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TEM IN - SITU OBSERVATION OF CARBON CLUSTERS GENERATION

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Carbon nanocapsules grown on carbon fibers were found and investigated by high - resolution electron microscopy. They began to be formed during heating up to 800-2000℃ in 1 atm. of N_2 gas. A part of them were hollow capsules and others were capsules enclosing a CaS single crystal. The growth mechanism of these carbon nanocapsules was discussed by comparing the structures of particles formed at several temperatures. Furthermore, in-situ observation of carbon clusters formation from hydrocarbons was performed by using a heating holder in a TEM under low electron irradiation. Isolated C_{60}-like or small onion-like spherical particles were produced at 800℃ on the surface of graphites transformed from the hydrocarbons . The carbon cluster formation at such a low temperature is considered to be due to a thermal decomposition of hydrocarbon.

1.INTRODUCTION

Fullerenes have received much attention because they have a unique structure which contributes to their peculiar physical properties. Most of new carbons such as the family of C_{60}[1], metallo-fullerene [2,3], carbon nanotubes [4] and carbon nanocapsules [5-7] were synthesized in plasma by the arc discharge method. Thus, high-temperature plasma and electric field generated by the arc discharge may play an important role in the synthesis of this new series of carbon-based materials. In this study, however, carbon nano-capsules were found to be generated on carbon fibers only by heating up to 800 - 2000℃ [8]. In order to clarify the growth mechanism of the carbon nanocapsules, the structures of carbon nanocapsules grown at several temperatures up to 2000℃ were investigated by high-resolution electron microscopy. Furthermore, we show the results obtained by in-situ observation of carbon clusters generation at high temperature under a low electron irradiation. A growth mechanism and some kinds of phenomena for carbon clusters by thermal heating is discussed on the basis of the observation results up to 800℃ in a TEM.

2.EXPERIMENTAL PROCEDURE

The pitch-based carbon fibers used in the present experiments were commercial materials (Nippon Carbon Co., Ltd.). Three types of specimens were prepared by heating at 800,1500 and 2000℃ for 7 hrs in 1 atm. of N_2 gas. High-resolution electron microscopy (HREM) observations were performed using a Topcon 002B electron microscope operating at 200kV.

The in-situ experiment was carried out with amorphous hydrocarbon deposited on the surface of ceramic particles ($BaTiO_3$) or edges of a molybdenum sheet used as a mount for the ceramic particles. The hydrocarbon began to be coated on the sample by electron beam irradiation at about 300-500℃. A 400kV transmission electron microscope (JEM-4000FX) with a heating stage (GATAN-628TA) was used for the in situ observation at temperatures up to 1000℃. The images were continuously recorded on a videotape during heating.

3.RESULTS AND DISCUSSIONS

3.1 Nanocapsules on carbon fibers

Carbon nanocapsules with the sizes of 20 - 200 nm were often observed on the surface of the fibers heated at 2000℃ in 1 atm. of N_2 gas. Figure 1 shows a carbon nanocapsule containing a single crystal of CaS, which electron diffraction pattern is also shown in Fig. 1. The calcium and sulfur atoms are considered to be impurities which were mixed during heating. Although CaS is a relatively oxidizable material, the CaS crystal surrounded by only six closed sheets of carbon in Fig. 1 was stable for over 3 months. This shows that the graphite film is fairly airtight.

In order to clarify the growth mechanism of these nanocapsules, carbon fibers were heated at several temperature. Spherical amorphous particles shown in Fig. 2 were frequently observed on the carbon fibers heated at 800℃. The sizes of these particles were 10-40 nm. Almost all of particles were completely amorphous and some particles had a thin graphite shell around the amorphous core, as shown in Fig. 2(a) and (b), respectively. Furthermore, there was a particle containing a small crystal of CaS which grew epitaxially on the inner surface of the graphite shell as shown in Fig. 2(c). From these micrographs, a growth mechanism was proposed, as schematically shown in Fig. 3. Cubic hollow capsules were frequently observed on the carbon fibers heated for 10 hrs in a vacuum.

These nanocapsules were easily peeled off the carbon fibers by using ultrasonic waves in acetone and could be collected in powdered form. In the near future, industrial production of carbon nanocapsules will become possible, and a new property of this material is expected.

3.2 In-situ observation of carbon clusters

Hydrocarbon deposited on the surface of ceramic particles were heated in TEM. Lattice fringes

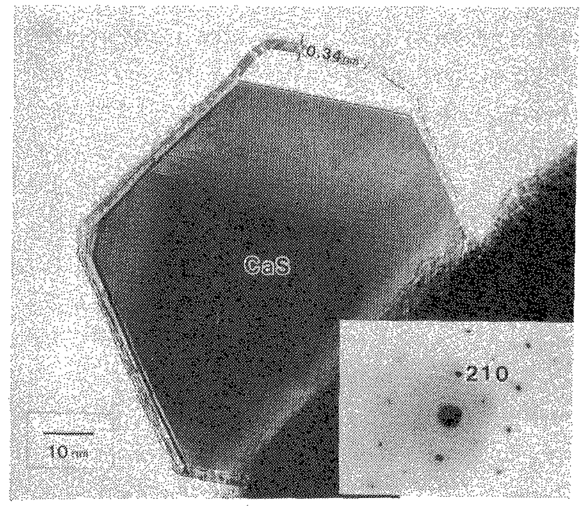

Fig. 1 HREM micrograph of a carbon nanocapsule containing a single crystal of CaS.

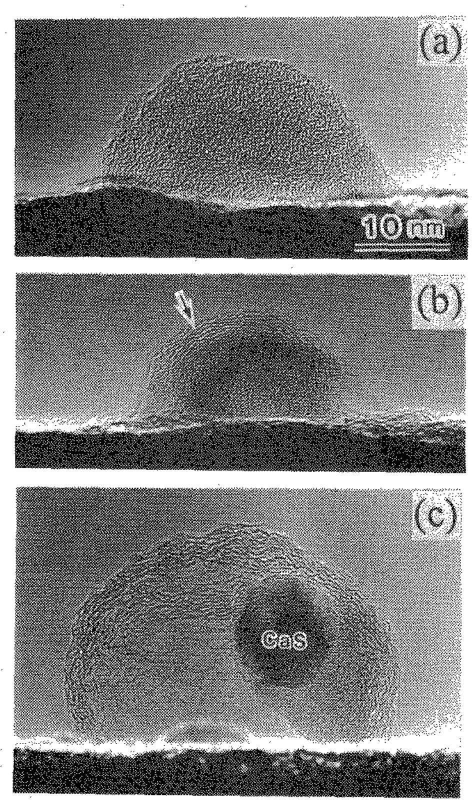

Fig. 2 HREM micrographs of spherical particles on the carbon fibers heated at 800℃. (a) an amorphous particle, (b) a particle with graphitization occurring on its surface indicated by an arrow and (c) a particle containing a small crystal of CaS.

appeared at 500℃, which were transformed from initial amorphous hydrocarbon. The lattice spacing on the ceramics particle is 0.34 nm which corresponds to the interplanar spacing of basal plane in graphite. Raising the temperature gradually up to 800℃, several graphite sheets on the surface began to change their shape and form small carbon particles as shown in Figs. 4(a) and (b). The diameters of sphere carbon particles are about (a) 0.8 and (b) 2.2nm which correspond to the size of C_{60} and C_{540} (containing C_{240}), respectively. These particles were clarified to be spherical shape by tilting the specimen in the electron microscope to ± 20 degrees. Ugarte [9] reported that the small onion-like particles composed of 2-5 concentric graphitic cages on large spheres generated by strong electron irradiation (100 - 200 A/cm^2 at 300kV). In our experiment, however, electron current density was only about 10A/cm^2. So, the formation of the small carbon particles is considered to be due mainly to the effect of thermal heating, though the effect of electron bombardment can not be neglected.

Endo et al. [10] presented that carbon nanotube could be produced by thermal decomposition of benzene at about 1000℃. Furthermore, Yamasaki et al.[11] found the existence of fullerenes (C_{60} and C_{70}) in Chinese ink stick ("Sumi"), which were made from soot and glue. These studies indicate that fullerenes or carbon nanotubes can be produced from hydrocarbon at relatively lower temperature, comparing with arc-discharge or laser method. Therefore, the phenomenon shown in Fig. 4 is considered to be a direct observation of the thermal decomposition process in hydrocarbon.

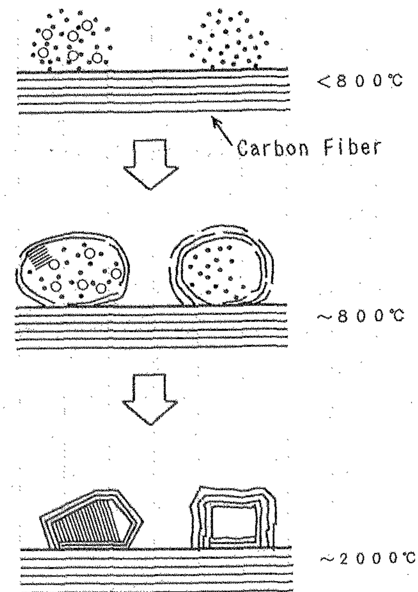

Fig. 3. Schematic of the growth mechanism of carbon nanocapsules.

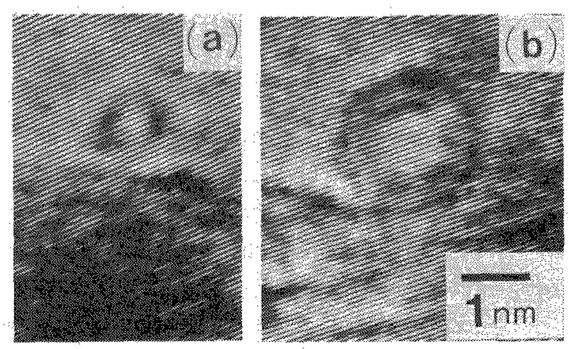

Fig. 4 Small carbon particles formed on the surface of the graphite at 800℃ in TEM. The number of atoms of the carbon particles are estimated to be (a) C_{60}; (b) C_{240} and C_{540}, respectively.

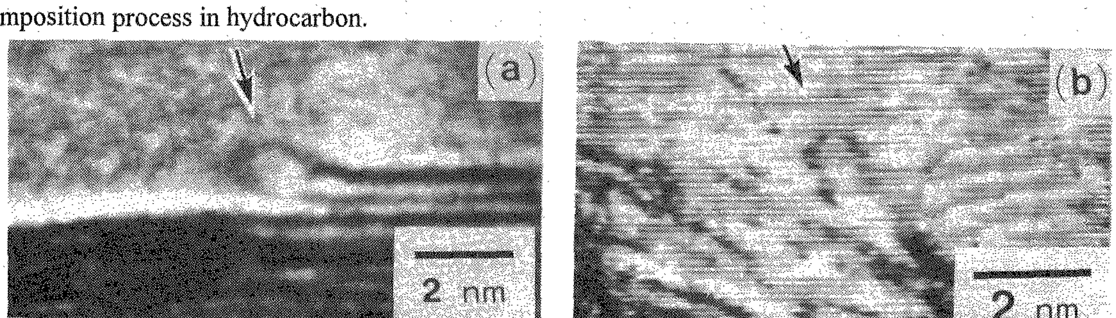

Fig. 5(a) One-shell carbon cluster generated at the step of a graphite shell. (b) an initial stage of growth for carbon nanotube.

The small carbon particles were frequently formed at the steps of the graphite as shown in Fig. 5(a). Since the number of dangling bonds of hexagons increases at the steps, it is presumably easy that a fullerene is formed by containing pentagons. In figure 5(b), a nanotube like contrast can be seen as indicated by the arrow, although very fine fringes due to reproduction process and computer enhancement are overlapped in this micrograph. The carbon particles generated at the steps occasionally began longitudinal growth as shown in Fig. 5(b). This phenomenon is presumed to be an initial stage of generation and growth for carbon nanotube. The cap of the nanotube composed of hexagons and some pentagons, is formed at first. Then, it is elongated along one direction. This model suggests that the tip of the nanotube is closed during growth. This model seemed to be similar to the one presented by Endo et al.[12]. However, it is considered that the tube in the present case grows by the transformation of the graphite sheet at the root of the tube, not with gas phase, though the tube was damaged by electron irradiation after growing a little.

4.CONCLUSIONS

Carbon nanocapsules grown on carbon fibers were investigated by HREM and TEM in-situ observation. The results obtained are summarized as follows.

1. They were formed during the heating of carbon fibers up to 2000℃.
2. Two types of nanocapsules, a capsule enclosing a CaS single crystal and a cubic hollow capsule, were found.
3. The growth mechanism of these carbon nanocapsules was proposed .
4. The generation of carbon particles from hydrocarbons was observed in-situ by TEM at high temperature.
5. Individual C_{60}-like and onion-like spherical particles were produced at 800℃ on the surface of graphites.
6. An initial stage of carbon nanotube generation was observed.

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REFERENCE

1. H. W. Kroto, J. R. Heath, S. C. Brien,R. F.Curl, R. E. Smalley, Nature, 318(1985) 162.
2. Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford and R.E. Smalley, J. Phys. Chem., 95(1991) 7564.
3. H. Shinohara, H. Sato, M. Ohkohchi, Y. Ando, T. Kodama, T. Shida, T. Kato and Y. Saito, Nature, 357(1992)52.
4. S. Iijima, Nature, 354(1991)56.
5. R. S. Ruoff, D. C. Lorents, B. Chan, R. Malhotra and S. Subramoney, Science, 259 (1993)346.
6. M. Tomita, Y. Saito and T. Hayashi, Jpn. J. Appl. Phys., 32(1993)L280.
7. Y. Saito, T. Yoshikawa, M. Okuda, M. Ohkohchi, Y. Ando, A. Kasuya and Y. Nishina, Chem. Phys., 209(1993)72.
8. M. Kusunoki, Y. Ikuhara and J. Kon, J. Jpn. Appl. Phys.,34(1995)1610.
9. D. Ugarte, Europhys. Lett., 22(1993) 45.
10. M. Endo, K. Takeuchi, S. Igarashi, K. Kiyohara, M. Shiraishi and H. W. Kroto, Fullerenes'93 Colloquium.(1993).
11. A. Yamasaki, T. Iizuka and E. Osawa, Fullerene Sci. Thechnol., in press.
12. M. Endo and H. Kroto, J. Phys. Chem.,96 (1991)6941.