

# INTERCALATE VAPORIZATION DURING THE EXFOLIATION OF GRAPHITE INTERCALATED WITH BROMINE

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**Abstract**—Pressure-volume-temperature measurement during the exfoliation of graphite intercalated with bromine showed that exfoliation involved the vaporization of 1/8 of the intercalate, which formed aggregates of at least 8 monolayers thick on the average. At the point of completion of the vaporization, one vaporized intercalate monolayer was about 400 Å thick.

**Key Words**—Bromine, intercalation, exfoliation, vaporized intercalate, pressure.

## 1. INTRODUCTION

Intercalate vaporization in a graphite intercalation compound is a phase transition which causes large (up to hundreds of times) expansions along the *c*-axis. This phenomenon is known as exfoliation. The phase transition is reversible so that collapse of the exfoliated material occurs upon cooling due to the condensation of the intercalate[1]. However, excessive heating causes the exfoliation to be irreversible[1]. Irreversibly exfoliated graphite has a honeycomb microstructure[1-3], which suggests the existence of gaseous bubbles within the graphite crystals[1].

Irreversibly exfoliated graphite is technologically important for numerous applications, including high temperature gaskets and packings[4-9], fire extinguisher agent[10,11], thermal insulator[12], conductive resin composites[13], electrodes[14], protective layers on carbon crucibles[15], lubricant support[16], battlefield obscurant[17] and molded graphite products[18].

In spite of the technological importance of exfoliated graphite, there has been little work on the process of exfoliation or on the nature of the vaporization. Mazieres *et al.* showed that intercalate vaporization in graphite obeys the Clapeyron-Clausius equation[19]. From the slope of the plot of  $\log P$  versus  $1/T$  (where  $P$  = pressure and  $T$  = temperature), they found that the enthalpy change  $\Delta H$  ranges from 11 to 17 kcal/mole, which is much higher than that associated with the vaporization of bulk liquid bromine (7.3 kcal/mole). Martin and Brocklehurst showed that the exfoliation temperature increases linearly with applied load[1]. Dowell showed that the volume change due to exfoliation is smaller than that predicted for ideal-gas expansion, such that the ideal-gas expansion is approached as rates of expansion greatly exceeds intercalate desorption rates[3]. A similar ideal-gas expansion was also reported by Mazieres *et al.*[20].

In these previous works, either the temperature  $T$  and the pressure  $P$  were measured without measuring the volume  $V$ [19], or the volume alone was measured[3,20], so a rigorous test of the extent of ideal-gas behavior was not possible. In the present work,  $P$ ,  $V$ , and  $T$  were all measured simultaneously, thus allowing a quantitative study of the vaporization process.

## 2. EXPERIMENTAL

### 2.1 Sample preparation

Highly oriented pyrolytic graphite (HOPG), which was kindly provided by Union Carbide Corporation, was intercalated with bromine to stage 2 by exposure to bromine vapor at room temperature. Subsequently it was allowed to desorb in air at room temperature. At the beginning of the experiment, weight measurement showed that the sample contained 73 wt.% bromine; at the end of the experiment, the sample contained 22 wt.% bromine. During the experiment, the sample was first heated up to 210°C to allow significant desorption to take place, so that in the subsequent time when data collection was made, little desorption took place. As the rate of desorption is much higher above 100°C (melting temperature of intercalated bromine) than below 100°C, the heat treatment at 210°C ensured significant desorption[21]. Using previous thermogravimetric results[21], it is clear that, during the period of data collection, the sample's intercalate concentration was greater than but relatively close to 22 wt.% bromine.

The sample thickness (along the *c*-axis) was 0.58 mm. The cross-sectional area of the sample (perpendicular to the *c*-axis) was 0.281 cm<sup>2</sup>.

### 2.2 Experimental techniques

The graphite-bromine sample was placed between the ends of two glass (Pyrex) rods. The other end

of each of the glass rods had been fixed to one of the steel compression plates of an Instron Model 1125 (22,000 lb. load frame) mechanical testing system, which had a machine stiffness of  $1 \times 10^6$  lb/in operating in the compression mode. A 10,000 lb load cell was used at a full scale of 0.2% (or 20 lb). A chromel–alumel thermocouple was placed beside the sample, such that it almost touched the sample. The sample and parts of the glass rods were surrounded by a small resistance heater coil, which extended about 2.5 cm both above and below the sample. The temperature detected by the thermocouple was controlled by a TECCO temperature programmer.

The sample was heated gradually from room temperature to 210°C over a period of about 1 hr and was then held at 210°C for about 5 min in order to complete most of the desorption and to bring the intercalate concentration to a value which was stable even at the highest temperature used in the experiment. Subsequently the temperature was lowered to 200°C and the cross-head above the sample was allowed to move upward at a speed of 1 mm/min for 2 min and then downward at the same speed for 2 min while the stress was continuously measured. After this, the temperature was lowered stepwise to 190, 180, 160, 140 and 120°C; at each temperature, the cross-head was moved up and down as described above.

### 2.3 Experimental results

At each constant temperature, the stress decreased as the cross-head moved up (the sample thickness increased) and the stress increased as the cross-head subsequently moved down (the sample thickness decreased). The magnitude of the change in stress increased with increasing temperature. Figure 1 shows the stress–strain curves obtained at 180°C during expansion and collapse of the sample. The curves almost overlapped, indicating the reversibility of the process. The curve during collapse

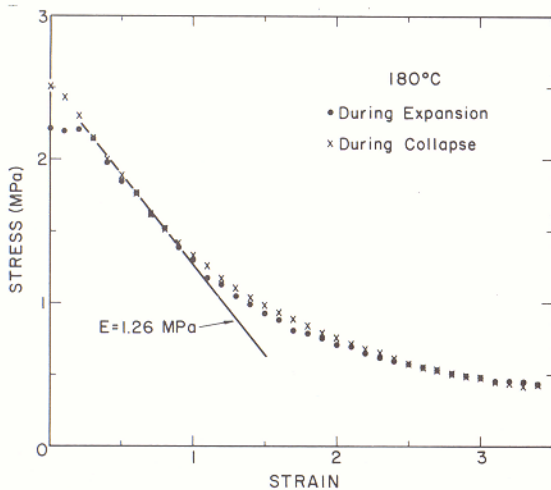


Fig. 1. Stress-strain curves obtained at 180°C during the expansion and collapse of graphite-bromine.

can be viewed as the compression stress–strain curve of exfoliated graphite if the strain axis in Fig. 1 is reversed. The curve during expansion reveals the thermomechanical behavior of intercalated graphite. The curve during collapse shows that the ease of compressing exfoliated graphite decreased as the collapse occurred, such that the maximum “Young’s modulus”  $E$  of exfoliated graphite at 180°C was given by the slope of the solid line in Fig. 1, i.e., 1.3 MPa. The value of  $E$  was 1.8 MPa at 190°C and was 1.5 MPa at 200°C. At temperatures below 180°C, the stress changes were too small for quantitative analysis.

As the stress was related to the pressure  $P$  and the strain was related to the volume  $V$ , the product of stress and strain was related to the product of  $P$  and  $V$ . Therefore, the product of stress and strain was plotted against the strain for each constant temperature, as shown in Fig. 2 for 180°C. This product increased with strain up to a strain of about 2 and then levelled off at a constant value of 1.45 MPa. Similar behavior was observed during expansion and collapse. The levelled off value of this product was 1.40 MPa during expansion at 190°C and was 1.32 MPa during expansion at 200°C. In general, a flatter curve was obtained during expansion than collapse, so the values obtained during expansion were more representative.

At 180°C, the stress–strain product of 1.45 MPa at a strain of about 2 corresponds to a  $PV$  product of  $2.35 \times 10^{-4}$  1.atm. Hence,  $PV/RT = 6.32 \times 10^{-6}$ . Since the compressibility factor of bromine is 1.0[22],  $PV/RT$  gives the number of moles of bromine that vaporized. From this, it was found that the ratio of the number of moles of vaporized  $\text{Br}_2$

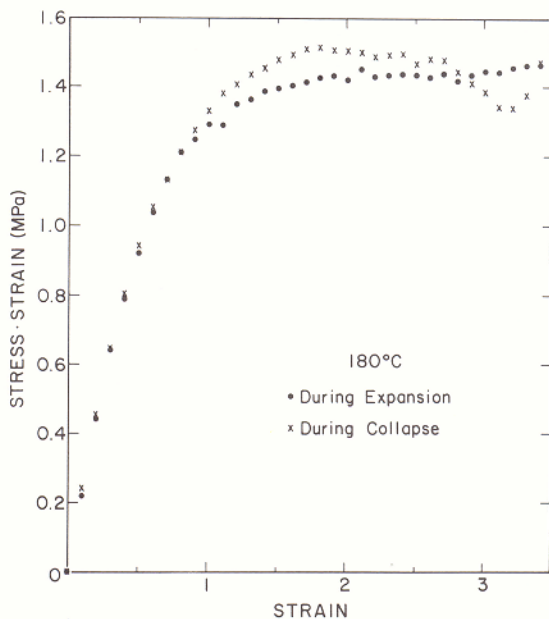


Fig. 2. The product of stress and strain as a function of strain at 180°C during the expansion and collapse of graphite-bromine.

molecules to the number of moles of carbon atoms was 0.0033. This implies that the fraction of bromine intercalate that vaporized was  $0.13 \pm 0.03$ ; the error limits in this value reflect the error in estimating the bromine concentration in the sample. Similar analysis of the 190°C data showed that the fraction of bromine intercalate that vaporized was  $0.12 \pm 0.03$ ; similar analysis of the 200°C data showed this fraction to be  $0.115 \pm 0.025$ .

Little or no variation of the Young's modulus of exfoliated graphite or the fraction of bromine intercalate that vaporized was found with temperature. However, because of the limited temperature range used in this work, the presence of some temperature dependence cannot be ruled out. In the temperature range from 180 to 200°C, the mean value of the Young's modulus of exfoliated graphite was 1.4 MPa and the mean value of the fraction of bromine intercalate that vaporized was  $0.12 \pm 0.03$ .

### 3. DISCUSSION

The fact that the sample used in this work had been desorbed at 210°C prior to the data collection and the fact that the data were reversible during expansion and collapse at various temperatures show that the results describe the intercalate vaporization in a state of equilibrium. It should be noted that the heat-treatment at 210°C was carried out while the sample was mechanically constrained from exfoliation as well as while the sample was allowed to expand. Thus, this heat-treatment ensured the occurrence of significant desorption, which typically accompanies first exfoliation. In this way, the occurrence of significant desorption during the data collection was avoided. The equilibrium and reversible nature of the exfoliation is in contrast to the non-equilibrium and irreversible nature of the exfoliation investigated by others[3,20]. In general, exfoliation becomes irreversible when the heating is excessive[23].

The results represented by Fig. 2 show that, during exfoliation expansion, the intercalated bromine gradually vaporized, with the fraction of intercalate vaporized increasing with strain up to a value of  $0.12 \pm 0.03$  at a strain of about 2. Beyond this strain, the fraction of intercalate vaporized remained constant up to a strain of 10. (Although a maximum strain of only 3.4 was used in Fig. 2, a separate experiment on another sample was carried out up to a strain of 10 and the constancy of the stress-strain product up to a strain of 10 was confirmed.) Therefore, only a small fraction of the intercalated bromine participated in the vaporization. The constancy of the stress-strain product indicates the ideal-gas behavior of the vaporized bromine. During collapse, condensation of the vaporized bromine occurred gradually below a strain of about 2.

Weight measurements and x-ray diffraction suggest the stage to be approximately 6 in the sample during the data collection. Assuming a stage of 6,

there would be a total of  $1.6 \times 10^5$  intercalate layers in the sample. Since about 0.12 of the intercalate underwent vaporization, the number of intercalate layers that underwent vaporization =  $(1.6 \times 10^5) \cdot 0.12 = 1.9 \times 10^4$ . At the point of completion of the vaporization, the strain was about 2. This means that, at the point of completion of the vaporization, the thickness of one vaporized intercalate monolayer would be 400 Å.

That the fraction of intercalate that vaporized was about 0.12 means that about 1/8 of the intercalate vaporized. For a stage of 6, the separation of nearest bromine layers is 23.8 Å. Hence, the separation of nearest vaporized bromine layers would be on the average  $23.8 \times 8 \sim 200$  Å, if one assumes that an entire intercalate monolayer vaporized uniformly without lateral migration of the intercalate.

The honeycomb microstructure of exfoliated graphite[1,2] suggests that the vaporized bromine occurs in the form of islands or bubbles. The width of an island is of the order of 1 μm, as suggested by transmission electron microscopy[24]. The thickness of the bubble wall is half of the separation between bubbles, or  $200 \text{ Å}/2 = 100 \text{ Å}$  if one assumes that an entire intercalate monolayer vaporizes uniformly without lateral migration of the intercalate.

Because of the error in stage determination and the error in determining the fraction of intercalate that vaporized, the values given above for the average height of a bubble and for the bubble wall thickness have errors of  $\pm 50\%$  and  $\pm 30\%$ , respectively. It should be emphasized that these values apply only at the point of completion of the vaporization and only if one assumes that an entire intercalate monolayer vaporizes uniformly without lateral migration of the intercalate. Further heating would cause ideal-gas expansion of the bubbles.

In order to measure the average thickness of the bubble wall, x-ray diffraction was performed on irreversibly exfoliated graphite-bromine at room temperature using  $\text{CuK}\alpha$  radiation. The irreversible exfoliation was achieved by heating graphite-bromine flakes at about 400°C for about 6 hr. The width of the line at  $\theta = 13.30^\circ$  (close to the 002 graphite line) showed that the  $L_c$  value was about 750 Å. A piece of pristine HOPG was used as a standard for linewidth measurement. This means that the bubble wall thickness was about 750 Å and the vertical separation between the nearest bubbles was about 1500 Å in irreversibly exfoliated graphite-bromine. As the strain of the graphite-bromine at the point of completion of the vaporization was smaller than that of the irreversibly exfoliated material, it is expected that  $L_c$  for irreversibly exfoliated graphite-bromine is smaller than that of graphite-bromine at the point of completion of the vaporization. Therefore, it can be concluded that, for graphite-bromine at the point of completion of the vaporization, the bubble wall thickness was at least 750 Å and the vertical separation between the bubbles was at least 1500 Å, in contrast to the respective values of 100 Å and 200

Å calculated from the *P-V-T* data by assuming that an entire intercalate monolayer vaporizes uniformly without lateral migration of the intercalate. This disagreement implies that the assumption was not valid, so that the intercalate migrates laterally and forms aggregates (at least 1500/200 ~ 8 monolayers thick on the average) that are separated laterally and vertically by graphitic regions. The aggregates evolve into bubbles. In this way, the vertical separation between the bubbles is at least 1500 Å while still 1/8 of the intercalate vaporized.

The  $L_c$  value determined here is greater than the value of 450 Å previously determined for irreversibly exfoliated graphite-HNO<sub>3</sub> that had been compressed into a foil[3].

The migration of the intercalate during exfoliation had been suggested by previous workers[1,3,19]. In particular, Dowell[3] suggested that the intercalate diffused from its position between the layers to defect sites at which it could form three-dimensional aggregates, which then vaporized. This work confirmed the existence of three-dimensional aggregates and furthermore showed that these aggregates are at least 8 monolayers thick on the average.

It should be emphasized that there is a wide distribution of the size of the bubbles, as indicated by scanning electron microscopy (SEM) of the irreversibly exfoliated material. The anomalously large bubbles may be a consequence of the presence of microcracks.

The reversibility of the exfoliation process pertains to the macroscopic expansion as well as the microscopic intercalate structure. X-ray diffraction showed that the in-plane intercalate structure, together with its three-fold twinning, are preserved after reversible exfoliation and collapse of graphite-bromine[24]. This reversibility means that the intercalate migration and aggregation are also reversible. Hence upon cooling, the bromine from the bubbles reintercalates to form condensed monolayers.

The formation of bubbles at defect sites has been suggested by previous workers[1,3,19]. On the other hand, single crystal graphite and HOPG intercalated with bromine exfoliated by similar amounts and with similar ease, so that grain boundaries cannot be the sites at which bubbles form[24]. It is possible that a bubble is associated with an intercalate island[23]. As the intercalate islands have a size distribution and the relatively large ones tend to form bubbles more easily than the others, not every island succeeds to evolve into a bubble. The mechanism for the intercalate migration and aggregation remains to be understood.

The physical origin for the fact that only 1/8 of the intercalate underwent vaporization is believed to be the wide distribution of intercalate island sizes. As larger cracks can buckle more easily, larger intercalate islands can form bubbles more easily. As a result, only a fraction of the intercalate islands manage to vaporize.

#### 4. CONCLUSION

By measuring the pressure and volume changes at constant temperatures during the exfoliation of graphite-bromine, it was found that exfoliation involved intercalate vaporization which occurred gradually up to a strain of 2, at which about 1/8 of the intercalate had vaporized. Beyond this point, negligible additional vaporization occurred and the vapor behaved like an ideal gas. Upon subsequent collapse of the exfoliated material, condensation began at a strain of 2 and occurred reversibly. From the average thickness of the bubble wall determined by X-ray diffraction, it was deduced that, during exfoliation, the intercalate migrated laterally and formed aggregates which were at least 8 monolayers thick on the average. The thickness of one vaporized intercalate monolayer was about 400 Å at the point of completion of the vaporization.

The stress-strain curves during exfoliation and collapse at various constant temperatures were determined, indicating that the compressive Young's modulus of exfoliated graphite was about 1.4 MPa at 180–200°C.

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