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Electrical Conductivity of Graphite Bromine Lamellar Compounds

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Polycrystalline graphite was allowed to react with bromine vapor, and the change of its electrical conductivity during the course of bromination and debromination was studied. The graphite was found to behave in two different ways depending on the process of bromination. When the vapor pressure of bromine was changed stepwise, following the equilibrium line of bromine absorption of graphite, the electrical conductivity showed a reversible change. On the other hand, when a graphite sample was brominated with the saturated vapor, an increase of the electrical conductivity steeper than that of the former case was observed. These results were discussed in relation to the structural analysis of the brominated graphite. A metastable phase of graphite bromide, the electrical conductivity of which remained unchanged in spite of a considerable increase of absorbed bromine, was found. The electrical conductivity of the residue compounds was also investigated, and a steep decrease was observed at high concentrations of bromine.

Graphite reacts with bromine at room temperature to form a lamellar compound. The saturated composition of the graphite bromine lamellar compound is C_8Br, and its structure was clarified by Rüdorff[1] as the second stage structure, where the bromine atoms are intercalated in every other layer spacing of graphite. The mechanism of bromine absorption of graphite has been investigated by several workers. Mukaibo and Takahashi[2] measured the rate of bromination of graphite, and obtained an apparent activation energy of the reaction of 5—7 kcal/mol. Saunders *et al.*[3] measured the dimensional change of pyrolytic graphite by bromine absorption, and observed a metastable structure which has a practically full expansion along the direction of *c*-axis by only about one-third of the limiting uptake. Hooley *et al.*[4,5] also investigated the rate of absorption and the dimensional change, and proposed a mechanism in which all layers are open to the intercalation at a relatively initial stage. The authors[6] measured the change of X-ray diffraction pattern of graphite during the course of bromination, and confirmed that the second stage structure of the lamellar compound appeared in the initial stage of the reaction.

Knowledge of electrical properties of the compounds gives valuable information about the electronic state of the species intercalated in graphite. Hennig[7] reported that the electrical resistance of polycrystalline graphite decreases with bromine uptake, and suggested that one-seventh of the intercalated bromine atoms would be ionized. Blackman *et al.*[8] measured the electrical resistance of pyrolytic graphite reacting with bromine vapor in the direction of both the *a*-axis, and the *c*-axis, and observed an initial steep decrease of the resistance in the *a*-axis direction.

We have investigated changes of the electrical conductivity of graphite with bromine absorption in two different processes, *i.e.*, the stepwise bromination and the rapid bromination. In the former case, the vapor pressure of bromine was increased stepwise, and the relation between the electrical conductivity and the equilibrium concentration of the absorbed bromine at every step has been investigated. In the latter, the change of the electrical conductivity of the graphite sample during the course of the reaction with saturated bromine vapor has been measured.

Experimental

Materials. The following three graphite samples have been used

1) High purity artificial graphite, heat-treated at

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1) W. Rüdorff, *Z. Anorg. Allg. Chem.*, **245**, 383 (1941).

2) T. Mukaibo and Y. Takahashi, This Bulletin, **36**, 625 (1963).

3) G. A. Saunders, A. R. Ubbelohde and D. A. Young, *Proc. Roy. Soc.*, *Ser. A*, **271**, 499 (1963).

4) J. G. Hooley and J. L. Smee, *Carbon*, **2**, 135 (1964).

5) J. G. Hooley, W. P. Garby and J. Valentin, *ibid.*, **3**, 7 (1965).

6) Y. Takahashi, T. Sasa and T. Mukaibo, *Tanso*, **1969** (No. 52), 199.

7) G. R. Hennig, *J. Chem. Phys.*, **20**, 1443 (1952).

8) L. C. F. Blackman, J. F. Mathews and A. R. Ubbelohde, *Proc. Roy. Soc.*, *Ser. A*, **256**, 15 (1960).

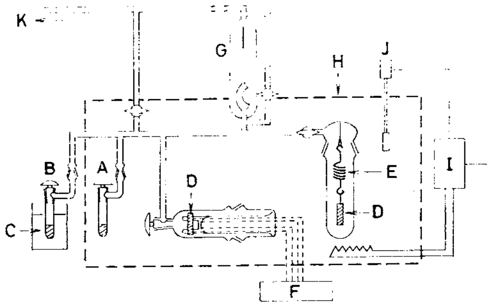

Fig. 1. Apparatus for the measurement of the electrical conductivity and the bromine content of graphite bromide.

A. Bromine container which provides saturated vapor of bromine.
B. Bromine container which provides bromine vapor of lower pressures.
C. Alcohol bath cooled by solid carbon dioxide.
D. Graphite specimen.
E. Quartz spring balance.
F. System for the measurement of electrical conductivity.
G. Glass spoon gauge for pressure measurement.
H. Water bath.
I. Temperature controller.
J. Photo-transistor detector.
K. To vacuum line.

2400°C, $c_0=3.364\pm0.001$ Å, specific resistivity 1.7×10^{-3} Ω·cm (type A).

2) Similar artificial graphite, heat-treated at 3000°C, $c_0=3.361\pm0.001$ Å, specific resistivity 1.4×10^{-3} Ω·cm (type B).

3) Natural graphite with pitch-binder, heat-treated at 3000°C, $c_0=3.356\pm0.002$ Å, specific resistivity 1.1×10^{-3} Ω·cm (type C).

The samples were cut in small specimen of 1.5 mm × 2 mm × 20 mm for measurements of the electrical conductivity and the weight gain.

GR-grade bromine was distilled and forced to pass through concentrated sulfuric acid before use.

Apparatus. The apparatus is shown in Fig. 1. It was difficult to measure both the electrical conductivity and the weight gain with the same specimen. Two graphite specimens cut from a homogeneous block were used for the measurements. The electrical conductivity was measured with one of the specimens by means of a four cantact potentiometric method, with a current of 60—80 mA and a detected potential of 0.3—3 mV. The specimen and the four platinum contacts are shown enlarged in Fig. 2. The other specimen was suspended by a quartz spring balance (sensitivity 20 mm/g), and the concentration of absorbed bromine was measured by means of a running microscope. The reaction temperature was in the range of 20—30°C, and was controlled to ±0.01°C by a controller connected with a photo-transistor detector. The bromine container A, in Fig. 1, provided the vapor of saturation pressure. The container B was controlled at desired temperatures by means of a water bath or an alcohol bath cooled by solid carbon dioxide. Thus the vapor pressure of bromine was controlled at desired values.

The whole system was evacuated before the run, and the bromine vapor was allowed to enter into the reaction tubes by the stop-cock A or B. On debromination, the container B was cooled so as to trap the bromine vapor. After the bromine vapor was completely pumped out, the electrical conductivity of the bromine residue compound was measured.

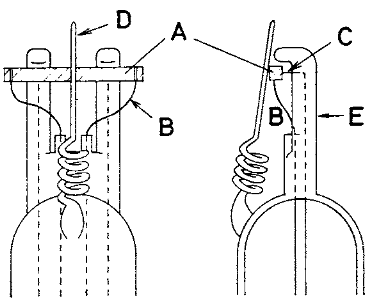

Fig. 2. Graphite specimen and electrodes for the measurement of electrical conductivity.

A. Graphite specimen, 1.5×2×20(mm).
B. Current electrode of platinum wire (0.2 mm).
C. Potential probe of platinum.
D. Glass spring to hold the sample.
E. Glass rod.

Results

Stepwise Bromination. Figure 3 shows the relation between the relative vapor pressure of bromine and the bromine uptake by graphite of the type C at 20.6°C. Open circles represent the equilibrium state of bromine absorption while the bromine vapor pressure was increased stepwise, and solid circles represent that while the vapor pressure was decreased. There existed a threshold pressure of bromine absorption, over which two stages of bromine absorption process was observed. It is consistent with the result obtained by Maire and Mering.[9] The electrical conductivity *vs.* bromine

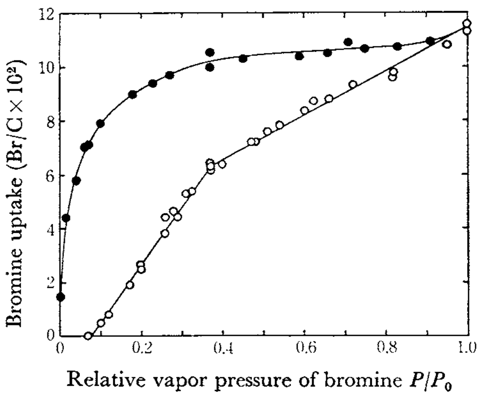

Fig. 3. Bromine vapor pressure and bromine absorption of graphite (type C) at 20.6°C.
○ on bromination
● on debromination

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[9] J. Maire and J. Mering, Proc. 3rd Conf. Carbon, 337 (1959).

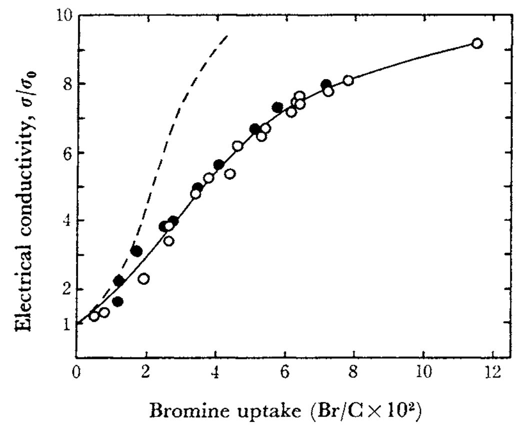

Fig. 4. Electrical conductivity of stepwise brominated graphite.
○ on bromination
● on debromination
dashed line: after Hennig

uptake curve corresponding to Fig. 3 is shown in Fig. 4. Here, σ represents the conductivity of the graphite bromide, and σ_0 that of the virgin graphite. The change was found to be almost completely reversible on bromination and debromination. The dashed line represents Hennig's work[7]) on polycrystalline graphite. Similar results have been obtained also with graphite of types A and B.

Rapid Bromination. The solid line in Fig. 5 shows the change of the electrical conductivity of type C graphite reacting with bromine vapor of saturation pressure. The dashed line represents the case of the stepwise bromination of Fig. 4. The electrical conductivity increased more steeply in the rapid bromination, and reached the final value on bromine uptake of only about one-third of the limiting value.

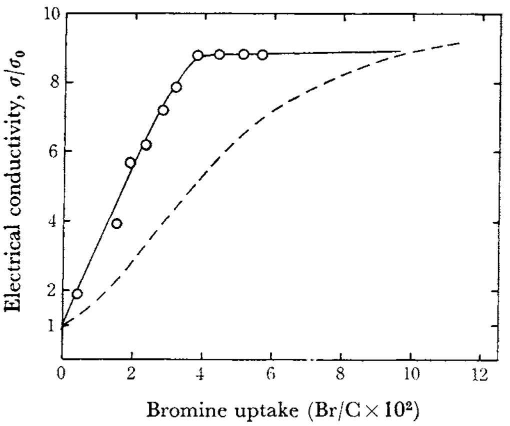

Fig. 5. Change of electrical conductivity of graphite (type C) by rapid bromination. (20.6°C)
Solid line: rapid bromination.
Dashed line: stepwise bromination

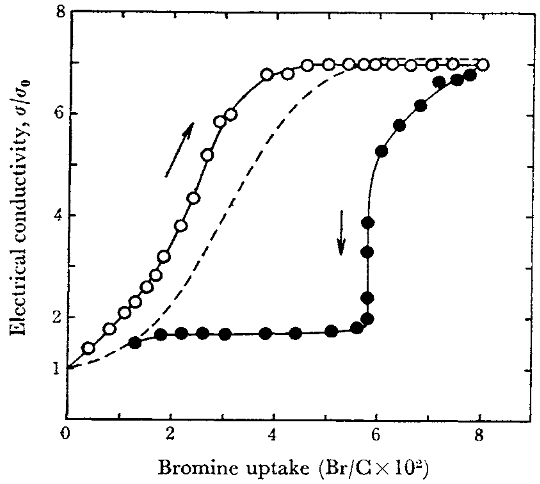

Fig. 6. Change of electrical conductivity of graphite (type B) by rapid bromination. (22°C)
○ on bromination
● on debromination
dashed line: stepwise bromination

Similar results have been obtained on graphite of types A and B. The latter case is shown in Fig. 6. A remarkable hysteresis has been observed. Moreover, an anomalous discontinuous change of electrical conductivity has been observed on debromination.

The residue compound thus formed was again allowed to absorb bromine by stepwise bromination. The curve of electrical conductivity *vs.* bromine content is shown in Fig. 7. In the earlier stage of this rebromination, the electrical conductivity of residue compound showed little change, while the

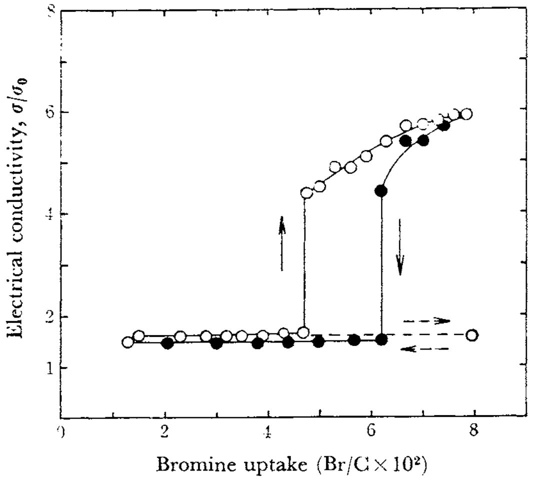

Fig. 7. Effect of stepwise bromination on electrical conductivity of the residue compound formed by the rapid bromination.
○ on bromination (stepwise)
● on debromination

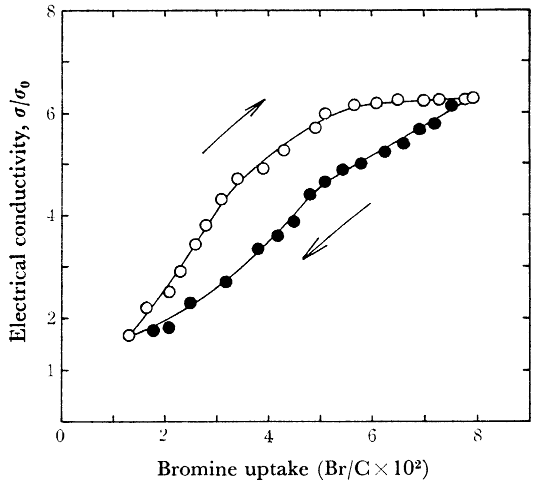

Fig. 8. Effect of rapid bromination on electrical conductivity of the residue compound formed by the stepwise bromination.
○ on bromination (rapid)
● on debromination

progress of bromine absorption was observed by weight gain. By a careful increase, a little at a time, of the reacting bromine vapor pressure, the graphite could absorb bromine almost to the saturated concentration without any change in electrical conductivity (dashed line). However, if the sample, during the course of rebromination of this type, was left to contact with bromine vapor of a constant pressure for a sufficient length of time such as 24 hr, the electrical conductivity increased to the value of the equilibrium state of the same bromine concentration (solid line). It should be noted that no bromine absorption or desorption was accompanied during the transition in electrical conductivity. The curve on debromination showed again a discontinuous change of conductivity.

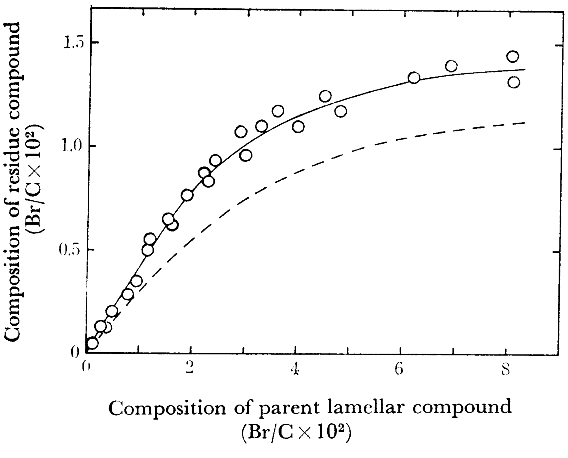

Fig. 9. Dependence of the composition of residue compound on the composition of parent lamellar compound. (dashed line: after Hennig)

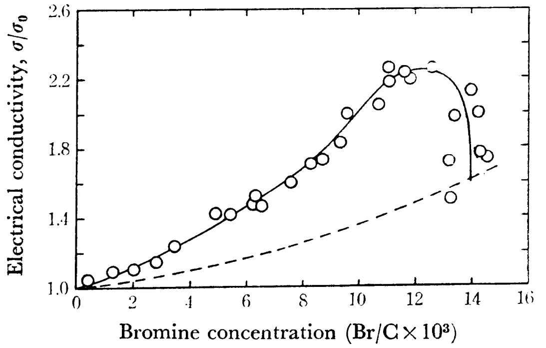

Fig. 10. Electrical conductivity of graphite bromine residue compound.
Solid line: residue compound
Dashed line: lamellar compound

The residue compound, on the other hand, formed by the stepwise bromination of the virgin graphite, followed by debromination, was later forced to absorb bromine by rapid bromination. Figure 8 shows the result of the reaction. The change was reversible, and such a discontinuous change of electrical conductivity as in Fig. 7 was not observed.

Residue Compounds. Figure 9 gives the dependence of the composition of the residue compound on the composition of the parent lamellar compound. The result coincides with Hennig's work[10] qualitatively. The electrical conductivity of the residue compound is plotted against the bromine content by the solid line in Fig. 10. The electrical conductivity increased with the bromine content over the range up to about Br/C$=1.2\times10^{-2}$. Beyond this concentration the conductivity decreased rather steeply.

The dashed line in Fig. 10 represents the electrical conductivity of the lamellar compound. The residue compound has a larger conductivity than the lamellar compound of the same bromine concentration. The results presented above are consistent with the works by Hennig[10] and Kosai[11].

Discussion

1) Electrical Conductivity of Graphite Bromide in Equilibrium. A single relation could be found between the electrical conductivity and the bromine concentration of the compound in equilibrium state of absorption.

Figure 3, which illustrates the relation between the vapor pressure and the bromine uptake, suggests that the bromine absorption of graphite can be divided into two stages at about half the saturated concentration of absorbed bromine. The curve of electrical conductivity *vs.* bromine content, however, did not show such a break. The single relation could be applied both during the course of bromina-

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[10] G. R. Hennig, *J. Chem. Phys.*, **20**, 1438 (1952).

[11] A. Kosai, *Oyobutsuri*, **30**, 402 (1961).

tion and debromination.

The curve in Fig. 4 shows a discrepancy from Hennig's result. It may be attributed to the differences in the type and the degree of crystallization of the graphite samples used.

2) The Mechanism of Bromine Absorption of Graphite. A steeper increase of the electrical conductivity was observed on the rapid bromination of graphite than in the case of the stepwise bromination for the same bromine concentration. It may be related to the difference in the structure between the rapidly brominated graphite bromide and the graphite bromide brominated stepwise.

The authors have reported[6] the change of the layer structure of graphite in the rapid bromination. As the reaction proceeded, distinct double peaks were observed in the X-ray diffraction pattern. These peaks were attributed respectively to the virgin graphite remaining and the second stage structure of the graphite bromine lamellar compound. No other phase could be found through the reaction. It is consistent with the result which Saunders *et al.*[3] reported on the measurement of the dimensional change of pyrolytic graphite with bromine absorption. The results suggest that the bromine intercalation into graphite layers would proceed as follows. At the first stage of the reaction, when the bromine vapor of saturation pressure contacts graphite, bromine begins to invade every other layer spacing of graphite. After a while, the absorbed bromine may be distributed dilutely in the crystallite and the second stage is formed.

It was also reported[6] that when the vapor pressure of the reacting bromine was increased stepwise, the (00*l*) peaks in the X-ray diffraction pattern of graphite showed gradual and continuous shifts to the lower diffraction angles, and finally reached that of the second stage structure of the saturated graphite bromide. Thus, bromine appears to be distributed rather orderly in the graphite lattice in the course of the stepwise bromination. The number of layer spacings occupied by bromine is dependent on the relative vapor pressure of bromine, and the bromine layer intercalated between the carbon layers seems to have a relatively high density. In the case of the above mentioned stepwise bromination, it may be probable that a certain fraction of the intercalated bromine is ionized as suggested by Hennig.[7] On the other hand, the more dilute distribution of bromine in the transient condition of the rapid bromination is supposed to increase the fraction of ionized bromine. It explains why the electrical conductivity of the rapidly brominated graphite for the same bromine concentration was higher than that of the sample brominated stepwise.

3) Metastable Phase of Graphite Bromide. In Figs. 6 and 7, a strange phase of graphite bromide is found, which contains a sufficient quantity of bromine, but the electrical conductivity of which remains unchanged. The phase was apparently not a stable one, and appeared only during the course of bromination and debromination. Only the normal phase is stable, the electrical conductivity of which increases with bromine concentration. The transition between the metastable phase and the normal phase was observed as a discontinuous change of electrical conductivity. The structural analysis of the metastable phase by X-ray diffraction was attempted, but adequate conditions for the appearance of the metastable phase could not be established.

The metastable phase was found only in rapidly brominated graphite, and the method of the first bromination process of virgin graphite is supposed to determine its succeeding behavior. Once a virgin graphite sample has been rapidly brominated, the memory strongly remains in it, and the residue compound also forms the metastable phase in any condition of bromination. No satisfactory explanation is found for the phenomena at present. The role of the bromine in the metastable phase of graphite bromide is interesting.

4) Residue Compounds. Figure 9 shows the retention of bromine in the graphite lattice. About half of the bromine absorbed by graphite was retained in the dilute region. The fraction of the retained bromine is higher than Hennig's result, which may be attributed to the difference of the type of the graphite sample.

The steep decrease of the electrical conductivity of the bromine residue compound at the higher bromine concentration was also observed by Hennig[7] and Kosai.[11] They explained this phenomenon to be the result of the mechanical disintegration of graphite crystal by a considerable dimensional change with bromination. This is plausible in a way. The reproducibility of the data was fairly good, and the point of the saturated residue compound coincided with the line of lamellar compound. It may be possible to consider the decrease of the electrical conductivity as a transition from the electronic state of the residue compound to that of the lamellar compound.