

Preparation and Thermal Expansion of Pyrolytic Graphite-Bromine Residual Compounds

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Stable pyrolytic graphite-bromine residual compounds (PG(Br)) of various bromine concentrations ($100.\text{Br}/\text{C}=0.3\text{--}12$) were prepared using PG deposited at 1900, 2100 and 2300° C. Preparation conditions and the thermal expansion in the direction of the *c*-axis of these compounds are described. Up to 1000° C the general characteristics of the thermal expansion of these PG(Br) are similar to that of PG(Br) made from PG heat-treated at 3000° C, but the thermal expansion coefficient of PG(Br) varies with bromine concentration and the properties of the original PG. The experimental results are interpreted by the following model: Bromine in the PG(Br) is bonded to the carbon network ionically at room temperature, but begins to vaporise to make gaseous bubbles between graphite layer planes at higher temperatures. These bromine gas bubbles expand against internal stress according to the ideal gas law. Therefore an increase in the average *c*-spacing of PG(Br) results upon heating.

1. Introduction

Pyrolytic graphite (PG) is used extensively as a high temperature material, a coating material for various purposes, and for some parts of electronic devices [1-3], because of its anisotropy in thermal and electrical properties. In order to extend the potentiality of PG for industrial applications, PG-compounds, i.e. PG doped with foreign elements, are currently studied. PG-compounds are classified into PG-deposited compounds and PG-lamellar compounds. The former are produced by pyrolytic decomposition of a mixture of hydrocarbon gas and halide of the foreign element, such as boron trichloride [4] and silicon tetrachloride [5]. The latter is formed by intercalation of foreign elements such as bromine [6] or potassium [7] into the PG-specimen. Usually most of the intercalated foreign element in PG-lamellar compounds escapes from the PG matrix, if the atmosphere of the foreign element is removed, but small amounts are retained even at considerably higher temperatures and in vacuum. These PG specimens are called PG-residual compounds [8]. The physical and chemical properties of the PG-residual compounds are different from those of the usual types of PG, and therefore some new

fields of application are anticipated. In this work, the peculiar behaviour of the thermal expansion of PG-bromine residual compounds was studied between room temperature and 1000° C.

Brocklehurst [9] measured the thermal expansion of extruded graphite-bromine residual compounds, and observed an extraordinary increase of the thermal expansion coefficient depending on the bromine concentration. Martin and Brocklehurst [10] studied the thermal expansion behaviour of PG-bromine residual compounds made from heat-treated PG. Specimens were prepared with their length axis perpendicular to the deposition plane, and varying loads were applied. They found a tendency for the behaviour of the thermal expansion similar to that in the extruded graphite-bromine residual compounds. They also recorded the hysteresis of the thermal expansion up to 500° C. During thermal cycling, the expansion of a specimen on heating always appeared to be lower than the contraction during cooling. The large thermal expansion in the *c*-direction was explained by the model of bromine gas bubbles: Bromine, existing as gas bubbles between the graphite layer planes, expands according to the

ideal gas law, with increasing temperature and spreads between the graphite layer planes, causing a net thermal expansion of the lattice spacing.

Yajima, Hirai, and Aoki [11] measured the thermal expansion behaviour of PG-bromine residual compounds, which contained various concentrations of bromine, in the temperature range from room temperature to 1000° C. The PG specimens used in the study had been heat-treated at 3000° C. The experimental results obtained are similar to those of Martin and Brocklehurst [10]. However, three stages of thermal expansion were observed both on heating and on cooling, which were not reported by Martin and Brocklehurst. The following model was used to explain this phenomenon. At room temperature, the bromine in PG is chemically bonded to the graphite layers (probably by ionic bonding [12]) rather than existing as gas bubbles. With an increase in temperature, the bonding force is decreased and the liberated bromine starts to form gas bubbles. Only then do the bromine gas bubbles expand between the layer planes as indicated by Martin and Brocklehurst [10].

PG-bromine residual compound, which is made of heat-treated PG, shows exfoliation to form flakes during the heat treatment process [13], but the PG-bromine residual compound made from as-deposited PG does not show such behaviour, even at high temperatures. The thermal expansion measurements were, therefore, made on such specimens. Preparation conditions of the PG-bromine residual compounds are described briefly.

2. Experimental

The PG specimens used in this experiment had been prepared in a graphite furnace by pyrolytic deposition of propane gas on heated graphite substrates at three different temperatures, 1900, 2100 and 2300° C. These PG specimens have a turbostratic structure and resemble each other in appearance. Their cross-sections are shown in fig. 1, and some physical properties are summarised in Table I. In these specimens, the crystallite arrangement cannot so clearly be described as in the case of heat-treated PG. Blocks of about 3 mm thickness perpendicular to the deposition plane and 4 mm square, were sawed from the PG specimens and used to form PG-bromine residual compounds.

As shown in fig. 2, a PG block was reacted

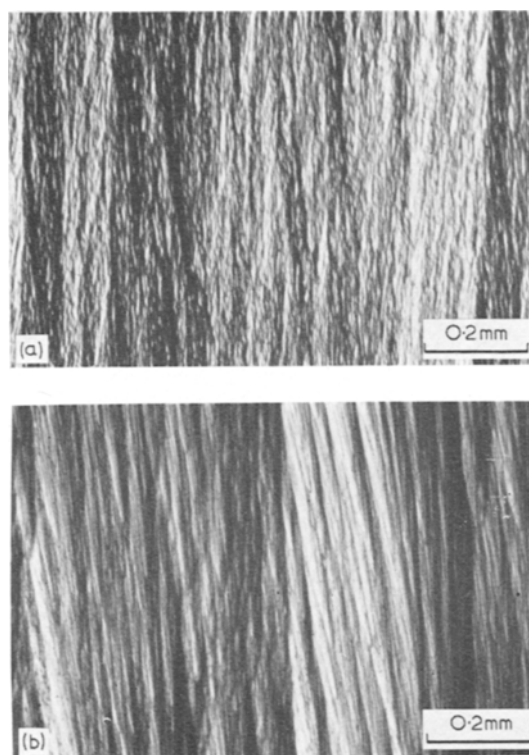


Figure 1 Cross sections of PG as deposited at (a) 1900° C. (b) 2300° C.

TABLE I Some physical properties of PG specimens used in this work.

Deposition temperature (°C)	2300	2100	1900
<i>c</i> -spacing (Å)	6.84	6.84	6.85
Thermal expansion coefficient ($\alpha_c \times 10^6 / ^\circ\text{C}$)	26.8	26.6	24.7
Preferred orientation parameter (β deg.)	22	22	25
Electrical resistivity $\rho_a (\times 10^4 \Omega \cdot \text{cm})$	7.1	11	10
$\rho_c (\times 10 \Omega \cdot \text{cm})$	6.9	6.3	5.4
Density (g/cm ³)	2.20	2.17	2.11

with bromine vapour to form the PG-bromine lamellar compound in a glass reaction tube. The bromine concentration in the PG block was measured by a quartz spring balance. When the PG-bromine specimen was removed from the bromine atmosphere, the intercalated bromine began to escape. The bromine desorption was measured as the weight decrease of the PG-bromine compound. As it was intended to measure the thermal expansion up to 1000° C, PG-bromine compounds were needed which would show little change in bromine concentration during the experiment. For this purpose,

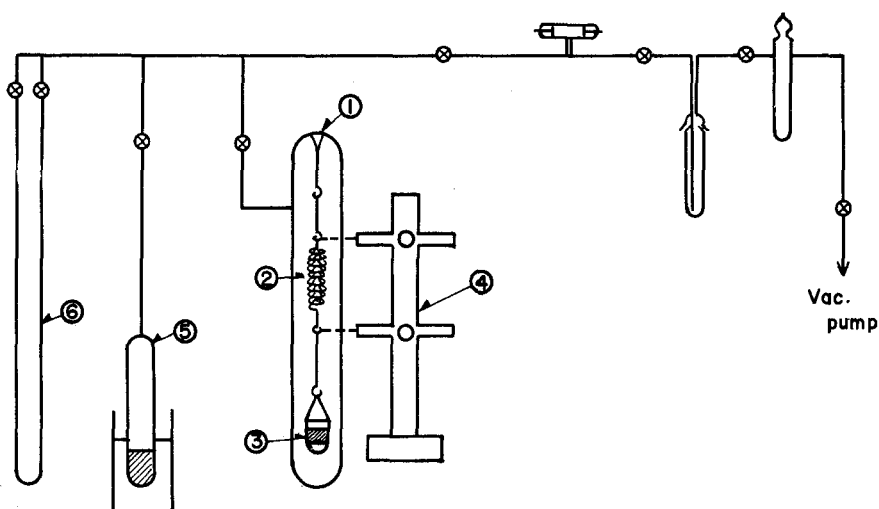


Figure 2 The experimental apparatus for bromination of PG. 1. Reaction vessel. 2. Quartz spring balance. 3. PG sample in quartz basket. 4. Cathetometer. 5. Bromine reservoir. 6. Mercury manometer.

debromination at 1000°C in vacuum was carried out, using graphite vessels to protect the PG-bromine specimen from oxidation. To distinguish the weight loss due to specimen oxidation from that due to debromination, a PG block without bromine was subjected to the same heat-treatment. As in this case no weight loss could be observed, the weight decrease of the PG-bromine specimens can be considered to be due to bromine loss alone. When the weight change became hardly recognisable, the specimen was taken as the PG-bromine residual compound (PG(Br)), and was used for the measurements of thermal expansion.

The thermal expansion measurements were made with the graphite dilatometer shown in fig. 3, between room temperature and 1000°C in flowing nitrogen gas. Measurements were made during heating as well as during cooling. The dilatometer was calibrated with quartz glass, and the thermal expansion of the specimen could be detected to $0.1\ \mu\text{m}$ using dial-gauges. The specimen was subjected to a load of 100 g, the weight of the graphite rod.

3. Results

The debromination process of PG-bromine lamellar compounds with a composition of approximately C_8Br at room temperature is shown in fig. 4, whereby bromine concentration is given as the weight ratio (Bromine weight/carbon weight) $\times 100$. Hereafter, bromine weight ratio is shown as 100.Br/C. Desorption started

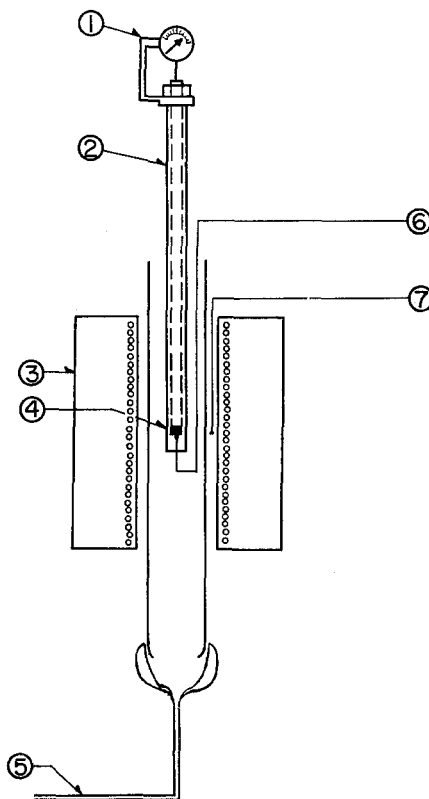


Figure 3 Thermal expansion apparatus. 1. Dial gauge. 2. Graphite dilatometer. 3. Resistance furnace. 4. Specimen. 5. Nitrogen inlet. 6, 7. Thermocouple.

immediately after removal of the bromine vapour, and 75% of the total intercalated

bromine was lost during the first 50 h. However, after 1500 h debromination practically stopped and the stable PG-bromine compounds which are stable at room temperature were obtained. No further weight loss was observed in these specimens even during vacuum-treatment. However, at elevated temperatures, further desorption occurred and therefore a further debromination treatment was made at 1000° C in vacuum. Fig. 5 shows the change in Br-concentration during heating at 1000° C using the same specimens as in fig. 4. Stable PG-bromine compounds (PG(Br)) can be obtained after 100 h.

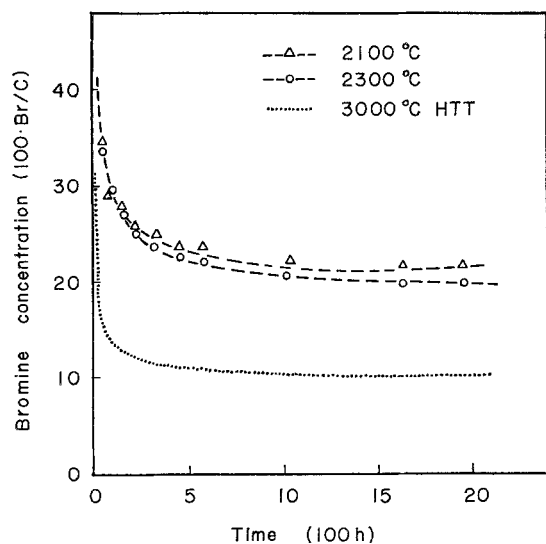


Figure 4 Debromination curves of PG-bromine lamellar compounds (nearly C_8Br , $100.Br/C = 83$) in air at room temperature. Dotted line shows the case of PG-bromine lamellar compound made of PG heat treated at 3000° C.

In fig. 6 the bromine concentration of PG(Br) is correlated with that of the initial PG-bromine lamellar compounds. It is seen that the bromine concentration of PG(Br) increases with that of the PG-bromine lamellar compound. There exists also a tendency for the PG of higher deposition temperature to have a lower residual bromine concentration.

Typical thermal expansion measurements are shown in fig. 7 for the PG(Br) made from PG deposited at 2300° C (23-PG(Br)). The as-deposited PG, which had not been reacted with bromine, expands linearly in the temperature range between room temperature and 1000° C, and the thermal expansion is the same on heating

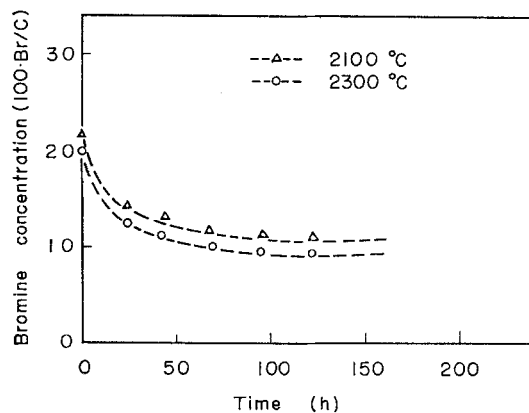


Figure 5 Debromination curves of PG-bromine compounds in vacuum at 1000° C. The specimens shown had been debrominated in air at room temperature about 2000 h.

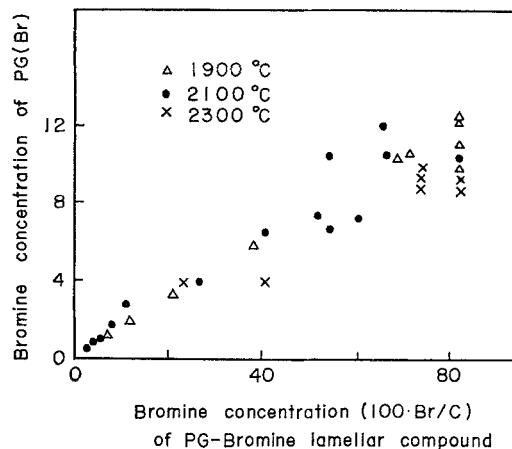


Figure 6 Correlation between bromine concentration in PG-bromine lamellar compounds and PG-bromine residual compounds.

and on cooling (curve (a) in fig. 7). Thermal expansion of 23-PG(Br) however, exhibits a different behaviour. In the case of low bromine concentration ($100.Br/C = 1.35$), thermal expansion is nearly the same as that of as-deposited PG up to about 120° C. At this temperature, a sudden increase in thermal expansion occurs. Martin and Brocklehurst called this the *break-away expansion* [10]. Above 120° C the thermal expansion increases linearly with temperature up to 1000° C, but on subsequent cooling, contraction follows another curve. At higher temperatures the rate of shrinkage is smaller than the expansion rate, but it becomes larger at about

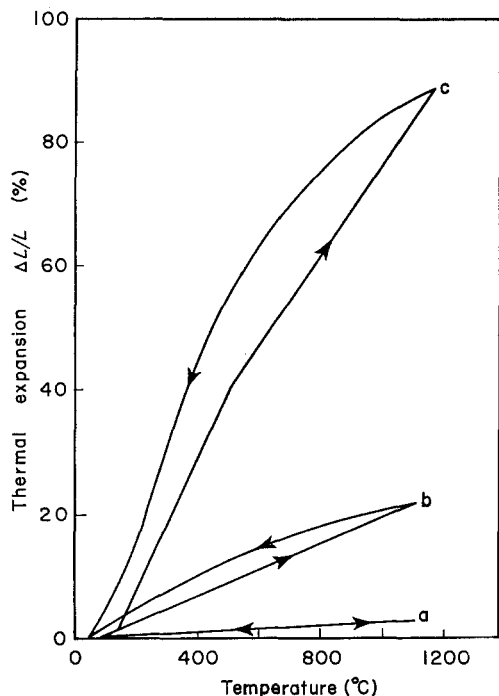


Figure 7 Thermal expansion behaviour of PG as-deposited at 2300°C and 23-PG(Br). (a) PG as-deposited. (b) 23-PG(Br): 100.Br/C = 1.35. (c) 23-PG(Br): 100.Br/C = 8.17.

500°C. When the temperature was decreased to room temperature, thermal expansion was zero. This thermal hysteresis is represented by curve (b) in fig. 7. In the case of higher bromine concentration (100.Br/C = 8.17), again thermal expansion shows nearly the same curve as that of as-deposited PG below 120°C. At that temperature breakaway expansion occurs, as with the lower bromine concentration, but the change is more pronounced. In the temperature range of 120°C up to about 500°C, linear expansion with increasing temperature is observed. At about 500°C there is a discontinuity in the expansion curve. Above 500°C, thermal expansion increases, again linearly with temperature up to 1000°C. Shrinkage during cooling, on the contrary, shows nearly the same behaviour as in the case of the lower bromine concentration. The length of the specimen before and after the thermal expansion measurement is the same within 1 μm. Thus in this case too, thermal hysteresis is observed. The area of the hysteresis loop is larger for the higher bromine concentration.

The same thermal expansion behaviour was observed with PG(Br) made from PG deposited

at various temperatures. Figs. 8 and 9 show the examples of the thermal expansion behaviour of PG(Br) made from PG deposited at 2100°C (21-PG(Br)), and at 1900°C (19-PG(Br)) respectively.

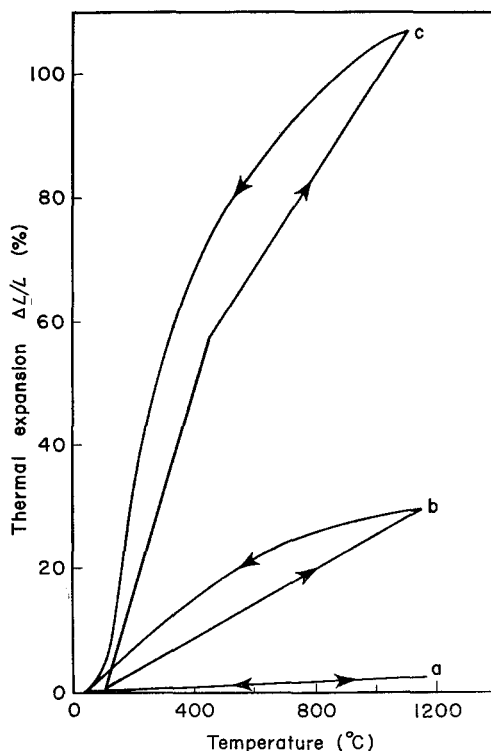


Figure 8 Thermal expansion behaviour of PG as-deposited at 2100°C and 21-PG(Br): (a) PG as-deposited. (b) 21-PG(Br): 100.Br/C = 2.78. (c) 21-PG(Br): 100.Br/C = 12.18.

The thermal expansion coefficients of these PG(Br) was defined as the value of the inclination of the linear part of the expansion curve above 500°C, divided by the specimen length at room temperature, L_0 . The thermal expansion coefficient α_c , therefore, is expressed by the following equation:

$$\alpha_c = \frac{1}{L_0} \left(\frac{\Delta L}{\Delta T} \right) \quad (T \geq 500^\circ \text{C}) \quad (1)$$

In fig. 10 the thermal expansion coefficient of PG(Br) is plotted against bromine concentration, and shows a linear relationship between these two parameters. For the same bromine concentration the thermal expansion coefficient of 23-PG(Br) is larger than that of 21-PG(Br).

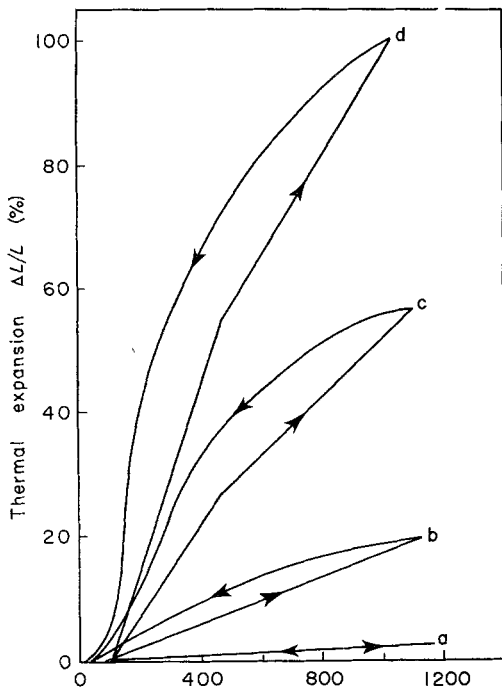


Figure 9 Thermal expansion behaviour of PG as-deposited at 1900°C and 19-PG(Br). (a) PG as-deposited. (b) 19-PG(Br): 100.Br/C = 3.22. (c) 19-PG(Br): 100.Br/C = 5.79. (d) 19-PG(Br): 100.Br/C = 10.39.

4. Discussion

Martin and Brocklehurst [10] measured the c -axis thermal expansion of PG-bromine residual compounds (2.2 at. % bromine) and found that the breakaway temperature (T_B) of those compounds varies with the load applied to the specimen. They proposed a model to explain this behaviour in terms of gaseous bromine bubbles within the lamellar structure of the graphite crystal, whereby the bubbles are considered to be analogous to Griffith cracks. At the temperature of T_B , the pressure of the bromine bubbles (P) becomes greater than the sum of the bonding force between the layers (F) and the pressure due to the load on the specimen (S). Then the following relationship exists:

$$P = F + S. \quad (2)$$

In this formula, P and F are represented by

$$P = nkT/\pi r^2 c_s \quad (3)$$

$$F = [\pi \gamma G / 2(1 - \sigma^2) \cdot r]^{\frac{1}{2}} \quad (4)$$

where n = number of bromine atoms in the bubbles, k = Boltzmann constant, r = radius

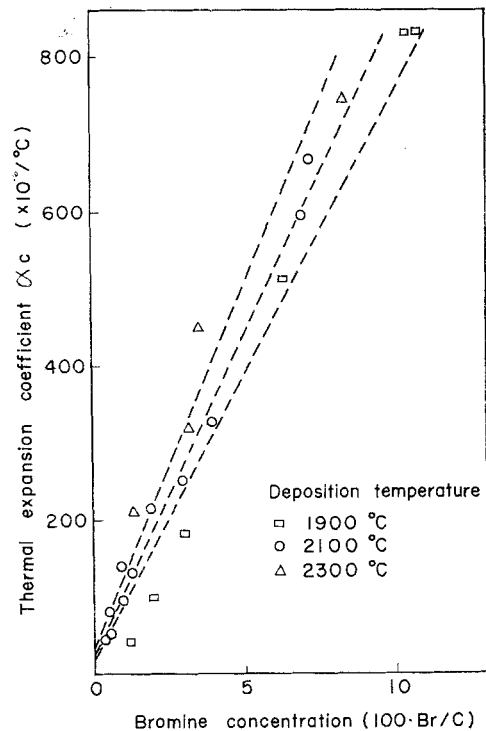


Figure 10 Correlations between thermal expansion coefficient of PG(Br) and bromine concentration.

of bromine gas bubble, c_s = c -spacing of the crystal compound, γ = effective surface energy per unit area of the bubble, G = shear modulus of the graphite, and σ = Poisson ratio of graphite.

From equations 2, 3 and 4, S may be obtained as follows:

$$S = \frac{nk}{\pi r^2 c_s} T - \sqrt{\frac{\pi \gamma G}{2(1 - \sigma^2) r}}. \quad (5)$$

As T in equation 5 represents T_B , there is a linear relationship between T_B and S . The experimental results obtained by Martin and Brocklehurst [10] are shown in fig. 11. From the slope of the line and the value of the intersection, the following values can be calculated

$$\begin{aligned} r &= 0.024 \text{ cm} \\ P &= 4.2 \times 10^4 \cdot T_B \text{ dyne/cm}^2 \\ n &= 4 \times 10^{10} \end{aligned}$$

The thermal expansion coefficient was given by the following equation,

$$\frac{1}{\alpha c} = \frac{V_0}{Nnk} S + \frac{3V_0}{4Nnk} \left(\frac{\pi \gamma G}{2(1 - \sigma^2)} \right)^{\frac{1}{2}} \cdot r^{-\frac{1}{2}} \quad (6)$$

where N is the number of bromine gas bubbles, V_0 is the bromine gas volume at room temperature. The experimental results obtained in reference [10] was more than ten times the value calculated from equation 6. This difference may be considered to be due to the application of the gas bubble model at room temperature, since the discontinuity in the thermal expansion curve at 300° C could not be explained.

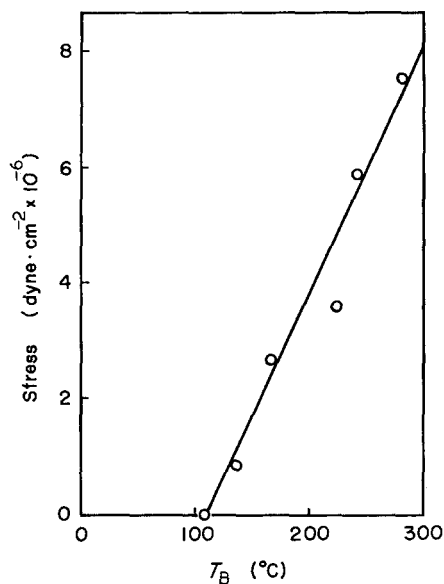


Figure 11 Relation between the applied stress and the breakaway temperature (T_B) in the PG-bromine residual compound (after Martin and Brocklehurst [10]).

Yajima *et al* [11] measured the thermal expansion of HT-PG(Br) which were made from PG heat treated at 3000° C, at various bromine concentrations, and interpreted the thermal expansion behaviour by the following model: Bromine in PG(Br) is ionically bonded to carbon networks [12], and exists in PG in the solid state rather than as gas bubbles. But this ionic bond is weakened as the temperature increases until bromine vaporisation starts. This bromine vaporisation causes a large volume change. With increasing temperature, the number of bromine gas bubbles increases, and bromine vapour pressure between the graphite layer planes becomes higher. As the bromine gas bubbles begin to spread between the graphite layer planes, a net thermal expansion of the specimen results. The volume change in PG(Br) due to the phase change of bromine explains the pronounced increase in thermal expansion in the temperature

range of 120 to 300° C. After the bromine in PG(Br) is completely vaporised, only the gaseous expansion of bromine, which follows the ideal gas law, is responsible for the further thermal expansion of PG(Br). Therefore, at a temperature higher than 300° C, the thermal expansion coefficient will be constant. Considering these thermal expansion processes, the thermal expansion coefficient due to the bromine volume change at temperatures higher than 300° C is expressed by

$$\alpha_c = \frac{nNk}{V_0} \left(S + \frac{3}{4} \sqrt{\frac{\pi\gamma G}{2(1-\sigma^2)r}} \right)^{-1} \quad (7)$$

Using numerical values, equation 7 is written as

$$\alpha_c = 2.1 c \times 10^{-3} \quad (8)$$

where c is the bromine weight ratio in PG(Br). In fig. 12, experimental values are correlated with the calculated ones. There is a good agreement between the experimental and the calculated values.

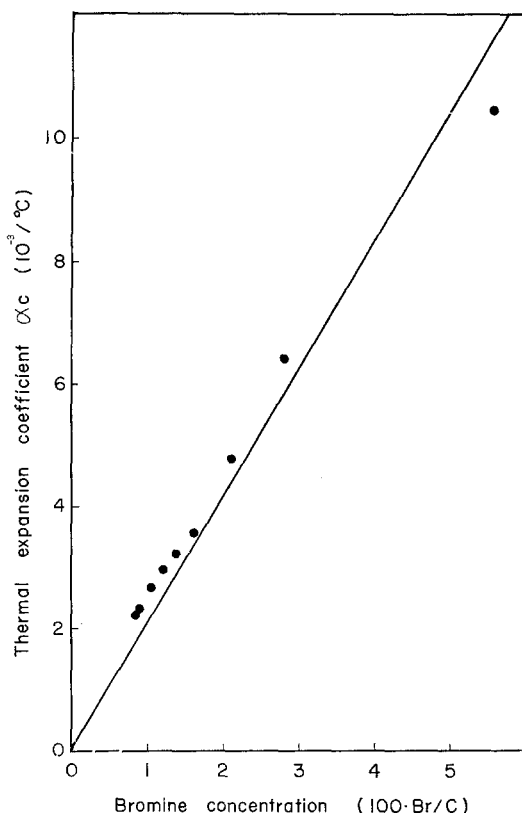


Figure 12 Relation between thermal expansion coefficient and bromine concentration of 3000° C heat-treated PG-bromine residual compounds. Solid line shows the calculated values shown by equation 7.

In the present study, the thermal expansion measurements of PG(Br) made from as-deposited PG show that the breakaway expansion occurs at about 120°C and the thermal expansion coefficient is reduced at about 500°C, if the bromine concentration is large. This thermal expansion behaviour is analogous to that of HT-PG(Br). In the case of low bromine concentration, however, the discontinuity in the thermal expansion curve cannot be observed at about 500°C. In this case too, at 120°C, ionically bonded bromine begins to vaporise to form gas bubbles, and to induce the breakaway expansion, but this thermal expansion due to the phase change of bromine is restricted to a value lower than that due to the gaseous expansion of bromine, and therefore no change in the thermal expansion coefficient at about 500°C is observed. This restriction may come from the mechanical stress due to a complex crystallite arrangement, where each crystallite expands and exerts a stress on the neighbouring crystallites and vice versa.

If the mechanism of thermal expansion of PG(Br) is interpreted by the above-mentioned model, expansion due to bromine gas bubbles should begin at 500°C. The thermal expansion coefficient of PG(Br) is determined by using equation 1 for the linear part in the thermal expansion curve above 500°C. In fig. 10, the thermal expansion coefficients of PG(Br) are shown as a function of bromine concentration. It is seen that the thermal expansion coefficient of PG(Br) depends on the concentration of bromine and the deposition condition of the original PG. With an increase in the deposition temperature, the thermal expansion coefficient of PG(Br) becomes higher. This tendency may be explained by the preferred orientation of the crystallites in the as-deposited PG block, as the preferred orientation of crystallites in PG becomes better with increasing deposition temperature. A better preferred orientation causes a larger contribution of the *c*-axis to the crystallite thermal expansion of the PG(Br) block, and will decrease the resistance to thermal expansion of the bromine gas bubbles. This is due to the decrease in the complex stacking of the crystallite arrangement in the PG specimen, and the elastic restraint between adjacent crystallites [14]. The thermal expansion coefficients of PG(Br) in this experiment are in the range of 1/20 to 1/30 of that of HT-PG(Br). This difference may be due to the mechanical stress caused by the complex arrangements of the crystallites. If

this stress be called *E*, equation 2 becomes

$$P = F + S + E. \quad (9)$$

The thermal expansion coefficient is rewritten by the following equation (if the values of *F* and *S* are considered to be unchanged):

$$\alpha_c = \frac{Nnk}{V_0} \left(S + \frac{3}{4} \sqrt{\frac{\pi\gamma G}{2(1-\sigma^2)r}} + E \right)^{-1}. \quad (10)$$

If the value of *E* in the case of the as-deposited PG is large enough when compared with the value of (*S* + *F*), thermal expansion differences between PG(Br) of different origin are largely due to the value of *E*. A large value of *E* in as-deposited PG is expected from X-ray strain analysis [15] and from the fact that the temperature at which all the bromine be vaporised is much higher than that of HT-PG(Br).

When the temperature is decreased, shrinkage of PG(Br) does not follow the same path as during expansion. This effect was also observed with HT-PG(Br). However, in the case of 23-, 21-, 19-PG(Br) the length differences, measured at the same temperature on heating and on cooling, are largest for the 23-PG(Br), but are all smaller than for HT-PG(Br). The high temperature behaviour of HT-PG(Br) during cooling is explained as follows: Above 300°C, expanded bromine gas bubbles exist between the graphite layer planes or crystallite boundaries, and subsequently there is a disturbance in the crystallite arrangement. With a decrease in temperature, the pressure of the bromine gas bubbles is reduced, but it is still larger than the bonding force between the graphite layer planes plus the weight on the specimen. This means that at the same temperature the specimen length is larger during cooling than during heating. When the temperature is lowered to below 300°C, the bromine gas again reacts with carbon and this reduces the pressure of the bromine gas rapidly. Below 100°C, nearly all of the bromine gas had disappeared, and at room temperature, the specimen length became the same as that before the thermal expansion measurement.

In the case of PG(Br) made of as-deposited PG, the bromine behaviour during cooling may be explained by the same bromine gas bubble model. The smaller difference in thermal expansion between heating and cooling, in this case is explained by the presence of a stress (*E*), which accompanies the disturbance in the crystallite arrangement.

In fig. 13, a cross-section perpendicular to the

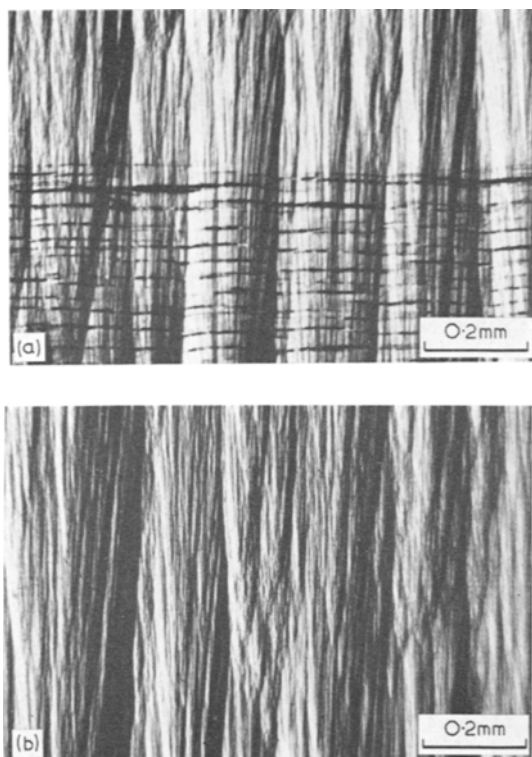


Figure 13 Lower part of the cross-section of 21-PG(Br) after thermal expansion measurements. (a) $100.\text{Br}/\text{C} = 6.83$. (b) $100.\text{Br}/\text{C} = 0.52$.

deposition plane of a 21-PG(Br) specimen, which was used for thermal expansion measurements, is shown. Fig. 13a shows a part of the cross-section of 21-PG(Br) with higher bromine concentration ($100.\text{Br}/\text{C} = 6.83$). There are cracks of about 0.5 mm length parallel to the deposition plane in the lower part. These cracks are observed on either side of the specimen, but no cracks are seen in the central portion of the specimen, as shown in the upper half of fig. 13a. In the case of PG(Br) with lower bromine concentration (fig. 13b, $100.\text{Br}/\text{C} = 0.52$), only two or three cracks can be observed on both sides of the specimen. There is little difference in appearance between as-deposited PG and PG(Br). These cracks may be considered to be formed by the internal stress accumulation caused by the expansion of the bromine gas bubbles between the layer planes. Bromine gas bubbles should be formed uniformly between the graphite layer planes in PG(Br), but in the central portion, these cracks are closed by the complex stress system caused by the crystallite arrange-

ment. The existence of these cracks thus substantiates the above-mentioned thermal expansion model.

5. Conclusion

Stable PG(Br) compounds, prepared from as deposited PG at 1900, 2100 and 2300° C, do not show exfoliation upon heating. They are obtained from PG-bromine lamellar compounds by debromination at room temperature in air, succeeded by vacuum heat-treatment at 1000° C for more than 100 h. The bromine concentration in 100.Br/C ranged from 0.3 to 12.

The *c*-axis thermal expansion behaviour of these PG(Br) was measured between room temperature and 1000° C. In the case of PG(Br) of higher bromine concentration, the thermal expansion behaviour is analogous to that of HT-PG(Br), but the thermal expansion coefficient is only one twentieth to one thirtieth of that of HT-PG(Br). These results are explained as follows. Bromine in PG(Br) is ionically bonded to carbon, but this bond is weakened as the temperature is increased until bromine vaporisation starts. This bromine vaporisation causes a large volume change and explains the breakaway expansion at 120° C. At about 500° C the thermal expansion coefficient decreases to a lower value. This is attributed to the complete vaporisation of the bromine in the PG(Br). Only the gaseous expansion of bromine is responsible for the further *c*-axis thermal expansion of PG(Br). In the case of PG(Br) with a lower bromine concentration, the change in the thermal expansion curve at about 500° C cannot be observed clearly. Although in this case also, all the bromine in the PG(Br) may be completely vaporised, the volume change due to the vaporisation process is rather gradual because of a larger stress in the specimen.

Thermal expansion coefficients of PG(Br) were defined in the temperature range of about 500 to 1000° C. The small values of the thermal expansion coefficient compared to those of HT-PG(Br) may be due to a stress in the original PG specimens. The thermal expansion coefficient of PG(Br) depends on the bromine concentration and on the deposition temperature of the original PG.

During cooling, the pressure of the bromine gas bubbles is reduced with temperature, but the bonding force between the graphite layer planes cannot be recovered, and therefore the volume of the bromine gas bubbles does not change in the

same manner as during heating. When the temperature is lowered below 300° C, bromine begins to react with carbon again, and the pressure of the bromine gas is very quickly reduced so that the bonding force is recovered, and PG(Br) shrinks rapidly. At room temperature the length of PG(Br) before and after the thermal expansion measurements are the same.

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