

Structure of Carbon Coils observed by Neutron Diffraction

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Carbon nanocoils and microcoils have been reported to have a 3D-helical/spiral structure with a coil diameter of few tens nanometers and a few micrometer. X-ray diffraction pattern for the as-grown carbon coil is smooth and haloed, and is characterized by the lack of a long range order at an atomic level as a glassy carbon. The structure of the carbon coils apparently changed from a glassy state into a crystalline one with long range regularity when annealing at 3000°C. The observation of the structural rearrangement subjected to the heat treatment was carried out by neutron diffraction. The reduced pair distribution function $G(r)$ indicates that atomic rearrangements took place and the regularity of the layer stacking recovered through the heat treatment at the temperature of 1500, 2000, 2500 and 3000°C, together with long range reordering of the winding graphene sheets. The RMC modeling based on the experimental diffraction data reveals the buckled and irregularly stacked graphene sheets in the as-grown carbon coil gradually changes to the graphite with great regularity through the heat treatment

Key words: Carbon coil, atomic structure, neutron diffraction, graphite

1. INTRODUCTION

Up to date, various kinds of carbon materials have been synthesized and the interesting properties have been paid attention. Recently, carbon coils which have been prepared regularly by Motojima et al. is characterized a 3D-helical/spiral structure with a coil diameter of few tens nanometers and a few micrometer [1-7]. The carbon coils have a bright prospect of using functional materials such as novel electromagnetic wave absorbers and tunable microdevices, etc. The structural information of the carbon coils has been investigated by X-ray diffraction and transmission electron microscopy (TEM) techniques before and after the heat treatment. The as-grown carbon coil indicates a halo X-ray pattern, which is attributed to disordered state. Moreover, after the heat treatment at 3000°C the graphite with regular hexagonal layer structure has been observed by TEM. However, the detailed structural change from disordered to crystal state at an atomic level through the heat treatment has not been clarified yet.

In this work, we have carried out a structural study on a set of five samples of the as-grown carbon coil and heat treated ones at 1500, 2000, 2500 and 3000°C for 6 hrs by taking advantage of the T-O-F neutron diffraction at a spallation neutron source. Since the pulsed source provides high fluxes of short-wavelength, that is, "epithermal" neutrons, structure factors $S(Q)$ were measured to large values of momentum transfer $Q=500 \text{ nm}^{-1}$, the extended Q -range data of which gives us a high resolved atomic distribution in real space. In order to visualize a three-dimensional structure the reverse Monte Carlo (RMC) modeling [8] was carried out using structure factors observed by neutron diffraction. The RMC modeling has been recognized a good method for

reproducing the detailed atom configuration of disordered or distorted materials.

2. EXPERIMENTAL

Carbon coils were synthesized on a graphite substrate by the catalytic pyrolysis of acetylene at 700 to 800°C. Fine Ni metal powder (about 5 μm in diameter) was used as a catalyst. Heat treatments were carried out at 1500, 2000, 2500 and 3000°C for 6 hrs in a $\text{CO}+\text{CO}_2$ gas atmosphere.

The neutron diffraction experiment was carried out using the High Intensity Total scattering spectrometer (HIT-II) at the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. Time-of-Flight (TOF) neutron scattering technique using the spallation neutron source gives us detailed information of the short range atomic arrangement through a structure factor $S(Q)$ with higher Q region up to 500 nm^{-1} .

X-ray diffraction data were measured by using a horizontal sample goniometer (RIGAKU RINT-Ultima) with Mo-K α radiation operated at 40 kV, 30 mA and the horizontal two-axis diffractometer on BL04B2 beam line at SPring-8. After corrections for polarization, absorption and Compton scattering, the scattering intensity, $I(Q)$, was converted to the structure factor, $S(Q)$, where $Q=4\pi\sin\theta/\lambda$.

The structure factor, $S(Q)$, was derived as follows,

$$S(Q) = \frac{I(Q)}{Nb^2} \quad (1)$$

where $I(Q)$ is a coherent intensity per atom and Q is a scattering vector. b is the coherent scattering length of an element and N is a number of atoms. Fourier

transformation of $S(Q)$ gives a reduced pair distribution function, $G(r)$, in real space as follows;

$$G(r) = 4\pi\rho_o(g(r)-1) = \frac{2}{\pi} \int_0^{Q_{max}} Q(S(Q)-1)\sin(Qr)dQ, \quad (2)$$

where ρ_o is an atomic number of density of the sample. $G(r)$ is a reduced pair distribution function and $g(r)$ is a pair distribution function.

Reverse Monte Carlo (RMC) modeling [8] has been recognized to be a method for producing three dimensional atom arrangements of disordered materials that is consistent with an inputted experimental static structure factor $S^E(Q)$. In RMC method the difference between the 'real' structure factor $S^C(Q)$ which can be calculated from a model of the 'real' atomic arrangement, and an experimentally measured structure factor $S^E(Q)$ is

$$\varepsilon = S^E(Q) - S^C(Q), \quad (3)$$

and has probability

$$P(\varepsilon) = \frac{1}{(2\pi)^{1/2}\sigma(Q)} \exp(-\varepsilon^2 / 2\sigma^2(Q)), \quad (4)$$

where $\sigma(Q)$ is the standard deviation of the normal distribution.

In order to model the structure of a system using $S^E(Q)$ we iterated to create a statistical ensemble of atoms whose structure factor satisfies the totally summed probability distribution. Therefore, we searched the minimized value of the exponent;

$$\chi^2 = \sum_{i=1}^m [S^C(Q) - S^E(Q)]^2 / \sigma^2(Q). \quad (5)$$

In this experiment, the simulation starts with an appropriate initial configuration of about 4000 atoms with periodic boundary condition, the size of which was 1.7 nm cube.

3. RESULTS AND DISCUSSION

Figure 1 shows the structure factors $S(Q)$ measured up to $Q=500 \text{ nm}^{-1}$, which shows significantly oscillatory structure at higher Q -range, for the as-grown carbon coil, heat treated ones at 1500, 2000 and 3000°C for 6 hrs and the pure graphite. The high Q -data in $S(Q)$ is very important to get characteristic knowledge of the short range structure. We can easily recognize that the $S(Q)$ for the as-grown carbon coil sample has characteristic feature of disordered carbon and after the heat-treatment the long range order of the structure was recovered. TEM images of the as-grown and 3000°C heat-treated carbon coils have shown a tortuous pattern and an approximate periodicity, respectively [5,6]. However, the structural characteristics of the as-grown carbon coil are distinct from that of the amorphous 'diamond-like' carbon reported by P.H. Gaskell et al. [9]. Specifically, the $S(Q)$ of the as-grown carbon coil has a peak around 18 nm^{-1} which was scarcely observed in $S(Q)$ of the amorphous 'diamond-like' carbon. Since the

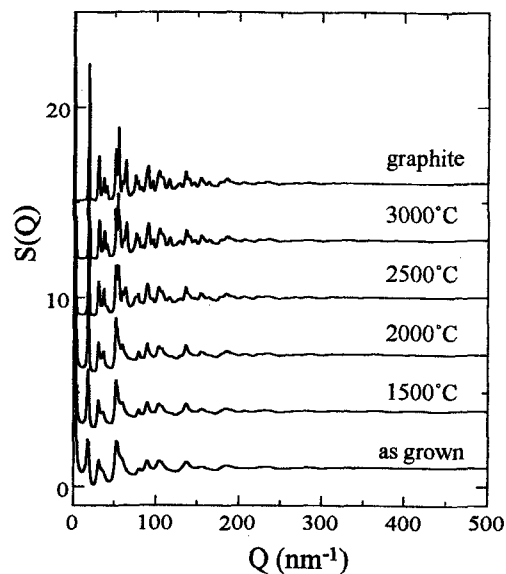


Fig. 1. Structure factors, $S(Q)$, observed by neutron diffraction for the as-grown carbon coil, the heat treated carbon coils at 1500, 2000, 2500 and 3000°C, and the pure hexagonal graphite.

amorphous 'diamond-like' carbon. Since the first peak located at about $Q=18 \text{ nm}^{-1}$ is strongly associated with the layer structure of graphite, the as-grown carbon coil is understood to be made of stacked graphene sheets that is more or less buckled and have various kinds of defects.

When the heat treatment of the carbon coil at 1500, 2000, 2500 and 3000°C was carried out, the location and intensity of the first peak (related to (002) plane) in $S(Q)$ drastically varied with the heat treated temperature. The shift of the location of the first peak around $Q=18 \text{ nm}^{-1}$ to the higher Q side indicates a decrease of the interlayer distance of the graphene sheets as shown in Fig 2. The interlayer spacing became decreased from 0.349 nm for the as-grown carbon coil to 0.335 nm after 3000°C heat-treatment, the value of which is the same as that in fully dense graphite. Therefore, the interlayer spacing is

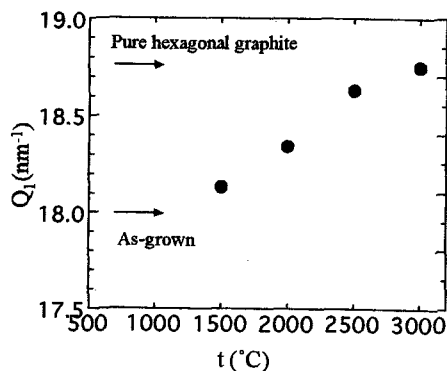


Fig. 2. The first peak positions of $S(Q)$ for the as-grown carbon coil, the heat-treated carbon coils at 1500, 2000, 2500 and 3000°C, and the pure hexagonal graphite.

strongly related with the density of the carbon coil sample, which increased with increasing the annealing temperature and achieved to 2.211 g/cm. Moreover, we can recognize remarkable growth of (112), (114) and (116) peaks in $S(Q)$ after the heat treatment at 1500, 2000, 2500 and 3000°C as shown in Fig. 3, which is the enlarged $S(Q)$. Graphite has a stacking sequence of layer ABABAB... Therefore, it is worth to note that the growth of (112), (114) and (116) peaks means reordering of the stacking sequence of layer ABABAB..., that is, layers were stacked again in symmetry-related way through the heat-treatment. In other words, the absence of the intense (11 h) reflections in the diffraction pattern of the as-grown carbon coil is attributed to the lack of correct ABABAB... stacking of the graphite.

In order to get high resolved structural information in real space the reduced pair distribution function $G(r)$ was derived from Fourier transformation of $S(Q)$ at $Q=500 \text{ nm}^{-1}$. Figure 4 shows $G(r)$ s for the as-grown carbon coil, heat treated ones at 1500, 2000 and 3000°C for 6 hrs and the pure graphite. The first, second and third peaks are located at $r=0.142, 0.246$ and 0.284 nm , respectively, which exactly accord the in-plane carbon-carbon bond distances in the aromatic-type ring of graphite. Although these three peak positions did not change after heat-treatment at 1500, 2000, 2500 and 3000°C, another peaks located at higher r region than the third carbon-carbon distance were found to move in position by the heat treatment. Especially we can observe newly grown correlation peaks around $r=0.7 \text{ nm}$ (the arrow in Fig. 4), which is attributed to the increasing regularity of the spacing of the A-A layer planes. Therefore, the results allow us to understand that there is disorder in the planar array of the hexagonal network and consequently the disordered arrangement develops not only in the plane but also in the direction of the vertical axis of the graphene sheet.

The coordination number of the nearest carbon-carbon correlation was calculated from the area of the first peak of the $G(r)$. Surprisingly, the value of the coordination number keeps constant to be 3.0 atoms for all carbon coils. For nanoporous carbons made of curved and defective graphene sheets the

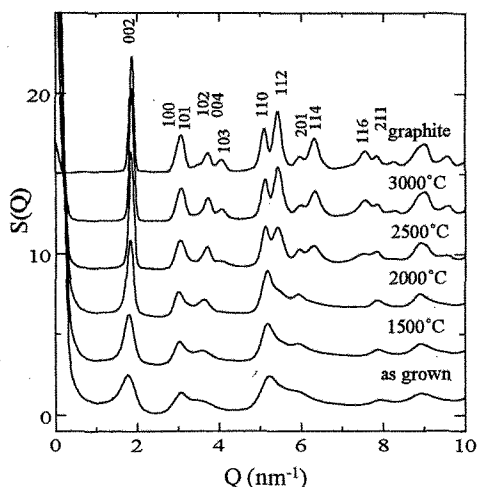


Fig. 3. Enlarged $S(Q)$ for the as-grown carbon coil, the heat-treated carbon coils at 1500, 2000, 2500 and 3000°C, and the pure hexagonal graphite

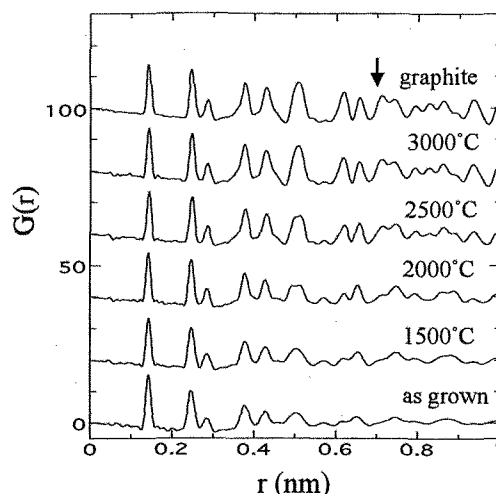


Fig. 4. Reduced pair distribution functions, $G(r)$, for the as-grown carbon coil, the heat-treated carbon coils at 1500, 2000, 2500 and 3000°C, and the pure hexagonal graphite. The arrow indicate the 2nd interlayer distances of graphene sheets in graphite

and defective graphene sheets the coordination number of the first nearest neighbour was reported to be 2.6 atoms [10]. In this case, one may imagine that nanoporous carbons is heavily disordered and do not seem to be built of regular aromatic-type structural units (hexagonal rings). In contrast, our work indicates that the local structure of the carbon coils is similar to that of graphite and exhibits the expected hexagonal network because of the coordination number of 3.0 atoms even for the as-grown carbon coil. Therefore, it can be concluded that the structure of the as-grown carbon coil is made of tortuous or winding layers with regular aromatic-type rings but with irregular ABABAB... stacking of the graphene sheets.

The RMC modeling was utilized in order to get information of a three-dimensional atom configuration for clarifying the structure of the carbon coils. The experimental static structure factors $S(Q)$ (line) as well as the RMC results (dot) are shown in Fig. 5. The quite good agreement between the experimental and RMC structure factors for the as-grown carbon coil and the heat treatment ones at 1500 and 3000°C was achieved by modifying the atomic positions and occupancies in the starting atomic configuration through the RMC modeling algorithm. Figure 6 shows visualized atom configurations, which reveal a side- and surface-on view of the graphene sheets stacked in the c-axis direction for the as-grown and heat-treated carbon coils, respectively. We can recognize that the side-on view of the graphene sheets for the as-grown carbon coil shows much winding shape, which becomes a flat hexagonal network with after the heat treatment. Moreover, an irregular ABABAB... stacking of graphene sheets in the vertical axis is definitely observed in the as-grown carbon coil. The graphene sheets become to stack regularly like the pure hexagonal graphite after the heat treatment at 3000°C for 6 hrs. Thus, the RMC modeling structure of the carbon coils apparently supports the structural image obtained from the experimental results, which reveal the

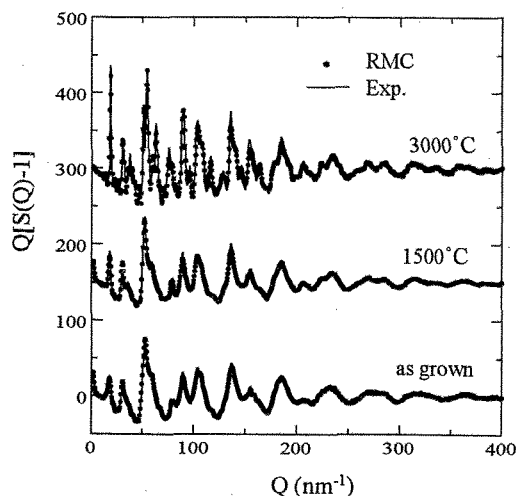


Fig. 5. Experimental structure factors, $S(Q)$ (line) and the RMC results (dot) for the as-grown carbon coil and the heat-treated carbon coils at 1500 and 3000°C.

change from the tortuous or winding graphene sheets to the smooth ones and the recovery from the irregular ABABAB... stacking of the graphene sheets in the direction of c-axis after heat treatment.

4. CONCLUSIONS

The structural characteristics of the as-grown carbon coil and its structural change subjected to the heat treatment at the temperatures of 1500, 2000, 2500 and 3000°C were observed by neutron diffraction.

The $S(Q)$ of the as-grown carbon coil shows characteristics of amorphous state. The decrease of the interlayer distance of the graphene sheets attributed to the (002) diffraction peak and the remarkable growth of (112), (114) and (116) peak were observed in $S(Q)$ when the carbon coils were annealed at 1500, 2000, 2500 and 3000°C. Moreover, it was found that the coordination number of the first atomic correlation keeps constant to be 3.0 atoms but the distances of the atomic correlations over the third atomic distance in the $G(r)$ changed after the heat treatment. These results lead us to conclude that the structure of the as-grown carbon coil is characterized as the buckled atom configuration within the basal plane and the lack of correct ABABAB... stacking of graphene sheets.

The three dimensional visualization by the RMC modeling was carried out using the experimental diffraction data. The RMC modeling definitely also taught us that the graphene sheets are winding and the regular ABAB... stacking is lost for the as-grown carbon coil. Moreover, the configuration of the buckled and irregularly stacked graphene sheets gradually changes to the hexagonal network of the graphite with great regularity through the heat treatment.

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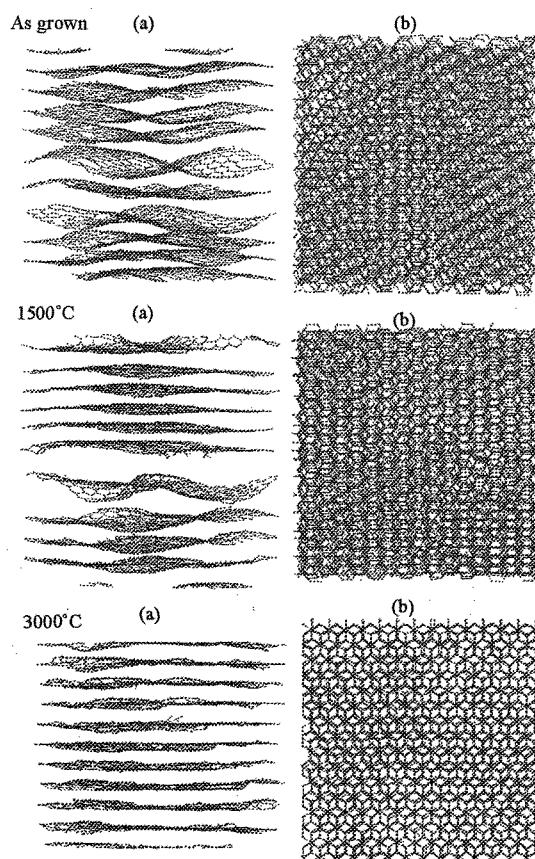


Fig. 6. A side- (a) and surface-on view (b) of the graphene sheets for the as-grown carbon coil and the heat-treated carbon coils at 1500 and 3000°C.

References

- [1] S. Motojima, S. Asakura, T. Kasemura, S. Takeuchi and H. Iwanaga, *Carbon* 34, 289-296 (1996)
- [2] S. Motojima, S. Asakuma, M. Hirata, H. Iwanaga, *Mat. Sci. & Eng.*, B34, L9-L11 (1995)
- [3] S. Motojima, S. Kagiya, H. Iwanaga, *Mat. Sci. & Eng.*, B34, 47-52 (1995)
- [4] S. Motojima, I. Hasegawa, S. Kagiya, K. Andoh and H. Iwanaga, *Carbon* 33, 1167-1173 (1995)
- [5] X. Chen, T. Saito, M. Kuzunoki and S. Motojima, *J. Mater. Res.*, 14, 4329-4336 (1999)
- [6] W. Im-Hwang, T. Kuzuya, H. Iwanaga and S. Motojima, *J. Mater. Sci.*, 36, 1-8 (2001)
- [7] S. Motojima, M. Hirata and H. Iwanaga, *J. Chem. Vapor Deposition* 3, 87-99 (1994)
- [8] R. L. McGreevy and L. Pusztai, *Mol. Simulation* 1, 359-368 (1988)
- [9] P.H. Gaskell, A. Saeed, P. Chieux, D.R. McKenzie, *Phys. Rev. Lett.*, 67, 1286-1289 (1991)
- [10] V. Petkov, R.G. Difrancesco, S.J.L. Billinge, M. Acharya and H.C. Foley, *Phil. Mag.*, B79, 1519-1530 (1999)

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