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Graphite Intercalation Compound With Iodine as the Major Intercalant

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ABSTRACT

Halogenated graphite CBr_xI_y ($1 < y/x < 10$) was made by exposing graphite materials with interplanar spacing in the 3.35 to 3.41 Å range to either pure Br_2 or an I_2-Br_2 mixture, and then to iodine vapor containing a small amount of Br_2. Electrical resistivity of this product is from 3 times to 6.5 times the pristine value. The presence of a small amount of isoprene rubber in the reaction significantly increased the iodine to bromine ratio in the product. In this reaction, rubber is known to generate HBr and to slowly remove bromine from the vapor. The halogenation generally caused a 22 to 25 percent weight increase. The halogens were found uniformly distributed in the product interior. However, although the surface contains very little iodine, it has high concentrations of bromine and oxygen. It is believed that the high concentrations of bromine and oxygen in this surface cause the halogenated fiber to be more resistant to fluorine attack during subsequent fluorination to fabricate graphite fluoride fibers.

INTRODUCTION

The reaction between graphite and iodine has been studied extensively for decades. It was concluded that iodine did not intercalate with graphite in the -78 to 950 °C temperature range (Ref. 1). However, iodine does react, very slowly, with the residue compound of bromine

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intercalated graphite (Refs. 2 and 3). This residue compound can be obtained by first brominating graphite in a bromine environment, and then debrominating the brominated product in ambient air for a long time.

The graphite materials used in these bromination-debromination reactions was natural graphite crystals. Whether graphitized carbon fibers behave the same as the natural graphite crystals in such reactions was not studied before. However, after exposing a bromine residue compound of graphitized carbon fibers to iodine at NASA Lewis Research Center, the product contained no iodine under SEM examination. Iodine intercalated graphitized carbon fiber, however, is desirable because such a product may lead to the following advances in science and technology:

(1) It may be electrically very conductive. The electrical resistivity of the graphitized carbon fibers decreases to 1/3 to 1/4 of the original (pristine) value after the process of fluorine intercalation (Ref. 4). It decreases to 1/5 of the pristine value after the process of bromine intercalation (Ref. 5). Therefore, based on the chemistry of halogens, iodine intercalated fibers might be expected to be more conductive than the bromine intercalated fibers.

(2) It may be very stable at high temperature. Fluorine intercalated fibers were found to be less thermally stable than bromine intercalated fibers, which are thermally stable at 200 °C (Refs. 4 and 5). Again, based on halogen chemistry, iodine intercalated fibers might be expected to be more thermally stable than bromine intercalated fibers.

(3) It may be a better intermediate product to produce graphite fluoride. Graphite fluoride made from fluorine intercalated fibers was found to be less electrically insulating, more fragile, and have more structural damage than those made from bromine intercalated fibers (Ref. 6). Again, based on halogen chemistry, the graphite fluoride made from the iodine intercalated fibers could be more electrically insulating, stronger, and less structurally damaged than those made from the bromine intercalated fibers.

(4) The process of iodine intercalation may reveal the mechanism of intercalation. Intercalation of iodine in graphite is difficult. Therefore, a successful process to intercalate iodine with graphite could reveal the important driving forces of graphite intercalation. Such information could be helpful in controlling the intercalation process in order to obtain the desired extent of intercalation, which, in turn, is needed in order to obtain the desired physical properties of the intercalated products.

This report describes several slightly different processes which successfully intercalate iodine into graphite materials. These products are then characterized. Their results and implications are also described in this report.

EXPERIMENTAL METHODS

The graphite materials used in this work include six different graphitized carbon fibers (Amoco P-55, P-75, P-100, and du Pont E-130, E-105, and E-55 with interplanar spacings of 3.43, 3.41, 3.37, 3.38, 3.42, and 3.43 Å, respectively), a Showa Denco experimental vapor grown fiber heat treated to 3000 °C, and highly oriented pyrolytic graphite (HOPG) from Amoco Inc. The products described in this report were characterizeded using electrical conductivity, weight, x-ray diffraction, SEM, and ESCA data.

A large number of intercalation experiments were performed in this work. The six sets of experiments described in the following paragraphs of this section are summarized in Tables 1 and 2. They were selected because they were typical, revealing, or unusual.

(1) The first set of experiments explored the possibility of achieving iodine intercalation after initiating the reaction with other chemicals, e.g., Br_2, HBr, or IBr. The aparatus is described in Fig. 1. A test tube plugged with an isoprene rubber stopper was used to contain Amoco P-100 fibers and two small vials. One of the vials contained a small amount of liquid bromine, isoprene rubber, and a small piece of nickel (99 percent pure). The other vial contained excess iodine.

This system was kept at room temperature for 15 min, and then at 75 °C for 3 days before removing the sample from the halogen environment and allowing it to stablize in ambient air. The rubber was in the system because it reacts with bromine to produce HBr, which, based on the intercalation mechanism proposed by Forseman (Ref. 7), could initiate the iodine intercalation reaction. Nickel was in the system because it was thought to be a catalyst for the rubber-bromine reaction. Another purpose of the rubber is to serve as a bromine sink because it reacts with bromine but not iodine. Therefore, the fibers in the test tube were in direct contact with mostly bromine and HBr at the beginning of the experiment, but with mostly iodine at the end of the experiment.

After the above described reaction, the fibers were examined by electrical resistivity and weight data. SEM was also used to examine the polished flat cross sections of strands of the iodinated fiber, which were embedded in an epoxy block. Results of this work suggested that iodine was uniformly distributed in the fibers. After these data were obtained, additional experiments were designed to study this reaction. They are described in the following paragraphs.

(2) The second set of experiments was performed to experimentally determine the effects of rubber and nickel in the iodination reaction described above. Two P-100 samples were treated by a process described in Table 1, which was similar to that described above, except that pure bromine (no nickel and no rubber) was used as the bromine source in one of the samples, and a bromine-rubber mixture was used (no nickel) as the bromine source in the other sample. Weight, electrical resistivity, and SEM-EDS data from these samples were obtained after the reactions. Results of these experiments indicated that the effects of nickel are not obvious, but the functions of rubber are indeed important, although more complicated than originally thought. Nickel, therefore, was not used in the later experiments.

(3) The third set of experiments was designed to study iodine intercalation in detail, and to produce iodine intercalated graphite products for detailed characterization. Four test tubes of reactants were treated by four different processes detailed in Table 2. Iodine intercalation reactions in these four tubes were initiated by exposing the graphite materials to, respectively, a room temperature rubber-bromine mixture for 2 hr, a room temperature rubber-bromine mixture for 1 hr, a 75 to 120 °C bromine-(excess)iodine mixture, and a 75 to 120 °C rubber-bromine-(excess)iodine mixture. The four test tubes were then heated and kept at 120 °C for 7 days, during which time the bromine reacted with rubber, and solid iodine in the test tubes evaporated and was in direct contact with the graphite materials. After 7 days of 120 °C iodination, the test tubes were cooled to near room temperature in 15 min. The fiber samples were then removed from the test tube and allowed to stablize in ambient air.

Every tube contained three different graphite materials: Amoco Inc. P-100 fibers, vapor grown carbon fibers treated to 3000 °C, and HOPG. All four test tubes were sealed with rubber stoppers, but the rubber stopper for the third tube was protected by layers of Teflon tape in order to minimize the rubber effects.

SEM-EDS and weight data were determined for all samples. X-ray diffraction data were obtained from all but two damaged HOPG products. Electrical resistivity was measured for all pitch based fibers. ESCA data were obtained for one of the pitch based fiber products and one of the vapor grown fiber products.

(4) The fourth set of experiments was performed to determine whether rubber in this reaction can be replaced by iron powder. The function of iron powder was thought to be similar to that of rubber because both react with bromine but are inert to iodine. However, these two materials function differently in that the iron-bromine reaction is faster, more complete, and does not produce HBr.

Two samples of du Pont E-130 graphitized carbon fibers were iodinated by a process detailed in Table 1. The two samples were treated by the same process, except that one used rubber to remove bromine vapor, and the other used iron powder to remove bromine vapor during the reaction. The fiber products were then examined by weight, conductivity, and SEM-EDS data.

(5) The fifth set of experiments, also described in Table 1, was to determine whether the intercalants already in graphite can be replaced by intercalants surrounding the graphite. Two experiments were conducted for this purpose. In the first experiment, an iodine and bromine intercalated fiber made from P-100, $CBr_{0.0168}I_{0.0120}$, was iodinated by exposure to vapor containing bromine and excess iodine at 100 °C. In the second experiment, identical iodine and bromine intercalated fibers were brominated by exposure to saturated bromine vapors at room temperature. After the reactions, the weight and SEM-EDS data were used to determine whether iodine and bromine content in the fiber products increased, did not change, or decreased during the reaction.

(6) The sixth set of experiments, also described in Table 1, was to determine if it is possible to iodinate carbon fibers less graphitized than P-100 fibers. Amoco P-55, P-75, du Pont E-105, and E-55 were used in this set of experiments. The weight data and SEM were used to detect the presence of iodine and bromine in the fibers after the reactions.

RESULTS AND DISCUSSION

(1) In the first set of experiments (in which P-100 fibers were first reacted with a bromine, rubber, and nickel mixture before reacting with iodine at 75 °C), the color of the vapor in the test tube was at first orange, then turned to a reddish brown color similar to that of iron rust, and finally became purple. This indicates that the majority of vapor was at first bromine, then an iodine-bromine mixture, and finally iodine. The product was 22.3 percent heavier than the pristine fiber and had electrical resistivity of 100 $\pm$ 20 $\mu\Omega$-cm. In comparison, bromine

intercalated P-100 fibers are typically 18 percent heavier than pristine, with resistivities of 80 $\mu\Omega$-cm. It is noted that the particular pristine P-100 used in this work had a resistivity value of 440 $\mu\Omega$-cm. A typical SEM micrograph of the polished flat cross sections of the iodinated product embedded in epoxy is shown in Fig. 2(a). The EDS (energy disperse spectrum) data on both the inner 2 μm and the outer 2 μm (right underneath the fiber surface) of one of the fiber cross sections are also shown (Figs. 2(a) and (b)). Comparison of the iodine and bromine peaks leads to the conclusion that both iodine and bromine are uniformly distributed in the interior of the fiber. The atomic iodine to bromine ratio was 3.46 as determined by the quantitative Kevex software package. Therefore, the empirical formula of this intercalated fiber is $CBr_{0.0052}I_{0.018}$.

(2) In the second set of experiments, the same experiments as those in the first set of experiments, but without the presence of nickel and/or rubber, were conducted. It was observed that the process and product of these reactions were similar whether the nickel was in the liquid bromine or not. However, under the conditions described in Table 1, if there was no rubber in the liquid bromine, the color of the vapor turned reddish brown and never became purple, and bromine became the major intercalant in the product. In this case the bromine to iodine ratio was determined by EDS as 57:43. This ratio is similar to the 55:45 ratio obtained from IBr intercalation with graphite (Ref. 8).

(3) The third experiment involved characterization, using mass, electrical resistivity, SEM, ESCA, and x-ray diffraction data, on 12 samples obtained from treating three different kinds of graphite materials by four different kinds of processes. Because of the large number of data, not all data points are included in this report. The followings are the important findings from this experiment:

It was visually observed that no graphite materials were intercalated with iodine without being wetted by the intercalants containing bromine at the beginning of the initiation reaction. Such wetting did not happen in many experimental runs similar to those described in this set of

experiments, especially in the cases in which the fiber temperatures were kept high at all times when exposed to bromine and iodine. This result agrees with the intercalation mechanism suggesting that adsorption of intercalants by the graphite materials is the first step of intercalation reaction.

The surfaces of both iodinated P-100 and iodinated vapor grown fibers which were exposed to a 75-120 °C iodine-Br (with rubber) mixture during intercalation initiation were studied. These samples were from the fourth test tube described in Table 2. The ESCA data were taken 3 months after the products were made (Ref. 9). The chemical compositions of these fiber surfaces are described in Table 3. For comparison, the bulk chemical composition of these fibers calculated from the bromine to iodine ratio data from EDS and mass gain data are also included in this table. They indicated that both samples had very high concentrations of bromine and oxygen, but very low concentrations of iodine on the surfaces. The surface bromine concentration was so high that it was similar to that of stage 2 bromine intercalated graphite. The surface oxygen concentration was so high that it was similar to that of graphite oxide.

The low iodine concentration on the iodinated fiber surface is comparable to the low bromine concentration on the brominated fiber surface. However, the high bromine and oxygen concentration on the iodine intercalated fiber surfaces is in contrast to the near-zero intercalant concentration on the bromine intercalated fiber surfaces (Ref. 10). Knowing intercalation improves graphite's ability to withstand fluorine gas attack (Ref. 11), this phenomenon has the implication that the high temperature reaction between bromine intercalated fibers with fluorine gas will result in extensive fiber surface damage, but that between iodine intercalated fibers and fluorine gas will not. This was verified experimentally and is described in Fig. 3. Also, the high intercalant concentration on the fiber surface could strengthen the fiber-epoxy interface. This, however, needs to be confirmed experimentally.

The ESCA data also indicated that there were two different electronic states for the bromine on the surface.

The x-ray diffraction data for the iodinated P-100 fibers did not show new peaks. However, after the reaction the graphite interplanar spacings increase from 3.37 to 3.42±0.02 Å. This compares to the 3.37 to 3.39 Å increase during bromine intercalation of P-100 fibers. No such increase in interplanar spacing of vapor grown fibers was observed. It remained unchanged at 3.35 Å. However, a small new peak near 2.0 Å D spacing was found for all iodinated vapor grown fiber. This indicates some superlattice structure in vapor grown fibers. The x-ray diffraction of HOPG after bromine and iodine reaction, on the other hand, is complicated. It showed a large number of new peaks. This indicates a possible mixed-stage product with bromine, iodine, and iodine bromide as intercalants.

The weight data were monitored after the samples were removed from the halogen enviornment. After 39 days of room temperature air exposure, total halogen to carbon weight ratios were estimated and listed in Table 2. This table also includes the bromine to iodine ratio estimated from the EDS data.

The EDS data from SEM indicated that all samples contained more iodine atoms than bromine, except for the vapor grown fibers and the HOPG intercalated with minimum exposure to rubber. Such effects of rubber on the I/Br ratio in P-100 fibers, however, cannot be found.

It was later on observed that the large I/Br ratio of 9.2 shown in Table 2 is typical for highly graphitized pitch based carbon fibers, e.g., Amoco P-100 and Du Pont E-130, simultaneously brominated and iodinated in 75 to 160°C range. This ratio decreases if the fibers were first brominated before the simultaneous bromination and iodination.

The resistivity of the fibers before the iodination reaction was 440 $\mu\Omega$-cm. After the iodination reaction, this value became 67 $\mu\Omega$-cm if a minimum amount of rubber was present during the reaction, and 73 $\mu\Omega$-cm if a larger amount of rubber was present during the reaction.

In the second set of experiments described earlier, the electrical resistivity value of the iodinated fibers was 100 $\mu\Omega$-cm if no rubber was present during the reaction, and 150 $\mu\Omega$-cm if excess rubber was present during the reaction.

The results described in the above paragraph indicated that iodine intercalated fibers with very low bromine content can have lower electrical resistivity than the bromine intercalated fibers. For example, the iodine intercalated P-100 obtained from the process using minimum rubber, $CBr_{0.00333}I_{0.0248}$, has electrical resistivity of 67$\mu\Omega$-cm (6.5 times of pristine value), but a bromine intercalated fiber, $CBr_{0.028}$, has electrical resistivity value of 85$\mu\Omega$-cm (5 times the pristine value). This phenomenon suggests that, with proper help from the isoprene rubber, the charge transfer between iodine and carbon in graphite could be greater than the charge transfer between bromine and carbon in graphite.

The weight of the iodinated vapor grown fibers was monitored for 2 months following intercalation, and it was concluded to be unchanged since removal from the halogen environment and placed in the room temperature air, with no mechanical disturbance. The same was observed for HOPG after 21 months of weight monitoring. The iodinated P-100, on the other hand, lost weight gradually but continuously. It was later observed that the halogen to carbon weight ratio of the iodinated P-100 stablized at 21 percent after 1 week of heating at 100 °C air.

The color of the vapors in all test tubes described in this set of experiments changed from orange to reddish brown to purple. This change seemed to near completion in 1 hr for all test tubes except the one where the rubber effects were minimized by wrapping Teflon tape on the rubber stopper (6 hrs for this particular run). The rubber effects were obvious in that the vapor color changes began at the top part of the test tubes, where the rubber stopper was located, and then spread to the bottom part of the tube.

(4) In the fourth set of experiments, after 2 hr of reaction, iron powder was added to the 100 °C test tube containing Du pont E-130 graphitized carbon fibers, bromine, and iodine, but

no rubber. The vapor turned from orange to purple which characterizes pure iodine vapor in a few minutes. From EDS data and weight analysis, the iodinated E-130 product from this reaction was found to contain 20.2 wt% of iodine and 0.80 wt% of bromine. These are somewhat different from the 23.2 and 3.2 percent, respectively, for the other E-130 sample which went through the same process in the presence of rubber but no iron. The large difference between these two samples, however, is their electrical resistivity. The values were 207 $\mu\Omega$-cm if iron was used, and 89 $\mu\Omega$-cm if rubber was used. Again, the resistivity was 440 $\mu\Omega$-cm before the reaction.

It appears that, after the intercalation reaction is initiated by bromine and/or iodine bromide, iodine is able to enter the graphite, but is not able to have charge transfer to/from the graphite without the help of a small amount of bromine.

The results obtained in this experiment suggest that, for the reaction described in this report, iodine first enters the fibers' surface, then experiences charge transfer from/to the graphite. The "entering" process needs to be initiated by a small amount of bromine, but can continue to progress in pure iodine after it is initiated. The charge transfer between iodine and graphite, however, could not be completed without the presence of bromine and/or IBr.

(5) In the fifth set of experiments described in Table 1, after treating a residue compound of P-100, $CBr_{0.0168}I_{0.0120}$, with a small amount of liquid bromine and a large amount of solid iodine, the fibers became $CBr_{0.0126}I_{0.0192}$. Also, after treating the same kind of fibers with saturated bromine vapor at room temperature for 30 hr, the fibers became $CBr_{0.0275}I_{0.0063}$. From these compositions, it is clear that in both bromination and iodination processes, both halogen addition and halogen substitution reactions took place. However, the electrical resistivity differences between the reactant residue compound and the product residue compounds were small, indicating that the total number of carbon-halogen charge transfers changed very little during the reactions.

(6) In the sixth set of experiments, attempts were made to iodinate carbon fibers less graphitized than P-100 or E-130. Numerous experiments were conducted using the method described in this report. It was observed that the process and products of P-75 iodination are very similar to those of P-100. However, iodination of Amoco P-55, du Pont E-105 and E-55 resulted only in a very low concentration of halogen (<5 percent). It may be possible to iodinate a bromine residue compound of P-55, which contains 13.5 percent bromine (Ref. 12). This, however, was not tried. This result suggests that iodine intercalation is possible only when the degree of graphitization of the carbon fibers is higher than a certain minimum, which is close to that of the Amoco P-75.

CONCLUSIONS

Graphite intercalation compounds with iodine as the major intercalant were fabricated. The graphite materials used for this purpose need to be at least as graphitized as Amoco P-75, whose interplanar spacing is 3.41 Å. The fabrication process involves exposing the graphite to the vapors from two vials containing a bromine-isoprene rubber mixture and iodine, respectively. The vapor, a Br_2/HBr/IBr mixture, initiates the intercalation reaction. The graphite materials are then exposed to iodine vapor containing a small amount of Br_2/HBr/IBr to complete the intercalation reaction. A small amount of rubber in this vaporous mixture helps to produce HBr vapor, and remove bromine from the vapor. During the intercalation reaction, the intercalant enters the graphite structure to either take a new site or replace an old intercalant.

The halogenated graphitized carbon fibers P-100 thus formed were found to lose weight slowly, but stablized after 100 °C air heating for 1 week, resulted in a product 21 percent heavier and 3 to 6.5 times more conductive than the pristine P-100 fibers. The halogenated HOPG and vapor grown fibers, on the other hand, were stable after gaining 16 to 30 wt% during intercalation and exposure to ambient air for a few minutes.

Iodine and bromine concentration distributions in the fibers appear to be uniform. The atomic iodine to bromine ratio was estimated to be in the 1.6 to 9.2 range. Higher values for this ratio were obtained from the runs which were initiated by bromine/iodine/IBr vapor mixture.

The ESCA data indicated that the chemical composition at the fiber surface was very different from that at the fiber interior. At the surface, the oxygen and bromine concentrations are high (atomic ratios to carbon were 1:3.0 and 1:9.1, respectively), but the iodine was barely detectable. Similar ESCA results were observed at the surfaces of vapor grown fibers.

The x-ray diffraction data on P-100 fibers indicated that intercalation causes an increase in the interplanar spacings from 3.37 to 3.42 Å, but no new peaks. However, x-ray diffraction of vapor grown fibers showed a new peak at D = 2.0 Å; the diffraction pattern of HOPG showed a large number of new peaks, possibly indicating a mixed stage product containing bromine, iodine, and iodine bromide.

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TABLE 1.—SUMMARY OF EXPERIMENTS DESCRIBED IN THIS REPORT

Experiment	Experimental set							
	I	II		IV[a]		V		VI
	Experiment run							
	1	1	2	1	2	1	2	1-4
Reactants in test tube at beginning of initiation reaction[b]								
In first vial	Bromine, rubber[c] nickel (99%)	Bromine	Bromine, rubber	Bromine	Bromine	Bromine	Bromine	Bromine, rubber
In second vial	Iodine[d]	None	None	None	None	Iodine[d]	None	Iodine[d]
Fibers	P-100	P-100	P-100	E-130	E-130	$CBr_{0.017}I_{0.012}$	$CBr_{0.017}I_{0.012}$	(e)
Stopper material	Rubber[c]	Glass	Rubber	Rubber	Glass	Rubber	Rubber	Rubber
Reactants added to test tube after initial reactions								
In separate vials	None	Iodine[d]	Iodine,[d] rubber,[f] bromine	Iodine[d]	Iodine, (2 hr later), iron powder	Rubber	None	None
Reaction temperature histogram								
During initiation reaction	RT,[g] 15 min	RT, overnight	RT, overnight	RT, overnight	RT, overnight	RT, 7 days	RT, 30 hr	RT to 100 °C, 1 hr
After initiation reaction	75 °C, 3 days	110 °C, 72 hr	110 °C, 72 hr	(h)	(h)	100 °C, 2 days	----------	100 °C, 4 days
Treatment after intercalation reaction								
	RT, air	(i)	(i)	RT, air	RT, air	(j)	RT, air	RT, air

[a]Experiment set III is described in Table 2.
[b]Every test tube contained graphitized carbon fibers and two vials, which contained chemicals for the intercalation reactions (Fig. 1).
[c]Isoprene rubber was the material for rubber stopper and extra rubber added to the system.
[d]There will be iodine left after the reaction is 100 percent complete.
[e]The fibers included Amoco P-55, P-75, Du Pont E-55, and E-105.
[f]Bromine and rubber were in the same vial.
[g]Room temperature.
[h]90-105 °C for 65 hr; except accidental overnight heating to 160 °C.
[i]70 °C in air for 90 hr then RT in air.
[j]200 °C for 15 min then RT in air.

TABLE 2.—CHEMICAL COMPOSITION AND ELECTRICAL RESISTIVITY OF CB_rI_y PRODUCED FROM DIFFERENT PROCESSES AND DIFFERENT GRAPHITE MATERIALS

Process				
Rubber in bromine vial	Yes	Yes	No	Yes
Rubber stopper	Yes	Yes	Minimum[a]	Yes
First step:				
Iodine vial	Yes	Yes	Yes	Yes
Bromine vial	Yes	Yes	No	No
Temperature	RT[b]	RT	75 °C	75 °C
Time, (hr)	2	1	16	16
Second step:	Yes	Yes	Yes	Yes
Iodine vial	Yes	Yes	Yes	Yes
Bromine vial				
Temperature histogram:	1 hr, 5 hr	1 hr, 5 hr	0, 5 hr	0, 5 hr
RT→75 °C, 75°C→120 °C	7 days	7 days	7 days	7 days
120 °C	15 min	15 min	15 min	15 min
120 °C→RT				
Iodine-to-bromine atomic ratio				
P-100 (D = 3.37 Å)	1.59	3.72	7.44	9.18
Vapor-grown fibers (HTT = 3000 °C, D = 3.35 Å)	2.64	2.26	0.77	1.84
HOPG (ZYX, D = 3.35 Å)	1.78	1.85	0.97	1.52
Total halogen-to-carbon weight ratio				
P-100 (D = 3.37 Å)	0.273	0.265	0.284	0.292
Vapor-grown fibers (HTT = 3000 °C, D = 3.35 Å)	0.156	0.130	0.274	0.304
HOPG (ZYX, D = 3.35 Å)	0.242	0.241	0.242	0.237
Electrical resistivity ($\mu\omega$cm)				
P-100 (D = 3.37 Å (440 $\mu\Omega$cm before halogenation)	72	82	67	73

[a]Teflon tape was used to wrap the rubber stopper used in this experiment.
[b]Room temperature.

TABLE 3.—APPROXIMATE CHEMICAL COMPOSITION ON SURFACE AND IN BULK OF GRAPHITE FLUORIDE FIBERS

Element	Surface concentration, percent	Bulk concentration, percent
$CBr_{0.0116}I_{0.0214}$ from vapor-grown fibers (interplanar spacing, 3.35 Å)		
C	78	97
O	18	0
Br	4	1
I	.1	2
$CBr_{0.00281}I_{0.0258}$ from P-100 (interplanar spacing, 3.37 Å)		
C	69	97
O	23	0
Br	8	.3
I	.05	3

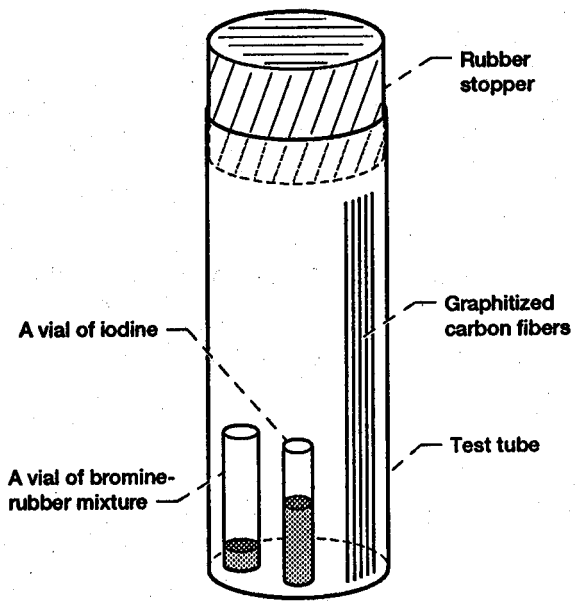
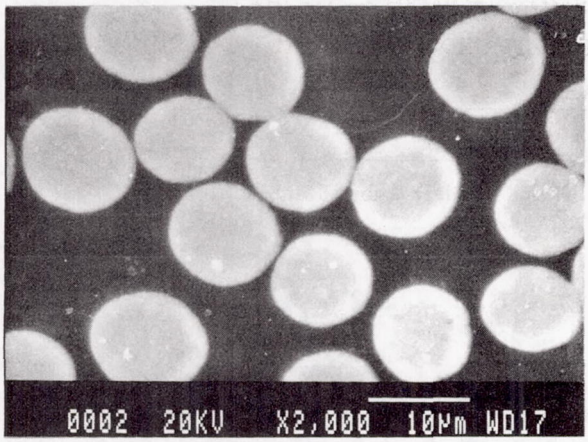
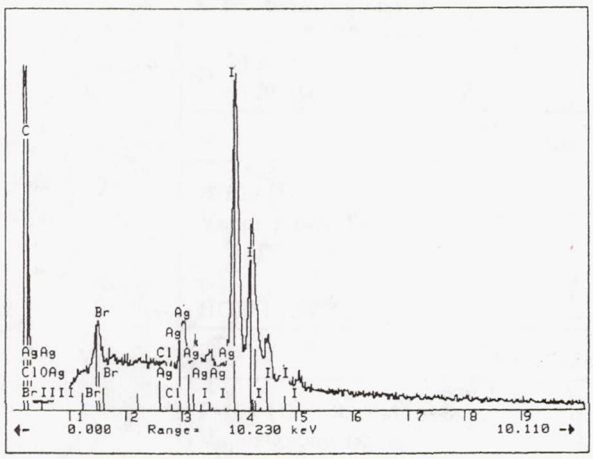


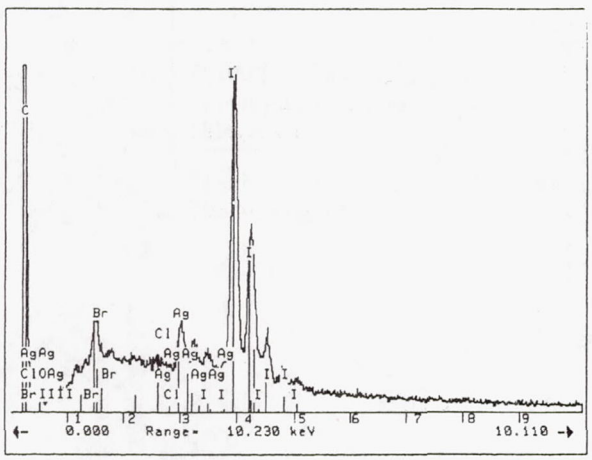
Figure 1.—Apparatus for iodine intercalation of graphite.



(a) Cross sections.

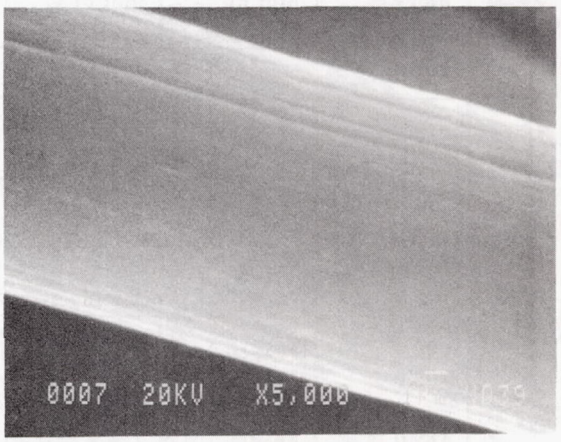


(b) EDS near the center of a fiber cross section.

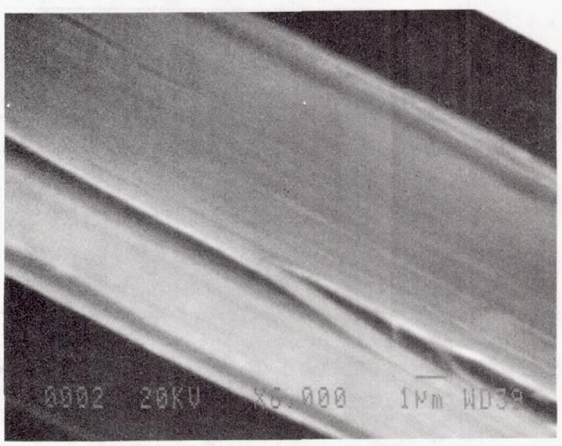


(c) EDS near the surface of a fiber cross section.

Figure 2.—SEM data from iodine intercalated graphitized carbon fibers.



(a) From fluorination of iodine intercalated P-100.



(b) From fluorination of bromine intercalated P-100.

Figure 3.—SEM micrographs of graphite fluoride fibers.

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13. ABSTRACT ***(Maximum 200 words)***

Halogenated graphite CBr_xI_y ($1<y/x<10$) was made by exposing graphite materials with interplanar spacing in the 3.35 to 3.41Å range to either pure Br_2 or an I_2-Br_2 mixture, and then to iodine vapor containing a small amount of Br_2. The presence of a small amount of isoprene rubber in the reaction caused the electrical resistivity of the product to increase from 4 times to 6.5 times the pristine value. It also significantly increased the iodine to bromine ratio in the product. In this reaction, rubber is known to generate HBr and to slowly remove bromine from the vapor. The halogenation generally caused a 22–25% weight increase. The halogens were found uniformly distributed in the product interior. However, although the surface contains very little iodine, it has high concentrations of bromine and oxygen. It is believed the high concentrations of bromine and oxygen in this surface cause the halogenated fiber to be more resistant to fluorine attack during subsequent fluorination to fabricate graphite fluoride fibers.

14. SUBJECT TERMS

Intercalation; Iodine; Graphite; Fiber surface

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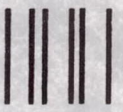

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