

A solid-state process for formation of boron nitride nanotubes

Ying Chen^{a)}

Joint Department of Engineering, Department of Electronic Materials and Engineering, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

Lewis T. Chadderton

Atomic and Molecular Physics Laboratories, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

John Fitz Gerald

Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

James S. Williams

Department of Electronic Materials and Engineering, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

(Received 27 January 1999; accepted for publication 26 March 1999)

The formation of boron nitride (BN) nanotubes via a solid-state process is demonstrated. The nanotubes are produced by first ball-milling hexagonal BN powder to generate highly disordered or amorphous nanostructures, followed by annealing at temperatures up to 1300 °C. The annealing leads to the nucleation and growth of hexagonal BN nanotubes of both cylindrical and bamboo-like morphology. Unlike previous mechanisms for nanotube formation, the reordering and solid-state growth process of our nanotubes does not involve deposition from the vapor phase nor chemical reactions. © 1999 American Institute of Physics. [S0003-6951(99)04320-X]

Hollow nanostructures, in particular, nanotubes and nanocages, which can be formed in carbon¹ and other compound materials such as boron nitride,² are currently generating much interest. Such structures are normally formed at high temperature by deposition² or chemical reaction³ from a vapor phase. We recently reported that boron nitride (BN) nanotubes can be prepared by a reactive ball-milling process at room temperature,⁴ during which elemental boron powder was first ball milled in an atmosphere of ammonia gas, followed by annealing in nitrogen up to 1400 °C. Nanotubes with diameters varying from 20 to 150 nm were obtained. This formation process for nanotubes occurred at a temperature far below that of the familiar arc-discharge² or laser-ablation⁵ methods. In particular, the starting material for ball milling is elemental boron powder rather than a BN compound and the nanotube formation process during annealing may have been initiated by chemical reaction. In the present letter we demonstrate that ball milling of hexagonal BN powder, followed by annealing, leads to the nucleation and growth of BN nanotubes via a solid-state process which does not involve deposition from the vapor phase nor chemical reactions.

Hexagonal boron nitride powder of a purity of 98% or better was used as the starting material. The ball-milling process was carried out in a rolling laboratory ball mill using hardened steel balls with a diameter of 25.4 mm and a stainless-steel cell.⁶ The containment cell was loaded with several grams of BN powder together with four balls. To prevent contamination with oxygen, the cell was purged with nitrogen gas several times and a pressure of 300 kPa was established prior to milling. Following milling, as-milled

powders were heated under N₂ gas flow (1 ml min⁻¹) at different temperatures up to 1300 °C for about 10 h. Structures of samples were investigated by means of x-ray diffraction (XRD) analysis using Co radiation ($\lambda=0.1789$ nm) at room temperature. Chemical compositions were examined using x-ray energy-dispersive spectroscopy (XEDS) in a JEOL (JSM6400) scanning electron microscope. Transmission electron microscopy (TEM) was carried out using both a Philips EM430 (300 kV) and a JEOL 2000 scanning transmission electron microscopy (200 kV) instruments. Powder samples were dispersed in acetone using an ultrasonic bath, and a drop of the suspension was placed on a copper support grid covered with holey carbon film. Differential thermal analyses (DTA) were made in a Shimadzu analyzer under nitrogen flow.

Figure 1(a) shows a TEM micrograph of hexagonal BN powder first ball milled for 140 h at room temperature in nitrogen gas, followed by annealing at a temperature of 1200 °C for 10 h in a nitrogen flow. BN nanotubes are clearly observed which have an outer diameter of about 11 nm and an inner diameter of 3 nm. Microdiffraction on individual tubes reveals that walls are multilayers of BN (002) planes, with a lattice spacing of 3.38 ± 0.04 Å.

Different microstructures of tubes can be observed in annealed samples. For example, a sample annealed at 1300 °C for 10 h [Fig. 1(b)] shows three “bamboo-like” tubes, each of which are divided into several segments by transverse internal walls. The biggest has a diameter of 280 nm and the smallest a diameter of about 120 nm. Each tube contains a metal particle at its tip. XEDS reveals that these particles are mainly Fe with a little Ni and Cr, which are contaminants from the stainless-steel container. The electron diffraction inset shows that the wall has a hexagonal struc-

^{a)}Electronic mail: ying.chen@anu.edu.au

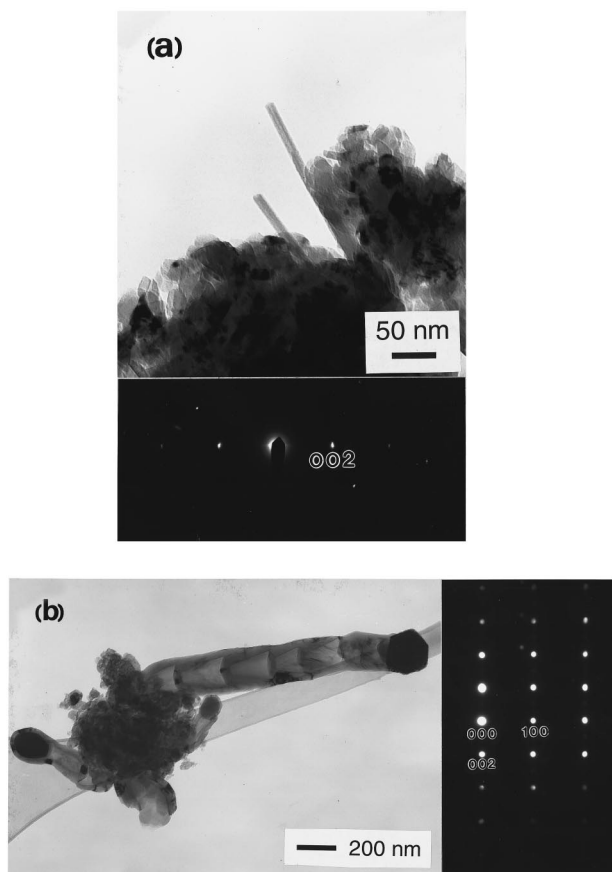


FIG. 1. TEM micrographs taken from the 140 h milled sample following two different heat treatments: (a) 1200 °C for 10 h, the electron diffraction pattern inset is taken from the two filaments; and (b) 1300 °C for 10 h, the electron diffraction pattern inset is taken from the wall of the longest tube.

ture. The outer diameter seems to be determined by the overall size of the metal particles and the inner diameter is close to the projected width of the edge of the Fe particle. These tubes are analogous to carbon “bamboo” tubes.⁷

Nanotubes are not observed in milled samples which have not been heated, nor are they observed when unmilled BN powder is heated. This shows that formation of nanostructures can only take place during annealing of ball-milled powders. The nanostructure of the ball-milled BN powder is essential to the ultimate growth of nanotubes during annealing. Figure 2 is a typical TEM micrograph showing the typical morphology of a sample after milling. Aggregates consisting of particles below 50 nm are observed. The selected area diffraction pattern (inset) shows three diffuse rings, which suggests a disordered nanocrystalline BN structure, associated with (002), (100), and (110) planes with lattice spacings of 3.61, 2.14, and 1.24 Å, respectively. The larger (002) interlayer distance and the absence of a three-dimensional structure are features characteristic of a turbostratic structure.^{8,9} TEM also reveals that iron particles with a size below 1 μm are dispersed in milled BN powders as inclusions.

XRD analysis also supports the conclusion that the hexagonal BN phase is transformed to a highly disordered BN phase after ball milling. The turbostratic BN structure is indicated by two weak and broadened peaks (referred to as α1 and α2) in the XRD pattern shown in Fig. 3(a). The mean

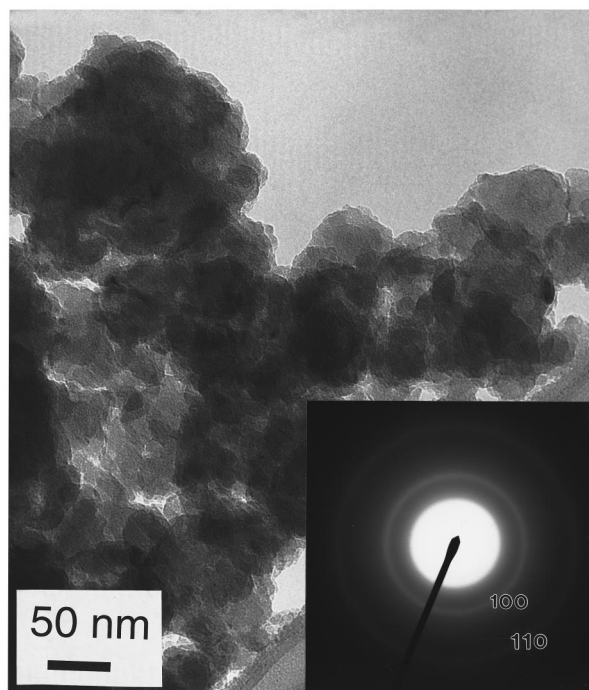


FIG. 2. TEM micrograph taken from the BN sample after ball milling for 140 h without heat treatment.

lattice spacing for the α1 peak is about 3.56 Å (though this value has a high level of uncertainty because of the background correction). The XRD patterns including XEDS data also show the presence of iron contaminant from the milling balls and the cell itself. The measured overall Fe level is about 3.8 wt %. After heating at 1200 °C for 10 h in flowing nitrogen, the hexagonal BN structure was recovered, as evidenced by the XRD pattern shown in Fig. 3(b). Pronounced diffraction peaks of the Fe and Fe(C) phases are also observed [see Fig. 3(b)]. A sample milled for 140 h was also analyzed using DTA up to 1250 °C in nitrogen gas. The somewhat featureless curve obtained (not shown) strongly suggests that no activated chemical reactions take place during heating. Also, no evidence for a sharp crystallization event is observed from DTA and the behavior during anneal-

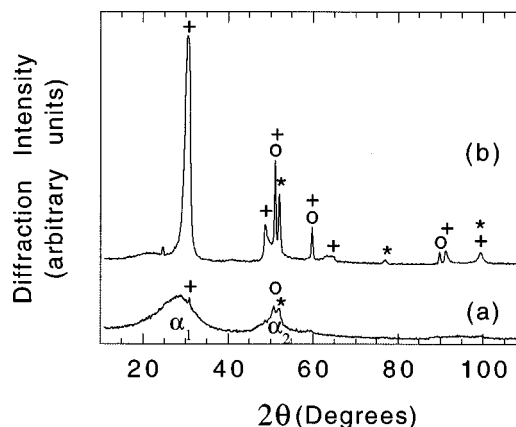


FIG. 3. X-ray diffraction patterns taken from the BN sample after milling for 140 h (a), and from the milled sample after heating at 1200 °C for 10 h (b). α1, α2: turbostratic BN, +: hexagonal BN, *: α-Fe, and O: Fe(C) austenite alloy (stainless steel).

ing is more consistent with gradual reordering, defects annealing, and grain growth.

The above results clearly show formation of BN nanotubes during annealing of disordered BN nanostructures at 1200 °C and above. It is important to note that precipitation from vapor or liquid BN phases is impossible: the annealing temperatures are simply too low. Nanotubes appear to grow directly from adjacent disordered, nanosized BN grains, both with and without the aid of Fe (contaminant) particles. Furthermore, since the starting phase is BN and no chemical reaction has been detected by DTA during the heat treatment, there is no reason to suggest that chemical reactions are involved in the formation process of the nanotubes. Therefore, the current results clearly demonstrate a solid-state nucleation and growth process for the formation of BN nanotubes, which is distinctly different from either a vapor phase (arc-discharge and laser-ablation)^{2,5} or chemical reaction (catalysis)³ method identified previously.

The metastable disordered BN nanostructure after ball milling and its structural rearrangement during annealing hold the key to understanding the process. The metastable nanostructure contains a large surface area. Fine Fe (Cr and Ni) particles with sizes in the range from several nanometers to 1 μm are also dispersed through the sample. During annealing, the (002) lowest free-energy¹⁰ layers for hexagonal BN grow from the disordered BN powder. Indeed, many two-dimensional (002) sheets are observed in samples annealed at low temperatures (less than 1100 °C) and these may be the precursors of nanotubes. The (002) layers appear to grow to a particular thickness depending on temperature and then extend into various tubular morphologies, with or with-

out the catalytic effect of metal particles. At higher annealing temperatures (around 1300 °C), the growth is faster and most tubes are both thicker and longer. It is interesting that some cylindrical tubes appear to have grown without the presence of a contaminant particle whereas the bamboo-like tubes are most often capped with an Fe particle which appears to have catalyzed the growth.

In conclusion, boron nitride nanotubes have been produced by the annealing of ball-milled BN powders in nitrogen. Ball milling is crucial in forming disordered BN nanostructures from which the nanotubes appear to grow via a solid-state process, quite distinct from other known methods for nanotube synthesis.

The authors thank P. Willis for providing them with some hexagonal BN powders, and also S. Stowe and F. Brink for assistance with the TEM.

¹S. Iijima, *Nature (London)* **354**, 56 (1991).

²N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettle, *Science* **269**, 2045 (1995).

³P. Gleize, M. C. Schouler, P. Gadelle, and M. Caillet, *J. Mater. Sci.* **29**, 1575 (1994).

⁴Y. Chen, J. Fitz Gerald, J. S. Williams, and S. Bulcock, *Chem. Phys. Lett.* **299**, 260 (1999).

⁵D. Golberg, Y. Bando, M. Eremets, K. Takemura, K. Kurashima, and H. Yusa, *Appl. Phys. Lett.* **69**, 2045 (1996).

⁶Y. Chen, T. Halstead, and J. S. Williams, *Mater. Sci. Eng., A* **206**, 24 (1996).

⁷Y. Saito and T. Yoshikawa, *J. Cryst. Growth* **134**, 154 (1993).

⁸J. Thomas, N. E. Weston, and T. E. O'Connor, *J. Am. Chem. Soc.* **84**, 4619 (1963).

⁹S. I. Hirano, T. Yogo, S. Asada, and S. Naka, *J. Am. Ceram. Soc.* **72**, 66 (1989).

¹⁰J. Abrahamson, *Carbon* **19**, 217 (1973).