Exfoliation of Benzene-Derived Graphite Fibers

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<u>Abstract</u>. The exfoliation of bulk graphite produces volume increases of factors of >300. Previous attempts to exfoliate graphite fibers have met with limited success. Utilizing the unique microstructure of benzenederived fibers, we have achieved volume increases of factors ~150 upon exfoliation. These results and the underlying physics are reported.

Introduction

The application of a rapid heat pulse to graphite intercalation compounds above some critical temperature causes expansions by as much as two orders of magnitude along the c-axis direction. This phenomenon is called exfoliation and has been reported to occur in HOPG intercalated with many intercalants, such as Br2, HNO3-H2SO4, FeCl3-NH3 and SbCl5. However, attempts to exfoliate graphite fibers have had only limited success.¹ Only one report of fiber exfoliation is available in which a diameter increase by a factor of \sim 3 was attained, in this case using a pitch-based Union Carbide Thornel fiber.² Pitch-based fibers have a structure in which the basal planes are stacked such that the a-axis perpendicular to the fiber axis is oriented in the radial direction. This arrangement is not particularly convenient for expansion along the c-axis; in the case of pitch fibers, expansion could be expected to result in a "fanning-out" of the planes.

A more favorable geometry for exfoliation is found in the structure of BDF (benzene-derived fibers)³ where the basal planes are stacked like "rings of a tree", forming polygons centered around the fiber axis with the c-axis pointing in the radial direction (see Fig. 1). For this geometry the expansion can occur radially, thus maintaining the basic morphology of the fiber. In the present work the feasibility of significant exfoliation in fibers is demonstrated and new factors involved in the mechanism of exfoliation are discussed.

Experimental Details

Prior to exfoliation, BDF which were heat treated at 3000°C were intercalated. Intercalation with SbCls was carried out for two weeks at 160°C in a two-zone furnace with a small temperature difference between the zones. The diameter of these fibers was accurately determined using the SEM before and after intercalation.



Figure 1: SEM micrograph of a typical BDF cross section before intercalation.

Two different batches of fibers were used in these studies. The stage of the first group was calculated from the size increase. In the second group the stage was determined using TEM bright field images. Before measurement of the diameter in the intercalated fibers, the SbCl_s on the surface of the samples was removed by washing the fibers with a dilute solution of HCl. Following characterization of the batch of intercalated fibers, the fibers were exfoliated irreversibly by very rapid heating (~400°C/s) inside an open quartz tube.

Results and Discussion

Figure 1 shows a SEM micrograph of a BDF fiber which was heat treated at 3000°C. The picture reveals, not only the expected layered polygonal cross sectional structure of BDFs but also signs of non-uniformity around the fiber axis. Among the fibers from the first batch the measured diameters varied from 7 to 11μ m. In the second group of fibers the diameter ranged from 10 to 15μ m.

Figure 2 shows a fiber after intercalation. The basic structure of the fiber remains unchanged. For a typical fiber in the first group, the diameter increased from $\sim 10\mu m$ before intercalation to $\sim 31\mu m$ after intercalation, suggesting a stage 1 SbCl₅-GIC for which $(I_s/c_0) = 2.81$. It is interesting to note, that many of the intercalated fibers showed cracks along the fiber axis, which probably result from the fiber non-uniformity (see Fig. 1).

In the second group of fibers, the stage was characterized using lattice fringe images obtained with a high resolution TEM. Stages 2 and 3 were the predominant species among these fibers.

The exfoliation process takes place in the first second of the rapid heating process. An exfoliated fiber is shown in Figs. 3a and b (note that the c-axis is normal to the plane of the pictures). In the first batch of fibers the measured increase in volume amounted to a factor of ~15 in the case of the larger diameter fibers and a factor of 13-14 in the smaller (17-31 μ m) pre-exfoliated fibers. In the second group of fibers a factor of ~150 was obtained for the volume increase. The reasons behind this dramatic difference between the two batches of fibers are not yet understood. However the ratio of graphitized to disordered carbon is larger in the thicker fibers, where the disordered region is associated with the joining of two adjacent polygonal faces. We suggest that the well staged GIC exfoliated more completely than the disordered carbon.

Under higher magnification (Fig. 3b), a ridge and furrowlike structure is revealed, with dimensions in the range of 1μ m to 15μ m. This is suggestive of a very fast and explosive process that breaks the layers shown in Fig. 2. The characteristic dimensions of these structures are about one order of magnitude larger than the estimated platelet size (in-plane coherence lengths) for SbCl₅-GICs, which implies that the fractures occur at platelet boundaries.

A uniform radial expansion of the fiber is not observed upon exfoliation for several reasons, including non-uniformity of the fibers along their lengths and cross sections and spatial variations of the applied heat pulse on the fiber sur-



Figure 3: SEM micrograph of a BDF after exfoliation. (a)The magnification is 90X. The graphite c-axis is normal to the plane of the picture. (b)Same view magnified 2300X (see text).

face. These observations are consistent with an exfoliation process nucleated at the position of maximum thermal stress. Work is in progress to examine this phenomenon more quantitatively.



This work is supported by DOE Grant #DE-AC02-83ER45041. We are also grateful to Drs. M. Endo, G. Dresselhaus and K. Sugihara for valuable suggestions.

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Figure 2; SEM micrograph of a BDF after intercalation with SbCl₅ showing the polygonal cross sectional structure.