Carbon Vol. 28, No. 4, pp. 521–528, 1990
Printed in Great Britain.

0008–6223/90 $3.00 + .00

CARBON FIBERS BROMINATED BY ELECTROCHEMICAL INTERCALATION

C. T. Ho and D. D. L. Chung
Composite Materials Research Laboratory, Furnas Hall, State University of New York at Buffalo, Buffalo, NY 14260, U.S.A.

(*Received* 7 *September* 1989; *accepted in revised form* 24 *October* 1989)

Abstract—Bromine was intercalated in pitch-based carbon fibers (Thornel P-100 of Amoco) by either exposure to Br_2 or anodic oxidation (i.e., electrochemical intercalation). The former method resulted in fibers that exhibited in-plane disorder at room temperature and in-plane melting at 271 K, whereas the latter method resulted in fibers that exhibited in-plane superlattice order at room temperature and in-plane melting at 373 K. Compared to fibers prepared by the former method, fibers prepared by the latter method exhibited more homogeneous intercalation, a more uniform chemical state of the intercalated bromine, a higher electron transfer from bromine to carbon, a lower bromine concentration, a lower electrical conductivity, enhanced oxidation resistance, and an increased activation energy for oxidation. Highly oriented pyrolytic graphite did not undergo electrochemical intercalation under the same conditions as the fibers.

Key Words—Carbon fibers, bromine, intercalation, oxidation, pitch, Raman, electrochemical, anodic oxidation.

1. INTRODUCTION

Pitch-based carbon fibers (Thornel P-100 of Amoco) that have been brominated by exposure to bromine (liquid or vapor) have received much attention recently[1] because they have an electrical resistivity of 50 $\mu\Omega$ cm (comparable to the value for stainless steel) and are stable in air, vacuum, high humidity and temperatures up to 200°C[2]. Moreover, the electromagnetic interference (EMI) shielding effectiveness is greatly improved by the bromination[1]. Even though the mechanical properties of the fibers themselves are essentially not affected by the bromination, the interlaminar shear strength of the brominated fiber-epoxy composite is 18% greater than its pristine counterpart[1]. Furthermore, the oxidation resistance of the fibers is improved by the bromination[3].

Raman scattering showed that Thornel P-100 fibers brominated by exposure to bromine are graphite intercalation compounds, but X-ray and electron diffraction showed that the bromine layers in the fibers are disordered at room temperature[4]. In contrast, all other graphite–bromine phases exhibit in-plane superlattice ordering at room temperature[5]. Upon cooling these fibers to below 271 K, in-plane superlattice ordering occurs[4].

Intercalation in general can be carried out in two ways, namely

1. direct exposure to the intercalate vapor or liquid, and
2. electrochemical intercalation.

The first method is the method widely used for almost all intercalate species, whereas the second method is used for many fewer intercalate species (e.g., H_2SO_4[6]). The intercalation of bromine in graphite as well as carbon fibers has always been carried out by using the first method. However, recently Tillgner and Ruland[7] successfully carried out electrochemical intercalation of bromine in Thornel P-100 carbon fibers and observed with X-ray diffraction in-plane superlattice ordering at room temperature. In this paper, we have confirmed the report of Tillgner and Ruland and have furthermore shown that the electrochemically brominated P-100 fibers are more oxidation resistant than those brominated by exposure to bromine, and that the bromine in the electrochemically brominated P-100 fibers undergoes more charge transfer than that in the fibers brominated by exposure to bromine.

2. INTERCALATION METHODS

Two bromination methods were used for the sake of comparison. The first method involved direct exposure of Thornel P-100 carbon fibers (without resin sizing) to bromine vapor in air at room temperature for at least 6 days. After that, the fibers were removed from the bromine reservoir and allowed to desorb in air at room temperature. The fibers prepared by using this method are labeled Type I.

The second method involved anodic oxidation of the Thornel P-100 carbon fibers in an electrolyte, which was a saturated aqueous potassium bromide solution[7]. The electrochemical intercalation set-up is illustrated in Fig. 1. The carbon fibers were suspended in the electrolyte by a platinum wire and basket, which served as the anode. Electrical contact between the fibers and the platinum basket was ren-

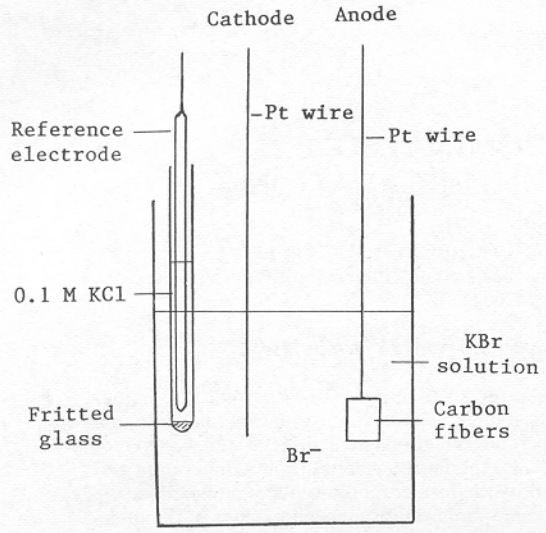

Fig. 1. Schematic of apparatus for electrochemical intercalation of bromine in carbon fibers.

dered by pressure. Another platinum wire served as the cathode. The reference electrode was a commercial (Orion) Ag/AgCl electrode, which was filled with a 4 M KCl solution and connected to the electrolyte by fritted glass. Above the fritted glass was a 0.1 M KCl solution. Anodic oxidation was performed either at constant voltage (1.8–2.2 V) or constant current (0.5 mA) between the anode and the cathode. With a constant current of 0.5 mA for 80 h, the potential between the anode and the reference electrode (Fig. 2) was recorded continuously in a pulse mode, such that each data point was obtained after disconnecting the anode and cathode for 2 min. No step was observed in Fig. 2, in contrast to the steps typical for the electrochemical intercalation of graphite (such as highly oriented pyrolytic graphite, or HOPG) with H_2SO_4[6]. After the anodic oxidation, the fibers were rinsed with distilled water and dried in air at room temperature for 2 days. The fibers prepared by using this method are labeled Type II.

3. WEIGHT UPTAKE

The fractional weight increase relative to the weight of the pristine fibers was about 20% for Type I and 12.2% for Type II, as measured by using a Perkin-Elmer AD-2Z autobalance. The weight increase for Type II includes the weight of the small amount of KBr crystals which remained on the surface of the fibers after drying.

4. STRUCTURE

X-ray diffraction was performed at room temperature in the transmission mode with the diffraction plane perpendicular to the fiber axis. A Stoe X-ray diffractometer system was used, with CuKα radiation and a 45° curved position sensitive detector. Figure 3 shows a diffraction pattern obtained on a Type II sample, which weighed 3.9 mg. The counting time was 1500 s. Most of the peaks in the diffraction pattern were labeled with the Miller indices of graphite (G) or of graphite–bromine intercalation compound (B). The intercalate peaks are due to in-plane intercalate superlattice ordering. No staging peak was observed. One peak is due to KBr. In contrast, Type I at room temperature gave an X-ray diffraction pattern that consisted of only graphite peaks[4].

Electron diffraction was performed on a Type II sample at room temperature. The diffraction pattern (Fig. 4) was the same in-plane superlattice pattern as that of HOPG intercalated with bromine[8]. In contrast, the electron diffraction pattern of Type I at room temperature (Fig. 4) was just a graphite pattern, without any superlattice spot.

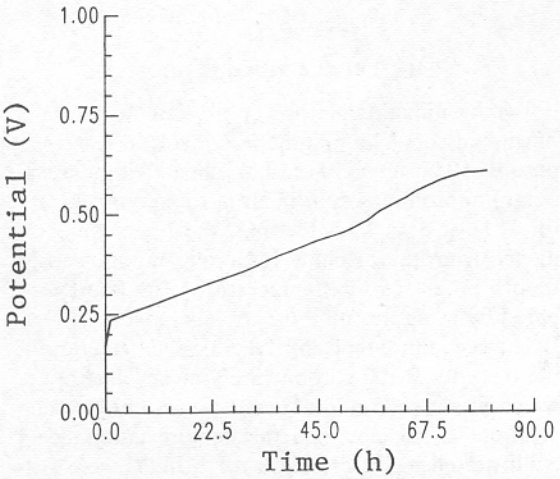

Fig. 2. Variation of the potential between the anode and the reference electrode during electrochemical intercalation of bromine in carbon fibers.

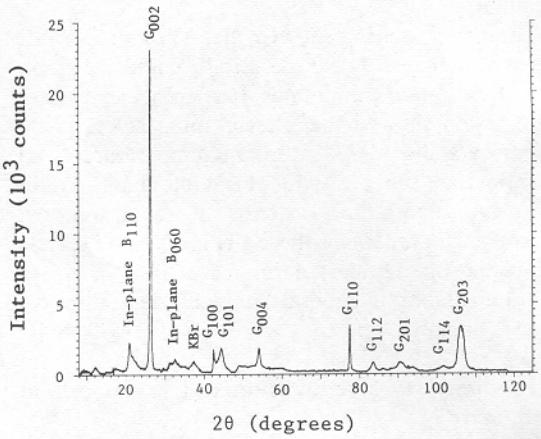

Fig. 3. X-ray diffraction pattern of carbon fibers brominated by electrochemical intercalation (Type II). The peaks are labelled by the Miller indices, with G signifying graphite peaks and B signifying bromine intercalate peaks.

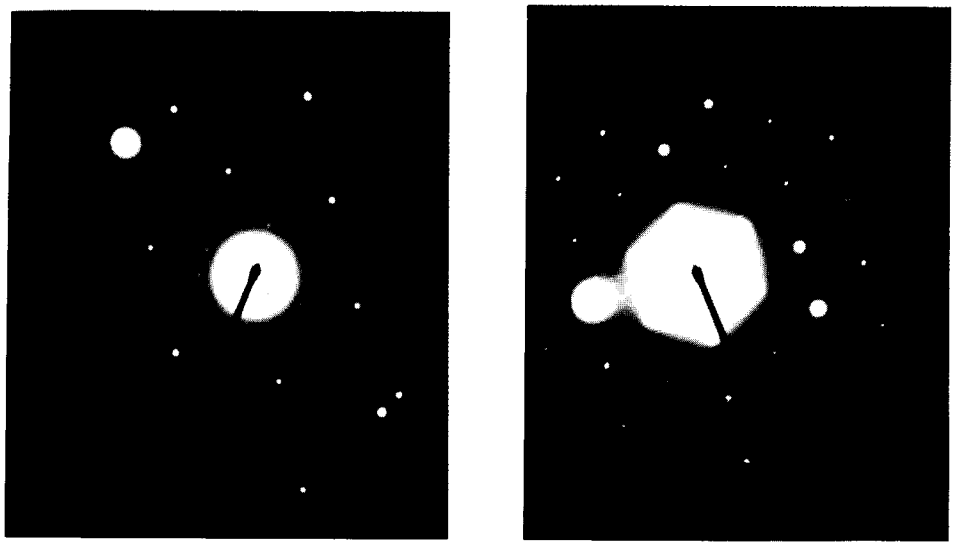

Fig. 4. Electron diffraction patterns of Type II and Type I fibers at room temperature. The camera length is different for the two photographs.

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-2 system in order to look for the melting of the intercalate layers—a phase transition which occurs at 100°C in HOPG intercalated with bromine[9,10]. This peak was indeed observed as an endothermic peak at 100°C (373 K) upon heating at a heating rate of 40°C/min for a 15 mg Type II sample prepared with a voltage of 2.2 V between the anode and cathode (Fig. 5(a)). Upon cooling this sample at 20°C/min, an exothermic peak was observed at 96°C (369 K) (Fig. 5(b)). For Type I samples, the only peak observed was at −2°C (271 K)[4]; no peak was observed in the vicinity of 100°C.

Raman scattering was performed in the 180°C back-scattering geometry using the 5145 Å line of an argon ion laser operating at a power of 250 mW. The scattered light was detected by using a photomultiplier tube and photon counting. The doublet corresponding to the E_{2g2} mode of graphite (as previously observed in HOPG intercalated with bromine[11,12]) was observed in both Type I and Type II samples, as shown in Fig. 6(a). The high frequency component of the doublet is associated with the graphite layers bounding the intercalate layers, whereas the low frequency component is associated with the graphite layers that are not immediately adjacent to an intercalate layer[11]. The intensity ratio of the high frequency component to the low frequency component increases with increasing intercalate concentration[11]. This ratio is 0.42 and 0.29 for Type I and Type II samples respectively. According to Fig. 7 of Ref. 11, these values correspond to residue compound intercalate concentrations of 1.4 mole % Br_2 (18.6 wt. % Br_2) and 0.87

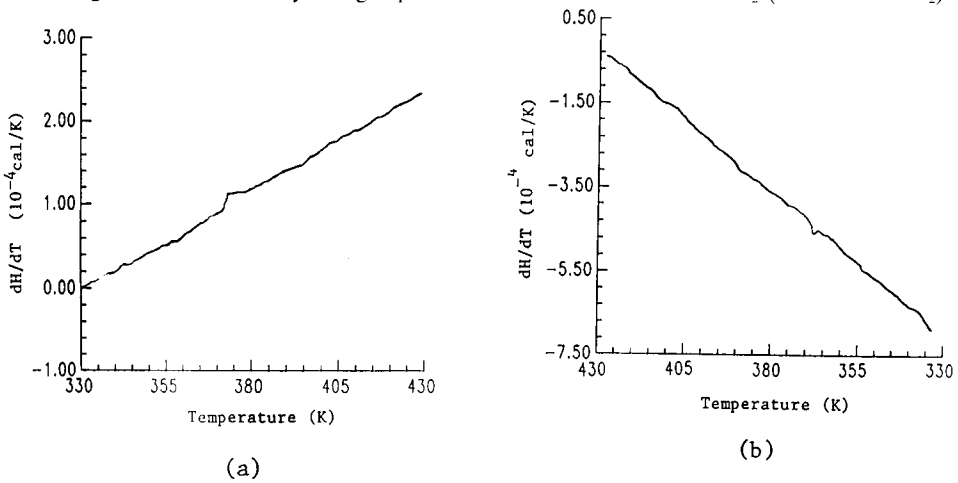

Fig. 5. DSC thermograms of carbon fibers brominated by electrochemical intercalation (Type II) (a) during heating at 40°C/min, and (b) during cooling at 20°C/min.

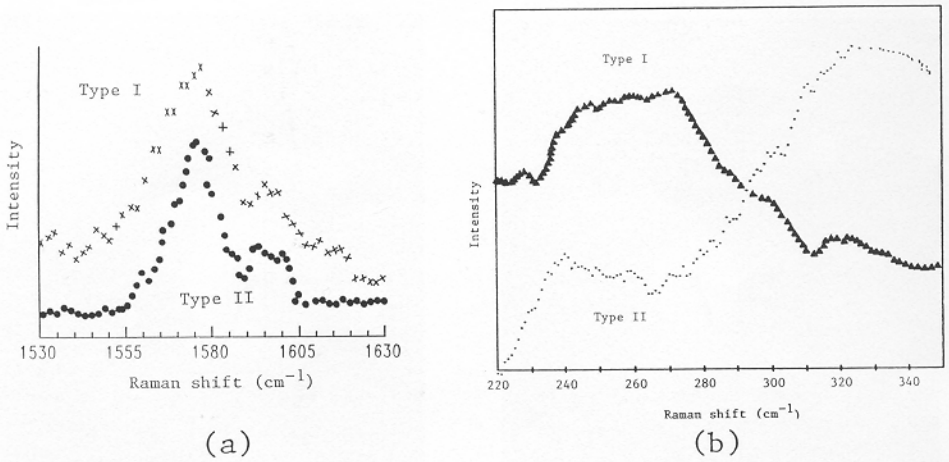

Fig. 6. (a) Raman spectra of brominated carbon fibers, showing the doublet associated with the E_{2g2} mode of graphite; (b) Raman spectra of brominated carbon fibers showing the intercalate peak near 240 cm^{-1} superimposed on a scattering background.

mole % Br_2 (11.6 wt. % Br_2), respectively. Since the measured weight uptake (including that due to the KBr crystals on the surface) is 12.2% for Type II, this result indicates that the weight uptake due to KBr is only about $0 \approx 1$ wt.%. A difference between Type I and Type II is that the high frequency component is more well resolved in Type II than Type I. Another difference is that the full width at half maximum of the low frequency component is 25 and 16 cm^{-1} for Type I and Type II respectively (compared to 15 cm^{-1} for HOPG intercalated with bromine[11]). These Raman observations suggest that intercalation is more homogeneous in Type II than Type I.

Figure 6(b) shows the only observed Raman peak other than the doublet for Type I and Type II. Both Type I and Type II show a peak at about 240 cm^{-1}, which is the frequency for the intercalate mode in HOPG intercalated with bromine[11,12]. However, this peak for Type I and Type II is much broader than in HOPG, though the peak for Type II is more well defined and closer to 240 cm^{-1} than that for Type I. This difference between Type I and Type II suggests that the chemical state of bromine in Type I is less uniform than that in Type II. (It should be mentioned that Raman peaks quite close to 240 cm^{-1} also exist for Br^{-3} and Br^{-5} ions[13]).

For both Type I and Type II, no Raman peak was observed around 1360 cm^{-1} (due to crystallite boundaries[14]) or around 323 cm^{-1} (the vibration frequency of a free bromine molecule).

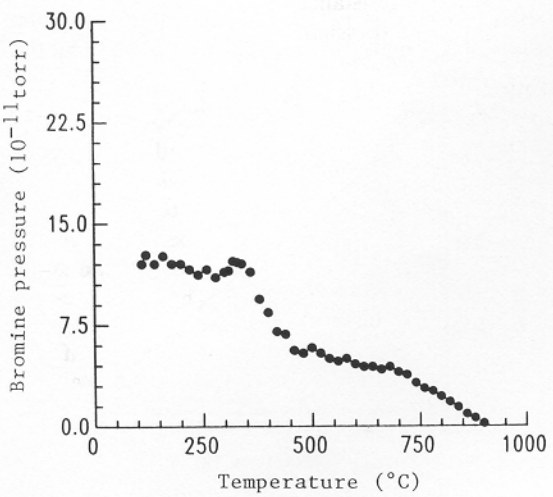

Fig. 7. Bromine pressure measured by mass spectrometry versus temperature during heating of carbon fibers brominated by exposure to bromine vapor (Type I).

5. ELECTRONIC PROPERTIES

The electrical conductivity, Hall coefficient and magnetoresistance of pristine fibers, Type I and Type II were measured at room temperature and 77 K. Unidirectional fiber tows that had been pressed to make contact were used for these galvanomagnetic studies. The method of measurement was as described by Marchand *et al.*[15,16]. The electric current was passed along the fiber axis (x direction). The magnetic field (0.75 T) was applied perpendicular to the x direction, i.e., along the z direction. The Hall voltage was directed perpendicular to both the x and z directions, i.e., along the y direction. The results on the electrical conductivity, magnetoresistance and Hall coefficient are shown in Table 1. The electrical conductivity is higher for Type I than Type II at both temperatures. The magnetoresistance is much less for both types of brominated fibers than for pristine fibers. The Hall coefficient is negative for the pristine fibers and is positive for both types of brominated fibers.

At room temperature the following four equations were used to determine the mobilities (μ_e, μ_h) and

Table 1. Galvanomagnetic properties of carbon fibers

Fiber type	Temperature (K)	Electrical conductivity σ ($10^5\ \Omega^{-1}m^{-1}$)	Magneto-resistance $\Delta R/R$ (10^{-4})	Hall coefficient A ($10^{-8}m^3C^{-1}$)
Pristine	300	4.72	31.0	−0.27
	77	2.92	23.6	−0.35
Type I	300	18.69	8.12	0.647
	77	19.37	−10.08	0.410
Type II	300	8.02	7.40	0.718
	77	9.47	−9.32	0.341

concentrations (n_e, n_h) of both electrons (e) and holes (h)[16]:

$$\sigma = e(n_e\mu_e + n_h\mu_h) \quad (1)$$

$$A\,\sigma^2/e = n_h\mu_h^2 - n_e\mu_e^2 \quad (2)$$

$$2\,\sigma^2\,(\Delta R/R)/e^2\beta^2 = n_e n_n \mu_e\mu_h\,(\mu_e + \mu_h)^2 \quad (3)$$

$$n_e n_h \text{ (brominated)} = n_e n_h \text{ (pristine)}, \quad (4)$$

where,

σ = electrical conductivity,
e = electronic charge,
A = Hall coefficient
$\Delta R/R$ = magnetoresistance,

and,

β = magnetic field.

When the magnetoresistance values are negative at (77 K), eqn. (3) is no longer valid[16], but the problem can be solved by eqns (1), (2) and (4), and also by using the notion that the (n_h–n_e) difference is the same at 77 K and at room temperature. The results of the calculations are listed in Table 2. From the bromine content of each sample and the corresponding value of n_h–n_e, it is possible to determine the charge transfer coefficient, that is, the number of electronic charge transferred per bromine atom, as listed in Table 2. The charge transfer coefficient for Type II is larger than that for Type I. If we had excluded the weight of KBr, then the charge transfer coefficient would have been even higher for Type II. The electrical conductivity is higher for Type I than Type II. This is because Type II has a lower carrier concentration and a lower carrier mobility than Type I.

Marchand and Mathur[16] investigated the galvanomagnetic properties of UCC-3200 (a Union Carbide pitch-based carbon fiber heat-treated at 3200°C) and UCC-3000 (the same fiber heat-treated at 3000°C) instead of Thornel P-100. The electrical conductivity of pristine P-100 is higher than that of UCC-3200 or UCC-3000. After bromination by exposure to vapor bromine (this work) or liquid bromine[16] and subsequent desorption, the weight uptake for P-100 (20%) was much less than that of UCC-3200 (84%) or UCC-3000 (47%). Marchand and Mathur[16] did not use electrochemical intercalation. They reported a charge transfer coefficient of approximately 0.3. Thus, in spite of the difference in material between this work and Ref. 16, the charge transfer coefficient determined was similar for the two works.

6. OXIDATION RESISTANCE

The oxidation resistance of the fibers was studied during temperature scanning at a heating rate of 20°C/min. During heating the weight of the fibers was measured in situ using a Perkin-Elmer AD-2Z autobalance, while the relative amount of evolved bromine vapor and the relative amount of evolved

Table 2. Carrier concentrations, carrier mobilities and charge transfer

Fiber type	Temperature (K)	Carrier concentration (cm^{-3}) Electrons n_e	Carrier concentration (cm^{-3}) Holes n_h	Carrier mobility ($cm^2/V.s$) Electrons D_e	Carrier mobility ($cm^2/V.s$) Holes D_h	Charge transfer coefficient
Pristine	300	1.42×10^{19}	1.39×10^{19}	1050	1050	/
	77	1.01×10^{19}	9.9×10^{18}	916	916	/
Type I	300	2.04×10^{17}	9.65×10^{20}	5400	121	0.26
	77	1.03×10^{17}	9.65×10^{20}	7300	125	0.26
Type II	300	3.16×10^{17}	6.23×10^{20}	3420	80	0.30~0.33
	77	1.59×10^{17}	6.23×10^{20}	4830	95	0.30~0.33

CO_2 vapor were monitored by using a VG Instruments, Inc. 1–300 amu quadrupole mass spectrometer equipped with a glass-lined capillary inlet. Three types of fibers were used, namely pristine, Type I and Type II fibers. The weight of each type of fibers was about 20 mg prior to heating. Figures 7–9 show the mass spectrometry results obtained for Type I and Type II. The Type I fibers had been desorbed at room temperature for 4 days prior to heating; the Type II fibers had been desorbed at room temperature for 2 days prior to heating. Figures 7 and 8 show that bromine desorption is important at low temperatures, while Fig. 9 shows that the oxidation of carbon (thereby evolving CO_2) is negligible below 625°C for both Type I, Type II and pristine fibers. This means that the weight loss below 625°C is almost all due to the desorption of bromine. Comparison of the three curves in Fig. 9 shows that bromination by exposure to Br_2 (Type I) increases the oxidation resistance most significantly at 675–800°C, less significantly at 800–925°C and negligibly at other temperatures, whereas bromination by the electrochemical method (Type II) increases the oxidation resistance at all temperatures.

Table 3 shows, for the sake of comparison, the temperature (during temperature scanning at 20°C/min) required to achieve 5, 15, 25 and 40% burn-off (detected gravimetrically) in air for pristine, Type I and Type II fibers. At 5% burn-off, all three types of fibers are almost the same in this required temperature. This is because the contribution of bromine desorption to the weight loss is important for Type I and Type II below 626°C, thus overshadowing the effect of bromination on the oxidation resistance. For larger amounts of burn-off (i.e., higher required temperatures), the contribution of bromine desorption is relatively less and the required burn-off temperature clearly follows the trend: pristine < Type I < Type II.

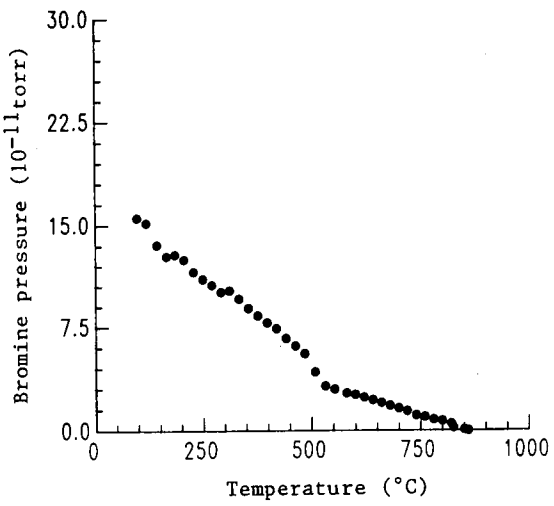

Fig. 8. Bromine pressure measured by mass spectrometry versus temperature during heating of carbon fibers brominated by electrochemical intercalation (Type II).

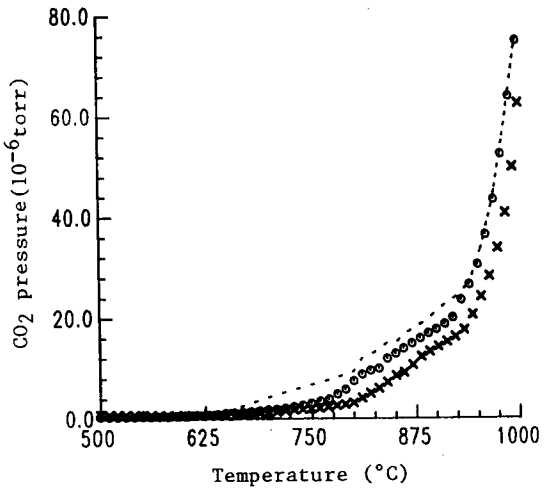

Fig. 9. CO_2 pressure measured by mass spectrometry versus temperature during heating of pristine fibers (dashed line), Type I fibers (circles) and Type II fibers (crosses).

The oxidation resistance of the fibers in air was also investigated isothermally at various temperatures as a function of time.

The isothermal study was carried out by measuring the weight of a bunch of fibers (typically about 20 mg in weight) after various periods of heating at a chosen temperature. The heating took place in static air in a box furnace with a heated volume of 0.0101 m^3. Due to the large volume of the furnace and the small volume of the fibers, the absence of forced air circulation in the furnace did not affect the quality of the results. Heating of a fiber sample was interrupted at 15 min intervals for the purpose of weighing.

The weight loss of the three types of fibers as a function of time at 700°C is shown in Fig. 10. The oxidation resistance of the fibers is again seen to follow the trend: pristine < Type I < Type II.

Table 4 shows the oxidation rate at 25% weight loss (determined from the slope of isothermal weight loss curves, such as Fig. 10, at 25% weight loss) for pristine, Type I and Type II fibers at 750, 700 and 650°C. The oxidation rate at each temperature was found to follow the trend: pristine > Type I > Type II.

The data of Table 4 were plotted in the form of an Arrhenius plot, as shown in Fig. 11. From the slope of this plot, the activation energy was determined. The activation energy is 162, 183 and 200 kJ/

Table 3. Burn-off temperature during heating at 20°C/min

	Burn-off temperature (K)			
Fiber type	5%	15%	25%	40%
Pristine	663	726	757	812
Type I	660	770	810	873
Type II	675	793	844	914

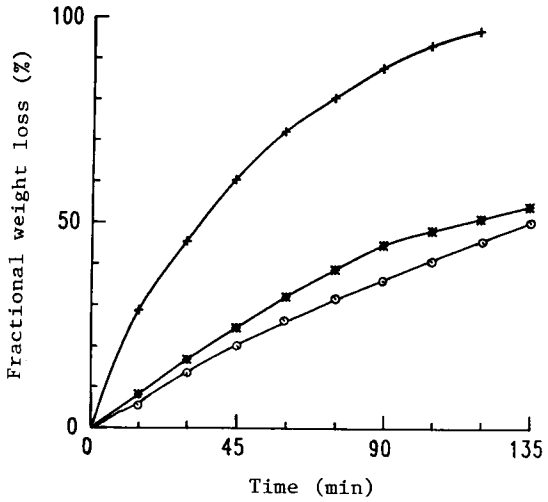

Fig. 10. Fractional weight loss versus time during isothermal heating at 700°C for pristine fibers (+), Type I fibers (*) and Type II fibers (○).

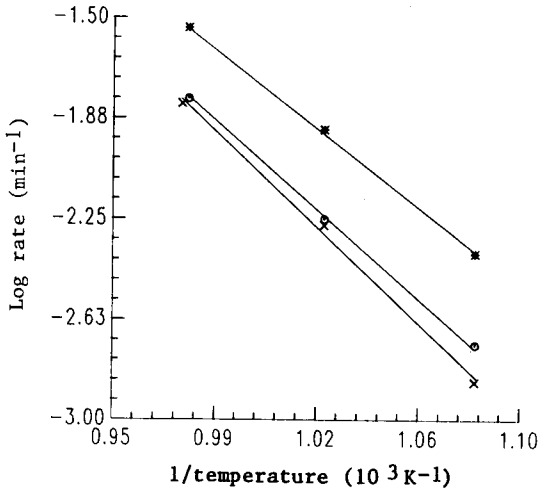

Fig. 11. Arrhenius plot of the oxidation rate at 25% weight loss versus 1/temperature for pristine fibers (*), Type I fibers (○) and Type II fibers (x).

mole for pristine, Type I and Type II fibers respectively. For the sake of comparison, we should mention that the activation energy at 5% burn-off is 240 kJ/mole for pristine Thornel P-55 fibers[17]. The activation energy of oxidation of Thornel P-100 fibers has not been previously reported.

7. COMPARISON WITH GRAPHITE

The same methods that produced Type I and Type II were applied to HOPG for the sake of comparison. HOPG exposed to bromine vapor resulted in a stage-2 intercalation compound with in-plane superlattice ordering, as shown by X-ray and electron diffraction.

Bromine intercalation did not occur in HOPG that had been electrochemically treated as for Type II, as indicated by a purely graphitic X-ray diffraction pattern (except for a very small amount of KBr remaining on the HOPG) and the lack of any change in the electrical conductivity after the electrochemical treatment. Figure 12 shows the potential between the anode and the reference electrode as a function of time during anodic oxidation at a constant voltage of 2.2 V between the anode and the cathode. As in Fig. 2, each data point in Fig. 12 was obtained after disconnecting the anode and cathode for 2 min. Comparison of Fig. 2 (for fibers) and Fig. 12 (for HOPG) shows that the potential is about ten times higher in Fig. 2 than in Fig. 12, although the potential increases smoothly with time in both figures. This suggests that a relatively small degree of charge transfer occurs in the anodic oxidation of HOPG, but the charge transfer may be associated with the adsorbed bromine and is not associated with intercalation.

Table 4. Oxidation rate measured at 25% burn-off

	Oxidation rate (min^{-1})		
Fiber type	750°C	700°C	650°C
Pristine	2.91	1.21	0.419
Type I	1.56	0.56	0.191
Type II	1.46	0.51	0.142

The difference between carbon fibers and HOPG in their response to anodic oxidation is probably due to the tendency of water in the electrolytic solution to dissolve bromine and this dissolution probably occurs more readily for bromine in HOPG than bromine in carbon fibers. This explanation is supported by the fact that the electrolyte turned more yellow and bromine-smelling for HOPG than fibers.

8. CONCLUSION

Type I and Type II fibers are different in the following ways:

1. Type I exhibits in-plane disorder at room temperature; Type II exhibits in-plane superlattice order at room temperature.
2. Type I undergoes in-plane melting at 271 K; Type II undergoes in-plane melting at 373 K.
3. Intercalation is more homogeneous in Type II than Type I.
4. The chemical state of the intercalated bromine is more uniform in Type II than Type I.
5. The electron transfer coefficient (from bromine to carbon) is higher in Type II than Type I.
6. The oxidation resistance is higher in Type II than Type I.
7. The activation energy for oxidation is higher for Type II than Type I.

The enhanced oxidation resistance of Type II compared to Type I is attributed to the increased charge

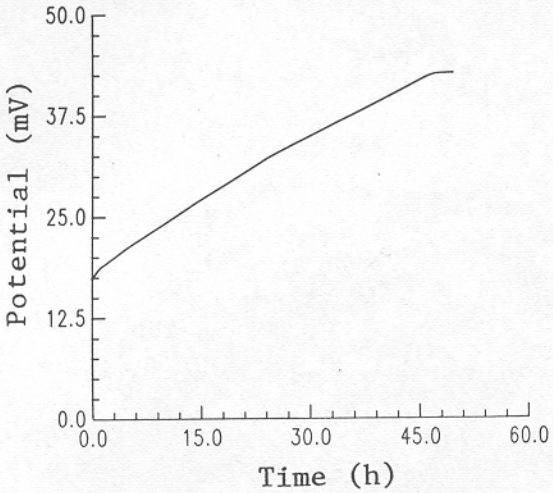

Fig. 12. Variation of the potential between the anode and the reference electrode during electrochemical treatment of HOPG.

transfer coefficient in Type II. Adsorbed halogens are known to inhibit carbon oxidation[18], but the bromine in both Type I and Type II is intercalated rather than adsorbed. Furthermore, the bromine concentration is higher in Type I than Type II. The increased activation energy for oxidation of Type II compared to Type I is consistent with the larger charge transfer coefficient in Type II than Type I.

In spite of the larger charge transfer coefficient in Type II than Type I, the electrical conductivity is lower in Type II than Type I. This is because of the lower bromine concentration in Type II than Type I.

That a difference in intercalation method yields different phases at the same temperature is related to the complex phase equilibria in the graphite–bromine system[5]. The origin of this difference is presently not clear.

Acknowledgements—The authors are grateful to L. Hwang of SUNY/Buffalo for the galvanomagnetic measurement, and to A. Petrou and X. Liu of SUNY/Buffalo for the Raman measurement.

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