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The local structure of hydrogen storage nanocrystalline graphite by neutron scattering

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Abstract

The total and inelastic neutron scattering measurements were employed in order to get more information on the local structure of nanocrystalline graphite prepared by mechanical milling under D_2 gas atmosphere. In the RDF(r) for the sample after 50 h of milling, newly grown peak around 0.154 nm was found at the larger r side of the first nearest peak corresponding to the C–C correlation. The distance 0.154 nm of the C–C correlation is attributed to 4-fold bonding. Moreover, the inelastic neutron scattering peak observed in the 160–190 meV region for the samples after 20 h of milling indicates new emergence of sp^3 bonding. The results apparently indicate that terminating D atoms at the edges of the nano-lattice plane of graphite create the new sp^3 bonding of C atoms during the milling process under D_2 gas atmosphere.

Keywords: Nanostructures; Hydrogen storage materials; Mechanical alloying; Neutron scattering; Diffraction

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1. Introduction

Various kinds of graphites have been paid much attention to as a prospective hydrogen storage material. Recently, it has been reported that the nanocrystalline graphite prepared by mechanical alloying absorbs a large amount of hydrogen through the solid–gas reaction [1,2]. The structural investigation by neutron diffraction teaches us two types of deuterium coordinations. One is a C–D covalent bond and the other is the D atom which locates between layers of the graphite [2].

In this work, we intend to get more insight on the local structure of nanocrystalline graphite prepared by mechanical milling under D_2 gas atmosphere by a combination of total and inelastic neutron scattering techniques. Inelastic neutron scattering measurement is a straightforward method for investigating hydrogen dynamics because of the much larger scattering cross-section of H atoms than that of C atoms. Therefore, we believe that a series of the vibration modes of C–H bonds in the inelastic neutron scattering spectrum give us new information on the local structure around D atoms for the nanocrystalline graphite.

2. Experimental procedure

3 g of hexagonal graphite powder (MCMB25-28, Osaka Gas, 99.999%, average size 25 μm) was put into a steel vial (80 cc volume) with 20 steel balls (10 mm in diameter). After the evacuation for 12 h below 10^{-4} Pa by a turbomolecular pump, high-purity H_2 gas (99.999%) or D_2 gas (99.999%) of 1 MPa as an initial pressure was introduced into the vial. A planetary ball mill (Fritsch P-5) was used with 400 rpm for the milling. In the course of milling, H_2 or D_2 gas was supplied after 5, 10, 20, 30 and 50 h of milling. The concentration of H or D in the samples was determined at the Center for Organic Elemental Microanalysis, Kyoto University.

The neutron diffraction measurement was carried out in HIT-II installed at the pulsed neutron source in the High

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Energy Accelerator Research Organization (KEK, Tsukuba, Japan). Each sample was put into a TiZr cell of inner diameter 8.0 mm with a 0.3 mm thick wall. The structure factor, $S(Q)$, was derived by applying various kinds of corrections to the background, absorption [5] and multiple scattering [6], and normalizing with a incident neutron beam profile. The radial distribution function, RDF(r), can be derived from the Fourier transformation of $S(Q)$ as follows,

$$\mathrm{RDF}(r) = 4\pi r^2 \rho + \frac{2r}{\pi} \int_0^\infty Q(S(Q) - 1)\sin Qr \, \mathrm{d}Q, \qquad (1)$$

where ρ is the average number density of atoms, which was measured by gas pycnometer (Micromeritics, Accupyc 1330) with He gas (99.999%).

Inelastic neutron scattering measurement was carried out by using CAT spectrometer installed at KEK. Thermal neutrons scattered by the sample are analyzed with a PG(002) analyzer mirror ($E_f = 4$ meV) and higher order reflections are eliminated with Be filter cooled at 70 K. The energy resolution is 2–3% over a wide energy range $E < 300$ meV. The sample was put into a flat aluminum cell with 0.3 mm wall in thickness. The thickness of the sample was 10 mm corresponding to transmission of a neutron beam of about 80%. The scattering data was corrected for the background and incident neutron beam profile.

3. Results and discussion

The concentration of D in the nanocrystalline graphite prepared by mechanical alloying under D_2 gas atmosphere is shown in Fig. 1. The content D increased when the milling proceeded and approached $CD_{0.80}$ after 50 h of milling.

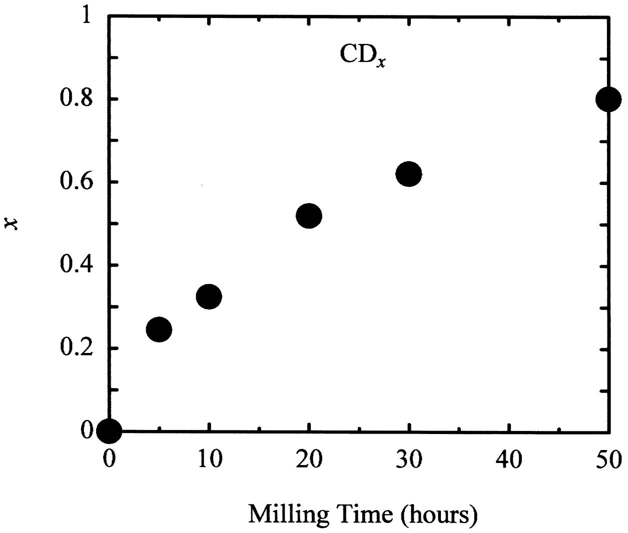

Fig. 1. The concentration of D in the nanocrystalline graphite after 5, 10, 20, 30 and 50 h of milling under D_2 gas atmosphere.

Fig. 2 shows $S(Q)$s for the samples before milling and after 5, 10, 20, 30 and 50 h of milling under D_2 gas atmosphere. The Bragg peak at $Q_1 = 18.6$ nm^{-1}, which corresponds to the distance between the layers of the graphite, broadened and shifted to lower Q side with increasing milling time. The change of the distance between the layers of the graphite, $2\pi/Q_1$, with milling time is shown in Fig. 3. The value of $2\pi/Q_1$ increased with milling time and reached to 0.42 nm after 50 h of milling. The result allows us to understand that the layer distance in the graphite broadened through absorbing D atoms during the milling process and accordingly the degree of disorder in the structure increased with increasing milling time.

Fig. 4 shows RDF(r)s which were derived from Fourier transformation of $S(Q)$s before milling and after 5, 10, 20, 30 and 50 h of milling under D_2 gas atmosphere. New peaks at 0.109 and 0.218 nm and a background peak around 0.18 nm were observed in nearest neighbour region. These results are in agreement with previous work [2] and indicate that there are two types of the D coordinations; one is C–D covalent bond and the other is

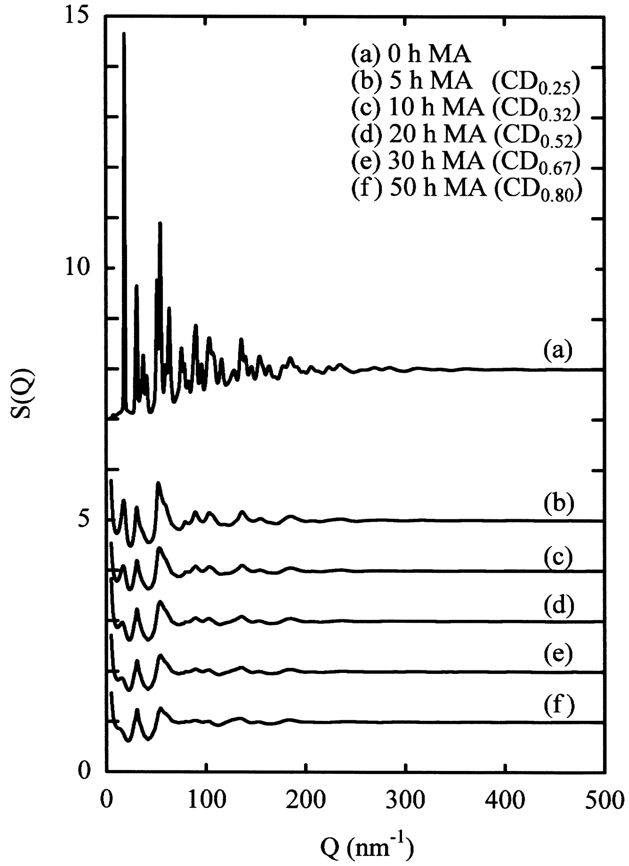

Fig. 2. Structure factors, $S(Q)$, observed by neutron diffraction for the sample before milling and after 5, 10, 20, 30 and 50 h of milling under D_2 gas atmosphere.

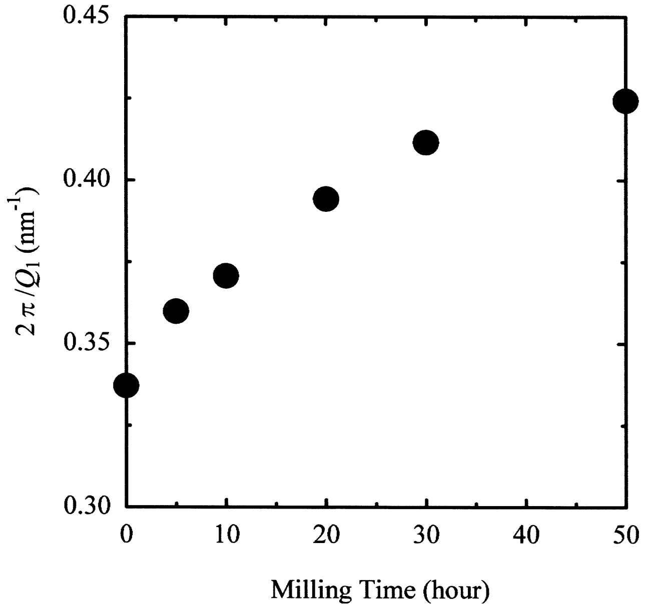

Fig. 3. The distance between the layers of the graphite, $2\pi/Q_1$, with milling time.

D atom located between layers of the graphite. It is noteworthy to realize that the peak around 0.145 nm consist of two peaks, the positions of which are 0.142 and 0.154 nm, respectively, in the RDF(*r*) for the sample after 50 h of milling. Since the C–C bond length for crystalline diamond is 0.1536 nm, the new C–C peak observed at 0.154 nm can be recognized as ascribing to the formation of a 4-fold bonding, which is described as sp^3 bonding.

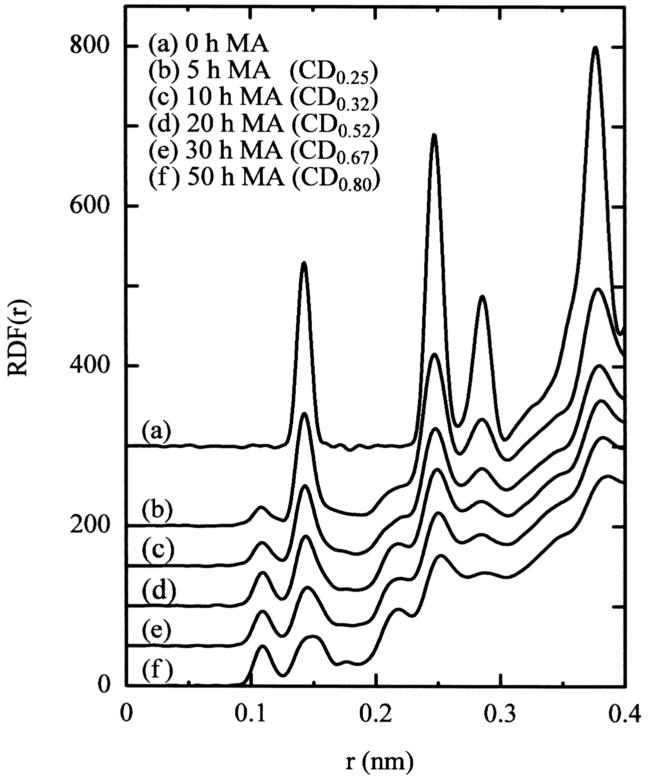

Fig. 4. Radial distribution functions, RDF(*r*), observed by neutron diffraction for the sample before milling and after 5, 10, 20, 30 and 50 h of milling under D_2 gas atmosphere.

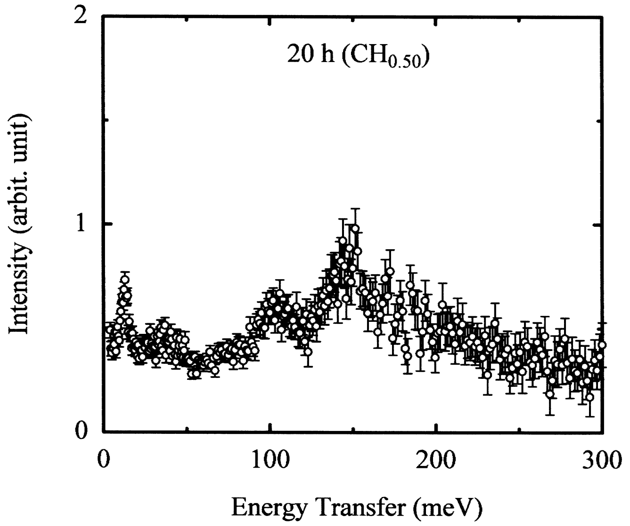

Fig. 5. Inelastic neutron scattering spectrum at 20 K for the sample after 20 h of milling under H_2 gas atmosphere.

The inelastic neutron scattering is capable of giving further structural information from a different point of view. Fig. 5 shows the inelastic neutron scattering spectrum observed at 20 K for the sample after 20 h of milling under H_2 gas atmosphere. The peaks around 110 and 145 meV can be ascribed to out-of-plane and in-plane bending mode of aromatic CH group, respectively [3,4]. Moreover, it is useful to note that weak peaks appeared in the 160–190 meV region where bending modes of non-aromatic CH group are anticipated. These results also indicate that sp^3 bonding was created with absorbing H atoms in the nanocrystalline graphite. A sharp peak at 13 meV which is due to lattice mode of graphite-like structure was observed in other carbon materials such as carbon blacks or coals [3,4].

4. Conclusion

Nanocrystalline hydrogenated graphite was prepared by mechanical milling under D_2 (or H_2) gas atmosphere. Detailed structural information was obtained by a combination of total and inelastic neutron scattering techniques. In the high resolved RDF(*r*) derived from $S(Q)$ up to 500 nm^{-1}, two peaks corresponding to the C–C correlations could be observed at about 0.142 and 0.154 nm. The result allows us to recognize the formation of the 4-fold (sp^3) bonding in the hydrogenated graphite prepared by milling. Moreover, we observed the inelastic peaks due to the CH_3 and CH_2 bending modes in the 160–190 meV region of the inelastic neutron spectrum. Therefore, total and inelastic neutron scattering data allow us to conclude that the 4-fold sp^3 bonding is generated in the nanocrystalline hydrogenated graphite prepared by milling.

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References

[1] S. Orimo, T. Fukunaga, G. Majer, A. Zuttel, L. Schlapbach, H. Fujii, J. Appl. Phys. Lett. 75 (1999) 3093.
[2] T. Fukunaga, K. Itoh, S. Orimo, M. Aoki, H. Fujii, J. Alloys Comp. 327 (2001) 224.
[3] P. Albers, G. Prescher, K. Seibold, D.K. Ross, F. Fillaux, Carbon 34 (1996) 903.
[4] F. Fillaux, R. Papoular, A. Lautie, J. Tomkinson, Fuel 74 (1995) 865.
[5] H.H. Paalman, C.J. Pings, J. Appl. Phys. 33 (1965) 2635.
[6] I.A. Blech, B.L. Averbach, Phys. Rev. 137 (1965) 1113.