DEVELOPMENT OF INTERFILAMENT MATRIX STRUCTURES IN CVD-INFILTRATED CARBON-CARBON

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Introduction

Some carbon-carbon composites have been processed by an initial infiltration with methane at low pressure to deposit pyrolytic (CVD) carbon on the fibers. When subsequently impregnated with coal tar pitch and baked at 100 MPa pressure, a graphite matrix is often formed within the bundles having basal planes perpendicular to the fiber direction. This structure, termed "transverse oriented graphite" (TOG)(1), provides an explanation for the lower values of thermal conductivity and elastic modulus in such composites, compared with identical materials in which the intrabundle matrix is primarily oriented with planes parallel to the fibers (POG). The TOG is readily identified by rotation of polished sections under plane polarized light, or by ion bombardment which etches cracks parallel to the basal planes. This presentation reviews observations made in connection with several programs relevant to the conditions required for TOG formation.

Origin of Transverse Oriented Graphite

The microstructures in several composites have been evaluated after the initial cycle of pitch impregnation and carbonization, using scanning electron microscopy and polarized light on polished sections. Supplementary information has been obtained from many billets after final processing. It has been observed that when a clean, high-modulus fiber preform is impregnated with pitch and carbonized under the same conditions as a CVD-infiltrated preform, TOG does not form next to the bare fibers. The pitch, and resulting mesophase, appear to wet the surfaces completely within the fiber bundles, and the primary matrix orientation is parallel to the filaments. Such composites, after final processing, may show some transverse structures in gaps filled in later cycles. Mesophase coating the broken ends of filaments can also develop planes transverse to the fiber bundle direction (parallel to the fractured surface).

When an isotropic CVD coating is applied, however, the only matrix in the bundles after the first cycle consists of nonwetting globules of mesophase, provided that fine particles present in the pitch have been filtered out by the preform; a fine-grained isotropic matrix may result if particles are present. The globules, characteristic of mesophase formation at high pressure, may contain a random orientation of planes in the final composite. This is more often the case if the gap between filaments is large, and if the CVD coating is relatively thick.

However, a standard CVD process has produced billets in which TOG has formed in the major portion of the initial globules within the fiber bundles. TOG formation frequently decreases near the surface, where the films are thicker, (1) and it may vary with location within some billets. Figure 1 illustrates such globules on the surface of coated bundles. Note that bladelike growths on the coated Thornel 50 have a transverse orientation, and appear to be wet by the droplets; most contact with the surface, however, has an angle greater than 90°. A variability in such "nucleating sites" in the coating is one hypothesis for the variability in TOG formation.

Changes during Successive Cycles

Several billets have been examined by excising samples after successive cycles. Figure 2 illustrates observations made on a 15-cm square section billet in which adjacent slabs were removed after each cycle at the Y-12 plant, Union Carbide Nuclear Division, Oak Ridge, Tenn. These were examined at GE-RESD. The amount of TOG present in the bundles increased, in subsequent cycles, with some variability due to exact differences in location.

The increase in TOG content is due primarily to filling cracks formed in the initial globules having the transverse orientation. Continuous TOG may be formed for long distances as a result. Parallel-oriented graphite, however, often develops on fibers which were not initially covered by the mesophase. The liquid in subsequent cycles wets these surfaces, in contrast to the first cycle.

Effects of Fiber and CVD Conditions

Minor changes in CVD conditions have not affected the amount of TOG formed in billets. However, changing conditions to produce a more anisotropic deposit resulted in no formation of TOG, and lower contact angles between the droplets and the surfaces. It has also been found that under similar deposition conditions, CVD coatings on fibers made from PAN (acrylic) or pitch precursors graphitize more readily than those on rayon-precursor Thornel 50, thus altering structure after the first graphitization.

Effects of Mesophase Formation Conditions

In autoclave runs where heater failures or other heating anomalies permitted the pressure to drop before the mesophase had stiffened, some of the matrix was removed from the material due to gas formation while the pitch was still liquid. Where a standard graphitization followed, involving a relatively high heating rate, the

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residual pitch carbonized at one atmosphere. No TOG formed under these conditions within the bundles, even if subsequent cycles were normal; the absence of globular structures in the bundles indicated that the CVD coating had been affected so as to permit wetting.

Conclusions

Formation of TOG requires (a) thin, isotropic coatings on the fibers which inhibit wetting by the pitch (or mesophase), (b) formation of mesophase at high pressures to produce globules within the bundles, and (c) a nucleus or other mechanism for formation of transverse molecular orientations within the globules, rather than a random orientation.

References

(1) R. H. McSwain and C. E. Bates (Southern Research Institute), AFML-TR-77-26, to be published.

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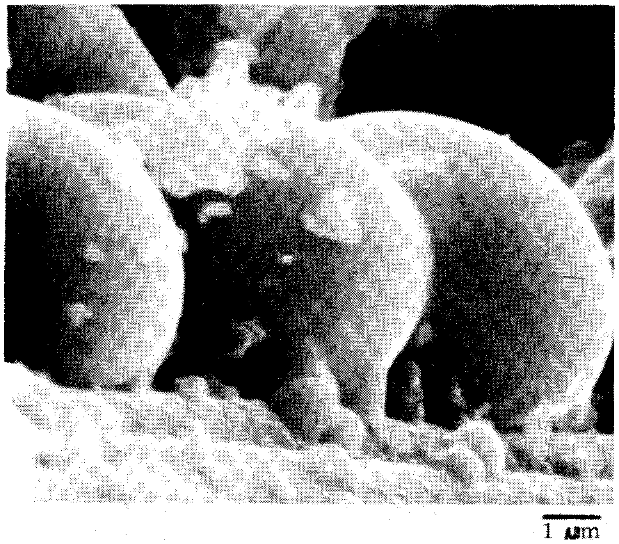

Fig. 1. Carbonized Mesophase Globules on the Surface of Thornel 50 Coated with CVD for 35 Hours at 1100°C; Note Transverse Oriented "Blades" on the Fiber Surface.

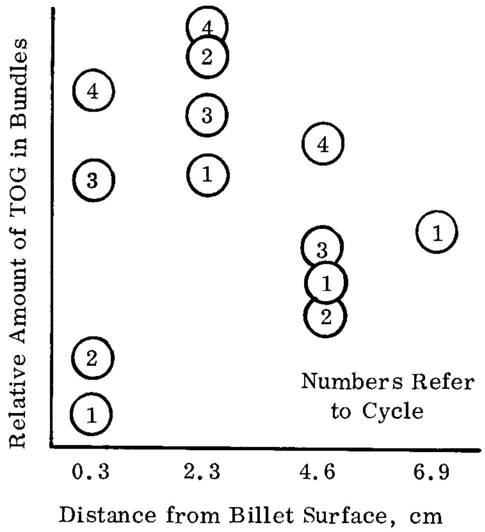

Fig. 2. Relative Amounts of TOG in Bundles of a 15 cm Square Section Billet after Successive Cycles of 100 MPa Carbonization to 650°C and Graphitization.