Ferromagnetic Properties of Super Surface Mesocarbon Micro Beads

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Introduction

Activated carbon whose specific surface area is greater than $2630 m^2 g^{-1}$, i.e., the surface area of a single infinite graphite sheet, may be called a superhigh surface area carbon or super surface carbon.[1] The super surface carbon is mainly composed of minute graphitic crystallites having a stacking structure of two or three layers.[2] Almost all carbon atoms of super surface carbon are on the surface, and thereby the super surface carbon should be called a surface solid. Their surface properties have attracted much attention.[3] The pore and surface structures have been characterized by various techniques[4-7] The main electronic states of the super surface carbon are the surface states and characteristic electronic properties are expected. Unusual photoconductivity and surface sensitive ESR relaxation of activated carbon fibers(ACFs) with large surface area were observed[8, 9] Activated mesocarbon microbeads(a-MCMBs) prepared from mesocarbon microbeads with an oriented polycyclic aromatic structure have greater surface area than ACF, which should be regarded as a representative surface solid. Furthermore, a-MCMBs are expected to have a more ordered micrographitic structure than ACF. This paper describes ferromagnetic properties of a-MCMBs.

Experimental Section

Two of M6 and M31 a-MCMBs were produced by Osaka Gas Co. through activation of MCMB with KOH. The N_2 adsorption isotherms were measured gravimetrically at 77 K. The micropore structures were determined by the subtracting pore effects(SPE) method using high resolution α_s-plot for the N_2 adsorption isotherm.[2] The micrographitic structures were examined by X-ray diffraction(XRD). The magnetic susceptibility was measured with a SQUID magnetometer (Quantum Design:MPMS2) over the temperature range of 1.7 to 300 K in vacuo. a-MCMB samples were sealed in a quartz tube after evacuation at 383 K and 1 mPa for 2 h.

Results and Discussion

The N_2 adsorption isotherms are basically of Type I, which is indicative of presence of uniform micropores.[10] Table 1 shows the specific surface area, the micropore volume and pore width. M31 has the surface area of $3090 m^2 g^{-1}$ which greater than $2630 m^2 g^{-1}$ even by the SPE method. Hence M31 can be regarded as a typical surface solid. The maximum position of the broad 002 X-ray diffraction peak due to the micrographites coincided with that of graphite. The stack height of M31 was 0.8 nm, which corresponds to the bilayer thickness of the graphitic layer. The combined peak of 100 and 101 peaks was more diffuse than that of ACF, and thereby the micrographitic units of M31 should be smaller than that of ACF. The above results indicate a bi-micrographitic structure of M31. As this micrographitic unit is so small that the ratio of edge carbon atom is 0.7. A part of the edge carbon atoms tend to form localized electronic states, and hence there should be many unpaired electrons in M31. The Fe impurities in M6 and M31 were 2 and 80ppm, respectively.

Figure 1 shows the temperature dependence of the magnetic susceptibility χ of M31 with an increase of temperature in vacuo. M6 showed a typical temperature dependence of paramagnetism at the whole temperature range. While M31 have a maximum at 4.2K±0.5K and the temperature dependence of the magnetic susceptibility in the temperature range of 30K to 200 K is expressed by the Curie-Weiss law. The Weiss constant was -227K in the range of 30K to 200K. However, a-MCMBs, especially M31, showed a slow relaxation of magnetization of several hours, and then the observed Weiss constant was not a real equilibrium value. As no maximum in the χ-T relation of ferromagnetic carbons at low temperature was reported in the literature,[11-13] super surface carbon shows an unusual ferromagnetic behavior. The magnified χ-T relation near the maximum is also shown in Figure 1, where a distinct difference between the χ-T behaviors with the increase and decrease in the measuring temperature is shown. Here the χ-T curve with the increase of temperature was measured after the sample was cooled down to 1.7K without applying the magnetic field. The χ value of M31 increases with the decrease in temperature, whereas the χ-T curve of M31 with the increase of temperature has the maximum at 4.2K. The irreversible temperature dependence of χ is quite close to that observed in spin glass or mictomagnetic compounds. [14-16] The spin glass behavior has been observed in the mixed dilute alloy system and in the isolated system of atomic impurities. As micrographitic units having spins are linked with each other to form spin clusters, there is an isolated spin on the micrographite. Therefore, the observed ferromagnetism can be ascribed to the spin glass mechanism or mictomagnetism.

M6 showed no magnetic hysteresis. Whereas a

marked the magnetic hysteresis was observed. Figure 2 shows the hysteresis of M31 in the magnetic field of -2000 to +2000G at 1.7K. The residual magnetization was 0.016emuGg^{-1}. The magnetic hysteresis became less marked with an increase of the measuring temperature. Nevertheless we observe a clear hysteresis even at 300K, but the loop is much smaller than that at 1.7K. We must take into account the magnetic contribution by Fe impurity. If we presume that Fe impurity of 80ppm originates from bulk Fe_3O_4, the estimated residual magnetization should be 0.008emuGg^{-1} at maximum, which is smaller than the observed value. Also there was no ferromagnetic resonance absorption due to Fe_3O_4 in the preliminary ESR examination. The fact that the magnetic hysteresis depends sensitively on the measuring temperature is completely different from the ferrimagnetism of Fe_3O_4. Hence we conclude that the observed ferromagnetism of super surface carbon is not extrinsic, but intrinsic. In the super surface carbon, there are clustered and isolated spins arising from the partially ordered micrographitic structures, and therefore both spin glass behavior and mictomagnetism can be assumed to be responsible for the observed ferromagnetism.[17]

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TABLE 1-Microporosity of samples

Sample	$a_{s,SPE}$ m^2g^{-1}	W_0 mlg^{-1}	w nm
M6	570	0.23	0.81
M31	3090	1.97	1.28

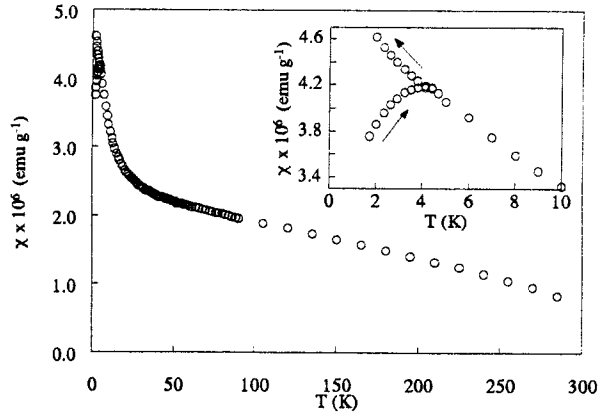

Figure 1-The temperature dependence of the magnetic susceptibility χ of M31 in vacuo.

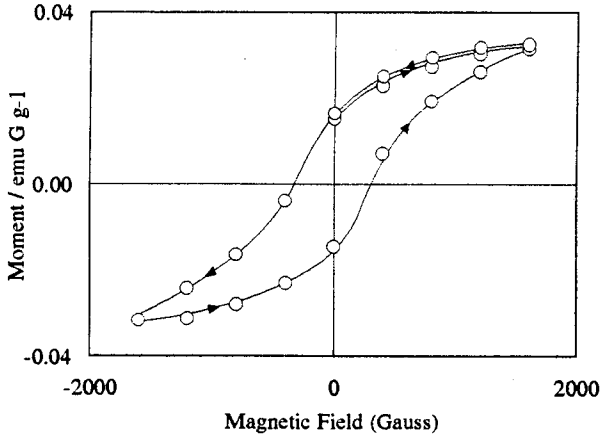

Figure 2-Magnetization curve of M31 at 1.7K.