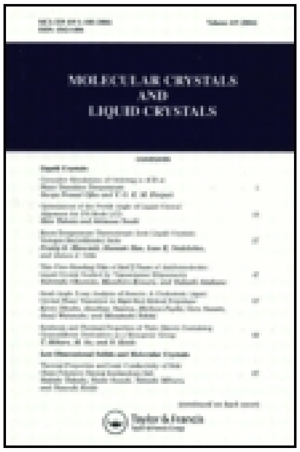

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Activated carbon fibers (ACFs) are microporous carbons consisting of a three-dimensional disordered network of micrographites. In order to clarify the correlation between the disordered structure and the electronic properties, we investigated the magnetic susceptibility of heat-treated and iodine-doped ACFs. The heat treatment reduced the Fermi energy of ACFs, but the carrier density per micrographite estimated from the Fermi energy is nearly equal to the density of dangling bond spins of as-prepared ACFs, irrespective of heat treatment temperature. In less graphitized ACFs, a charge transfer arises from ACFs to iodine, suggesting less graphitized micrographite has the electronic features of condensed polycyclic aromatic hydrocarbons. On the other hand, well graphitized micrographites in ACFs, are more graphitic in their electronic state, resulting in the absence of charge transfer to iodine.

Keywords; activated carbon fibers; orbital diamagnetism; disordered material; micrographite; iodine-doping

INTRODUCTION

Activated carbon fibers (ACFs), which have large specific surface areas (SSA) ranging about 1000–3000$\mathrm{m^2g^{-1}}$, are microporous carbons consisting of a three dimensional disordered network of micrographites[1], where each micrographite has three to four graphene sheets with an average in-plane size of about 30Å. This particular structure makes ACFs an interesting candidate for the issue of nano-graphite between bulk graphite and polycyclic condensed aromatic hydrocarbon, which is related to mesoscopic behavior and quantum size effects[2]. Heat treatment attenuates the disordered structure of the micrographite network and enhances the micrographite size[1,3]. Namely, we can modify the micrographite size from 30Å to infinity depending on the heat treatment temperature. Meanwhile, the nano-scale pores called micropores, which are the spaces surrounded by micrographites, are available for the accommodation of various guest molecules. It is expected that the interaction between ACFs and guest molecules due to their large SSA results in the change in the electronic states of ACFs. In the present paper, we investigated the magnetic properties of heat-treated and iodine-doped ACFs in order to clarify the electronic properties of micrographites in relation to the disordered structural feature and the interaction with doped iodine.

EXPERIMENTAL

The pitch-based ACFs (Osaka Gas Co.) with SSA = $1500 m^2 g^{-1}$ were heat-treated in argon gas atmosphere for 15 min in the temperature range 1300–2800°C. Magnetic susceptibilities were measured on about 15mg of the sample in magnetic fields up to 1T between liquid helium and room temperatures. The samples were vacuum-sealed in a Pyrex tube after heat-treatment at 200°C in a vacuum of 1×10^{-6}Torr, in order to avoid the influence of adsorbed gases, in particular, oxygen. For iodine-doping, the ACFs heat-treated at 1300–2800°C were reacted with about 40mg iodine in a Pyrex tube at 105°C for one day in an electric furnace. The amount of doped iodine in each ACFs was estimated by weight uptake.

EXPERIMENTAL RESULTS and DISCUSSION

FIGURE 1 shows the temperature dependence of magnetic susceptibility for non-doped and iodine-doped ACFs heat-treated at each temperature. The diamagnetic susceptibility is larger for all the samples than their expected Pascal diamagnetic susceptibility, 0.5×10^{-6}emu g^{-1}, which indicates an important role of the orbital diamagnetic contributions similar to regular graphite or other graphitic materials. Heat treatment enhances the orbital diamagnetic contributions and their temperature-dependent behavior, while the iodine-doping lessens the enhancement. According to McClure's theory[4], the increase in the orbital diamagnetism by the

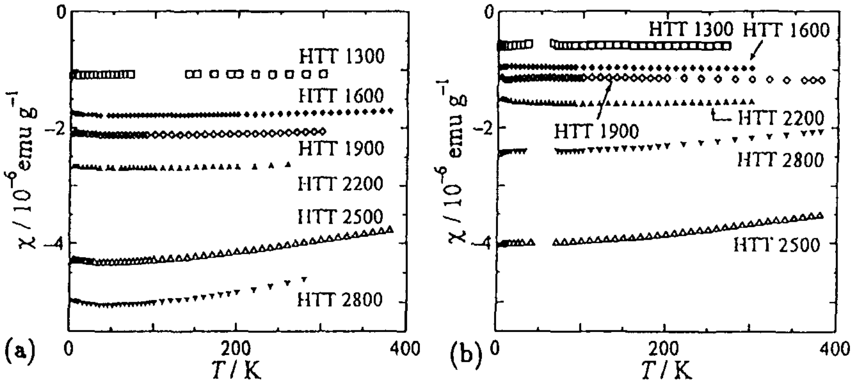

FIGURE I : The temperature dependence of magnetic susceptibility for non-doped ACFs (a) and iodine-doped ACFs (b). HTT denotes the heat treatment temperature (°C). The impurity spin contributions (~ 50ppm Fe) are subtracted from the observed magnetic susceptibility.

heat treatment corresponds to the decrease in the Fermi energy. By contrast iodine-doping tends to increase the Fermi energy, judging from the decrease in the orbital diamagnetic contribution.

There exists, however, a quantitative discrepancy between the observed orbital diamagnetic susceptibility and the calculated one based upon McClure's theory. Since the structural investigations for ACFs[1,3,5] suggest disordered features of the structure, the orbital diamagnetism has to be analyzed on the basis of the disordered network consisting of micrographites having finite sizes. Kotosonov introduced randomness in the theoretical treatment of the orbital diamagnetism for graphitic materials[6]. In his theory, which is a complement of McClure's theory by introducing the "degeneracy temperature" ΔT as an indication of the randomness in the electronic state, the temperature dependence of the orbital magnetic susceptibility is given by the following equation;

$$\chi_{\text{orbital}} /\text{emu g}^{-1} = -\frac{1.38\times 10^{-2}}{T+\Delta T}\,\text{sech}^2\left[\frac{E_{\text{F}}}{2k_{\text{B}}(T+\Delta T)}\right], \qquad (1)$$

where E_{F} and k_{B} are the Fermi energy and the Boltzmann constant, respectively. The analysis using Eq. (1) gives the Fermi energy and the degeneracy temperature as summarized in TABLE I. The decrease in the Fermi energy induced by heat treatment is explained in terms of the charge transfer from the π-band to the dangling bond sites, taking it into consideration that micrographites have dangling bonds around their peripheral

TABLE I : Fermi energies E_F, degeneracy temperatures ΔT and iodine concentrations x ($C(I_2)_x$) for ACFs heat-treated at 1300–2800°C.

HTT / °C	ACF		iodine-doped ACFs		
	E_F / eV	ΔT / K	E_F / eV	ΔT / K	x
1300	0.34	2.2×10^3	0.74	1.4×10^3	0.076
1600	0.20	1.4×10^3	0.68	1.5×10^3	0.071
1900	0.17	1.2×10^3	0.37	2.2×10^3	0.052
2200	0.14	0.95×10^3	0.23	1.7×10^3	0
2500	0.084	0.60×10^3	0.091	0.67×10^3	0
2800	0.073	0.49×10^3	0.15	1.3×10^3	0

region. The dangling bonds take electrons from the π-band, resulting in the generation of hole carriers in the π-band and the increase in the Fermi energy. The graphitization through heat treatment increases the in-plane sizes of micrographites at the expense of dangling bonds. As a consequence, the electrons trapped in the dangling bond sites are pushed back to the π-band, giving rise to decrease in the Fermi energy as the elevation of heat treatment temperature.

The degeneracy temperature which is an indication of the randomness is related to the relaxation time τ of carriers; $\tau = \hbar/\pi k_B \Delta T$. So we can estimate the mean free paths $\langle l \rangle = v_F \tau$ of the carriers by assuming the linear dispersion of the π-band like that in regular graphite, where v_F is the Fermi velocity. The correlation between $\langle l \rangle$ and the average micrographite in-plane size L_a for non-doped ACFs is shown in FIGURE II, where L_a is estimated by Raman spectra[7]. FIGURE II reveals that $\langle l \rangle$ is proportional to L_a, and $\langle l \rangle$ is about a half of the average micrographite in-plane size. This fact suggests that the carrier scattering is governed by processes taking place around the marginal region of micrographites.

Next, we discuss the correlation between the Fermi energy E_F and the relaxation time τ. FIGURE III reveals the proportionality between τ^{-1} and E_F, which can be related to L_a from the result in FIGURE II; $\langle l \rangle \propto L_a$. In addition, assuming the linear dispersion in the π-band, we obtain two following relations; $\langle l \rangle \propto \tau$ and $n \propto {E_F}^2$, where n is the carrier density. The above consideration gives $n \propto L_a^{-2}$ as an empirically derived result. Moreover, taking it into account that the number of micrographites N_{MG} in unit volume of ACFs is proportional to ${L_a}^{-2}$, the carrier density is estimated as 2.3 per micrographite and is independent of the

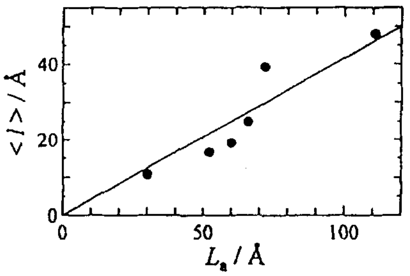

FIGURE II : The relation between the average micrographite in-plane size L_a and the mean free paths $\langle l \rangle$ of carriers for non-doped ACFs. The solid lines is the guide for the eyes.

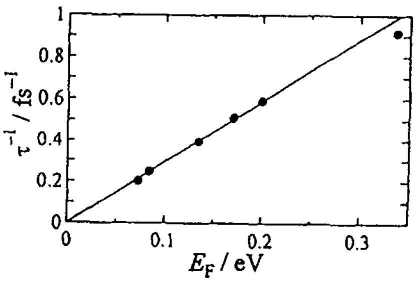

FIGURE III : The relation between the Fermi energy E_F and the relaxation rate τ^{-1} of carriers for non-doped ACFs. The solid line is the guide for the eyes.

micrographite in-plane size, as well. The as-prepared ACFs has about $4 \times 10^{19}g^{-1}$ dangling bonds[7,8], corresponding to about 4 dangling bond spins per micrographite, which is almost the same value as that of the carrier density. This suggests that the hole carriers are generated through the charge transfer from the π-band to dangling bonds.

Finally, we discuss the iodine-doping effect. The increase in the Fermi energy induced by iodine-doping suggests the presence of charge transfer from ACFs to iodine. Assuming the electronic state of ACFs has a linear π-band, we estimate the charge transfer rate from ACFs to iodine, as shown in FIGURE IV. The rate f_C, which is $f_C = 0.009$ at HTT 1300°C, decreases steeply with the elevation of the heat treatment temperature above 1600°C. It tends to be less temperature-dependent above 2200°C, and finally it approaches $f_C = 0$ around HTT 2800°C. In addition, this behavior is similar to that of the iodine concentration n_{I_2}/n_C doped in ACFs, which steeply decreases with the increasing heat treatment temperature above 1600–1700°C. The fact that iodine is not intercalated in bulk graphite[9] suggests the weakness in the interaction between iodine and graphite. Charge transfer salts, on the other hand, are formed between iodine and condensed polycyclic aromatic hydrocarbons; for example, perylene-iodine complex with $f_C = 0.02$[10]. The large charge transfer rate for the ACFs heat-treated below 1600°C demonstrates the formation of iodine intercalated system, that is, less graphitized micrographites are considered to have similar electronic features to those of small condensed polycyclic aromatic molecules. On the other hand the ACFs well graphitized does not accept iodine as an acceptor intercalate because of the more

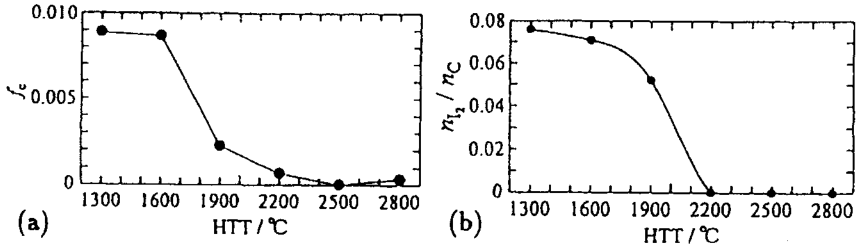

FIGURE IV : The charge transfer rate per carbon atom f_C for iodine-doped ACFs (a) and the iodine concentration n_{I_2}/c_C (b). The solid lines are the guides for the eyes.

graphitic nature in their electronic structures.

Acknowledgments

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