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# Synthesis of boron nitride nanotubes at low temperatures using reactive ball milling

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#### Abstract

Boron nitride (BN) nanotubes have been produced by thermal annealing at 1000°C of elemental boron powders which were previously ball milled in ammonia gas for 150 h at room temperature. High-energy ball milling induces nitriding reactions between the boron powder and the ammonia gas. A metastable material is formed consisting of disordered BN and nanocrystalline boron. BN nanotubes then grow out from this metastable and chemically activated structure during heat treatment in the presence of nitrogen gas. This novel process for forming BN nanotubes is distinctly different from arc discharge and laser-heating processes. © 1999 Elsevier Science B.V. All rights reserved.

# 1. Introduction

Chopra et al. [1] first synthesized pure boron nitride (BN) nanotubes using an arc-discharge method in 1995, and subsequently the same method was used to produce BN nanotubes with reduced size or varied structure [2,3]. It was suggested that nanotubes grew from metal nanoparticles present as seeds [1,2]. However, hexagonal BN nanotubes without metal particles were grown by the laser-heating of single crystal BN at a high nitrogen pressure [4]. Helical BN nanotubes were also obtained by the heating of

amorphous boron particles in a BN crucible [5]. All of these methods require pure BN as the starting material and most of them require a high temperature and/or a high gas pressure. In addition, large BN tubular filaments having external diameter more than 100 nm have been produced from the chemical reaction of B-trichloroborazine with cesium [6], or of N<sub>2</sub> or NH<sub>3</sub> with ZrB<sub>2</sub> [7] at 1100°C. However, true nanoscale tubular structures were not observed in either case. In this Letter we describe a new method for the synthesis of BN nanotubes at low temperatures. A room-temperature ball-milling treatment of elemental boron in NH<sub>3</sub> gas is followed by annealing at a relatively low temperature (1000°C). In this method, BN nanotubes over a large range of size can be produced under different conditions.

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High-energy ball milling can produce structural changes and chemical reactions at room temperature. The process embraces a complex mixture of fracturing, grinding, high-speed plastic deformation, cold welding, thermal shock, intimate mixing, etc. [8]. Because the structural changes and chemical reactions are induced by mechanical energy rather than thermal energy, reactions are possible at low temperatures and so are non-equilibrium in nature [9]. A large range of nanoscale materials, including nanocrystalline structures [10], nanoparticles [11] and nanocomposites [12], has been produced. Nanotubes, however, have not previously been synthesized using high-energy ball milling.

#### 2. Experimental

Elemental boron powder with a purity of 99.8% or better was used as the starting material and anhydrous ammonia as the reacting gas. Ball-milling process was performed at room temperature in a vertical planetary ball mill [13] using hardened steel balls with a diameter of 25.4 mm and a stainless steel cell. The cell was loaded with 4 g of the boron powder together with several balls. The cell was then purged with the reaction gas several times and a starting pressure of 300 kPa was established prior to milling. The pressure of the milling cell was monitored using an attached pressure gauge. Following milling, subsequent annealing of selected powders were carried out under N<sub>2</sub> gas or Ar gas flow at temperatures  $\geq 1000^{\circ}$ C. The milled and annealed samples were characterised using various techniques. Structure of samples was investigated by means of X-ray diffraction analysis (XRD) using Co radiation  $(\lambda = 0.1789 \text{ nm})$  at room temperature. Scanning electron microscopy (SEM) was carried out using a Hitachi S4500 Field Emission SEM. X-ray dispersive spectroscopy was made in a Jeol (JSM6400) SEM equipped with Oxford ISIS EDXA with ATW window analysis system. Transmission electron microscopy (TEM) was performed using Philips EM430 (300 kV) and VG601UX scanning transmission electron microscope (100 kV). Electron energy loss spectroscopy (EELS) analysis was carried out on the VG601UX field emission dedicated STEM fitted with a GATAN Model 666 PEELS spectrometer. The microscope was operated at 100 kV, with a 50  $\mu$ m objective aperture, and with the C2 lens focused on the selected area aperture, giving a nominal probe diameter of 1 nm. Specific surface area was measured using a Gemini 2375 surface area analyzer with nitrogen gas at liquid nitrogen temperature.

#### 3. Results and discussion

Pressure changes which occurred during milling are illustrated as a function of milling time in Fig. 1. The pressure decreases from 300 to 190 kPa during the first 36 h of milling, and then gradually increases again to a stable pressure of 315 kPa after 150 h. It is worth noting that the final pressure is higher than the initial ammonia pressure. According to our understanding from previous studies of similar pressure changes observed during milling of Ti and Zr in NH<sub>3</sub> [14,15], this pressure change suggests a nitriding reaction between the boron and the ammonia gas during milling. The pressure reduction at the first stage of milling is due to absorption of ammonia gas onto boron particle surfaces newly created by ball impacts. The rise of pressure during further milling results from dissociation of ammonia, leading to the release of hydrogen gas and to a nitriding reaction between boron and atomic nitrogen. Combustion analysis of the composition of the as-milled sample reveals that the nitrogen content is 10.1 wt% while the hydrogen content is 0.9 wt%, confirming nitridation of boron by NH<sub>3</sub>. An XRD pattern of the



Fig. 1. Pressure changes as a function of milling time during milling of boron powder in ammonia gas.

as-milled sample (Fig. 2a) reveals a high background and broad peaks from residual boron. The unreacted boron consists of nanocrystallites ( $\leq$  50 nm in size). The high background (and a possible broadened peak at about 25°) suggests that the nitride phase is either amorphous or consists of extremely small, highly disordered crystallites [16,17]. Despite a high nitrogen content in some sample regions, TEM analysis could not clearly identify a BN phase after milling. However, TEM reveals that a thin layer of BN with a thickness of about 10 nm covers the surface of B and Fe particles in a sample annealed at 1300°C for 6 h in flowing Ar gas. This suggests that, after milling, a BN phase may surround the boron nanoparticles as is discussed later.

Heat treatment of the as-milled sample under a nitrogen gas flow induces progress of the nitriding reaction at a temperature of 1000°C or higher. XRD analysis of a sample after heating at 1300°C for 6 h shows a dominant hexagonal BN phase and an iron boride ( $Fe_{2.12}B_{103.36}$ ) phase (Fig. 2b), which suggests nitridation of the residual boron and transformation of the disordered BN phase to a well-ordered hexagonal BN phase, as well as formation of the iron boride during heating. The iron contamination comes from abrasion of the steel ball and the containment cell. The total level of up to 5 wt% Fe has been approximately determined by X-ray energy dispersive spectroscopy in a scanning electron microscope.

No delicate nanotubes are expected in the highly mechanically damaged ball-milled material. However, an interesting morphology is revealed in the



Fig. 2. (a) X-ray diffraction pattern taken from the 150 h milled sample; (b) X-ray diffraction pattern for the 150 h milled sample subsequently annealed at 1300°C for 6 h in N<sub>2</sub>.  $\bigcirc$ , hexagonal BN; +, Fe<sub>2.12</sub>B<sub>103.36</sub>.



Fig. 3. SEM micrograph of the boron sample after 150 h milling and 6 h annealing at  $1300^{\circ}$ C in N<sub>2</sub>.

annealed samples by field emission SEM, as shown in Fig. 3. Fine filaments growing from BN aggregates of small individual and equant particles are observed. TEM reveals that these filaments are hollow with a tubular, multiwalled structure. Fig. 4 shows a typical micrograph from TEM examination of sample after heating at 1300°C for 6 h. The image is a projection through an entire 75 nm diameter BN nanotube. The 10–15 nm thick walls can be seen to



Fig. 4. TEM micrograph taken from the sample following heating at 1300°C for 6 h. The electron diffraction pattern insert is taken from the wall of the nanotube.

the left and right of the image as darker regions where diffraction occurred from BN layers oriented near-parallel to the incident electron beam. The core of the nanotube generally is of lower density (lighter grey in this image) although some higher density cross-cutting structures are also present. The electron diffraction pattern inset represents microdiffraction from one wall of this nanotube showing the characteristic orientation and spacing of basal planes of hexagonal BN. Selected area diffraction reveals that particles in the aggregates also have a hexagonal BN structure, in agreement with the XRD analysis.

The existence in the nanotube walls of a hexagonal BN compound is further confirmed by EELS. The analysis was performed on a portion of a nanotube suspended over a hole in the carbon support film. The EELS spectrum obtained is shown in Fig. 5, and exhibits two distinct K-shell ionisation edges (188 and 401 eV) of boron and nitrogen, respectively. The sharp  $\pi^*$  peak and the shape of  $\sigma^*$ peak are characteristic for hexagonal B–N bonding. The calculated B/N ratio is  $0.96 \pm 0.15$ . A similar composition was found in the particle aggregates from which the nanotubes appear to grow. The composition is uniform throughout the sample with the B/N ratio close to 1.

The number and size of the BN nanotubes depend on both milling and heating conditions. Longer milling time or high milling intensity (higher impact energy), as well as higher  $NH_3$  pressure, lead to a higher N content in the milled sample, and hence to a larger number of BN nanotubes after heat treatment. The size of the nanotubes can be controlled by changing the heating temperature and time. Nan-



Fig. 5. EELS spectrum for the nanotube shown in Fig. 4.

otubes with external diameter from 25 to 50 nm are obtained at 1000°C for about 6 h of heating. Heating at 1300°C for the same duration produces nanotubes with diameters in the range of 50-150 nm.

In terms of the mechanisms of formation of BN during milling and the growth of nanotubes during heating, the following process is tentatively proposed. High-energy ball milling at room temperature produces a chemically activated structure in which the boron particles are reduced in size and nitrogen is adsorbed onto particle surfaces. Although aggregate size is in the micrometer range, small individual particles in the milled B powder are less than 100 nm in size with a high surface area of about 45  $m^2/g$ . Iron particles are dispersed within the boron powder by ball milling and may catalyse the nitriding reaction during milling and subsequent heating [18]. These iron or iron boride particles appear important for the nanotube formation [1,19]. If heated in the presence of nitrogen gas, some nanotubes grow from these particles, as observed in TEM pictures taken of the samples after heating in  $N_2$  gas. In addition, it is also well accepted that ball-milled materials have a high level of microstrain and a high density of structural defects such as grain boundaries. Because of these structural changes and nanostructures produced by high-energy ball milling, the nitriding reaction can proceed at 1000°C under nitrogen flow. Without ball-milling treatment, direct elementary reaction between boron and nitrogen occurs only at a considerably higher temperature (above 1500°C) and under a high pressure (> 2 GPa) [20].

The low temperature formation of BN nanotubes following reactive ball milling is very different from those of other production techniques. In the case of arc discharge, BN nanotubes are probably formed during cooling of the B-N plasma from a temperature of at least 3700°C [1]. Laser heating leads to even higher temperatures of about 5000 K [4]. It is worth mentioning that crystallisation of disordered BN takes place above 2000°C, but the hexagonal BN phase so-formed does not show the tubular microstructure [21]. Also, BN nanotubes were not found in direct reaction of boron induced by laser heating at high temperature and under high nitrogen pressures [20]. These results suggest that BN nanotubes are formed during a non-equilibrium growth process, which clearly needs to be further investigated.

# 4. Conclusions

The reactive ball-milling method for preparing BN nanotubes, as demonstrated in this Letter, provides an alternative formation method which could form the basis of a practical production process with the advantages of low cost and ease of control. Furthermore, the apparent control over the growth of nanotubes during heat treatment, which is affected by ball-milled powders, may provide new information on the mechanisms of their formation.

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