURE OF CARBON-CARBON COMPOSITES

J. S. Evangelides
The Ivan A. Getting Laboratories
The Aerospace Corporation
P.O. Box 92957, Los Angeles, California 90009

Carbon-carbon composites are finding increasing use in thermostructural applications such as reentry vehicles and rocket nozzles. Although some increases in composite properties have been achieved, the development of advanced materials with improved performance and uniform properties will require a basic understanding of the macro/microstructural characteristics that control properties. A first step toward this goal is the description of the characteristics and changes that occur as a result of processing. The aerospace community has concentrated on the use of various pyrolysis pressures (6.9 to 103 Mpa) and filament coatings (with and without chemical-vapor-deposited carbon, CVD) as a means of improving performance. The objective of this experimental program was to study the effect of pyrolysis pressure and filament surface treatment on the resulting matrix structure. The description of the microstructural characteristics and thermal and physical properties of the constituents is essential to an understanding of processing stresses and is a vital part of the input data to analytical processing models. Ultimately, the correlation of performance to properties and structural characteristics can aid in establishing the optimum processing procedure.

The experimental approach has been to examine composites and bulk matrix after selected processing steps. After appropriate metallographic preparation and ion etching, the methods of optical and scanning electron microscopy were utilized to characterize microstructure. The xenon ion etching provided a simple means of observing the orientation of the graphitic layer planes with respect to the filament surfaces (Fig. 1). A well-defined etched lamellar structure in the matrix phase occurs when the graphitic basal planes were oriented within approximately 30 deg of the polished surface [1-4]. If the planes were parallel to the surface, a flat planar appearance was obtained while intermediate orientations yielded a fish-scale appearance.

The majority of the carbon-carbon composite samples were fabricated with Union Carbide Thornel 50 fibers and either Allied Chemical CP277 15V or Ashland A240 pitch. In order to supplement these specimens and represent extremes in processing pressure, miniature unidirectional samples were fabricated by low- (6.9 Mpa) and high-pressure (103 Mpa) procedures.

The effect of impregnation and pyrolysis pressure on matrix microstructure was most striking between individual filaments of a fiber bundle. Composites fabricated by the pyrolysis of coal tar (15V) or petroleum (A240) pitches under pressures of less than 6.9 Mpa resulted in the graphitic layer planes of the matrix being aligned parallel to the filament surface (Fig. 2). This highly aligned sheath of graphite basal planes formed irrespective of the type of filament (high- or low-modulus rayon, pitch, or polyacrylonitrile) or whether or not the filament had a CVD coating. Progressing away from the filament and sheath, the matrix structure became more complex or intertwined and, as such, more isotropic.

The pitch microstructure developed under high-pressure procedures (103 Mpa) was found to be significantly different. In the interfilament regions of a composite that had received an initial CVD coating, the graphite basal planes were randomly oriented to the filament surface (Fig. 3). Although regions of parallel orientation existed, the transverse orientation predominated. This random matrix had a characteristic structure indicative of inhibited mesophase spherule coalescence. In addition, this structure did not possess the long-range order of the composites fabricated by low-pressure procedures. Immediately at the CVD pitch interface, the basal planes were aligned at angles of 0 to 90 deg with the 0 deg or parallel alignment occurring the majority of the time. Examination of transverse sections of this composite indicated that the pitch matrix had penetrated those regions where the CVD coating had separated from the Thornel 50 filament [5].

The unidirectional composites fabricated by high-pressure impregnation procedures without an initial CVD coating also had the random basal plane orientation with respect to filament surface (Fig. 4). However, a qualitative assessment of the amount of random or transversely oriented matrix suggested that a slighly less random structure was obtained than when a CVD coating was present.

Since the pitch matrix microstructure is established during the mesophase pyrolysis occurring below 600°C and the interior of filament bundles density early in liquid impregnation procedures, the alignment of the graphite basal planes between filaments will be determined by the pyrolysis pressure employed during the initial densification cycles. Therefore, in those composites where initial low-pressure pyrolysis procedures are followed by high-pressure procedures, the graphite basal planes will be aligned parallel to the filament surfaces within the fiber bundles.

These microstructural observations indicated that high-pressure impregnation and pyrolysis results in a random orientation of botryoidal spheres, as was discussed by Marsh [6]. The effect of this pressure, then, appears to be to inhibit the coalescence of the mesophase spherules. Under low-pressure procedures, this coalescence results in a highly anisotropic sheath.

Although pressure was primarily responsible for imparting the random structure, it appears that the CVD coating increases the amount of random spherules or decreases the amount of coalescence. Since fiber surfaces promote parallel alignment between planes, the effect of the CVD coating may be to reduce the pitch wetting of filaments, thereby reducing coalescence [7].

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References

[1] J. S. Evangelides, et al., TOR-0076(6726-01)-1, The Aerospace Corporation (30 September 1976).

[2] J. L. White and J. E. Zimmer, Surface and Defect Properties of Solids 5, 16 (1976).

[3] R. D. Reiswig, et al., Carbon 5, 603 (1967).

[4] J. S. Evangelides, 12th Conference on Carbon, Extended Abstracts, p. 93 (1975).

[5] J. E. Zimmer, et al., TOR-0076(6726-02)-2, Vol. I, The Aerospace Corporation (September 1975).

[6] H. Marsh, et al., Carbon 9, 159 (1971).

[7] J. S. Evangelides, High Pressure Working Group (1976).

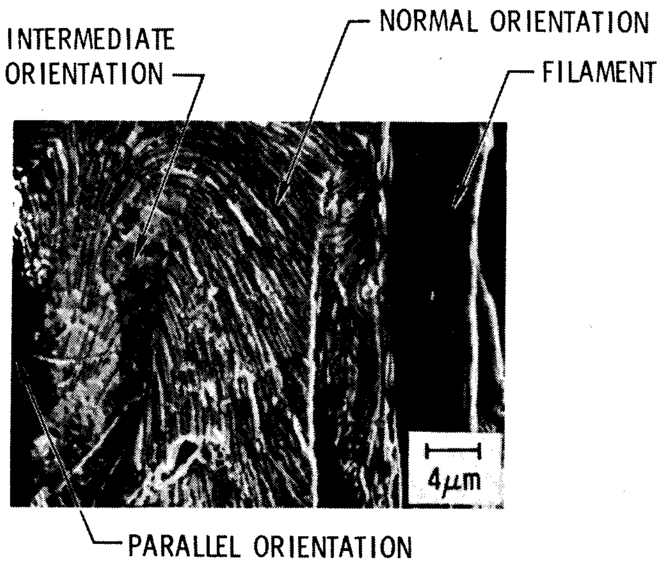

Fig. 1. Scanning electron micrograph of etch pattern orientations.

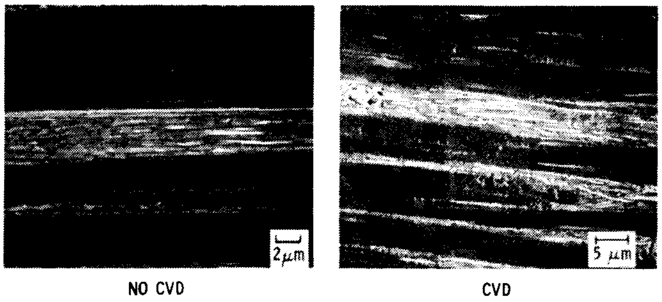

Fig. 2. Scanning electron micrographs of matrix structure due to low-pressure processing.

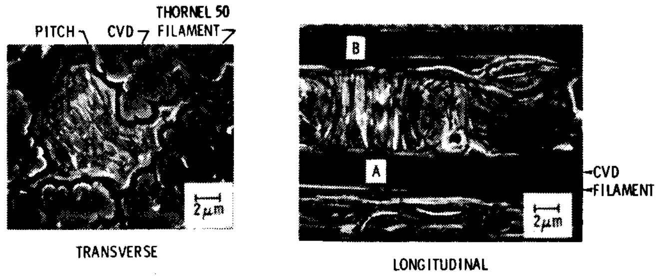

Fig. 3. Scanning electron micrographs of matrix structure due to high-pressure processing.

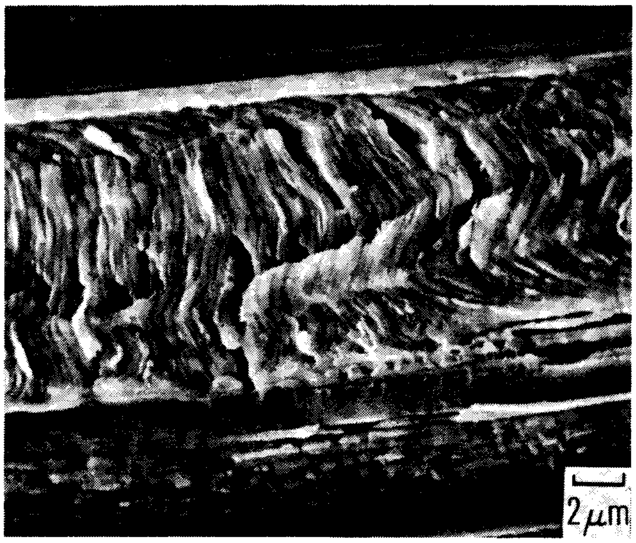

Fig. 4. Scanning electron micrograph of matrix structure due to high-pressure processing. No CVD.