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The effect of temperatures on the formation of nanotubes and nano-onions in boron-carbon-nitrogen system

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Abstract

Based on the microstructural data obtained in a heat-treated raw material, a relationship between temperatures and the formation of nanotubes and nano-onions was discussed. The segments in fibers existed in raw materials were suggested to be precursors for the formation of nanotubes and nano-onions. It was indicated that the most important factor for the formation of nanotubes and nano-onions was a temperature to heat the raw material. Experimental data showed that small nano-onions of 10 to 20nm in diameter were formed from the segments at lower temperatures than 2300K, while nanotubes and larger nano-onions than 50nm in diameter were formed at higher temperatures than 3000K

Key words: B-C-N nanotube, formation mechanism, precursor

1.Introduction

Carbon, boron nitride and composite nanotubes (B-C-N) of carbon with boron nitride have been prepared by the condensation processes from a vapor phase using a dc arc discharge, laser ablation, and so on.[1-8]. In these processes, the reaction rate is extremely rapid. So only the information about reactant and final products is available. Therefore, it is difficult to know what kind of reactions had proceeded. This makes the creation of the reliable formation mechanisms of nanotubes difficult. In order to build up the reliable formation mechanimes of them, it would be indispensable to specify the intermediate materials during the reactions. Thus, we have tried experimentally to clarify a relationship between intermediate materials and heat-treated temperatures. From the experimental data about intermediate materials obtained mainly by using electron microscopes, here we propose a formation mechanism of the nanotubes and nano-onions.

2. Experimental

BC_4N sintered disks were used as raw materials in this experiment. The preparation method of the disks was reported previously[9]. A direct current arc plasma jet was used for preparing nanotubes. Ar-5vol%H_2 gas was used as the plasma gas and the flow rate was 15 SLM. The chamber pressure was maintained at 100 Torr with the same as the plasma gas. Under these conditions, the dc arc plasma jet was generated at the power of about 8kW (300A-25~27V). A BC_4N sintered disk was set on a sample holder, which was made of copper and cooled with water. It was irradiated with the high temperature region of the dc arc plasma jet for 1 min [8,9]. The powders for the characterization were collected from the irradiated surface, and 1, 2, 3 mm inside regions from the surface. These powders and raw materials were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electron energy loss spectroscopy (EELS). The each temperature corresponding to the characterized regions was calculated by a computer simulation[10].

3. Results and discussions

The temperature distribution of the raw material irradiated by a dc arc plasma jet was obtained by a computer simulation as shown in Fig. 1. The results indicated that the surface temperature of the irradiated raw material was 3650K and the temperatures of the regions at 1,2, and 3mm inside from the surface were 3120, 2750, and 2380K, respectively.

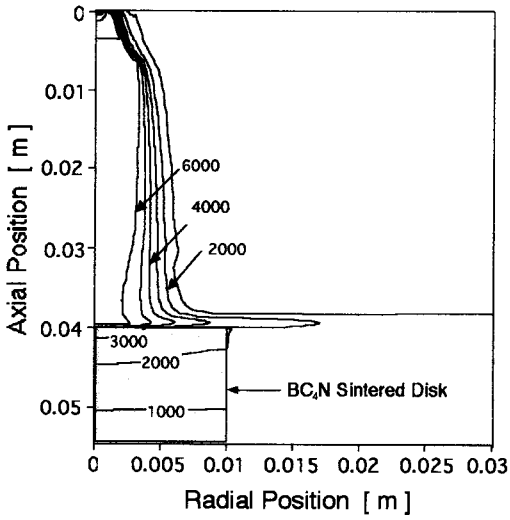

Fig.1 a diagram of the temperature distributions of plasma jet and the irradiated raw material under the condition of this experiment

The grain size of raw materials was about 10 μm.

The high-resolution TEM image of them was shown in Fig. 2(a) [11]. It showed a turbostratic structure something like overlapping multi-wall nanotubes of about 4nm in diameter. Among the raw materials, fibrous materials as shown in Fig. 2(b) existed.

Needle-like grains grown radially just like a sea urchin were formed on the surface of BC_4N sintered disks by the irradiation of the plasma jet as shown in Fig. 3(a) [11]. The corresponding TEM image clearly revealed the needle-like ones were nanotubes on the order of 15 to 25nm in diameter and up to 1 μm in length as shown in Fig. 3(b). In addition to them, spherical crystals formed with polyhedral concentric shells like as onion (nano-onion) of 10 to 100nm in outer diameter were observed as shown in Fig. 3(c). Their compositional elements were found to be carbon and boron nitride by analysis using EELS, however, mainly they were carbon (Fig.3 (d)). This would suggest that thermodynamically stable phase at higher temperatures as 3600K was in the mixture of carbon and boron nitride rather than in the homogeneous phase of B-C-N compounds.

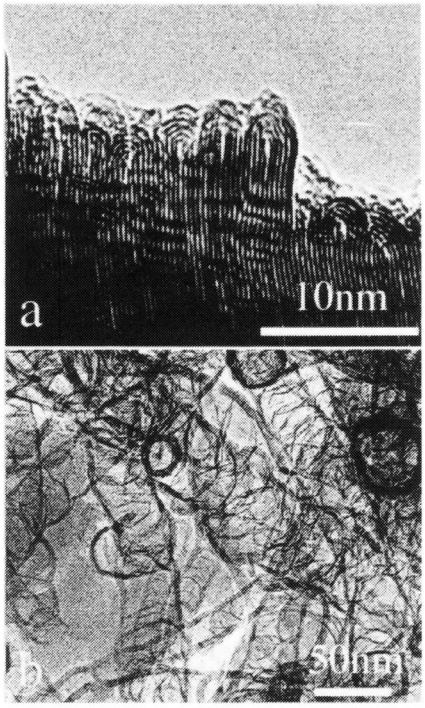

Fig. 2 High-resolution TEM images of raw materials: (a) turbostratic structure (b) fibrous materials

At the region of 1mm inside from the raw material's surface irradiated by a dc arc plasma jet, three kinds of products were observed. They were plate-like crystals, nanotubes of 10 to 20nm in diameter and 50 to 500nm in length, and nano-onions of 10 to 50nm in outer diameter. The compositional elements were mainly carbon. The nanotubes and nano-onions were small in size in comparison with the products generated on the surface irradiated by the plasma jet. However, the production of nanotubes and nano-onions by just heating the raw material is worthy of attention. This indicated an important possibility to produce them by just heating raw materials.

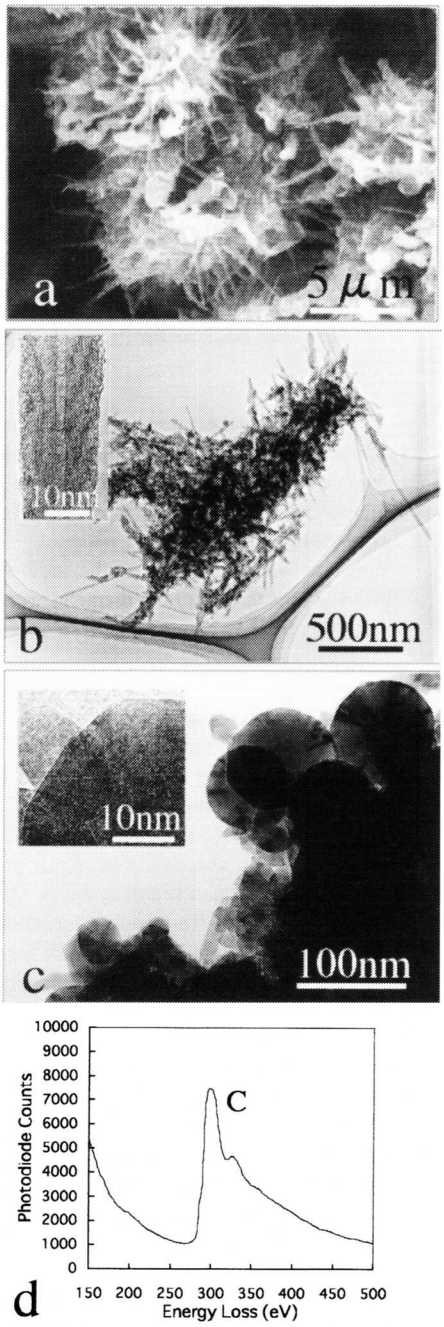

Fig. 3 (a) SEM and (b), (c) TEM images of the resultant products on the surface after the irradiation: the insets of (b) and (c) show the corresponding high-resolution TEM images. (d) one of the typical EELS spectra taken from the resultant products on the surface.

At the regions of 2 and 3mm inside from the surface of the raw material, dominant products were the agglomerated nano-onions of 10 to 20 nm in diameter as shown in Fig. 5(a) and (b). The structure was not as concentric as that of the nano-onions observed in a sample obtained from the surface of a raw material irradiated by the plasma jet. However, the

compositional elements of the products analyzed by EELS showed carbon, boron, and nitrogen (Fig. 5(c)). This may indicate that the homogeneous phase of B-C-N compounds is stable at the temperature as 2300 to 2700K. At the temperatures, no nanotubes were observed.

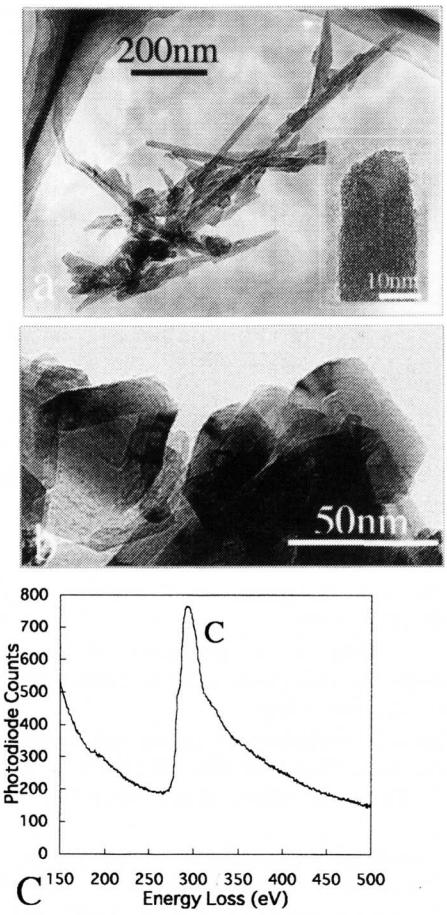

Fig. 4 TEM images of the resultant products at the region of 1mm inside: the insets of (a) and (b) show the corresponding high-resolution TEM images. (C) one of the typical EELS spectra taken from the resultant products observed at this region.

The results obtained above were summarized in Table. I .

Clearly from the table, the nanotubes were observed at higher temperature regions than 3000K, whereas the nano-onions were observed at lower temperature regions than 2700K.

The length and the diameter of nanotubes increased with increasing temperature. Also, the nano-onions increased the diameter at higher temperatures. This would indicate that very small nano-onion in size were firstly generated and with increasing temperatures large nano-onions were secondary produced and nanotubes were finally formed.

In order to check this, we tried to prepare nanotubes by just heating a raw material of porous BC_4N compounds at 3000K for 10 min in the flow of nitrogen gas. Resultant products were carbon, B-C-N nanotubes as shown in Figs. 6 and large nano-onions. The shape of them was fundamentally similar to those obtained at the temperature regions of 3000 to 3500K. However, compared with carbon nanotubes, B-C-N nanotubes were a few in number. Importantly, it was clarified that nanotubes and nano-onions were formed just by heating a raw material. This strongly suggested that the most important factor to produce nanotubes and nano-onions was a temperature to heat a raw material. Then, a question is, from what the first nano-onions are formed?

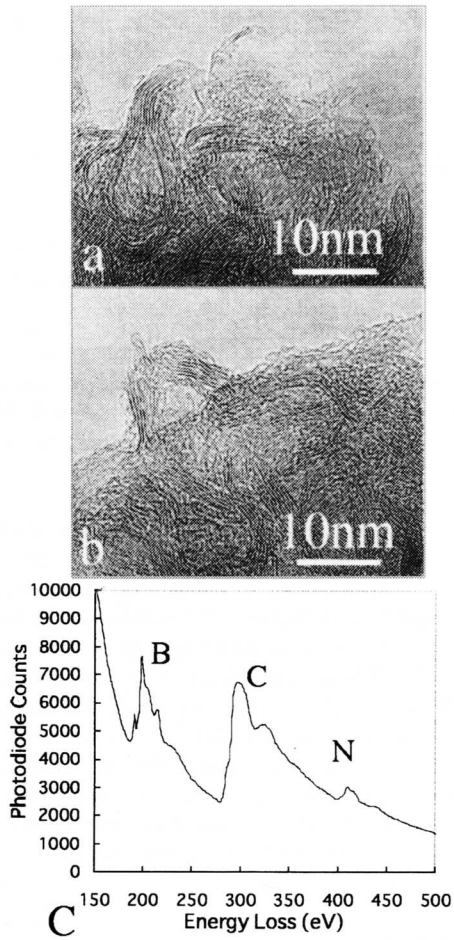

Fig. 5 (a) and (b) show the high-resolution TEM images of nano-onions observed at the regions of 2and 3mm inside, respectively. (c) one of the typical EELS spectra taken from the nano-onions observed at these regions.

Table. I The length of nanotubes, the diameters of nano-onions (maximum values), and the dominant component elements observed at the various regions and the temperatures corresponding to each region.

Observation regions	The irradiated surface	1mm inside	2mm inside	3mm inside
The temperatures	3650K	3120K	2750K	2380K
Nanotubes'length	1 μm	500nm	-	-
Nano-onions' diameter	100nm	50nm	20nm	20nm
The dominant components	C	C	B,C,N	B,C,N

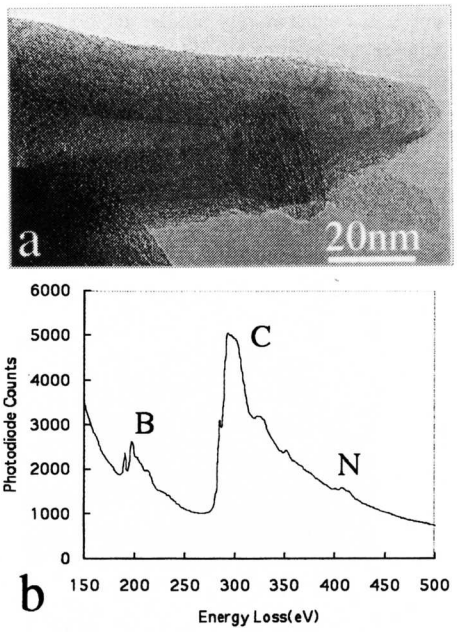

Fig.6 (a) a high-resolution TEM image of nanotube-structure obtained by just heating of raw material at 3000K for 10min and (b) the corresponding EELS spectra.

As reported previously [9], raw materials of porous BC_4N include fibrous ones, which consists of many segments (cups in shape) successively. These cups decomposed to each cup at high temperatures. Then, if its periphery is closed during heating, nano-onions would be formed. If it is open and grows to normal direction on periphery surface, nanotubes would be produced. For this, higher temperatures than 3000K would be very important, since higher temperature enhance the diffusion of chemical species to play an important role in growing them. The proposed formation mechanisms of nanotubes and large nano-onions were illustrated in Fig. 7.

4. Summary

One of the segments in fibers existed in a raw materials is considered to be precursors for the formation of nanotubes and nano-onions. Small nano-onions of 10 to 20nm in diameter are formed from the segments at lower temperatures than 2300K, while nanotubes and larger nano-onions than 50nm in diameter are formed at higher temperatures than 3000K.

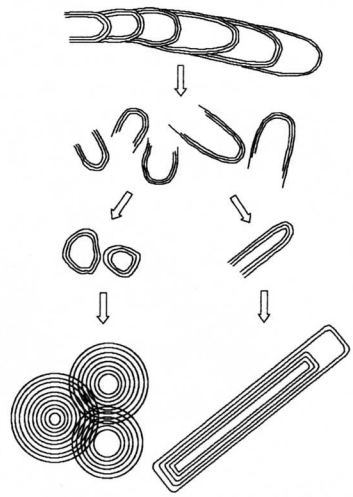

Fig. 7 the proposed formation mechanisms of nanotubes and large nano-onions

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, H.Tanaka, and S.Komatsu, Appl. Phys. Lett. **75**, 929 (1999)
9) Y.Shimizu, Y.Moriyoshi, S.Komatsu, T.Ikegami, T.Ishigaki, T.Sato, and Y.Bando, Thin.Solid.Films **316**,178 (1998)
10) T. Watanabe, Y. Shimizu, and Y. Moriyoshi, to be published.
11) Y.Shimizu, Y.Moriyoshi, H. Uono, T.Watamabe, N. Ekinaga, S. Komatsu, and T. Ishigaki, Proc.ISPC-14, Prague, 2179 (1999)

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