The effect of temperatures on the formation of boron-carbon-nitrogen nanotubes

Yoshiki Shimizu[1], Yusuke Moriyoshi[1], Hiroyuki Uono[1], Takayuki Watanabe[2], Naotaka. Ekinaga[3], Shojiro Komatsu[4], and Takamasa Ishigaki[4]

[1]Faculty of Engineering, Hosei University, 3-7-2 Kajino-cho Koganei-shi Tokyo, 184-8584
[2]Tokyo Institute of Technology, 2-12-1 O-okayama Meguro-ku Tokyo, 152-8550
[3]Tokai Carbon Co.Ltd., Oyama-cho Sunntou-gun Shizuoka, 410-1431
[4]National Institute for Research in Inorganic Materials,
1-1 Namiki Tsukubashi Ibaraki, 305-0044 Japan

Abstract

A relationship between microstructures and temperatures of porous BC_4N samples heat-treated in a dc arc plasma jet was examined by using mainly a transmission electron microscope. As a result, it was clarified that nanocapsules were formed at a temperature range from 1800 to 3500K and nanotubes, on the other hand, were formed at higher temperatures than 3500K. From the data, a model in the formation mechanism of B-C-N nanotubes was proposed, in which nanotubes grew from nanocapsules formed relatively at low temperatures.

1 Introduction

Nanotubes in carbon and boron nitride have been prepared by a rapid quenching immediately after a sample was evaporated at higher temperature than its melting points. They have been considered to form by the condensation of chemical species from a vapor phase. However, their formation processes are so rapid that it is difficult to obtain useful information for the analysis of the processes and to know what kinds of reactions proceed during the processes. So, formation mechanisms have been proposed so far are speculated only from the microstructures of obtained nanotubes [1-7] and are not necessarily accepted.

In order to create a reliable formation mechanism of nanotubes, it is necessary to have experimental data indicating intermediate reaction-products formed during the processes. In this connection, from a study about the preparation and characterization of boron-carbon-nitrogen nanotubes by a plasma evaporation method [8], we found some similarities in a microstructural relationship between a sample and obtained nanotubes. These results strongly suggested a possibility that the precursors of nanotubes were formed even in a sample heat-treated at lower temperatures. Then, we intended experimentally to clarify a relationship between intermediate products and temperatures in a sample heat-treated at given temperatures in a dc arc plasma. From the viewpoints, on the basis of a relationship between temperatures and microstructures obtained from the observations of porous B-C-N samples heated, in this paper, the formation processes of nanotubes were described.

2 Experimental

BC4N sintered disks were used as a sample in this experiment. They were prepared in the following as reported previously [9]. Boric acid, urea, and saccharose were mixed at the weight ratio of 1: 2.2: 2.6, respectively. The mixtures were put into a stainless beaker and heated at 220℃ in an electric furnace for 1 h in air. During the heating they melted and turned to a clear solution. Further heating, they gradually lost their transparency and finally turned to a dark brown solid. After cooling, it was pulverized in an agate mortar for 1 h. The resultant powders were uni-axially pressed at 10MPa and sintered at 1000℃ for 5 h in nitrogen atmosphere. They were set on a copper holder cooled with water.

The procedure of nanotube synthesis is schematically shown in Fig. 1. Ar-5mass % H_2 was used as a plasma gas. The flow rate was 15 SLM. The pressure in a reaction chamber was maintained at 100 Torr. A dc arc plasma jet was generated at 8 kW. Sintered disks were irradiated for 1 min by a dc arc plasma jet. The temperature of the disk surface irradiated was measured with an optical pyrometer. The temperatures inside the sintered disk were calculated by a computer simulation [10]. After the irradiation the powders were collected from the surface and the places of 1, 3, and 6 mm inside from the surface. They were ultrasonically dispersed in carbon tetrachloride and deposited on a copper grid coated with a carbon film. Then they were observed with a scanning electron microscope (SEM) and a transmission electron microscope (TEM).

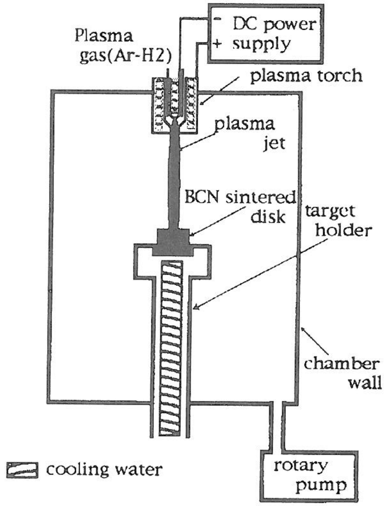
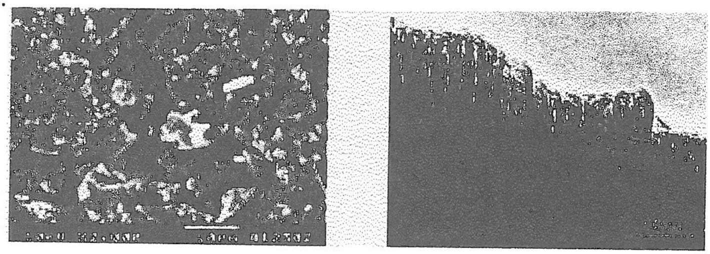


Fig. 1 A schematic illustration of apparatus for preparing nanotubes

3 Results and discussions

The temperatures of the surface irradiated by a dc arc plasma jet were measured by an optical pyrometer to be about 3500K. The temperatures at the places of 1, 3, and 6 mm inside from the surface were calculated by a computer simulation to be 3000, 2500, and 1800K, respectively.

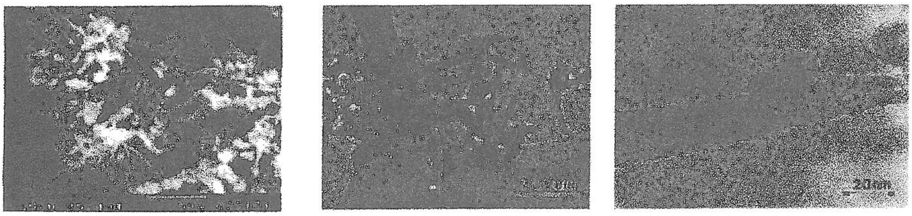


(a) (b)

Fig. 2 (a) SEM micrograph and (b) high magnification TEM images of raw materials

Figure 2(a) shows the SEM micrograph of sintered disks. There are a lot of pores among grains. The porosity of them was about 72 percents. The average grain size of them is about 10 μm. The TEM micrograph of a grain edge as shown in Fig. 2(b) indicated the presence of layer structures, something like overlapping multi-layered nanotubes. This would suggest even in a starting material the possibility of the existence of nanotube precursors, which are structurally similar to a nanotube.

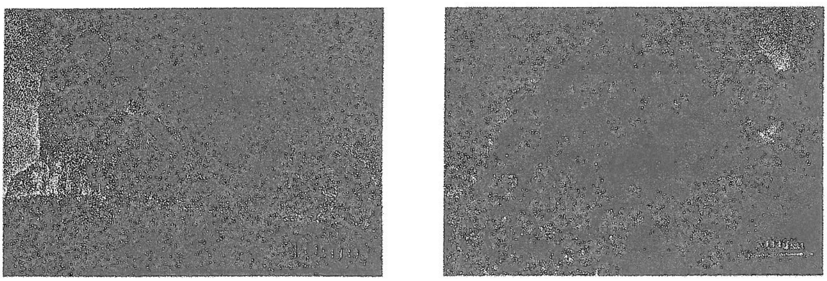
Figure 3(a) is the SEM micrograph of powders collected from the surface of a sintered disk after irradiation by a dc arc plasma jet. The observed grains are cylindrical. The average length and diameter of cylindrical grains are about 4 μm and less than 0.1 μm, respectively. The grains are agglomerated just like a sea urchin. Fig. 3(b) and (c) show TEM micrographs observed in low and high magnification. Clearly from the micrograph in high magnification, the cylindrical grains were found to be multi-layered nanotubes. Their diameter is from 10 to 20 nm. The average nanotube-length along nanotube axes is longer than 500nm. Also, nanocapsules were observed in the powders. Their diameter was from 20 to 25nm. This indicated that nanotubes and nanocapsules formed at high temperature such as 3500K.



(a) (b) (c)

Fig. 3 (a) SEM and (b) TEM micrographs of surface irradiated by a dc arc plasma jet. (c) high magnification TEM images of nanotubes obtained.

Nanotubes and nanocapsules were also observed in the powders collected at the place of 1mm inside from the irradiated surface. However, in comparison with the surface irradiated by the plasma jet, the temperature at the place was low. So, the size of nanotubes and nanocapsules would be small. Important evidence here is that nanotubes formed in even a solid just heated, although they have been so far considered to form by the condensation of chemical species from a vapor phase.



(a) (b)

Fig. 4 TEM images of nanocapsules observed at the region of (a) 3mm and (b) 6mm inside from the surface irradiated by a dc arc plasma jet.

Figures 4 (a) and (b) show the TEM micrographs observed at the place of 3 mm and 6 mm inside from the irradiated surface, respectively. No nanotubes but nanocapsules could be found in powders at the places. The data suggested that nanotubes could not form at lower temperature than at about 3000K and nanocapsules, on the other hand, generated at even lower temperatures such as 1800K. However, because of low temperatures, the size of nanocapsules was small in the order of 12 to 20 nm in diameter.

The results obtained here were summarized in Table 1 with calculated temperatures by computer simulation. That is, nanotubes were formed at from 3000K to 3500K and nanocapsules, on the other hand, were formed at even lower temperatures such as 1800K. Higher temperatures tended to elongate the length of nanotubes and the diameter of nanocapsules.

Table.1: The length of nanotubes and the diameter of nanocapsules observed at the various regions and the respective temperatures calculated by the computer simulation.

Observation region	Irradiated surface	1mm inside	3mm inside	6mm inside
Nanotubes (length)	Over 500nm	300nm	no	no
Nanocapsules(diameter)	20-25nm	20-25nm	12-20nm	12-20nm
Calculated temperatures by computer simulation	3500K	3000K	2500K	1800K

In the discussions about the formation of BN or BCN fullerenes, it has been so far reported that the collision processes of electrons under the irradiation of high-density electron beam play an important role on the formation [11-13]. However, our data in this experiment suggests a possibility that nanocapsules become as precursors for the formation of nanotube, since nanocapsules form at lower temperatures than nanotubes.

Based on the data, we would speculate the following mechanisms as schematically shown in Fig. 5. Firstly, BC_4N sintered disks decompose to BN and carbon at high temperatures [8]. During the decomposition process, nanocapsules are formed by the decomposition of the layered structures of BC_4N sintered disks. Secondly, nanocapsules grow to nanotubes or large nanocapsules in large size as shown in Fig. 5. In this case, as higher temperatures enhance diffusivity of chemical species, the growth rate of nanotubes and nanocapsules would be fast.

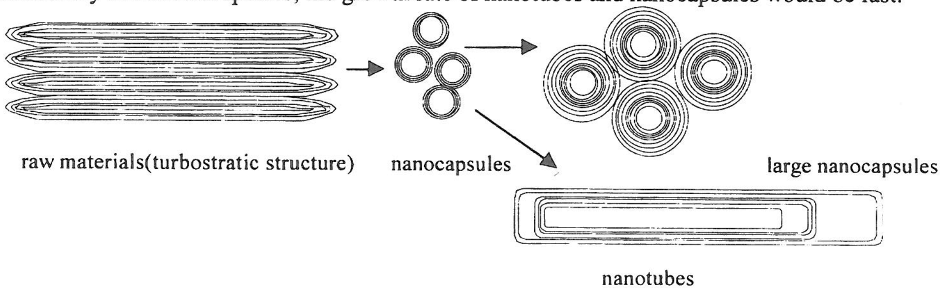


Fig.5 Schematic illustration of growth mechanism speculated on the basis of the results obtained.

In summary, from a relationship between microstructures and temperatures of sintered disks heat-treated, the formation mechanism of nanotubes was discussed. Consequently, a model that nanotubes grew from nanocapsules formed by the decomposition of the layered structures of BC_4N sintered disks was proposed.

References

[1] S. Iijima, P. M. Ajayan, and T. Ichihashi, Phys. Rev. Lett. **69**, 3100 (1992)

[2] X. F. Zhang, X. B. Zhang, G. V. Tendeloo, S. Amelinckx, M. O. de Beeck, and J. V. Landuty, J. Crystal. Growth. **130**, 398 (1993)

[3] Y. Saito, T. Yoshikawa, M. Inagaki, M. Tomita, and T. Hayashi, Chem. Phys. Lett. **204**, 277 (1993)

[4] N. Hatta, and K. Murata, Chem. Phys. Lett. **217**, 398 (1994)

[5] S. Amelinckx, D.Bernaerts, X. B. Zhang, G. V. Tendeloo, and J. V. Landuty, Sciense **267**,1334 (1995)

[6] O. A. Louchev, Appl. Phys. Lett. **71**, 3522 (1997)

[7] F. Jensen, and H. Toflund, Chem. Phys. Lett. **201**, 89(1993)

[8] Y. Shimizu, Y. Moriyoshi, S. Komatsu, T. Ikegami, T. Ishigaki, T. Sato, and Y.Bando, Thin. Solid. Films. **316**, 178 (1998)

[9] M. hubacek, and T. Sato, J. Solid. State. Chem. **114**, 258 (1995)

[10] T. Watanabe, Y. Shimizu, and Y. Moriyoshi, to be published.

[11] O. Stephan, Y. Bando, A. Loiseau, F. Willaime, N. Shramchenko, T. Tamiya, and T. Sato, Appl. Phys. **A67**, 107(1998)

[12] D. Golberg, Y.Bando, O. Stephan, and K. Kurashima, Appl. Phys. Lett. **73**, 2441(1998)

[13] O. Stephan, Y. Bando, C. Dussarrat, K. Kurashima, T. Sasaki, T. Tamiya, and M. Akaishi, Appl. Phys. Lett. **70**, 2383 (1997)