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High Temperature Resistivity of Pyrolytic Graphite Bromine Residual Compounds

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The electrical resistivity of pyrolytic graphite (PG) deposited at 2300°C decreases in both the *a*- and *c*-axis directions as the temperature is increased up to 1000°C, but the high temperature resistivity of PG-bromine residual compounds differ somewhat from that of the original PG. When the temperature is increased, the *a*-axis resistivity remains nearly constant at the lower temperature range but increases rapidly between 300 and 500°C. Above 500°C the value of the resistivity approaches that of the original PG. On cooling, the change of the electrical resistivity of PG-bromine residual compounds is the same as that on heating, but its value is larger between 500 and 100°C. At room temperature, the *a*-axis resistivity of the compound before and after the cyclic heat-treatment is the same. This behaviour is closely related to the *c*-axis thermal expansion and is well explained by the same bromine vaporisation model. As to the *c*-axis direction, the electrical resistivity of PG-bromine residual compounds show a different behaviour. However, the factors affecting the electrical conduction in this case are complicated and cannot be resolved.

1. Introduction

Graphite compounds are made by reacting some elements or compounds such as halogens, alkali metals, chlorides with graphite [1]. These graphite lamellar compounds are in general unstable. In the case of the graphite-bromine reaction, a lamellar compound of maximum composition C_8Br is formed in a bromine atmosphere [2]. On removal of bromine vapour from the reaction vessel. the bromine starts to escape from the graphite-bromine lamellar compound. The bromine concentration in the graphite matrix monotonically decreases with time [3]. However, some of the bromine is strongly held by the graphite and cannot be freed by a heat-treatment at 1000°C in vacuum for more than 100 h [4]. Such graphite compounds are usually called residual or residue compounds [5] and their properties differ from those of the original graphite [6].

Pyrolytic graphite-bromine residual compounds made by such a treatment using pyrolytic graphite (PG) as a starting material show extraordinarily large thermal expansion in the *c*-axis direction [4, 7, 8]. In addition to this, they show a peculiar thermal hysteresis. This phenomenon is explained by a phase change of bromine in the graphite matrix [4, 8]. That is, the bromine in the PG-bromine residual compounds is bound to the carbon networks at room temperature, but this bond is broken by thermal agitation at elevated temperatures. The freed bromine vaporises to form gas bubbles along the crystallite boundaries or between the layer planes. A large volume increase is hereby produced in the PG block, resulting in a large thermal expansion of the PG-bromine residual compound.

According to Blackman *et al* the electrical resistance of PG in both the *a*- and *c*-axis directions are decreased as the bromine reacts with the carbon [9]. In the *a*-axis direction, the rate of decrease in resistance is prominent at lower bromine concentrations, but for higher bromine concentrations, it becomes more pronounced in the *c*-axis direction. When bromine is reacted with PG, the bromine extracts π-electrons from the carbon and is ionised to form anions and therefore, positive holes are left in the carbon layers. Thus bromine changes the energy band scheme of the original PG, and depresses the Fermi level [9] and the electrical resistance changes as the bromine concentration increases.

This electrical resistance change also exists in

PG-bromine residual compounds. The electrical resistivity of PG-bromine residual compounds is changed by the number of carbon-bromine bonds [6]. As it is interesting to know the nature of the carbon-bromine bond in the graphite matrix, high temperature electrical properties are correlated to thermal expansion measurements [4]. In the present experiment especially, the *a*-axis electrical resistivity was measured in the temperature range from room temperature to 1000°C. A peculiar behaviour of the electrical resistivity was observed and is discussed with the same model as used for the thermal expansion measurement [4, 8].

TABLE I Some physical properties of the PG used.

Deposition temperature	2300°C
c-Spacing	6.84 Å
Preferred orientation parameter	22°
c-Axis thermal expansion coefficient	26.8×10^{-6}/°C
Density	2.20 g/cm^3

2. Experimental

The PG used in this experiment was supplied by Nippon Carbon Co., and was deposited at 2300°C on a graphite substrate heated in a graphite furnace. Some of its properties are shown in table I. From this PG, blocks of 3 × 15 mm along the layer plane and 3 mm thick, were cut for the *a*-axis measurement, while 4 × 4 mm and 3 mm thick blocks were used for measurement along the *c*-axis. These blocks were then introduced into a reaction vessel and were allowed to react with bromine. Thus PG-bromine lamellar compounds of various bromine concentrations were obtained. Stable PG-bromine residual compounds were then made following the same procedure reported elsewhere [4]. The bromine concentration in the specimen was determined by measuring the weight difference before and after the treatment.

Electrical resistivity measurements were made by the four probe arrangement shown in fig. 1. Platinum electrodes (0.1 mm in d) were attached to the specimen by pressing them between two quartz glass plates. Sometimes, platinum wires were attached to the specimens by silver paste. The resistivity and its temperature dependence were not affected by the type of electrode connection. Some of the conditions of the measurements are summarised in table II.

The temperature of the specimen was measured by an alumel-chromel thermocouple laid just below the quartz glass and it was recorded on a chart recorder. At the same time, the potential drop at the specimen was also measured and recorded on the same chart. A typical recorder trace is shown in fig. 2. The temperature of the Kantal furnace was automatically varied by a programmed controller and the temperature of the specimens was increased and decreased mainly at the rate of 300°C per h. To reduce the temperature difference between the potential leads, the specimens were placed perpendicular to the furnace axis. To measure the influence of the thermoelectric power, measurements using a reversed current were made at about 1000°C, 700°C and room temperature in some specimens. No difference before and after the current reversal was detected.

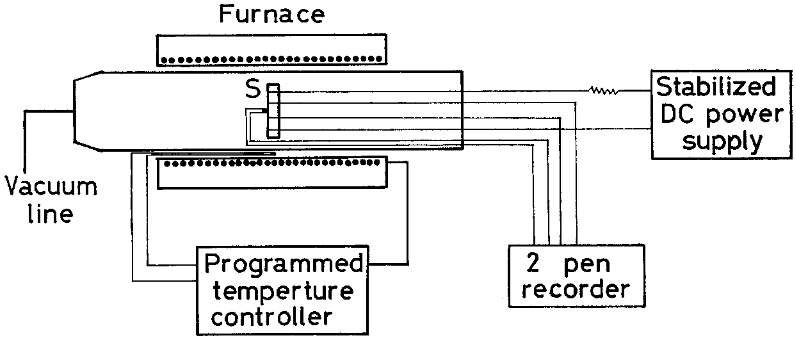
TABLE II Experimental conditions for high temperature resistivity measurements.

Dimension of the specimen	3 × 15 mm, 0.1 mm thick for *a*-axis measurement, 4 × 4 mm, 0.2 mm thick for *c*-axis
Potential lead length	4 mm for *a*-axis
Circuit current	60 mA stabilised
Potential drop	2 – 10 mV
Temperature range	20 – 1000°C
Atmosphere	vacuum (2×10^{-3} torr)
Amplifier and recorder	Hitachi Electric QPD 73

3. Results

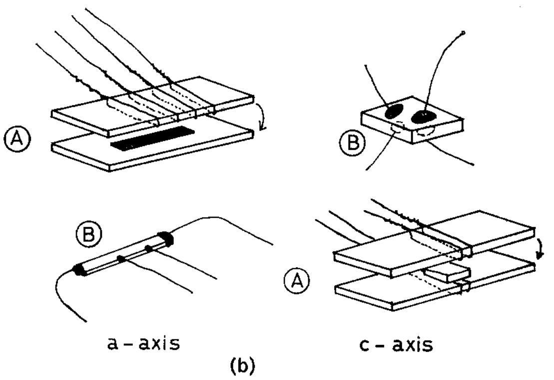
The electrical resistivities of PG and PG-bromine residual compounds at elevated temperatures are shown in figs. 3 and 4. In fig. 3, the high temperature *a*-axis electrical resistivity of as-deposited PG and of the PG-bromine residual compounds made from it are shown. Curve 1 represents the temperature dependence of the *a*-axis resistivity of as-deposited PG. The resistivity decreases with increasing temperature as is often observed in semiconductors, but the rate of the decrease is much smaller. The value of the resistivity is 6.8×10^{-4} Ωcm at room temperature and 2.8×10^{-4} Ωcm at 1000°C. Thus this specimen exhibits an increased conductivity at elevated temperatures.

On the other hand, the electrical resistivities of PG-bromine residual compounds have a very different temperature dependence. The *a*-axis resistivities at room temperature depend on the residual bromine concentrations, but at about 1000°C all of the specimens show the same value of about 2.8×10^{-4} Ωcm independent of the



(a)

Figure 1 Experimental arrangement for high temperature resistivity measurements. (a) Block diagram for measurement. S: the specimen. (b) Forms of electrode connection. Lead wires are 0.1 mm diameter platinum. A: Pressure contact between two quartz glass plates. B: Connection by silver paste.



(b)

bromine concentration. The *a*-axis resistivity of the PG-bromine residual compound with the highest bromine concentration (Br weight/C weight × 100 = 13.4) does not decrease at temperatures between 20 and 300° C as shown by curve 4. At 300° C, the resistivity begins to increase from 1.5×10^{-4} Ωcm to 2.8×10^{-4} Ωcm at 500° C. The resistivity above 500° C remains nearly constant and decreases only slightly up to 1000° C at which temperature the value of the resistivity is 2.6×10^{-4} Ωcm. When the temperature is decreased, the resistivity remains nearly constant from 1000 to 500° C as in the case of the temperature rise. In the temperature range of 500 to 250° C, it increases in a similar way as the resistivity of as-deposited PG. At about 250° C, the resistivity begins to decrease rapidly. At temperatures lower than 100° C the resistivity values for heating and cooling coincide. In a further experiment, the same resistivity-temperature curve was obtained within the precision of the recorder, thus a resistivity hysteresis versus temperature exists between room temperature and 1000° C. The shape of the resistivity curve is unaffected by a

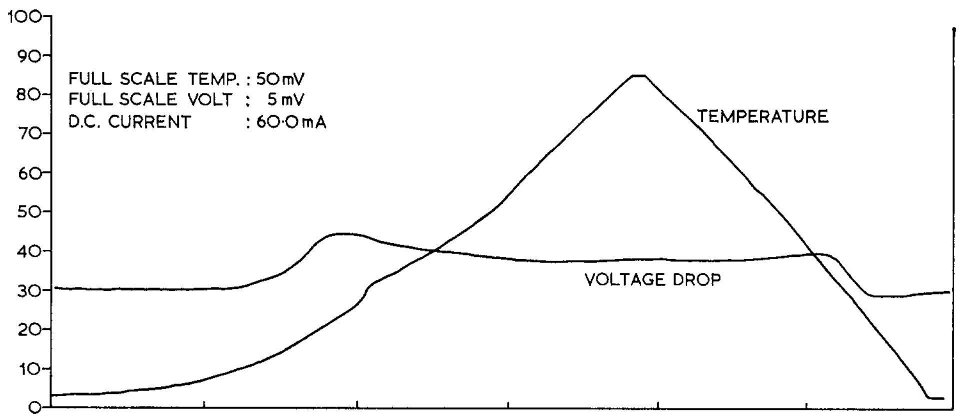


Figure 2 Typical recorder trace for the *a*-axis resistivity. This shows the case of PG-bromine residual compound whose bromine concentration is 13.4.

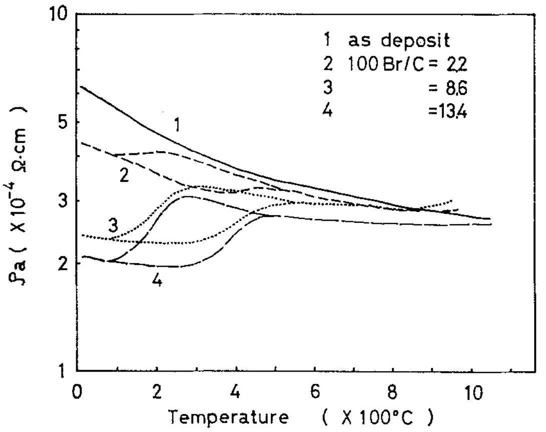


Figure 3 *a*-axis high temperature resistivity of PG deposited at 2300° C and of the PG-bromine residual compounds.

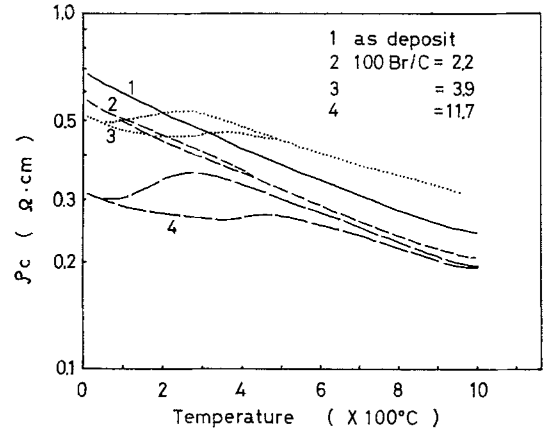


Figure 4 *c*-ay ,s high temperature resistivity of PG deposited at 2300° C and of the PG-bromine residual compounds.

change in the rate of heating by a factor 2. In the case of PG-bromine residual compounds with lower bromine concentration, the temperature dependence of the resistivity is shown by the curves 2 and 3 in fig. 3. These curves lie between the curves 1 and 4, and yet show the hysteresis phenomena between 100 and 500°C.

On the other hand, the *c*-axis high temperature resistivity is different from that of the *a*-axis. In fig. 4, the temperature dependence of the *c*-axis resistivity of as-deposited PG and of the PG-bromine residual compounds are shown. In the as-deposited PG, the resistivity decreases continuously with the temperature rise as in the case of the *a*-axis measurement. The value of the resistivity is 0.68 Ωcm at room temperature and 0.24 Ωcm at 1000°C. The *c*-axis resistivity of as-deposited PG also does not show a temperature hysteresis as in the case of the *a*-axis resistivity. Curve 4 shows the resistivity of the PG-bromine residual compound, whose bromine concentration is 11.7 (Br/C.100 = 11.7). From room temperature to about 300° C, the resistivity decreases with heating at nearly the same rate as in the case of as-deposited PG. At about 300°C, the rate of resistivity decrease becomes smaller. When the temperature is decreased, the resistivity increases more rapidly than on heating, but at about 250° C, the resistivity begins to decrease and reaches the same value as that on heating at about 100° C.

In the case of lower bromine concentrations, the behaviour of the *c*-axis resistivity is somewhat different from the above mentioned case. Curve 2 shows the result of the PG-bromine residual compound whose bromine concentration is 2.2. The rate of resistivity change with temperature is nearly the same as for the as-deposited PG; it shows a slight hysteresis between 100 and 500°C, and the resistivity at 1000°C is smaller than that of as-deposited PG. Curve 3 shows the result of the PG-bromine residual compound whose bromine concentration is 3.9. This curve rather resembles that of the *a*-axis resistivity. The value of the resistivity is larger than that of as-deposited PG at higher temperatures.

4. Discussion

The electrical resistivity of PG changes with the deposition condition. The higher the deposition temperature, the smaller is the *a*-axis resistivity and the larger is the *c*-axis resistivity [10]. This is explained by various factors such as crystallite size and orientation, and *c*-spacing of PG in bulk.

In fig. 5, the high temperature *a*-axis resistivity of as-deposited PG specimens is compared with those of polycrystalline [11] and other PG [12] specimens. In the PG specimen used in this experiment, the temperature at which the resistivity starts to rise is higher than that reported by Klein [12]. The resistivity drop with increasing temperature is tentatively explained by the presence of a small band gap between the conducting upper π-band and the lower filled band in the energy scheme of the graphite structure [12], but this explanation is not an exact one.

In the PG-bromine residual compounds, the

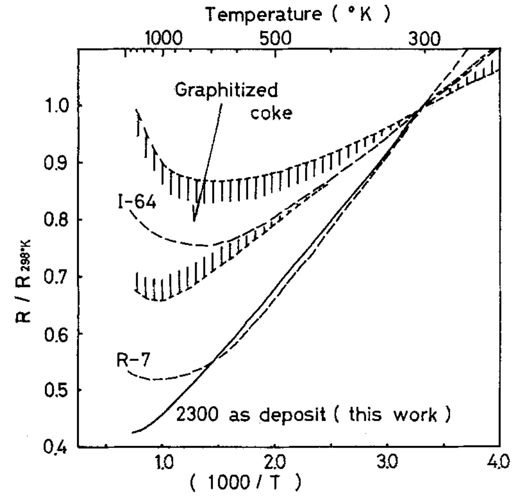


Figure 5 High temperature resistivity of PG and polycrystalline graphite. I-64, R-7 are Klein's data on PG deposited at 2300 and 2500° C respectively [12]. The data for graphitised coke were reported by Kinchin [11].

room temperature electrical resistivity of both the *a*- and *c*-axis is changed by bromine concentration [13]. This shows the presence of electronic coupling between carbon atoms constituting the graphite lattice and bromine atoms in the PG block. This bromine is considered to extract some of the electrons from the π-bonds between carbon-carbon in the graphite lattice as in the case of the PG-bromine lamellar compounds [9]. Some part of the bromine atoms change to bromine anions [6], and therefore the carbon networks or carbon macromolecules become a sort of cation. Thus, PG-bromine residual compounds can be considered as a kind of ionic crystal, Cn^+Br^-, as a result of which, positive holes are formed in the carbon networks in place of the π-electrons. Subsequently the Fermi level of graphite is depressed to change the energy scheme. Considering this, we can explain the peculiar behaviour of the resistivity change as follows.

The character of the carbon-bromine bond is not yet clearly resolved, but this bond seems to be very weak, as the activation energy of the bromine-carbon reaction is smaller than 10 kcal/mol [14]. Therefore this bond can easily be broken by a slight increase in temperature. Thus the positive holes in the graphite layer planes vanish with rising temperature and the energy scheme of the PG-bromine residual compound tends to return to that of the original PG. Subsequently, the *a*-axis resistivity becomes larger as the carbon-bromine bond is broken. When all the carbon-bromine bonds in the PG block are broken, the resistivity returns to the same value as that of the original PG. Therefore, the resistivity change above the temperature at which all the bromine is vaporised must be the same as that of the original PG. In fact, the room temperature *a*-axis resistivity of PG-bromine residual compounds deviates from that of as-deposited PG according to the bromine concentration [13], but it reaches nearly the same value as that of as-deposited PG above 500° C. This is the temperature at which all of the bromine is considered to be vaporised. When the temperature is decreased, all PG-bromine residual compounds – regardless of the bromine concentration – show the same temperature dependence between 1000 and 250° C as in the case of as-deposited PG. Below 250° C, electrical resistivities begin to differ according to the bromine concentration. This may be due to the recovery of the ionic bond between carbon and bromine [4]. Thus, the number of positive holes increase in PG and cause a decrease of the electrical resistivity.

This result of the high temperature resistivity is closely related to the vaporisation model of bromine at high temperature, which was used to explain the thermal expansion behaviour [4]. Fig. 6 shows examples of the thermal expansion behaviour of PG-bromine residual compounds made from PG deposited at 2300° C. In this case, bromine in PG begins to vaporise at about 120°C. This bromine vaporisation induces a large volume increase and a rapid thermal expansion. The bromine vaporisation ceases at about 500° C, and only the gas volume expansion is responsible for the further thermal expansion of the PG-bromine residual compound. This is concluded from the decrease of the thermal expansion rate at about 500° C. When the temperature is lowered, the thermal contraction is larger than the expansion on heating, due to some structural factors, but at temperatures between 300 and 100° C, the carbon-bromine ionic bond is recovered, and the bromine vapour pressure is reduced rapidly, resulting in a larger contraction rate. At temperatures below 100° C the specimen length reaches the same value as in the initial state.

Some difference exists between the behaviour of the thermal expansion and the electrical resistivity. In the thermal expansion measure-

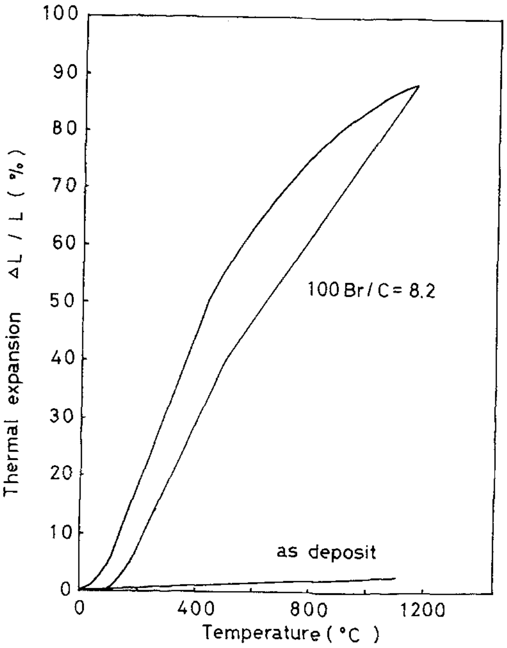


Figure 6 Thermal expansion behaviour of PG deposited at 2300° C and of the PG-bromine residual compound [4].

ment, bromine vaporisation is observed at about 120° C, but according to the electrical resistivity, ionic bond of carbon-bromine is broken above 300° C. Hennig considered that only a part of the bromine in graphite bromine lamellar and residual compounds is ionised [6]. If this is true, the nonionised bromine molecules in the graphite matrix may more easily be released by slight thermal agitation than the ionised bromine. It might be concluded that this nonionised bromine begins vaporisation at 120° C in the thermal expansion measurement.

This behaviour of bromine at high temperatures is also supported by the result of high temperature X-ray diffraction measurements made by Takahashi *et al.* [15]. They found that the *c*-spacing of the graphite bromine compound becomes larger as the temperature is increased up to about 300°C, but somewhat decreases between 300 and 450°C. At about 450°C, it reaches the same value as that of the original graphite, and above 450° C, the *c*-spacing begins to increase again, but the value is the same as that of the original graphite. This decrease in *c*-spacing between 300 and 450° C shows that the bromine, which was between the graphite layer planes, moved to the outside of the crystallite.

Considering the above mentioned behaviour of bromine in PG-bromine residual compounds, a correction of the *a*-axis resistivity, because of the influence of the thickness change due to the large thermal expansion in the *c*-axis, is not necessary in a first approximation. The reason is that the thermal expansion is induced by the formation of bromine gas bubbles between the graphite layer planes, and the gas bubbles expands along them, but the net thickness of graphite, responsible for electronic conduction, remains practically constant. For this reason, electrical resistivity can be used instead of resistance in fig. 3.

In the case of high temperature *c*-axis resistivity of PG-bromine residual compounds, a correction due to *c*-axis thermal expansion is not enough. The path for electronic conduction is greatly reduced by the bromine gas bubbles presented between the layer planes or crystallites. This effect cannot be estimated. In addition, the *a*-axis contribution to the *c*-axis electrical conduction is negligible in the PG specimens used. Therefore it is impossible to explain the *c*-axis resistivity change of PG-bromine residual compounds at high temperatures.

5. Conclusion

High temperature resistivity of PG deposited at 2300°C and PG-bromine residual compounds were measured. The measurements were made in vacuum and by a four-probe method. The temperature of the specimen, raised automatically by a programmed temperature controller, and the voltage drop, showing the resistance of the specimen, were recorded on the same recorder chart at once.

Both *a*- and *c*-axis resistivity of the original PG is decreased as the temperature is increased up to 1000°C. This is the typical temperature dependence of a narrow gap semiconductor, but the *a*-axis resistivities of PG-bromine residual compounds are different from that of the original PG. This difference increases with the bromine concentration. Resistivities of these compounds at room temperature are smaller than that of original PG.

The temperature dependence of the resistivity becomes smaller with bromine concentration at the lower temperature region. However at about 300° C, the resistivity increases rapidly up to about 500° C where it reaches the same value as that of the as-deposited PG. All of the resistivities show nearly the same value and temperature dependence between 500 and 1000° C, both on heating and cooling. On cooling, resistivity is larger than that on heating between 500 and 100°C. This peculiar phenomena is explained by the vaporisation model of bromine in the PG block, which was successfully used to explain the thermal expansion.

The *c*-axis resistivity of PG-bromine residual compounds is also different from that of original PG. But in this case, the factors affecting the electrical conduction are very complicated and therefore no proper explanation can be given for the change of the electrical resistivity.

6. Acknowledgement

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