



0008-6223(94)00093-X

## GRAPHITE INTERCALATION COMPOUND WITH IODINE AS THE MAJOR INTERCALATE

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(Received 8 February 1994; accepted in revised form 25 July 1994)

**Abstract**—Halogenated graphite  $\text{CBr}_x\text{I}_y$  ( $1 < y/x < 10$ ) was made by exposing graphite materials to either pure  $\text{Br}_2$  or an  $\text{I}_2/\text{Br}_2/\text{HBr}$  mixture to initiate the reaction, and then to iodine vapor containing a small amount of  $\text{Br}_2/\text{HBr}/\text{IBr}$  to complete the intercalation reaction. Wetting of the graphite materials by the  $\text{I}_2/\text{Br}_2/\text{HBr}$  mixture is needed to start the reaction, and a small amount of  $\text{Br}_2/\text{HBr}/\text{IBr}$  is needed to complete the charge transfer between iodine and carbon. The interplanar spacings for the graphite materials need to be in the 3.35 to 3.41 Å range. The X-ray diffraction data obtained from the halogenated HOPG indicate that the distance between the two carbon layers containing intercalate is 7.25 Å. Electrical resistivity of the fiber product is from 3 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  $\text{HBr}$  and to slowly remove bromine from the vapor. The halogenation generally caused a 22% to 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 that the high concentrations of bromine and oxygen in this surface cause the halogenated fiber to be more resistant to structural damage during subsequent fluorination to fabricate graphite fluoride fibers.

**Key Words**—Iodine intercalation, intercalation mechanism, halogen exchange, surface composition.

### 1. 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  $950^\circ\text{C}$  temperature range[1]. However, iodine does react, very slowly, with the residue compound of bromine-intercalated graphite[2,3]. 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 material used in the above-described bromination-debromination reactions was natural graphite crystals. Whether graphitized carbon fibers behave the same as the natural graphite crystals in such reactions has not been studied. However, after exposing a bromine residue compound of graphitized carbon fibers to iodine at NASA Lewis Research Center, the product contained no iodine under EDS (energy dispersive spectroscopic) examination. Iodine-intercalated graphitized carbon fiber is desirable, however, 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[4]; it decreases to 1/5 of the pristine value after the pro-

cess of bromine intercalation[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  $200^\circ\text{C}$ [4,5]. 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 for exposure to high-temperature fluorine 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 that made from bromine-intercalated fibers[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 for intercalating iodine with graphite could reveal the important driving forces of graphite intercalation. Such information could be helpful in controlling the intercalation process to obtain the desired extent of intercalation which, in turn, is needed in order to obtain the desired physical properties of the intercalated products.

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In this research, the intercalation mechanism proposed by Foreman[7] was used as the beginning point in designing the experiments to explore the possibility of quick and massive iodine intercalation. In general, this mechanism suggests that introduction of hydrogen halide could initiate the halogen intercalation reaction. In particular, this research introduced HBr, which was generated by the reaction of sufficient quantity of isoprene rubber and bromine, to a system where graphitized carbon was directly exposed to iodine vapor. The rubber is inert to iodine, but, it reacts to bromine slowly and completely, eventually leaving the graphitized carbon in the system exposed directly to only HBr and  $I_2$ .

Several slightly different processes based on that described above were found to successfully intercalate iodine into graphite materials. These products are then characterized; their results and implications are also described in this report.

## 2. EXPERIMENTAL

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 Denko 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 characterized using electrical conductivity, weight, X-ray diffraction, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and electron spectroscopy for chemical analysis (ESCA).

For a typical experiment, the apparatus is described in Fig. 1: a test tube plugged with isoprene rubber, used to contain graphitized carbon, and two small vials. One of the vials contained a small amount of liquid bromine and isoprene rubber, and the other vial

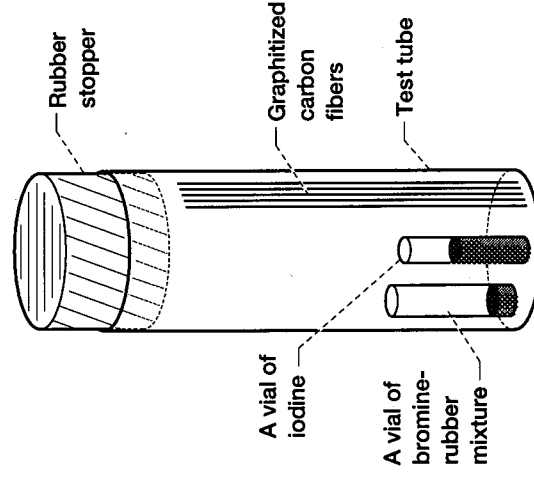


Fig. 1. Apparatus for iodine intercalation of graphite.

contained excess iodine. The chemical elements of the isoprene rubber used in this research were analyzed by EDS, and show the presence of small amounts of O, Na, Mg, Si, S, and Ca in the rubber.

The system described above was, in general, left at room temperature for 0 to 10 days and then heated from 75 to 120°C for 2 to 7 days. The room-temperature period was designed to allow HBr to be generated and the intercalation to be initiated. The high-temperature period was designed to allow iodine to be intercalated, and to allow the intercalated bromine, which entered the carbon materials during the room-temperature period, to be replaced by iodine.

The experimental procedure described above consistently resulted in intercalated carbon products with iodine as the major intercalate. Furthermore, the intercalate was found to be uniformly distributed in the interior of the carbon material. This is demonstrated in Fig. 2. This figure shows the data of SEM and EDS examination on different regions of the polished flat cross-sections of a strand of iodinated carbon fibers, which were embedded in an epoxy block.

A large number of intercalation experiments were performed in this work. The experiments described in the following paragraphs of this section are summarized in Tables 1 and 2. They were selected because they were either revealing or unusual. The purposes of these experiments are stated as the titles of the following sections.

### 2.1 Rubber effects demonstration

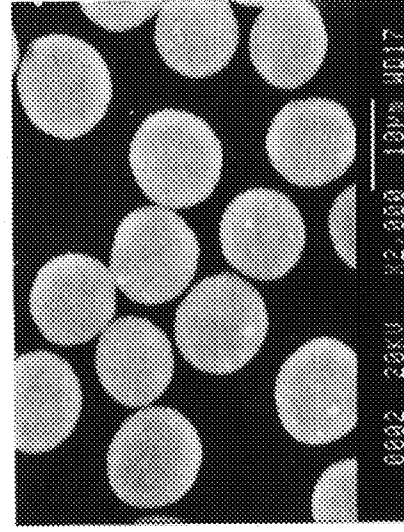
Two P-100 samples were treated by a process described in Table 1 and Fig. 1. Pure bromine (no rubber) was used as the bromine source in one of the samples, and a bromine-rubber mixture was used as the bromine source in the other sample. Weight, electrical resistivity, SEM, and EDS data from these samples were obtained after the reactions.

It was observed that 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 intercalate in the product ( $CBr_{0.0146}I_{0.0111}$ ). In this case, the electrical resistivity of the fiber product was 140  $\mu\Omega$ -cm, and the bromine to iodine ratio was similar to the 55:45 ratio obtained from IBr intercalation with graphite[8].

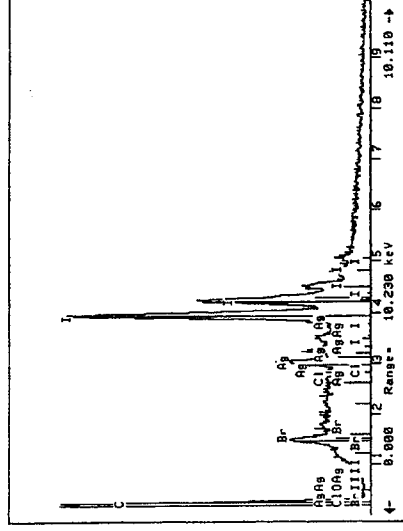
On the other hand, if there was rubber in the liquid bromine, the color of the halogen vapor in the test tube was at first orange, then turned to reddish brown, and finally became purple. This indicates that the majority of the vapor was at first bromine, then an iodine-bromine mixture, and finally iodine. The product was estimated to be  $CBr_{0.0054}I_{0.0193}$ . It had electrical resistivity of 120  $\mu\Omega$ -cm. In comparison, bromine-intercalated P-100 fibers are typically  $CBr_{0.025}$ , with resistivity of 80  $\mu\Omega$ -cm, and the pristine P-100 used in this work had a resistivity value of 440  $\mu\Omega$ -cm.

### 2.2 Iron powder as a rubber substitute

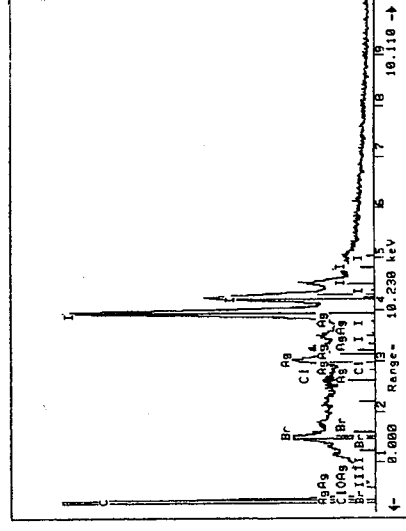
This set of experiments was performed to determine whether rubber in this reaction can be replaced



(a) Cross sections.



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



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

Fig. 2. SEM data from brominated and iodine-intercalated graphitized carbon fibers; (a) cross-sections, (b) EDS near the center of a fiber cross-section, (c) EDS near the surface of a fiber cross-section.

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 I. 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.

After iron powder was added to the test tube containing graphitized carbon fibers, bromine, and iodine, but no rubber, the vapor turned from orange (bromine) to purple (iodine) 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 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  $207 \mu\Omega\text{-cm}$  if iron was used, and  $89 \mu\Omega\text{-cm}$  if rubber was used. Again, the resistivity was  $440 \mu\Omega\text{-cm}$  before the reaction.

It appears that, after the intercalation reaction is initiated, 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, HBr or IBr.

The results obtained in this experiment suggest that, for the reaction described in this report, iodine first enters the fiber surface, then experiences charge transfer from/to the graphite. The "entering" process needs to be initiated by a small amount HBr 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 HBr, and/or IBr.

### 2.3 Halogen exchange during intercalation

This set of experiments, also described in Table 1, was to determine whether the intercalates already in graphite can be replaced by intercalates surrounding the graphite. Two experiments were conducted for this purpose. In the first experiment, an iodine- and bromine-intercalated fiber made from P-100,  $\text{CBr}_{0.0168}\text{I}_{0.0120}$ , was iodinated by exposure to vapor containing bromine and excess iodine at  $100^\circ\text{C}$ . In the second experiment, the same  $\text{CBr}_{0.0168}\text{I}_{0.0120}$  fibers were brominated by exposure to saturated bromine vapors at room temperature. In both experiments, rubber stoppers were used to seal the test-tube reactors.

After treating this fiber with a small amount of liquid bromine and a large amount of solid iodine, the fibers became  $\text{CBr}_{0.0126}\text{I}_{0.0192}$ . After treating the same kind of fibers with saturated bromine vapor at room temperature for 30 hours, the fibers became  $\text{CBr}_{0.0275}\text{I}_{0.0063}$ . From these compositions, it is clear that in either the bromination or iodination process, 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, indicat-

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

Table 1. Summary of experiments described in this report (Section 2.1 to 2.4)<sup>a</sup>

Section Number		Experiment									
Section	Experiment	Section 2.1		Section 2.2		Section 2.3		Section 2.4			
		Experiment Run 1	Experiment Run 2	Experiment Run 1	Experiment Run 2	Experiment Run 1	Experiment Run 2	Experiment Run 1-4	Experiment Run 1-4		
Reactants in test tube at beginning of initiation reaction <sup>b</sup>	In first vial	Bromine	Bromine, rubber <sup>c</sup>	Bromine	Bromine	Bromine	Bromine	Bromine	Bromine, rubber <sup>c</sup>		
	In second vial	None	None	None	None	None	None	None	Iodine <sup>d</sup>		
Fibers	Stopper material	P-100	Rubber	E-130	Rubber	CB <sub>0.017</sub> I <sub>0.012</sub>	CB <sub>0.017</sub> I <sub>0.012</sub>	CB <sub>0.017</sub> I <sub>0.012</sub>	Rubber		
Reactants added to test tube after initial reactions		Iodine <sup>d</sup>	Iodine, <sup>d</sup> rubber, <sup>f</sup>	Iodine <sup>d</sup>	Iodine (2 hr later), iron powder	Rubber	Rubber	Rubber	None		
In separate vials		Iodine <sup>d</sup>	Iodine, <sup>d</sup> rubber, <sup>f</sup>	Iodine <sup>d</sup>	Iodine (2 hr later), iron powder	Rubber	Rubber	Rubber	None		
Reaction temperature histogram		During initiation	RT, <sup>g</sup> overnight	RT, overnight	RT, overnight	RT, 7 days	RT, 30 hr	RT to 100°C, 1 hr	RT, 4 days		
After initiation reaction		110°C, 72 hr	110°C, 72 hr	h	h	100°C, 2 days	—	100°C, 4 days	RT, air		
Treatment after intercalation reaction		RT, air	RT, air	RT, air	RT, air	RT, air	RT, air	RT, air	RT, air		

<sup>a</sup>Experiment from Section 2.5 is described in Table 2.<sup>b</sup>Every test tube contained graphitized carbon fibers and two vials, which contained chemicals for the intercalation reactions (Fig. 1).<sup>c</sup>Isoprene rubber was the material for rubber stopper and extra rubber added to the system.<sup>d</sup>Excess iodine; that is, there will be iodine left after the reaction is 100% complete.<sup>e</sup>The fibers included Amoco P-55, P-75, DuPont E-55, and E-105.<sup>f</sup>Bromine and rubber were in the same vial.<sup>g</sup>Room temperature<sup>h</sup>90-105°C for 65 hr; except accidental overnight heating to 160°C.<sup>i</sup>70°C in air for 90 hr then RT in air<sup>j</sup>200°C for 15 min then RT in air

Table 2. Chemical composition and electrical resistivity of  $\text{CBr}_x\text{I}_y$  produced from different processes and different graphite materials described in 2.5

	Process			
	1	2	3	4
Rubber in bromine vial	Yes	Yes	No	Yes
Rubber stopper	Yes	Yes	Minimum <sup>a</sup>	Yes
First step:				
Iodine vial	Yes	Yes	Yes	Yes
Bromine vial	Yes	Yes	No	No
Temperature	RT <sup>b</sup>	RT	75°C	75°C
Time (hr)	2	1	16	16
Second step:				
Iodine vial	Yes	Yes	Yes	Yes
Bromine vial	Yes	Yes	Yes	Yes
Temperature histogram:				
RT → 75°C, 75°C → 120°C	1 hr, 5 hr 7 days	1 hr, 5 hr 7 days	0, 5 hr 7 days	0, 5 hr 7 days
120°C	15 min	15 min	15 min	15 min
120°C → RT				
Iodine-to-bromine atomic ratio				
P-100 ( $D = 3.37 \text{ \AA}$ )	1.59	3.72	7.44	9.18
Vapor-grown fibers				
(HTT = 3000°C, $D = 3.35 \text{ \AA}$ )	2.64	2.26	0.77	1.84
HOPG (ZYX, $D = 3.35 \text{ \AA}$ )	1.78	1.85	0.97	1.52
Total halogen-to-carbon weight ratio				
P-100 ( $D = 3.37 \text{ \AA}$ )	0.273	0.265	0.284	0.292
Vapor-grown fibers				
(HTT = 3000°C, $D = 3.35 \text{ \AA}$ )	0.156	0.130	0.274	0.304
HOPG (ZYX, $D = 3.35 \text{ \AA}$ )	0.242	0.241	0.242	0.237
Electrical resistivity ( $\mu\Omega \text{ cm}$ )				
P-100 ( $D = 3.37 \text{ \AA}$ ) (400 $\mu\Omega \text{ cm}$ before halogenation)	72	82	67	73

<sup>a</sup>Teflon tape was used to wrap the rubber stopper used in this experiment.<sup>b</sup>Room temperature

ing that the total number of carbon-halogen charge transfers changed very little during the reactions.

## 2.4 Intercalation of less-graphitized carbon

This 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 EDS were used to detect the presence of iodine and bromine in the fibers after the reactions.

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% bromine[9]; 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.

## 2.5 Effects of different types of reactants

This set of experiments was designed to compare the intercalation caused by different quantities of rubber, and different kinds of initiation chemicals (either bromine or mixture of bromine and iodine) in different

types of graphite. Four test tubes of reactants similar to that described in Fig. 1 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 (1) a room-temperature rubber-bromine mixture for 2 hours, (2) a room-temperature rubber-bromine mixture for 1 hour, (3) a 75 to 120°C bromine-(excess) iodine mixture, and (4) 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 minutes. The fiber samples were then removed from the test tube and allowed to stabilize 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 described above was protected by layers of Teflon tape in order to minimize the rubber effects.

The EDS data 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

quantity 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) which were intercalated after 75 to 120°C simultaneous iodine and bromine initiation. This ratio decreases if the fibers were first initiated by bromine at room temperature, before the simultaneous bromine and iodine intercalation in 75 to 160°C range.

The resistivity of the P-100 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 experiments described earlier, the electrical resistivity value of the iodinated fibers was 140  $\mu\Omega$ -cm if no rubber was present during the reaction.

The results described in the above paragraph indicate that iodine-intercalated fibers with very low rubber 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,  $\text{CBr}_{0.00333}\text{I}_{0.0248}$ , has electrical resistivity of 67  $\mu\Omega$ -cm (6.5 times pristine value), but a bromine intercalated fiber,  $\text{CBr}_{0.028}$ , 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 and bromine, the charge transfer between iodine and carbon in graphite could be greater than the charge transfer between bromine and carbon in graphite.

The weight data were monitored after the samples were removed from the halogen environment. 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.

After the vapor-grown fiber samples were removed from the halogen environment and placed in the room-temperature air, their weights were monitored for 2 months. No weight change was observed during this period. The same was observed for HOPG after 21 months of weight monitoring. The iodinated P-100, on the other hand, lost weight gradually and continuously. The halogen-to-carbon weight ratio of the iodinated P-100 stabilized at 21% 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 hour for all test tubes, except the one where the rubber effects were minimized by wrapping Teflon tape on the rubber stopper (6 hours for this particular run). The rubber effects on the chemical composition of vapor 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.

The surfaces of both iodinated P-100 and iodinated vapor-grown fibers which were exposed to a 75 to 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. 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 (obtained from EDS) and mass gain 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.

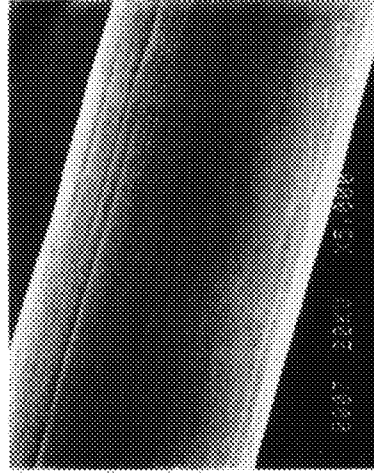
The low iodine concentration on the iodinated fiber surface is comparable to the low bromine concentration on the brominated fiber surface. However, the high bromine and oxygen concentration on the iodine-intercalated fiber surfaces is in contrast to the near-zero intercalate concentration on the bromine-intercalated fiber surfaces[10]. Knowing that intercalation improves the ability of graphite to withstand fluorine gas attack[11], this phenomenon implicates that the high-temperature reaction between bromine-intercalated fibers and 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, when the fiber-epoxy composite is made, the high intercalate 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  $3.42 \pm 0.02$  Å. This compares to the 3.37 to

Table 3. Approximate chemical composition on surface and in bulk of bromine and iodine intercalated fibers

Element	Surface concentration, %	Bulk concentration, %
$\text{CBr}_{0.0116}\text{I}_{0.0214}$ from vapor-grown fibers (interplanar spacing, 3.35 Å before intercalation)		
C	78	97
O	18	0
Br	4	1
I	0.1	2
$\text{CBr}_{0.00281}\text{I}_{0.0258}$ from P-100 (interplanar spacing, 3.37 Å before intercalation)		
C	69	97
O	23	0
Br	8	0.3
I	0.05	3



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



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

Fig. 3. SEM micrographs of graphite fluoride fibers, (a) from fluorination of iodine intercalated P-100, (b) from fluorination of bromine intercalated P-100.

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 was found for all iodinated vapor-grown fibers. 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. The positions of all major peaks obtained from the intercalated HOPG samples can be described by the eqn  $D = [7.25 + 3.35(N-1)]/L$  Å, where both  $N$  and  $L$  are integers, with  $L \geq 1$ , and  $N \geq 1$ . This suggests the distance between the two carbon layers containing the halogen layer ( $d_l$ ) is 7.25 Å, which is different from the 7.05 Å value for bromine-intercalated graphite.

Based on the eqn described in the previous paragraph, the structures of the two intercalated HOPG samples used in this set of experiments were determined. The sample whose intercalation was initiated by 1 hour room-temperature bromination was found to be a mixed-stage product (i.e.,  $N$  is not a constant). The sample whose intercalation was initiated by bromine-

Table 4. Peak position of the X ray diffraction data for a  $C(I_3Br)_{0.0078}$  HOPG, and  $N$  and  $L$  values obtained from the equation  $D = [7.25 + 3.35(N-1)]/L$  Å

$D$ (Å), data	$N$	$L$	$D$ (Å), calculated
17.147	4	1	17.300
8.607	4	2	8.650
6.904*	3	2	6.975
5.731	4	3	5.767
4.294	4	4	4.325
3.596*	1	2	3.625
3.461	4	5	3.460
3.426			
2.884	4	6	2.883
2.472	4	7	2.471
2.161	4	8	2.163
1.918	4	9	1.922
1.727	4	10	1.730
**	4	11	1.573
1.443	4	12	1.442
1.332	4	13	1.330
1.236	4	14	1.236

\*Small peaks.

\*\*There is a very small peak at  $D \approx 1.57$  Å, which can be observed on the diffractogram but was not detected by the instrument.

iodine mixture (in the presence of a minimum quantity of rubber) had at least 7 broad peaks suggesting an identity period ( $L$ ) of 30.7 Å, or a predominantly stage 8 product (i.e.,  $N=8$ ). For demonstration, the X-ray diffraction data from another intercalated HOPG obtained recently are described in Table 4. This sample weighed 0.0331 gm before intercalation, had sharp diffraction peaks, and was a predominantly stage 4 compound. Its intercalation was initiated by direct exposure to liquid bromine-iodine mixture at 85°C; its empirical formula was estimated to be  $C(I_3Br)_{0.0078}$ .

## 2.6 Importance of surface wetting during the initiation process

For all experimental runs conducted in this research, if the graphite materials were not wetted by the intercalates containing bromine at the beginning of the initiation reaction, the reaction could not start, and the products contained no intercalate. This was observed mostly in the cases where the temperatures of the carbon materials were kept high when exposed to bromine and iodine. This result agrees with the intercalation mechanism suggesting that adsorption of intercalates by the graphite materials is the first step of the intercalation reaction.

## 3. CONCLUSIONS

Graphite intercalation compounds with iodine as the major intercalate 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  $\text{Br}_2/\text{HBr}/\text{IBr}$  mixture, is at first absorbed by the graphite to initiate the intercalation reaction. The graphite materials are then exposed to iodine vapor containing a small amount of  $\text{Br}_2/\text{HBr}/\text{IBr}$  to complete the intercalation reaction, during which the small amount of  $\text{Br}_2/\text{HBr}/\text{IBr}$  enhances charge transfer between iodine and carbon. A small amount of rubber in this vaporous mixture helps to produce  $\text{HBr}$  vapor, and remove bromine from the vapor. When it enters the graphite structure, an intercalate either takes a new site or replaces an old intercalate. The halogenated graphitized carbon fibers P-100 thus formed were found to lose weight slowly, but stabilized after  $100^\circ\text{C}$  air heating for 1 week, and resulted in a product 21% 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 1:3-4.5 and 1:8.5-20, respectively), but the iodine was barely detectable.

The X-ray diffraction data on P-100 fibers indicated that intercalation causes an increase in the interplanar spacings from 3.37 to  $3.42\text{ \AA}$ , but no new peaks. However, X-ray diffraction of vapor-grown fibers showed a new peak at  $D = 2.0\text{ \AA}$ . The diffraction pattern of HOPG showed a large number of new peaks, all of which suggest that the two carbon layers containing intercalates are  $7.25\text{ \AA}$  apart.

## REFERENCES

1. F. J. Salzano, *Carbon* **2**, 73 (1964).
2. R. Juza, P. Jonck, and A. Schmeckenbecher, *Z. Anorg. Allgem. Chem.* **292**, 34 (1957).
3. G. Hennig, *J. Chem. Phys.* **20**, 1438 (1952).
4. C. Hung, M. Stahl, C. Mesia, and M. Slabe, *Effects of Sequential Treatment with Fluorine and Bromine on Graphite Fibers*, NASA TM-100106 (1987).
5. D. A. Jaworske, J. R. Gaier, C. C. Hung, and B. A. Banks, *SAMPE Q.* **18**, 9 (1986).
6. C. Hung and M. Long, *Fluorinated Graphite Fibers as a New Engineering Material: Promises and Challenges*, NASA TM-102511 (1989).
7. W. C. Forsman, T. Dziemianowicz, K. Leong, and D. Carl, *Synth. Met.* **5**, 77 (1983).
8. G. Colin and A. Hérault, *Compt. Rend.* **245**, 2294 (1957).
9. C. Hung, *Brominated Graphitized Carbon Fibers*, U.S. Patent 5,059,4090, (1991).
10. D. A. Jaworske and R. Zinolabedini, *Graphite Fiber Intercalation Dynamics of the Bromine Intercalation Process*, NASA TM-87015 (1985).
11. C. Hung, M. Long, and M. Stahl, *SAMPE Q.* **19**, 12 (1988).