

## INHIBITION OF THE OXIDATION OF CARBON-CARBON COMPOSITES BY BROMINATION

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**Abstract**—Bromination by exposure to bromine vapor at room temperature was effective for inhibiting the oxidation of carbon-carbon composites in the form of PAN-based carbon fibers impregnated with resin, which was subsequently carbonized at 1000 or 2000°C. The oxidation rate was decreased by up to 43%. In addition, electrical resistivity was decreased by up to 39%. However, the tensile modulus was decreased by 16–17% and tensile strength was decreased by 17–20%; the ductility was not affected. The increased oxidation resistance may be due to bromine adsorption or the electron transfer from graphite to bromine. The bromine resided in the matrix of the composite, particularly in pores within the matrix. Bromination was also attempted by the electrochemical method, but it resulted in negligible weight uptake in the carbon-carbon composite. Carbon-carbon composites that had been graphitized at 2700°C were damaged by bromination.

**Key Words**—Carbon-carbon composites, oxidation, oxidation rate, inhibition, bromine, electrical resistivity.

### 1. INTRODUCTION

Carbon in the form of carbon fiber reinforced carbon, or carbon-carbon composites, is a high temperature structural material of exceptionally low density, so it is important for aircrafts, spacecrafts, space radiators and many other aerospace applications. In a vacuum or inert atmosphere, it withstands temperatures above 2000°C. However, it suffers from being susceptible to oxidation at elevated temperatures (above 500°C). This oxidation reaction gasifies the carbon, increasing the porosity in the carbon and drastically weakening the material. To alleviate this problem, coatings such as boron oxide[1], silicon carbide[2–4], silicides[5], boron carbide[6], boron nitride[7], and alumina[8] have been used, but coatings are not desirable for applications such as space radiators, which need the good emissivity of carbon. A related method for carbon-carbon composites is to introduce a glass-forming phase to the pitch or resin matrix prior to the carbonization step in the fabrication of the carbon-carbon composite[9]. A basic requirement of the coating material is that it does not catalyze the oxidation of carbon.

Although there are numerous materials that function as catalysts, there are very few materials that function as inhibitors of the oxidation of carbon. For example, alkali metals such as potassium function as catalysts and this effect is attributed to the electron transfer from the alkali metal to the carbon, thereby raising the Fermi level and enhancing oxidation[10]. Potassium readily intercalates graphite[11–13] and carbon fibers[14–16]. It even intercalates relatively nongraphitic fibers[17]. However, the intercalated structure was shown to be lost in favor of the formation of free graphite prior to gasification[18]. An

example of an inhibitor is chlorine[19], which intercalates only at low temperatures such as  $-20^{\circ}\text{C}$ [20], and is believed to inhibit the oxidation by having chemisorbed (not intercalated) chlorine atoms strongly bonded at sites on the prismatic faces of the pit sides, thereby inhibiting growth of the hexagonal pits that propagate in the absence of chlorine[19]. Another inhibitor is phosphoric acid, which is believed to inhibit the oxidation of carbon-carbon composites because the phosphate may occupy some active sites in addition to removing impurity metals that might otherwise catalyze the oxidation[21]. Phosphoric acid prevents the oxidation of the carbon matrix as well as the fiber bundles in the carbon-carbon composite, whereas acetic acid prevents the oxidation of the fiber bundles in carbon-carbon composites[21].

Bromine is an electron acceptor that readily intercalates graphite[22]. It has recently been shown by Chung *et al.* that bromine inhibits oxidation of carbon fibers and the effect is attributed to the electron transfer from carbon to bromine, thereby lowering the Fermi level and inhibiting oxidation[23,24]. In addition, bromine serves to decrease the electrical resistivity of the fibers to  $50\ \mu\Omega\cdot\text{cm}$  (comparable to the value for stainless steel) and to increase the electromagnetic interference (EMI) shielding effectiveness[25,26]. The mechanical properties of the fibers are essentially not affected by the bromination[27]. Much research has taken place in NASA Lewis Research Center[25,26] on brominated carbon fibers (Amoco Thornel P-100) primarily because of the EMI shielding application. The added advantage of enhanced oxidation resistance makes brominated carbon fibers even more important technologically.

The research in NASA has been on carbon fibers

Table 1. Properties of carbon-carbon composites before bromination

Grade	CC1001D	CC1501D	CC1501G
Heat treatment temperature (°C)	1000	1000	2000
Bulk density (g/cm <sup>3</sup> )	1.35-1.40	1.40-1.45	1.40-1.45
Open porosity (%)	20-25	15-20	20-25
Bending strength (N/mm <sup>2</sup> )	140-160	230-280	210-250
Dynamic E modulus (kN/mm <sup>2</sup> )	30-35	55-60	60-65
Tensile strength (N/mm <sup>2</sup> )	90-110	280-350	260-330
Electrical resistivity parallel to fibers (Ω.μm)	35-40	30-35	25-30
Coefficient of permeability (cm <sup>2</sup> /s)	$4.4 \times 10^{-2}$	$5.9 \times 10^{-3}$	$4 \times 10^{-2}$
Interlaminar shear strength (N/mm <sup>2</sup> )	13-18	10-15	9-12
Ash content (%)	0.14	0.2	0.08

brominated by direct exposure to liquid or vapor bromine, as this method of intercalation is widely used for almost all intercalate species. This type of brominated carbon fibers (Type I) is more oxidation resistant than pristine carbon fibers[23]. On the other hand, carbon fibers can instead be brominated by electrochemical intercalation (i.e., anodic oxidation)[28]. This latter type of brominated carbon fibers (Type II) is even more oxidation resistant than Type I[24]. This difference between Type I and Type II is attributed to the larger charge transfer coefficient for Type II than Type I, as shown by Hall measurement[24]. Moreover, Type I and Type II differ in structure in the following ways[24].

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. Interaction 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.

Although much research work has been done on brominated carbon fibers, the bromination of carbon-carbon composites has not been previously explored. Hence, this is the subject of the present paper.

## 2. EXPERIMENTAL

### 2.1 Material preparation

The carbon-carbon composite materials used were kindly provided by Sigri Corporation (Somerville, NJ). They were all in the form of PAN-based carbon fibers that had been resin impregnated, laminated, and compressed into sheets. The matrix was subsequently carbonized by heating at either 1000°C (for Grades CC1001D and CC1501D) or 2000°C (for Grade CC1501G). The fibers used were in the form of either staple fiber fabric (for Grade CC1001D) or roving fabric (for Grades CC1501D and CC1501G). The properties of these three grades of carbon-carbon composites as received from Sigri are summarized in Table 1, which is taken from the product brochure of Sigri Corporation.

Bromination of the carbon-carbon composites was carried out by using two methods. Method 1 involved exposure of the composite to bromine vapor in air at room temperature for seven days. After that, the composites were removed from the bromination vessel and placed under a fume hood, where bromine desorption at room temperature was allowed from the brominated composites for three days. Method 2 involved anodic oxidation of the composite in an electrolyte, which was a saturated aqueous potassium bromide solution. The composite was suspended in the electrolyte by a platinum wire and basket, which served as the anode. Electrical contact between the composite and the platinum basket was

Table 2. Effect of bromination on electrical resistivity

Material	Electrical resistivity (Ω.μm)	Fractional decrease due to bromination
1001D	Untreated	$36 \pm 1$
	Brominated	$27 \pm 2$
1501D	Untreated	$32 \pm 2$
	Brominated	$21 \pm 1$
1501G	Untreated	$28 \pm 2$
	Brominated	$17 \pm 3$

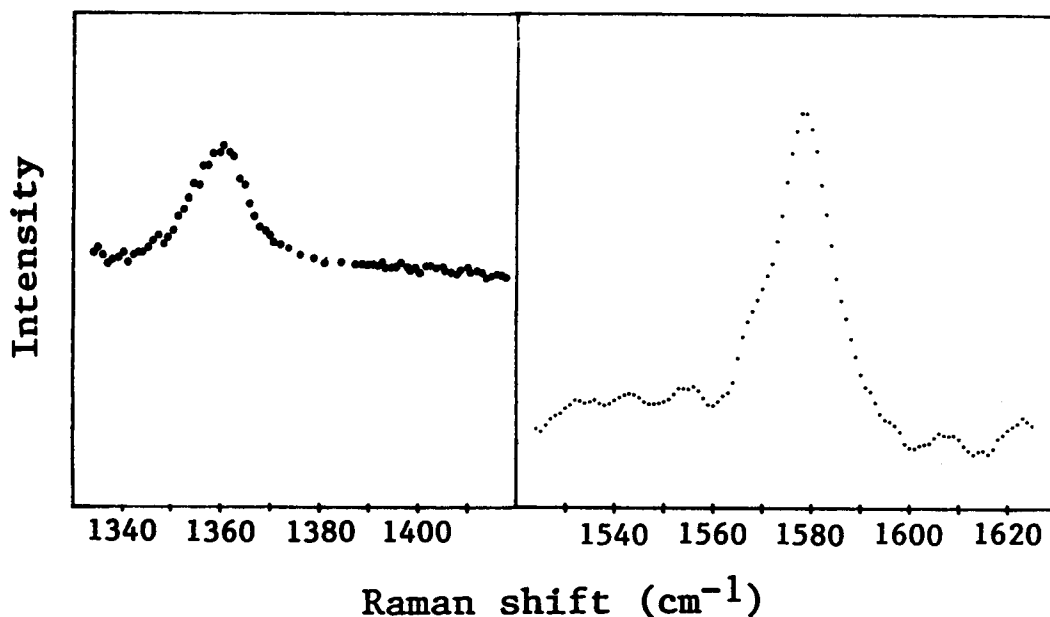


Fig. 1. Raman spectrum of brominated 1501G carbon-carbon composite. The vertical scale is the same for both segments of the figure.

rendered by pressure. Another platinum wire served as the cathode. Anodic oxidation was performed at a constant current of 0.5 mA for 72 h. The set-up was the same as that of ref. 24.

Method 1 corresponds to the method for preparing Type I brominated carbon fibers. Method 2 corresponds to the method for preparing Type II brominated carbon fibers. All results given in this paper are for composites treated by Method 1, unless stated otherwise.

## 2.2 Weight uptake

The difference between the initial and final (after both bromination and desorption) weights of a composite gave the weight uptake. For samples treated by Method 1, the weight uptake was 10.84% for CC1001D, 15.02% for CC1501D, and 15.16% for CC1501G. For samples treated by Method 2, the weight uptake was negligible for all types of composites. This means that Method 2 was not capable of brominating the composites, whereas Method 1 was. However, Tillgner and Ruland successfully car-

ried out electrochemical intercalation of bromine in Thormel P-100 carbon fibers[28]. The reason for this difference between carbon fibers and carbon-carbon composites 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 the matrix of carbon-carbon composites than for bromine in carbon fibers.

## 2.3 Electrical resistivity

The electrical resistivity of the composites was measured at room temperature by using the four-probe method. The electrical contacts were made by using silver paint. The results for untreated and brominated composites of each of the three types are shown in Table 2. Bromination decreased the resistivity by 39% for 1501G, 34% for 1501D, and 25% for 1001D. This indicates the occurrence of electron transfer (from carbon to bromine) in all types of brominated composites.

The percentage decrease in resistivity was larger

Table 3. Effect of bromination on tensile modulus

Material	Tensile modulus (GPa)	Fractional decrease due to bromination
1001D	Untreated	33.85 ± 1.1
	Brominated	28.44 ± 1.35
1501D	Untreated	57.71 ± 3.6
	Brominated	47.89 ± 3.46
1501G	Untreated	64.2 ± 4.1
	Brominated	53.6 ± 3.6

Table 4. Effect of bromination on tensile strength

Material	Tensile strength (MPa)	Fractional decrease due to bromination
1001D	Untreated	100.56 ± 5.12
	Brominated	83.46 ± 4.02
1501D	Untreated	323.10 ± 6.3
	Brominated	259.21 ± 5.7
1501G	Untreated	307.13 ± 6.3
	Brominated	256.12 ± 5.9

for 1501G than 1501D, even though the weight uptake was about the same for these two types of composites. As 1501G had undergone a 2000°C heat treatment, whereas 1501D had undergone a 1000°C heat treatment, 1501G was more graphitic than 1501D. This is probably why the percentage decrease in resistivity was larger for 1501G than 1501D.

The percentage decrease in resistivity was much larger for 1501D than 1001D. This is consistent with the much larger weight uptake for 1501D than 1001D.

#### 2.4 Structure

Bromination had no effect on the x-ray diffraction patterns of all types of composites. Only graphitic diffraction peaks were observed, namely 002, 100, and 110. Furthermore, no difference was observed between the diffraction pattern of the matrix alone and that of the fiber bundles alone. (The matrix and fiber bundles were mechanically separated and then further ground to powders.) Therefore, no diffraction evidence for the occurrence of intercalation was found.

As a further test for intercalation, differential scanning calorimetry (DSC) was performed in the temperature range from -45 to 300°C, using a Perkin-Elmer DSC-2 system. No peak was observed. The absence of a peak at 100°C indicates the absence of the bromine intercalate melting transition that occurs at 100°C in graphite-bromine prepared by Method 1[29]. The absence of a peak at -2°C indicates the absence of the bromine intercalate melting transition that occurs at -2°C in graphite-bromine prepared by Method 2[24]. The absence of a peak at 58°C indicates the absence of free bromine, which boils at 58°C.

Scanning electron microscopy (SEM) showed that bromination had no effect on surface morphology of the carbon-carbon composites. X-ray spectroscopy

was performed in conjunction with SEM to observe the bromine distribution in the composites after bromination. For all types of brominated composites, bromine was not detected in the fibers, but was detected in the matrix. The highest bromine concentration occurred in pores within the interbundle matrix. The pore size was typically about 20 μm.

Raman scattering was performed in the 180° 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. Figure 1 shows the only observed peaks, which occur at 1580 cm<sup>-1</sup> (E<sub>2g</sub> mode of graphite) and 1360 cm<sup>-1</sup> (due to crystallite boundaries) for CC1501G. All three grades of pristine or brominated carbon-carbon composites showed the same result. No doublet was observed near 1580 cm<sup>-1</sup>, implying the absence of intercalation in the brominated carbon-carbon composites. No Raman peak was observed around 323 cm<sup>-1</sup> (the vibration frequency of a free bromine molecule) or 240 cm<sup>-1</sup> (frequency for Br<sub>2</sub><sup>-</sup> or Br<sub>2</sub><sup>-</sup> ions[30]).

The above structural investigation revealed that a brominated carbon-carbon composite comprised a brominated (but not intercalated) carbon matrix and pristine (not brominated) carbon fibers. This is consistent with the fact that the fibers were PAN-based. PAN-based carbon fibers tend to be less graphitic than pitch-based carbon fibers. The effects of bromination on PAN-based carbon fibers are negligible compared to the much studied effects of bromination on pitch-based carbon fibers.

The absence of intercalation in the brominated carbon matrix is attributed to the relatively low heat treatment temperature of 2000°C or less. The low heat treatment temperature was not able to cause graphitization of the carbon matrix. Intercalation requires a graphitic structure. Although intercalation

Table 5. Effect of bromination on tensile ductility (elongation at break)

Material	Tensile ductility (%)	Fractional change due to bromination
1001D	Untreated	0.38 ± 0.08
	Brominated	0.39 ± 0.09
1501D	Untreated	0.69 ± 0.11
	Brominated	0.67 ± 0.04
1501G	Untreated	0.51 ± 0.06
	Brominated	0.53 ± 0.07

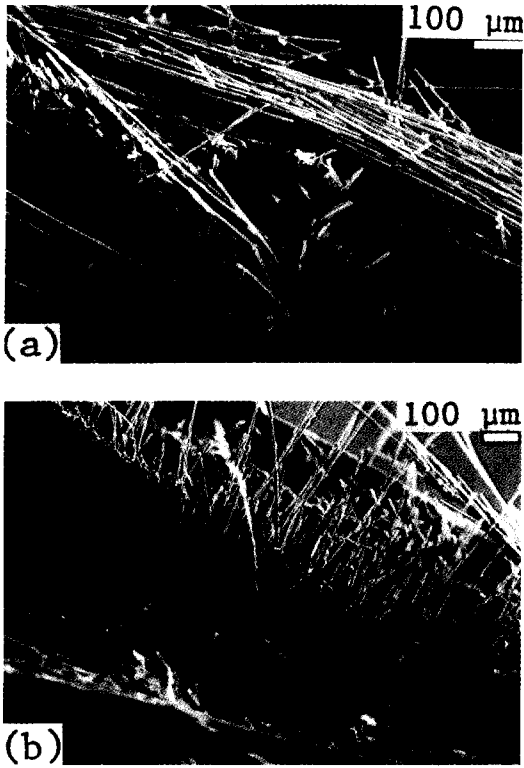


Fig. 2. SEM photographs of the fracture surfaces of carbon-carbon composite 1501D. (a) Untreated composite. (b) Brominated composite.

did not occur in the carbon matrix, electron transfer did occur, as indicated by the decrease in the electrical resistivity.

### 2.5 Mechanical properties

Tensile tests were performed on untreated composites and brominated composites. The tests were carried out using a hydraulic Materials Testing System (MTS). The strain was measured by using a strain gage (Measurements Group, Inc., gage type EA-13-120LZ-120, resistance =  $120.0 (\pm 0.3\%)$  ohms, gage factor =  $1.095 \pm 0.5\%$  at  $75^\circ\text{F}$ ). The gage length was 2 in.

Tables 3-5 show the tensile modulus, tensile strength, and tensile ductility (elongation) for the untreated and brominated composites. The modulus and strength were decreased by bromination by less than 20% and the tensile ductility was not affected by bromination.

Figure 2 shows the fracture surfaces after tensile testing of 1501D before and after bromination. Each is a low-magnification SEM photograph showing fiber bundles in various directions. These and other photographs show that debonding between the carbon fiber layers occurred much more extensively after bromination than before bromination. Similar observations were also made in 1501G and 1001D samples. This means that bromination degraded the

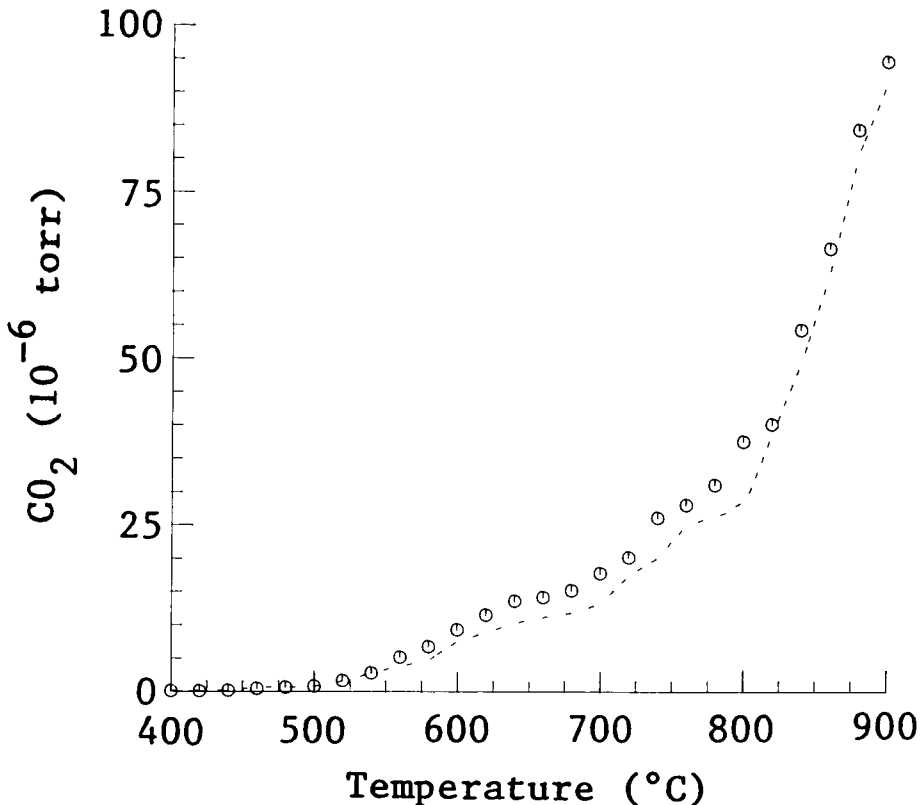


Fig. 3. Evolved  $\text{CO}_2$  gas pressure versus temperature during heating at  $10^\circ\text{C}/\text{min}$  for carbon-carbon composite 1001D. Circles: untreated composite. Dashed curve: brominated composite.

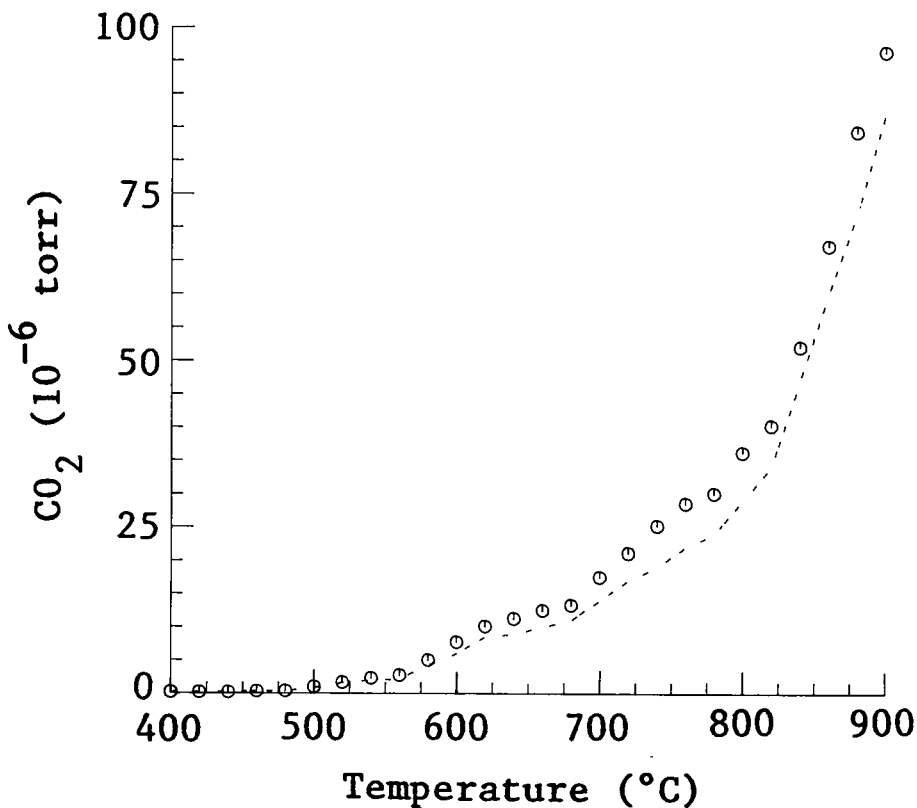


Fig. 4. Evolved CO<sub>2</sub> gas pressure versus temperature during heating at 10°C/min for carbon-carbon composite 1501D. Circles: untreated composite. Dashed curve: brominated composite.

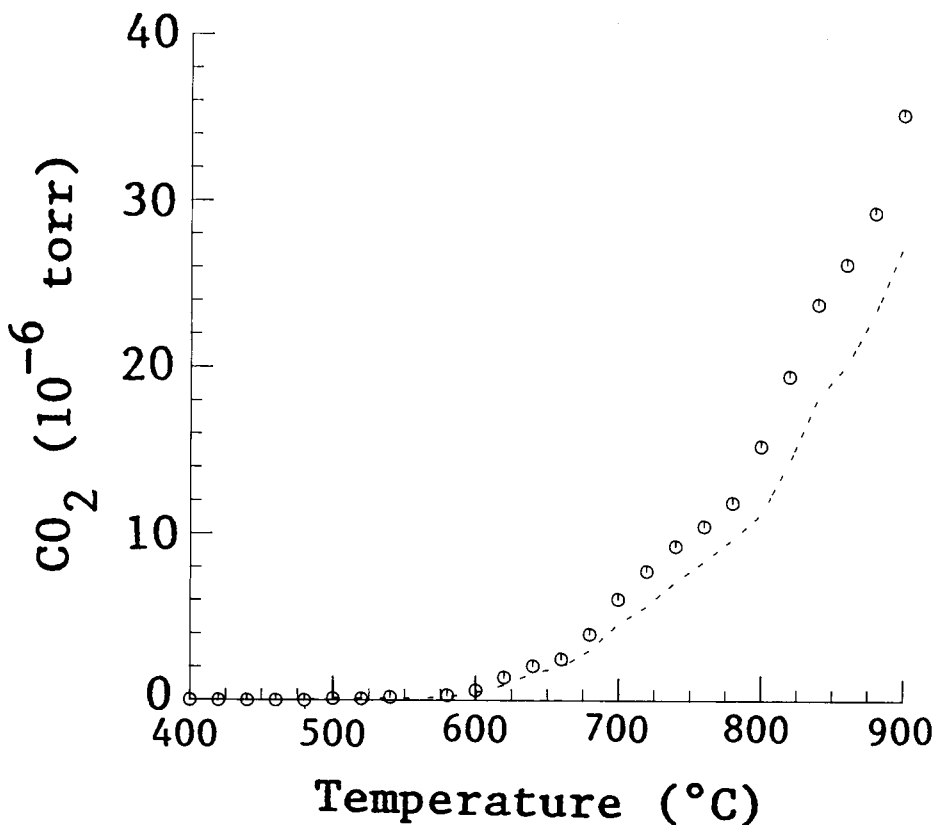


Fig. 5. Evolved CO<sub>2</sub> gas pressure versus temperature during heating at 10°C/min for carbon-carbon composite 1501G. Circles: untreated composite. Dashed curve: brominated composite.

Table 6. Temperatures in °C (during temperature scanning at 10°C/min) required to achieve various burn-off percentages

Material		10%	20%	30%	40%
1001D	Untreated	574	612	643	689
	Brominated	582	650	704	745
1501D	Untreated	593	631	664	684
	Brominated	615	682	740	780
1501G	Untreated	674	729	769	804
	Brominated	682	776	821	879

strength partly due to the weakening of the bonding between the fiber bundles and the matrix.

### 2.6 Oxidation resistance

The oxidation resistance of the composites in air was studied isothermally at various temperatures as well as during temperature scanning. The samples were cut with a diamond saw to  $0.5 \times 0.5$  in for measurement. The weight of each test specimen was about 210 mg prior to heating.

2.6.1 *Temperature scanning mode.* Oxidation resistance was investigated during temperature scan-

ning from 20 to 900°C at a heating rate of 10°C/min. During heating, the weight of the specimen was measured in situ using a Perkin-Elmer AD-2Z autobalance, and simultaneously the relative amount of evolved bromine vapor and the relative amount of evolved CO<sub>2</sub> vapor were monitored by using a VG Instruments, Inc. 1-300 amu quadrupole mass spectrometer equipped with a glass-lined capillary inlet.

The desorption of bromine began at about 180°C for all brominated composites. Figures 3-5 show the CO<sub>2</sub> (evolved due to the oxidation of carbon) pressure as a function of temperature during temperature scanning for the untreated composites (data points shown by circles) and the brominated composites (data shown by dashed curves). For 1001D and 1501D (both carbonized at 1000°C), CO<sub>2</sub> evolution was negligible below 500°C. For 1501G (carbonized at 2000°C), CO<sub>2</sub> evolution was negligible below 600°C. This difference between composites carbonized at different temperatures is consistent with the fact that the oxidation resistance of carbon increases with increasing degree of graphitization. This also means that the weight loss below 500°C for 1001D and 1501D and that below 600°C for 1501G were essentially all due to the desorption of bromine rather than the

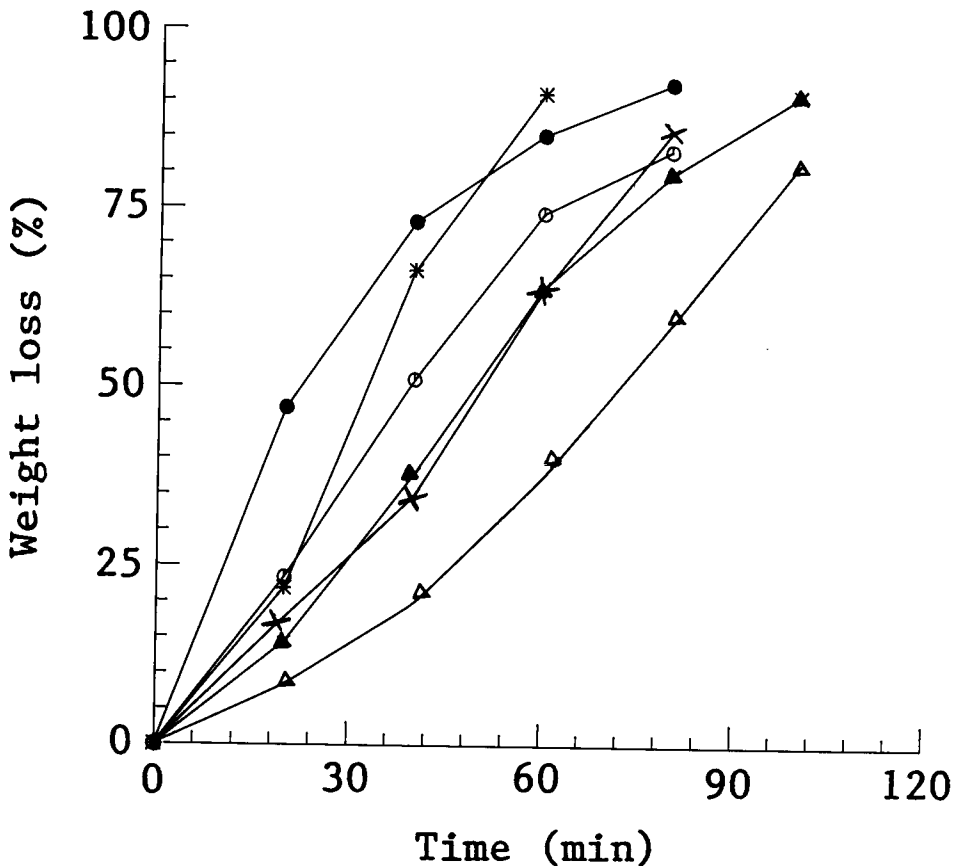


Fig. 6. Fractional weight loss versus time isothermally at 650°C.

- ▲: 1501G, untreated
- △: 1501G, brominated
- : 1501D, untreated
- : 1501D, brominated
- \*: 1001D, untreated
- X: 1001D, brominated.

Table 7. Oxidation rate measured at 25% burn-off

Material	Oxidation rate ( $10^{-2} \text{ min}^{-1}$ )			
	850°C	750°C	700°C	650°C
1001D Untreated	2.96	2.84	2.61	1.09
1001D Brominated	2.74	2.51	2.36	0.89
1501D Untreated	3.48	3.04	2.46	2.05
1501D Brominated	2.51	2.16	1.54	1.17
1501G Untreated	1.76	1.61	1.32	0.71
1501G Brominated	1.36	1.15	0.95	0.41

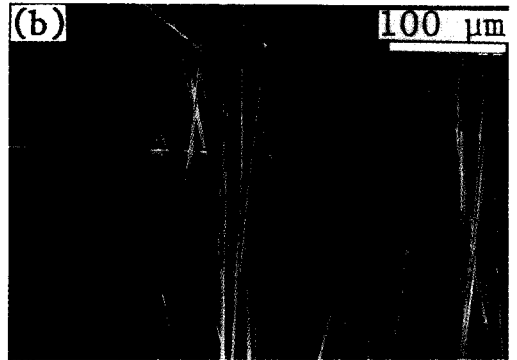
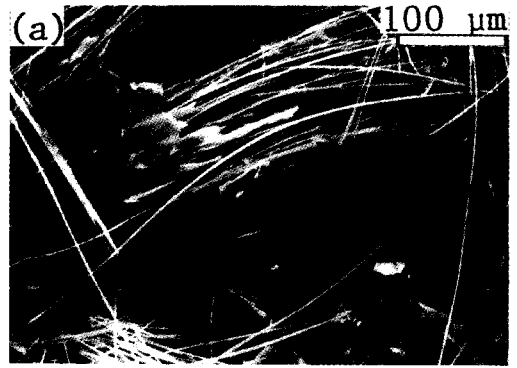
oxidation of carbon. Comparison of the data for untreated and brominated composites in each of Figs. 3–5 shows that bromination increased the oxidation resistance for all three types of composites. In particular, for 1001D (Fig. 3) and 1501D (Fig. 4), bromination increased the oxidation resistance most significantly at 640–820°C, whereas, for 1501G (Fig. 5), bromination increased the oxidation resistance most significantly at 750–900°C.

Table 6 shows the temperatures (during temperature scanning at  $10^\circ\text{C}/\text{min}$ ) required to achieve 10, 20, 30 and 40% burn-off (detected gravimetrically) in air. For each type of composite, these temperatures were increased by bromination, although the increases were much larger for the higher burn-off percentages. For example, for 1501G, the temperature increase was  $8^\circ\text{C}$  at 10% burn-off and  $75^\circ\text{C}$  at 40% burn-off; for 1501D, the temperature increase was  $22^\circ\text{C}$  at 10% burn-off and  $96^\circ\text{C}$  at 40% burn-off. This dependence on the burn-off percentage is due to the contribution of bromine desorption to weight loss in the brominated composites. This contribution is more important at low temperatures (corresponding to low burn-off percentages), so that it may overshadow the effect of bromination on the oxidation resistance. At high temperatures (corresponding to high burn-off percentages), this contribution is negligible and the difference in the required temperature for burn-off truly reflects the effect of bromination on oxidation resistance.

The required temperatures for burn-off are quite close between 1001D and 1501D, and are highest for 1501G for each burn-off percentage. This is attributed to the higher heat treatment temperature for 1501G (namely,  $2000^\circ\text{C}$ ). The increases (due to bromination) in the required temperatures for burn-off are much larger for 1501D than 1001D. This is

Table 8. Fractional decrease in the oxidation rate (measured at 25% burn-off) due to bromination

Material	Fractional decrease in oxidation rate (%)			
	850°C	750°C	700°C	650°C
1001D	7.4	11.6	9.6	18.4
1501D	27.9	29.0	37.4	42.9
1501G	22.7	28.6	28.0	42.3

Fig. 7. SEM photograph of brominated carbon-carbon composite 1501G after (a) 15% burn-off at  $650^\circ\text{C}$  and (b) 40% burn-off at  $700^\circ\text{C}$ .

consistent with the larger weight uptake for 1501D than 1001D.

**2.6.2 Isothermal mode.** 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 composite (typically about 210 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  $0.0101 \text{ m}^3$ . Because of the large volume of the furnace and the small volume of the specimens, the absence of forced air circulation in the furnace did not affect the quality of the results. The heating of each specimen was interrupted at 20 min intervals for the purpose of weighing. The weight loss of each type of composite as a function of time at  $650^\circ\text{C}$  is shown in Fig. 6. The oxidation resistance was increased by bromination for each type of composite.

Table 9. Properties of graphitized carbon-carbon composite before bromination

Treatment temperature	$2700^\circ\text{C}$
Tensile modulus	$73.2 \pm 6.1 \text{ GPa}$
Tensile strength	$275.2 \pm 6.4 \text{ MPa}$
Tensile ductility	$0.44 \pm 0.05\%$
Electrical resistivity	$21 \pm 6 \Omega \cdot \mu\text{m}$

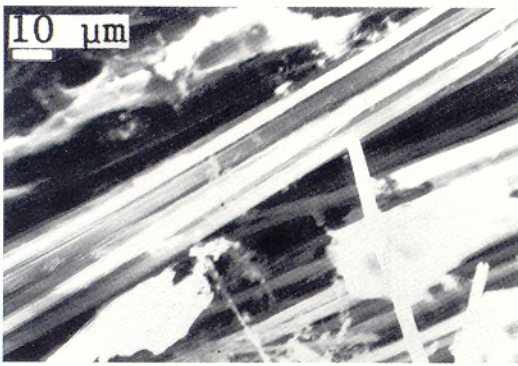


Fig. 8. SEM photograph of graphitized carbon-carbon composite after bromination.

Table 7 shows the oxidation rate at 25% weight loss (determined from the slope of isothermal weight loss curves, such as Fig. 6, at 25% weight loss) for all types of composites at 850, 750, 700, and 650°C. The oxidation rate was decreased by bromination at all temperatures for each type of composite.

Table 8 shows the percentage decrease in the oxidation rate (measured at 25% burn-off) due to bromination. The largest percentage decrease of the oxidation rate occurred at 650°C. In particular, for 1501D at 650°C, bromination decreased the oxidation rate by 43%.

Figure 7 shows scanning electron microscope (SEM) photographs of brominated 1501G after partial oxidation. Figure 7(a) was obtained after 15% burn-off at 650°C; Fig. 7(b) was obtained after 40% burn-off at 700°C. These photographs indicate that oxidation damaged the matrix rather than the fibers.

The percentage decrease in oxidation rate was greater for 1501D than 1501G at each temperature, especially at 700°C. Since 1501G is more graphitic than 1501D, this means that the effectiveness of

bromination in inhibiting the oxidation of carbon-carbon composites does not increase with increasing degree of graphitization, even though the ease of intercalation increases with increasing degree of graphitization[31]. This further implies that intercalation is not the origin of the oxidation inhibition. This effect on oxidation for carbon-carbon composites may be due to the chemisorption of bromine on active sites[19]. However, it may also be attributed to the electron transfer from the carbon to the bromine, which increases the oxidation resistance of carbon-carbon composites.

**2.6.3 Separated matrix and fiber bundles.** Each composite was ground to about 250 mesh in order to physically separate the matrix from the fiber bundles. The oxidation resistance of the matrix and the fiber bundles were then separately studied by weight loss measurement. It was thus found that bromination increased the oxidation resistance of the matrix, but had little effect on the oxidation resistance of the fiber bundles. This is consistent with the results of x-ray spectroscopy (Sec. 2.4), which showed that bromine resided in the matrix rather than in the fiber bundles.

### 2.7 Effects of the graphitization of carbon-carbon composites at 2700°C

The 1501G carbon-carbon composite was graphitized at 2700°C for 6 h in our Astro vacuum furnace. The properties of the resulting composite, labeled 1501H, are shown in Table 9. The measurements were made using the same methods as were used for the other composites. Graphitization decreased the electrical resistivity from  $28 \pm 2$  (Table 2) to  $21 \pm 6$  (Table 9)  $\Omega \cdot \mu\text{m}$ , increased the tensile modulus from  $64.2 \pm 4.1$  (Table 3) to  $73.2 \pm 6.1$  (Table 9) GPa, decreased the tensile strength from  $307.13 \pm 6.3$  (Table 4) to  $275.2 \pm 6.4$  (Table 9) MPa, and decreased the ductility from  $0.51 \pm 0.06\%$  (Table 5) to  $0.44 \pm 0.05\%$  (Table 9).

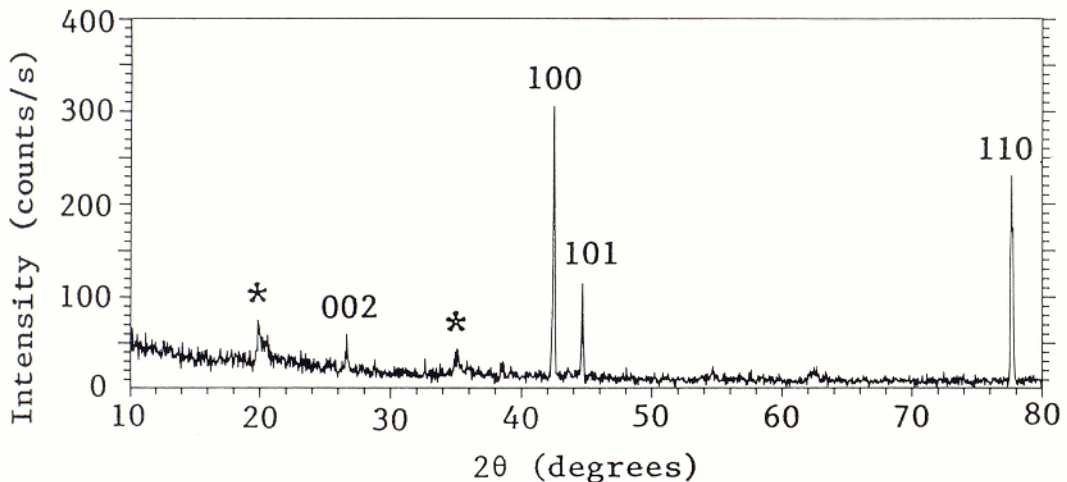


Fig. 9. X-ray diffraction pattern of graphitized carbon-carbon composite after bromination. The Miller indices shown correspond to graphite. The in-plane intercalate superlattice peaks are labeled with \*.

The 1501H composite was exposed to bromine vapor in air at room temperature. After two days, the composite was found to be damaged. Figure 8 shows an SEM photograph that indicates the damage was due to the cracking of the matrix.

Figure 9 shows the x-ray diffraction pattern of brominated 1501H. Two peaks associated with the in-plane intercalate superlattice were observed, indicating the occurrence of true intercalation, which is the origin of the matrix damage in Fig. 8.

### 3. CONCLUSION

Bromination by exposure to bromine vapor at room temperature was effective for inhibiting the oxidation of carbon-carbon composites in the form of resin impregnated carbon fibers carbonized at 1000 or 2000°C. The oxidation rate was decreased by up to 43%. In addition, the electrical resistivity was decreased by up to 39%. The tensile modulus decreased by 16–17%; the tensile strength decreased by 17–20%; the ductility was not affected. The weight uptake caused by bromination was up to 15%. The bromine resided in the matrix of the composite, particularly in pores within the matrix. The origin of the increased oxidation resistance is probably the electron transfer from the carbon matrix to the bromine. This transfer lowered the Fermi energy of the carbon. Bromination of the carbon-carbon composites was not possible with the electrochemical method. On the other hand, carbon-carbon composites graphitized at 2700°C were damaged by the bromination. Thus, the maximum heat treatment temperature of the carbon-carbon composite for bromination to be beneficial lies between 2000 and 2700°C.

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