# The preparation and Characterization of Boron-Carbon-Nitrogen Nanotubes by a dc Arc Plasma

by

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Abstract

B-C-N nanotubes prepared by a flush evaporation method using a dc arc plasma were mainly characterized by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). The nanotubes obtained were divided into three types such as carbon-, boron nitride-, and carbon or carbon nanotubes surrounded with boron nitride nanotubes. These types of nanotubes were obtained at higher temperatures than about 3000 K, however, these were not formed at lower temperatures than about 3000K. On the other hand, nanocapsules were formed at all the experimental temperatures and nanocapsules with a homogeneous phase were obtained at lower temperatures than about 3000 K. The effect of additives on the formation of B-C-N nanotubes was not clear. Based on these experimental data depending on temperatures and corresponding microstructures, the formation mechanisms of both nanotubes and nanocapsules were briefly discussed

Keywords: B-C-N nanotube, nanocapsule, microstructure, plasma

## 1 Introduction

As reported previously, nanotubes have unique electrical properties[1-3]. The preparations of nanotubes have been usually carried out by flush evaporation methods using either a dc arc plasma or a laser[4-5]. By these methods the reaction rate is so rapid that we have no data of intermediate products between initial raw materials and final products of nanotubes[6-9]. So, the formation mechanisms of nanotubes have been mainly speculated only from the microstructures of resultant nanotubes. In order to have more reliable formation mechanisms, it is particularly important to have the information of intermediate products at the corresponding temperatures. From the viewpoints, we have studied about the effects of temperatures on the preparation of nanotubes. Here we report on firstly some problems on the preparation of B-C-N nanotubes[10], secondly the effects of temperatures on the preparation of B-C-N nanotubes, and finally the formation mechanisms of nanotubes.

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2 Experimental

Porous $BC_4N$ sintered bodies were used as raw materials. The synthetic principle of the compounds was reported previously[10-11]. Two moles of boric acid and one mole of urea were mixed in an agate mortar. The mixtures were added to a solution with saccharose. The C/BN molar ratio in the mixture was 4. The mixed solution was heated in a Pyrex beaker at 130-150℃ for 1 h and then it was raised to 220℃, at which it was heated again for 2h. The atmosphere during the heating was nitrogen. The reaction began by complete melting of the mixture. Then the melt gradually lost its transparency, turned to a brown viscous liquid, and later foamed, finally solidification of the foam took place. After cooling, the $BC_4N$ precursor obtained was pulverized in an agate mortar. The resultant powders were filled in an alumina tube, which was annealed in an RF induction furnace with a carbon susceptor at 1500℃ for 3h in the stream of $N_2$ gas. The chemical analysis of the sintered bodies obtained was confirmed to be $BC_4N$. The porosity of the compound was about 70%.

Porous $BC_4N$ compounds containing additives such as potassium and cerium were prepared in the following. $BC_4N$ compounds were mixed with the additives in an agate mortar for 30min. The mixing ratio of $BC_4N$ compounds with the additives was 99:1, 97:3, 95:5, and 90:10. The mixture was pressed to compacts at 30 MPa. The resultant compacts were heated at given temperatures for 5 h in the stream of $N_2$.

The procedure of nanotube synthesis was carried out in the following as reported previously[11]. The reaction chamber was maintained at 100 torr. The dc arc plasma was operated under the condition of 25V and 300A by using Ar and $N_2$-$H_2$ for plasma gas and sheath gas, respectively. The temperatures of the porous $BC_4N$ sintered body irradiated by a dc arc plasma were calculated by a computer simulation [11] and measured by using an optical pyrometer. The porous $BC_4N$ sintered body set up on a copper disk cooled with water was evaporated by the irradiation of the plasma flame. The surface temperature irradiated by the plasma flame was 3650 K. The temperatures at 1, 2, and 3 mm inside from the surface were 3120, 2750, and 2380K, respectively. The powder samples deposited on chamber walls by the condensation of chemical-species evaporated and ionized from the porous $BC_4N$ sintered body were collected. Also, the samples cut from given places of porous $BC_4N$ sintered body at a given temperature were collected. They were ultrasonically dispersed in carbon tetrachloride, and were deposited on a copper grid coated with a holey carbon film in order to characterize by TEM and EELS, which were operated at 200kV.

3 Results and discussion

Typical nanotubes obtained were usually in an aggregated state. Outer diameters of them were from 5 to 20 nm, and the lengths were longer than 300 nm. Their aspect ratio was larger than 50. Figure 1 showed a TEM micrograph of a nanotube observed at high magnification and a corresponding electron diffraction pattern. The electron diffraction pattern indicated that the c-axis was the radial direction, which was normal to the axis of the nanotube. That is, its basal planes are parallel to the nanotube axis. The lattice fringes of inter-spacing distance between two (002) planes could be clearly seen in the figure.

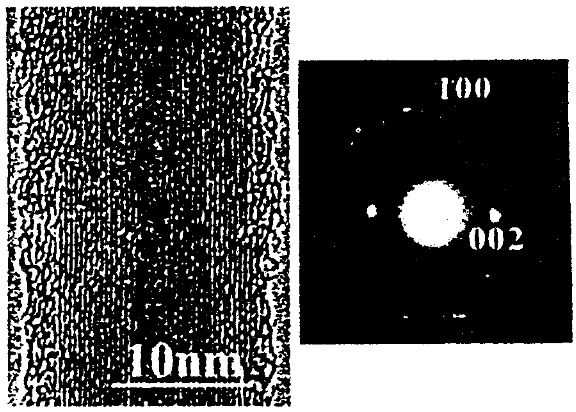


Figure 1: A high magnification TEM micrograph of a nanotube and the corresponding electron diffraction pattern.

Figure 2 showed TEM micrographs and corresponding EELS data of a nanotube. Almost all the nanotubes had closed tips similar to those of carbon nanotubes[13] and BN nanotubes[7]. The EELS data indicated the ionization edges at approximately 188 and 401 eV, corresponding to the characteristic K-shell ionization edges of boron and nitrogen, respectively. The sharp $\pi^*$ peak was typical for hexagonal B-N bonding[14]. This indicates that it is a BN nanotube. However, carbon was not detected in the nanotube. This is a strange result, since $BC_4N$ compound used as a sample for evaporation consisted of three elements: boron, carbon, and nitrogen. So, we tried again to analyze carefully the different positions in a single nanotube.

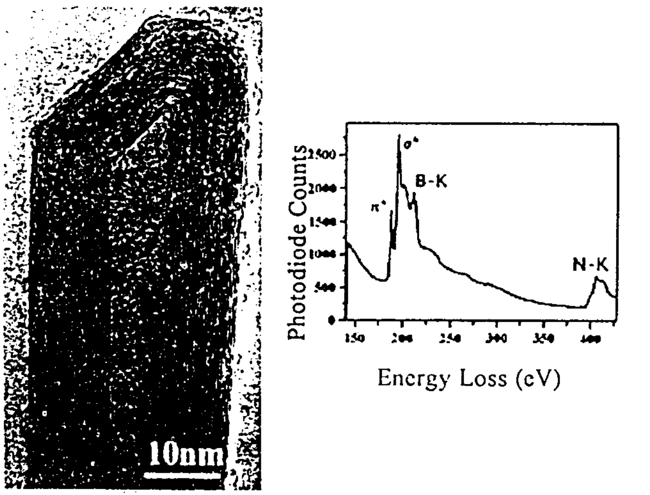


Figure 2: A high magnification TEM micrograph of a nanotube and the corresponding EELS data, which indicates the nanotube is consisted of boron and nitrogen.

Figure 3 showed a TEM micrograph and corresponding EELS data[11]. Boron and nitrogen were clearly detected in the positions (a), (b), and (c) but carbon peak was very weak. Careful analysis suggested that the carbon peak was related to contamination due to hydrocarbon vapors derived from vacuum system in a TEM. Therefore, the positions analyzed were concluded to be parts of a BN nanotube. On the other hand, at the center position (d) of the nanotube, three elements of boron, carbon, and nitrogen were detected. Particularly high concentration of carbon was noticeable. It is noted in the position (d) that another nanotube was present inside the BN nanotube. Since electron beams could penetrate through the nanotube, high carbon peak in EELS data is considered to come from the inner nanotube. So, the nanotube shown in Fig. 3 is a combined one, that a carbon nanotube is surrounded with a BN nanotube. The same types of combined nanotubes are much found in the samples observed. This would show that a stable phase was in the mixed state of carbon and BN rather than in the homogeneous phase of B-C-N nanotubes. Previously, Weng-Sieh et al synthesized successfully $BC_2N$ nanotubes using dc arc discharge[3], however, in our experiments the homogeneous phase of B-C-N nanotubes was not obtained.

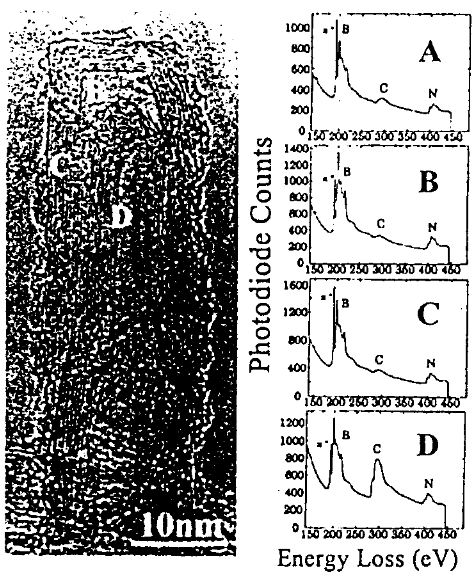


Figure 3: A high magnification TEM micrograph of a nanotube and the EELS data taken from various regions of the nanotube. Boron and nitrogen were mainly detected and carbon was hardly detected in the regions of (a), (b) and (c). On the other hand, three elements of boron, carbon, and nitrogen were clearly detected in the region of (d). Consequently, this nanotube is considered to be a carbon nanotube surrounded with a BN nanotube.

In summary carbon, boron nitride, and combined nanotubes of carbon and BN were prepared from a porous $BC_4N$ sintered body by a flush evaporation method in a dc arc plasma. The surface temperatures irradiated by the plasma flame were estimated to be 5000 K. In such high temperatures the homogeneous nanotubes in composition of carbon, boron, and nitrogen could not be obtained because of the decomposition of porous $BC_4N$ compound.

The reaction rate of nanotubes and nanocapsules by a flush evaporation method is so rapid that we have no data about intermediate products between initial raw materials and final products of them. So, various formation mechanisms of them have been speculated only from the microstructures of final products of nanotubes. In order to have more reliable formation mechanisms, it would be important to have information about intermediate products at corresponding temperatures. From the viewpoints, we have studied a relationship between intermediate products and temperatures.

The temperature distribution of a porous $BC_4N$ sintered body irradiated by a dc arc plasma were obtained by a computer simulation as shown in Fig. 4. Resultantly, the surface temperature of the porous $BC_4N$ sintered body irradiated was 3650K and the temperatures of the regions at 1, 2, and 3 mm inside from the surface were 3120, 2750, and 2380K, respectively.

In the samples obtained from the surface, fibrous substances grown to radial directions just like a sea urchin were formed. The corresponding SEM images clearly revealed that the substances were nanotubes. These were from 15 to 25 nm in diameter and from to 5 μm in length. Also, spherical substances formed with polyhedral shells like an onion(nanocapsule) were observed. These were from 10 to 100 nm in outer diameter. Their compositions were found to be either carbon or boron nitride. This also suggested that a stable phase at as high temperature as 3600K was in the mixture of carbon and boron nitride rather than in the homogeneous phase of B-C-N compounds.

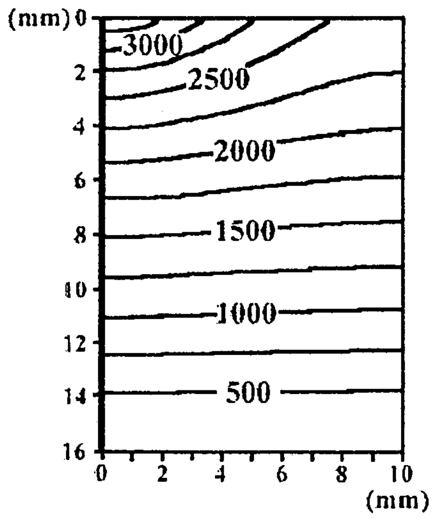


Figure 4: The temperature distribution of a porous BC4N sintered body irradiated with a dc arc plasma. The temperature of the irradiated surface was estimated to be 3650K. The temperatures of the regions at 1, 2, and 3 mm inside from the surface were estimated to be 3120, 2750, and 2380K, respectively.

At the region of 1mm inside from the surface, three kinds of products were observed. They were plate-like crystals, nanotubes of 10 to 20 nm in diameter and 50 to 500 nm in length, and nanocapsules of 10 to 50 in outer diameter. The nanotubes and nanocapsules were small in size in comparison with the products generated on the surface.

At the regions of 2 and 3 mm inside from the surface of a porous $BC_4N$ sintered body, dominant products were the agglomerated nanocapsules of 10 to 20 nm in diameter. Their structure was not as concentric as that of the nanocapsules observed in the sample obtained from the surface. The compositions of them analyzed by EELS were carbon, boron, and nitrogen, which are distributed homogeniously. This indicates that the homogeneous phase of B-C-N compounds is stable at lower temperatures than about 3000K. However, at such temperatures no nanotubes were generated.

The above data show the following results. The nanotubes were formed at higher temperatures than about 3000K, whereas the nanocapsules were formed at lower temperatures than about 3000K. The length and the diameter of nanotubes increased with increasing temperature. Also, the nanocapsules increased the diameter at higher temperatures. Very small nanocapsules in size were firstly generated, thereafter, large nanocapsules were produced with increasing temperatures and then nanotubes were finally formed.

In order to check the data, we tried to prepare nanotubes by further heating a $BC_4N$ sintered body in a furnace at 3000K for 10 min in the flow of nitrogen gas. Resultant products were carbon, B-C-N nanotubes, and large nanocapsules. The shape of them was fundamentally similar to those obtained at higher temperatures than 3000 K. This indicates that nanotubes and nanocapsules are formed just by heating a porous $BC_4N$ sintered body and that one of the most important factors to produce nanotubes and nanocapsules is its heating temperature. The effect of additives on the formation of B-C-N nanotubes and nanocapsules was not clear, however, in higher concentration than 5 wt % additives such as potassium and cerium, nanocapsules containing their carbides inside were detected.

Detail observation of a porous $BC_4N$ sintered body, provides us the information suggesting precursors for nanotube growth. The structure of the precursors, something like successive cups, already existed in the $BC_4N$ sintered body. The cups would decompose to each cup when the $BC_4N$ sintered body was irradiated by a dc arc plasma. If we assumed that the periphery of a cup became a growth site for a nanotube, which would grow to the direction parallel to the nanotube axis. That is, chemical species adsorbed on the periphery made crystal lattice toward outer direction. To attain this process, higher temperatures than 3000K may be required, since higher temperatures enhance the diffusion of chemical species on the periphery to a site for the lattice formation. Such formation mechanisms of nanotubes and large nanocapsules were schematically illustrated in Fig. 5.

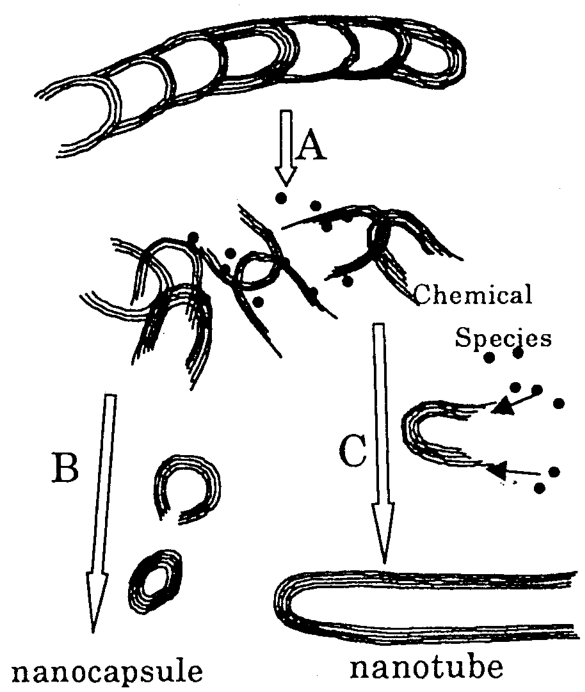


Figure 5: A Schematic illustration of the formation mechanism of nanotubes, which was discussed on the basis of the results obtained. Firstly, the substance whose structure is something like successive cups is decomposed into each cup by irradiation of dc arc plasma (process A). In the resultant cups, some are closed and form into nanocapsules (process B), others form into nanotubes by the diffusion of chemical species to the sites of the lattice formation on the periphery (process C).

In summary, B-C-N nanotubes were prepared by a flush evaporation method using a dc arc plasma. The nanotubes obtained were divided into three types such as carbon-, boron nitride-, and carbon or carbon nanotubes surrounded with boron nitride nanotubes. These were formed at higher temperatures than about 3000 K, but not formed at lower temperatures than about

3000K. On the other hand, nanocapsules were formed at all the experimental temperatures and nanoapsules with a homogeneous phase were obtained at lower temperatures than about 3000 K. The effect of additives on the formation of B-C-N nanotubes was not clear. Based on these experimental data depending on temperatures and corresponding microstructures, the formation mechanisms of both nanotubes and nanocapsules were briefly discussed

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