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# Synthesis and state of art characterization of BN bamboo-like nanotubes: Evidence of a root growth mechanism catalyzed by Fe

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#### Abstract

We report the synthesis of bamboo-like BN nanotubes by annealing amorphous BN powders at 1100 °C in an Ar atmosphere. The amorphous powders were obtained after ball-milling h-BN for times longer than 60 h. The materials were characterized using high-resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), elemental mapping, energy dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Based on our observations, we propose a novel root growth mechanism catalyzed by Fe-based alloy nanoparticles that arise from the ball-milling container. © 2005 Elsevier B.V. All rights reserved.

## 1. Introduction

Hexagonal boron nitride (h-BN), considered as a structural analogue of graphite, has motivated the synthesis of curved BN nanostructures using high temperature methods [1]. As a result, intense theoretical and experimental studies on inorganic nanotubes have been triggered due to their unconventional mechanic, electronic and thermal properties [2].

In particular, BN nanotubes become extremely important, because they behave as nano-insulators with extremely high Young's moduli, and photo-luminescent properties [3,4]. BN nanotubes were first synthesized by Chopra et al. [5], using an arc discharge between tungsten electrodes filled with BN powder. Subsequently, this method was modified by Loiseau et al. [6], Terrones et al. [7] and others [8,9]. Nowadays, various techniques have been implemented for producing different types of BN nanotubes. For example, single, double and multi-walled BN nanotubes have been generated using laser ablation [10,11], plasma jets [12], thermal heating [13], carbothermal reduction [14], substitution reactions using carbon nanotubes as templates [15–17], and chemical vapor deposition (CVD) synthesis [18–23].

As an alternative, a low cost route based on ball milling processes in conjunction with a subsequent thermal annealing (at temperatures higher than 1700 °C), has been used to produce BN nanotubes based on boron nitride or boron powders [8,24–29]. A metal tip growth model describing the BN nanotube formation has been proposed by Chadderton and Chen [30]. These authors believed that an iron particle always located at the tip of the growing tube is responsible for the BN nucleation. In this communication, we have carefully characterized BN nanotubes produced by ball-milling/heat-treatment techniques using h-BN powders. We have now used lower annealing temperatures and shorter milling times when compared to previous reports [30]. We characterized our samples using the state-of-art electron microscopy characterization techniques that

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include EELS elemental mappings, HRSEM, EDX spectroscopy and HRTEM. Based on our observations, we propose a novel root growth mechanism that has never been reported hitherto for BN nanotubes obtained by this synthesis method.

# 2. Experimental

Hexagonal BN powder with a purity of 99% was used as the starting material. Four grams of the crystalline material was introduced into a stainless steel vessel as well as four steel balls of different diameter (two of 25.4 mm and the others of 14.7 mm). The vessel was sealed and Ar was introduced in order to avoid oxidation. These BN powders were milled for different periods of time. Subsequently, the milled samples were annealed during 4 h at 1100 °C under a N<sub>2</sub> atmosphere. The milled and milled-annealed samples were characterized by X-ray powder diffraction, scanning electron microscopy (SEM) using a FEI Field Emission XL30 microscope operating at 1–5 kV, and high-resolution transmission electron microscopy (HRTEM) using a JEOL-JEM 4000 EX operating at 400 kV and a Philips CM 200 operating at 200 kV. In order to determine the nitrogen and boron content in our material, the samples were characterized by electron energy loss spectroscopy (EELS) in a Zeiss 912 Omega filter microscope operated at 120 kV and equipped with an EDX detector. Samples for TEM studies were prepared by placing directly the powder material onto a holey carbon TEM grid.

# 3. Results and discussion

Fig. 1a shows XRD patterns corresponding to ballmilled h-BN powders obtained at different milling times. Here, we clearly observe an amorphization process of the material as the time is increased. After 4 h of milling, the damage of the BN crystallites is not considerable and almost all crystalline reflections are present. After 16 h of



Fig. 1. (a) X-ray powder diffraction patterns of ball-milled BN materials obtained before thermal annealing at 1100 °C. The numbers next to each pattern denote the ball milling time used to prepare each sample (4, 16, 32, 60 and 72 h). It is interesting to note that that after 60 h of milling, amorphous material is obtained. (b) and (c) correspond to representative SEM images of ball-milled (amorphous) BN powders obtained after 60 and 72 h, respectively. The size of particle agglomerates exhibit diameters ranging from 100 to 1000 nm.

milling, the reflections corresponding to the (004) plane have disappeared and the reflections corresponding to the (104) and (103) planes became broad. After 32 h of milling, the XRD pattern exhibits the absence of various reflections, thus confirming that the starting crystalline BNphase is transforming into an amorphous material. For 60 and 72 h, the presence of an amorphous material was clear and only two main broad peaks corresponding to the (002) and (100-101) planes were observed. Fig. 1b,c reveal SEM micrographs of powders ball-milled for 60 and 72 h, respectively. These two images show the presence of amorphous-like material consisting of particle aggregates. SEM images and XRD patterns corresponding to 60 and 72 h of milling time, exhibit similar morphologies and crystallinity, thus indicating that 60 h of ball-milling is sufficient for producing amorphous-like BN.

After carrying out thermal treatments of all powders at 1100 °C in a N<sub>2</sub> atmosphere for 4 h, we noted (using XRD) that the material suffered no considerable structural changes, except for the powders milled for 62 and 72 h (not shown here). We clearly observed strong reflections corresponding to h-BN, indicating that the majority of the BN material recovered their original crystallinity. In addition, we observed the presence of Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe peaks that arise as a result of reactions occurring between the milled BN material and the eroded surface residues coming from the steel milling container.

TEM observations of the annealed products (previously milled for 60 and 72 h) exhibit numerous nanotubes with a compartmentalized structure (bamboo-type; Fig. 2). These tubes always contain a metallic particle at one end, whereas the other end is closed and does not include any particle. Thus, the metal particle appears to be responsible for the BN agglomeration and subsequent nanotube growth.



Fig. 2. EDX spectrum of a metal nanoparticle, shown in the TEM image (inset), which is located at the tip of a typical BN bamboo-type nanotube. The tube was grown after annealing amorphous BN powders at 1100 °C for 4 h. Note that the amorphous BN was obtained after 72 h of ball milling. The particle is clearly an alloy formed by Fe (94%), Ni (5%), and Cr (1%). The stoichiometry of this alloy is commensurate with that of the wall-steel container of the ball-milling device. The Cu signal arises from the TEM used to analyze the sample.

EDX spectrum of a metallic nanoparticle located at the tip of a BN bamboo-type nanotube (produced after ballmilling h-BN for 72 h and annealed for 4 h in a N<sub>2</sub>) displayed Fe (94%), Ni (5%) and Cr (1%) (Fig. 2). The presence of this alloy confirms that the catalytic material responsible for the formation of our BN nanotubes, arises from the side wall of the milling container. HRTEM images of the metallic particles generally indicate that they are composed of agglomerated nano-crystals (polycrystalline). Therefore, we could not observe any epitaxial relationship between the crystallographic planes of the Fe particle and the (002) plane of BN (see below).

Fig. 3 shows elemental mapping studies on two different annealed samples that were previously milled for 60 and 72 h. It is clear that the presence of B and N are uniform within each nanotube (Fig. 3b,c,f,g). The presence of Fe was also detected at one end of the nanotubes (Fig. 3d,h). These results are consistent with the XRD patterns of the annealed samples (not shown here), which reveal the presence of Fe (110) reflections.

Fig. 4a depicts a typical EELS spectrum of an individual BN nanotube exhibiting an overall BN stoichiometry. The spectrum displays sharp core-ionization K-edges corresponding to B and N located at 188 and 401 eV, respectively. The adsorption edges of B and N of this EELS spectrum also exhibit the  $1s \rightarrow \pi^*$  (left-hand side peak of the edge) and  $1s \rightarrow \sigma^*$  (right-hand side band of the edge) transition features, implying the existence of a sp<sup>2</sup>-hybridized BN material.

HRTEM images of two different BN bamboo-type nanotubes are depicted in Fig. 4b,d. Fig. 4c,e show closer views of the nanostructures shown in Fig. 4b,d, respectively. In some occasions, the inner layers of the compartments exhibit dangling bonds that result in open BN conical structures (Fig. 4c). It is important to note that diameter of the inner cones are similar to the size of the Fe particle located at the tip of the growing nanotube. From Fig. 4d,e, it is possible to confirm that the catalytic particle is not a homogenous monocrystal but an agglomeration of various Fe nanocrystals which somehow control the diameter of the BN bamboo-type nanotubes during growth. In addition, this figure demonstrates that these metallic particles consist of various crystalline domains oriented in different directions.

In order to understand further the growth of such BN bamboo-shaped nanotubes, we carried out careful SEM studies on the annealed bulk BN powders. In particular, annealed powders that had been previously ball-milled for 60 h are depicted in Fig. 5a,b, whereas SEM images of the powders that had been milled for 72 h prior to thermal annealing are shown in Fig. 5c,d. In all samples, we noted that BN nanotubes were always protruding from the amorphous BN material (indicated by arrows in the figures). White squares point out the opposite ends of the nanotubes that are always free standing. In some SEM images, we could clearly observe an internal stacked-cup or bamboo-type morphology.



Fig. 3. Elemental mapping of two different BN nanotubes obtained using EELS in conjunction with an Omega Filter. The BN nanotubes were obtained after annealing samples for 4 h under  $N_2$ , which were previously milled for 60 h (a–d) and 72 h (e–h). (a) and (e) correspond to the bright field images of the BN nanotubes; (b) and (f) match the boron maps; (c) and (g) the nitrogen maps; (d) and (h) iron maps; and (i) the carbon map corresponding only to the holey carbon TEM. From these mappings, it is clear that the B and N coexist within the same tube region, thus suggesting that they are homogeneously distributed within the nanostructure. Note the absence of carbon within the BN tubes (i).

From our observations, one could easily note that the initial cups (located at the free-standing tips) within the staked cup-like nanotubes have narrower diameter and it starts to enlarge as we approach the base of the fiber where the amorphous BN could be extruded (see figures from EDX analysis and SEM images).

Based on all our observations, we propose a possible root-growth mechanism (see Fig. 5e–k). Soon after ball milling h-BN for 60–72 h, nanoparticles with different crystalline orientations consisting of Fe–Ni–Cr (94–5–1%) arise from the steel milling container, and are evenly distributed within the amorphous milled BN-powder (see Fig. 5e). As the milled products are annealed under Ar, these Fe–Ni–Cr nanoparticles start reacting with amorphous BN, and result in the crystallization of BN layers that adopt the shape of the crystalline particle (see Fig. 5f). Following the formation of successive BN layers, precipitated from the amorphous material, mechanical strains occur within the inner BN cups that result in a sudden sliding of the first BN multi-cup, thus leaving an empty gap behind (Fig. 5g). By repeating the latter process, it is possible to obtain the extrusion of a stacked-cup tubular structure (Fig. 5h). During the tube extrusion process, it is likely that additional Fe-based nanoparticles attach to the main metallic system, thus initiating a coalescence-clustering process (Fig. 5i). At this point, the catalytic particle is increased in size, becomes polycrystalline and results in the precipitation of additional BN multi-cups of larger



Fig. 4. (a) EELS spectrum recorded from on an individual BN nanotube showing edges at ca. 188 and 399 eV, corresponding to the K-shell ionization edges of boron and nitrogen, respectively. Notice that the B and N edges exhibit sharply defined  $\pi^*$  and  $\sigma^*$  fine structural features, which are commensurate with the sp<sup>2</sup> hybridization. (b–e) HRTEM images of a BN nanotube produced by annealing amorphous BN powders that were ball milled for 72 h. The filaments consist of compartmentalized stacked cone structures, roughly aligned along the tube axis, which adopt the alloy particle morphology; (c) an enlargement of (b) (marked inside a white square) exhibits how the BN layers curve and adopt the conical morphology (interlayer spacing 0.33 nm); (d) HRTEM image of a BN nanotube end containing the Fe-based alloy particle; (e) higher magnification of the selected area shown in (d) reveals a polycrystalline particle that strongly suggests the lack of epitaxial correlation between the metal particles and the deposited BN (002) planes. The latter image shows different crystalline orientations of the conglomerated particle (see white parallel lines).

diameter within the growing fiber (Fig. 5j,k). As the polycrystalline Fe–Ni–Cr nanoparticle reaches a specific size, the BN precipitation/crystallization process stops so that the growth of the bamboo-type BN tube is inhibited.

We should point out that Chadderton and Chen [30] proposed a distinct growth model for BN nanotubes via annealing ball-milled powders. The authors propose a catalytic capillarity process that results in the tube epitaxial growth involving preferential planes of Fe and the (002) plane of BN. However, in our Letter, we never observed any epitaxial relationship between the metal particle and the (002) plane of h-BN. We believe that the root growth



Fig. 5. (a–d) SEM images showing BN nanotubes produced after annealing amorphous BN powders obtained from h-BN powders ball-milled for 60 h (a– b) and 72 h (c–d). Note that these fibers are always attached to a lager particle (pointed with white arrows). A TEM image of a typical BN nanotube end is also shown in the inset of (c). Squares denote the thin end of the tubular BN structure. (e–k) Schematic diagram accounting for the BN nanotube growth during the annealing process: (e) small Fe-based alloy nanoparticles are spread in the BN amorphous material after ball-milling; (f) as the temperature is increased, BN material starts migrating and precipitates layers which adopt the shape of small Fe-based alloy nanoparticle; (g) sliding of the first cone shaped cup-like structure occurs due to the strains created inside of cup, thus leaving a gap below the tip; (h) repetition of the precedent process takes place, and agglomeration of additional Fe-based alloy nanoparticles start to attach to the to the previous metal particle; (i) following the coalescence of various metallic particles, the seeding particle increases in size, and results in an enlargement of the precipitated BN cups; (j) the metal agglomeration process continues, as well as the sliding of the cups, thus resulting in the nanotube growth; (k) the Fe-based particle reaches a critical size that inhibits the formation of additional BN layers, and the growth process is interrupted.

mechanism could be considered as a general formation scenario when using the ball-milling/thermal-annealing technique, even if the milling times and annealing temperatures are increased. However a careful study, using SEM, TEM and allied techniques, on the materials produced previously by other authors should be carried out.

## 4. Conclusions

In summary, we have reported the production of BN nanotubes by a ball-milling-annealing method. Using state-of-the-art characterization techniques, we proposed a novel growth mechanism accounting for the formation of BN nanotubes. This mechanism is based on the agglomeration, crystallization and precipitation of BN material around Fe-based alloyed nanoparticles arising from the ball-milling container. A sliding mechanism of the growing BN cups is responsible for the formation of the bamboo-shaped tubes. Our results are able to explain the presence of free-standing tube ends observed in our BN tubes (thin tails and thick heads). The information presented in this Letter adds new insights into the growth of BN nanotubes that could result in the preparation of larger amounts of this material for industrial applications.

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