Doping of Bromine into Carbon Materials with Different Heat-Treatment Temperatures

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熱処理温度の異なる炭素材料への臭素のドーピング

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Behavior of bromine doping into carbon materials with different heat-treatment temperatures (HTT) from 1000 to 2800°C were investigated, together with the characteristics such as XRD patterns, Raman spectra and electric conductivities of the respective bromine residue compounds prepared by debromination of the doped samples. It was found that there are two different cases in the behavior of the carbon materials for bromine doping depending on their HTTs; one is the carbons with high HTT (HTT $\geq$ 2000°C), the other those with low HTT (HTT $\leq$ 1900°C). The carbons of high HTT group form intercalation compounds with compositions up to C₁₀Br, and considerable fractions, such as 13–25%, of the intercalated bromine remain in the interlayer space of graphite after the debromination process, thus forming the bromine residue compounds. On the other hand, the carbons of HTT $\leq$ 1900°C, except for HTT1000, absorb only small amounts of bromine, which are almost completely expelled by the debromination process. They apparently do not form residue compounds with bromine. The carbon with HTT1000 was found to have a unique character: It absorbed an appreciable amount of bromine and the remaining fraction of the bromine after debromination was rather large, although the XRD pattern and the electric conductivity were unchanged. It is thus suggested that the remaining bromine may exist on the edge of the crystallites by forming weak bonding with carbon atoms.

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1. Introduction

The graphite intercalation compound with bromine has been studied extensively^{1)–3)} because of the ease of its synthesis, high electric conductivity of the resulting compound and the existence of the residue compound. In particular, the high electric conductivity and the unusual stability of the residue compound have attracted attention of many investigators in the field of carbon fiber technology.^{4)–6)} However, studies on the bromine-carbon system with emphasis on the effect of graphitization degree of host carbons are rare. Mukaibo and Takahashi⁷⁾ studied on the samples of artificial graphite heat-treated at 800, 1500, 2000 and 2600°C and found that for the samples heat-treated above 1500°C, both the saturated amount of absorbed bromine and absorption rate increased with the heat-treated temperature, whereas the sample heat-treated at 800°C had exceptionally large bromine absorption, almost twice as much as that of the sample heat-treated at 1500°C. Hooley and Deitz,⁸⁾ and Mathur et al.⁹⁾ also pointed out, in their studies using carbon fibers, that intercalation of bromine became difficult with the carbon fiber samples having low graphitization degree. A systematic investigation on the behavior of bromine doping into samples with different degree of graphitization has not been hitherto seen.

We have recently reported¹⁰⁾ some results of IBr doping into several carbon samples of different heat-treatment temperature, in view of their electric conductivity change. Here, we report on the host-effect of bromine doping into the carbon samples with different heat-treatment temperatures,

which are the same materials used for the IBr doping study.¹⁰⁾

2. Experimental

The carbon samples used were taken from artificial graphite kindly provided by SEC Corp., which were derived from petroleum coke particles with a pitch binder and heat-treated at about 1000°C (hereafter designated as HTT1000). Small blocks of the raw graphite were then heat-treated at respective temperatures of 1500, 1750, 1900, 2000, 2200, 2400 and 2800°C (HTT1500–HTT2800). Bromine with purity of >99% (Wako Junyaku Kogyo Co.) was used after distillation in vacuum.

Specimens (2 × 3 × 20 mm) of each carbon sample were placed in an evacuated glass reaction vessel equipped with a bromine reservoir, and doping of bromine was made by allowing the specimens to contact with saturated bromine vapor at room temperature for several hours until the saturation of bromine absorption was achieved. The amount of bromine absorption was determined by observing the lowering of liquid bromine level in an upper capillary part of the bromine reservoir. The saturated compounds thus prepared were debrominated by cooling the bromine reservoir to liquid nitrogen temperature and then heating the sample in a vacuum of 10⁻¹ Pa at 300°C for several hours to complete the debromination. The resulting bromine residue compounds were confirmed to be quite stable in the air. For the carbon samples of HTT2200, 2400 and 2800, the bromine absorption process was performed under several controlled

bromine vapor pressures (P) such as $P/P_0=0.5$ and 0.25 , where P_0 is the saturated vapor pressure of the sample temperature, and the residue compounds of each were prepared in the same way. The compositions of the residue compounds were determined from the weight increase of the specimens.

The measurements of X-ray diffraction (XRD) (Rigaku RINT2000, Cu K α), Raman spectroscopy (Renishaw Raman Microscopy System 2000, He-Ne laser), electric conductivity (four-terminal method) and thermoelectric power were made on each residue compounds.

3. Results and discussion

3.1 Doping of bromine into carbons with different heat-treatment temperatures and their bromine residue compounds

The concentrations of absorbed bromine at saturation into the carbon samples of different HTT under the saturated bromine pressure at room temperature are shown in Fig. 1, together with those of remaining bromine after the debromination process. For the host carbons of $\text{HTT} \geq 2000^\circ\text{C}$, the concentration of absorbed bromine at saturation increased with HTT of the host carbon and the atomic ratio of bromine to carbon, ($n_{\text{Br}}/n_{\text{C}}$), became 0.08–0.1. The saturation composition for HTT2800 carbon becomes nearly C_{10}Br . This can be compared with the literature values for artificial graphites,⁷⁾ whereas for well graphitized carbons such as natural graphite, the saturation composition is known to be C_8Br .^{1),2)} On the other hand, for the carbons of $\text{HTT} \leq 1900^\circ\text{C}$, it decreased with HTT and the values of ($n_{\text{Br}}/n_{\text{C}}$) at saturation were rather small, less than 0.03.

As for the residue compounds after debromination treatment, again rather different behavior was seen between the host carbons of high HTT and of low HTT. For the residue compounds prepared from carbons of $\text{HTT} \geq 2000^\circ\text{C}$, the concentrations of remaining bromine were appreciable, ($n_{\text{Br}}/n_{\text{C}} = 0.01\text{--}0.02$), which were 20–25% of those at saturation, though HTT2800 has a little small remaining fraction of bromine of about 13%. On the other hand, the remaining fractions for the carbons of $\text{HTT} 1500\text{--}1900^\circ\text{C}$ were fairly small, virtually zero.

The X-ray diffractograms of the host carbons and the bromine residue compounds are shown in Fig. 2. The usual graphitization behavior with increasing heat-treatment temperature was observed for the host carbons. The residue compounds prepared from the samples of $\text{HTT} \leq 1900^\circ\text{C}$ showed very similar patterns to the respective host carbons, while the peak positions of the residue compounds from the samples of $\text{HTT} \geq 2000^\circ\text{C}$ shifted appreciably towards lower diffraction angles, indicating that the interlayer distance is slightly expanded by the remaining bromine. Since any indications of higher stages were not recognized in the patterns, these bromine molecules are considered to be randomly distributed in the interlayer spaces of the host carbons.

As stated above, the mechanisms of bromine doping are clearly different between the cases of low HTT and high HTT carbons, and the boundary of the two cases seems to lie between 1900 and 2000°C . For the samples of high HTT carbons, bromine molecules are considered to be intercalated in the interlayer space of graphite in the similar way to other ordinary graphite intercalation compounds, and in this case a considerable fraction of the intercalated bromine still remain in the interlayer spaces in the residue compounds after the debromination process. On the other hand, the samples of low HTT carbons, except for that of $\text{HTT} 1000$, absorb rather small amounts of bromine even under saturated bromine pressure, and their remaining fractions after debromination process are very small. The results of XRD

Fig. 1. Bromine concentrations in saturation and residue compounds. □: in saturation, ■: in residue.

Fig. 2. XRD patterns of host carbons and bromine residue compounds. —: host carbons, —: residue compounds.

measurements also suggest that for low HTT carbons there exist no bromine molecules in the interlayer space. For the sample of $\text{HTT} 1000$, discussion will be made in Sec. 3.5.

3.2 Electric conductivity of the residue compounds

The residue compounds prepared from the host carbons of $\text{HTT} \leq 1900^\circ\text{C}$ showed almost the same electric conductivity as the respective host carbons, in accord with their virtually negligible remaining bromine as stated in the preceding section, while an appreciable increase in electric conductivity by bromine doping was observed on the host carbons of $\text{HTT} \geq 2000^\circ\text{C}$. Similar behavior was also reported¹⁰⁾ for IBr doping into the same host carbons. For the high HTT carbons, the dependence of bromine concentration in the residue compounds upon their electric conductivity was examined by controlling the relative bromine pressure (P/P_0). In Fig. 3 the results are shown as the relative electric conductivity (σ/σ_0) vs. the bromine concentration of the

Fig. 3. Relative electric conductivity vs. bromine concentration of residue compounds. Δ : HTT2200, $\circ$: HTT2400, $\blacksquare$: HTT2800, —: Sasa et al.¹¹⁾

residue compounds, where σ_0 is the electric conductivity of the respective host carbons. As shown in Fig. 3, these results on the samples of different HTTs agree fairly well with those of Sasa et al.,¹¹⁾ though they used well-graphitized carbons such as heat-treated pyrolytic graphites. Among the residue compounds, two samples of $n_{\text{Br}}/n_{\text{C}} > 0.012$ showed the values of (σ/σ_0) less than one, which are indicated in parentheses in Fig. 3. It is probably because that the specimens of these samples would have some cracks in their structure during the process of bromine intercalation owing to large expansion of interlayer distances, as was indicated by Hennig.²⁾ Except for these two samples, the effects of bromine concentration on the electric conductivity are almost similar, irrespective of heat-treatment temperature of host carbons. This fact suggests that the main part of remaining bromine molecules exist in the interlayer space and contribute to the increase of charge carrier of the residue compounds, in accord with the conclusion of Miyauchi and Takahashi.¹²⁾

The temperature dependence of the electric conductivity was also examined from 80 to 450 K on each residue compound. The samples of $\text{HTT} \leq 1900^\circ\text{C}$ showed the same temperature dependence as the respective host carbons, whereas for those of $\text{HTT} \geq 2000^\circ\text{C}$ it was observed a tendency to shift to metallic behavior from semi-conductive one of the host carbons.

3.3 Raman spectra of the bromine residue compound

Raman spectra of the host carbons of different heat-treatment temperature showed the ordinary tendency to change, similarly to the results of XRD measurement, with increasing HTT. We observed so-called G-, D-, and D'-band at around 1580, 1330 and 1620 cm^{-1} , respectively. The frequency of D-band, around 1330 cm^{-1} , is fairly low as compared with the normally observed value of 1360 cm^{-1} . This shift is attributable to the fact that the exciting wave-length of the He-Ne laser used in this experiment is 632.8 nm and considerably long as compared with 514.5 nm of Ar^+ laser usually used.¹³⁾

The Raman spectra of the residue compounds prepared from the carbons of low HTT were found to be almost the same as those of the host carbons. On the other hand, for the residue compounds prepared from the HTT2400 and HTT2800 carbons, the intensities of D-band and D'-band, at around 1330 and 1620 cm^{-1} , respectively, were observed to decrease with the concentration of the remaining bromine. Figure 4 shows the Raman spectra of the HTT2800 host

Fig. 4. Raman spectra of HTT2800 host carbon and its bromine residue compounds.

Fig. 5. Relative Intensity ($I_{\text{D}}/I_{\text{G}}$) vs. bromine concentration of residue compounds. $\circ$: HTT2400, $\blacksquare$: HTT2800.

carbon and its bromine residue compounds. It is to be noted that in the spectra of Fig. 4, a small sharp peak at around 1650 cm^{-1} are seen near the D'-band at 1620 cm^{-1} . This peak is considered to be caused by undesirable instrumental stray light and is to be disregarded. In Fig. 5, the changes of the relative intensity, $I_{\text{D}}/I_{\text{G}}$, of D-band to G-band with the bromine concentration are shown on the residue compounds of HTT2400 and HTT2800. The decreasing tendency of $I_{\text{D}}/I_{\text{G}}$ with bromine concentration indicates that the bromination-debromination process apparently caused some rearrangements in the texture of the host carbons because of the large expansion of interlayer distances by the intercalation of bromine molecules. It is to be added here that the results on the same samples which we showed in parentheses in Fig. 3 were also included in Figs. 4 and 5, and they showed

the normal, similar behavior to other samples of the residue compounds.

Song et al.¹⁴⁾ reported that in the Raman spectra of the graphite-bromine compound ($n_{\text{Br}}/n_{\text{C}}=0.0114$) prepared from highly oriented pyrolytic graphite (HOPG), the G-band peak at 1580 cm^{-1} splitted into a doublet signal at around 1580 cm^{-1} and 1600 cm^{-1} . They studied also on ICl-, IBr-, HNO_3 -graphite system as well as on Br_2 -graphite, and revealed that this doublet signal was observed commonly on these intercalation and/or residue compounds. In the present study, we also observed the doublet signals, which appeared at around 1580 and 1596 cm^{-1} for HTT2400, and at 1580 and 1593 cm^{-1} for HTT2800. These bands showed a tendency to shift towards slightly higher wave length, with the bromine concentration in the samples, in accord with the results of Song et al.¹⁴⁾

3.4 Thermoelectric power of the bromine residue compounds

The experimental results of thermoelectric power measurements at 273 K are shown in Fig. 6 against the bromine concentration in the residue compounds. Although Fig. 6 shows some scatter, it is seen that the absolute thermoelectric power tends to increase at first with the bromine concentration, probably because of the increase of positive holes as the charge carrier in the samples, and then for $n_{\text{Br}}/n_{\text{C}}$ above 0.01 , it appears to converge on $30\text{--}45\text{ }\mu\text{V K}^{-1}$, irrespective of HTT of the host carbons. The samples shown in parentheses in Fig. 3, which were considered to have some cracks, showed the values slightly lower than the average, but in general their behavior was almost the same as other samples. The temperature dependence of thermoelectric power was also found to increase with the bromine concentration.

3.5 Bromine doping into the carbon of HTT1000

The behavior of the carbon of HTT1000 upon bromine doping was unique as compared with that of the other low HTT carbons. Namely, the concentration of absorbed bromine under the saturated bromine pressure was comparatively small, whereas the remaining fraction of bromine after debromination process was considerably large and was more than 30%. Similar unusual behavior was also reported by Mukaibo and Takahashi,⁷⁾ on the carbon sample heat-treated at 800°C . Nevertheless, the XRD patterns of the residue compound were found to be almost the same as those of the host HTT1000 carbon. It was also found that

there was negligibly small effect on the electric conductivity. These observations indicate that the remaining bromine molecules in the HTT1000 carbon do not exist in the interlayer space. The bromine molecules are considered to make weak bonding with the carbon atoms at the edge of the crystallite of the host carbon.

4. Conclusions

The behavior of bromine doping into carbon materials of artificial graphite derived from petroleum coke and heat-treated at several different temperatures from 1000 to 2800°C (designated as HTT1000 etc.) was investigated. The characteristics of the bromine residue compounds after the debromination process of the respective bromine-carbon system were also examined. The results are summarized as follows.

(1) For the carbons of $\text{HTT} \leq 1900^\circ\text{C}$, except for HTT1000, the concentrations of absorbed bromine under the saturated bromine pressure were rather small, and the remaining fractions of the bromine after the debromination process were virtually zero. It is considered that the bromine residue compounds are hardly formed for these low HTT carbons.

(2) The carbons of $\text{HTT} \geq 2000^\circ\text{C}$ were found to absorb bromine under the saturated bromine pressure up to $n_{\text{Br}}/n_{\text{C}} \cong 0.1$, and the remaining fractions of the bromine after the debromination process were 13–25% of the saturation concentrations, thus resulting the bromine residue compounds.

(3) In the bromine residue compounds, the main part of the bromine molecules are considered to exist in random distribution in the interlayer space of the graphite, and contribute apparently by charge transfer to the increase in the electric conductivity, irrespective of HTT of host carbons.

(4) The thermoelectric powers of the residue compounds of $n_{\text{Br}}/n_{\text{C}} \geq 0.01$ were found to converge on the value $30\text{--}45\text{ }\mu\text{V K}^{-1}$, irrespective of HTT of the host carbons.

(5) The carbon sample of HTT1000 showed an unique character in the behavior for bromine doping. It absorbed an appreciable amount of bromine under the saturated bromine pressure, and considerable fraction of the bromine remained after the debromination process. In this case, however, little effects on the electric conductivity and the XRD pattern were observed, and consequently the bromine molecules are considered to exist not in the interlayer space of the graphite, but probably on the edge of the crystallites by forming weak bonding.

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Fig. 6. Thermoelectric power vs. bromine concentration of residue compounds. $\triangle$: HTT2200, $\circ$: HTT2400, $\blacksquare$: HTT2800.

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