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Boron nitride nanotube growth via boron oxide-assisted chemical vapor transport-deposition process using LiNO₃ as a promoter

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TABLE OF CONTENTS (TOC)

BoronNitrideNanotubeGrowthviaBoronOxide-AssistedChemicalVaporTransport-DepositionProcessUsingLiNO3 as aPromoter

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High purity straight and discrete multiwalled boron nitride nanotubes (BNNTs) were grown via a boron oxide vapor reaction with ammonia using LiNO₃ as a promoter. BNNTs with an average diameter of 30-50 nm and length above 50 μ m were mostly observed in a temperature range of 1280 -1320 °C.



Boron Nitride Nanotube Growth via Boron Oxide-Assisted Chemical Vapor Transport-Deposition Process Using LiNO₃ as a Promoter

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ABSTRACT

High purity straight and discrete multiwalled boron nitride nanotubes (BNNTs) were grown via a boron oxide vapor reaction with ammonia using LiNO₃ as a promoter. Only a trace amount of boron oxide was detected as an impurity in the BNNTs by energy-dispersive X-ray (EDX) and Raman spectroscopies. Boron oxide vapor was generated from a mixture of B, FeO, and MgO powders heated up to 1150°C and transported to a reaction zone by flowing ammonia. Lithium nitrate was pasted on the upper side of a BN bar from a water solution. The bar was placed along a temperature gradient zone in a horizontal tubular furnace. BNNTs with an average diameter of 30-50 nm were mostly observed in a temperature range of 1280-1320°C. At higher temperatures curled polycrystalline BN-fibers appeared. The amount of BNNTs drastically decreased whereas quantity and diameter of the fibers increased above 1320°C. The mechanism of BNNTs and fibers growth is proposed and discussed.

1 Introduction

Historically, boron nitride nanotubes (BNNTs) are well known rivals of popular carbon nanotubes (CNTs). Both tube types possess hexagonal honeycomb-like shells where alternating boron and nitrogen, or carbon atoms are assembled while revealing pure sp² type hybridization. CNTs have evidenced many potential applications ranging from nanoelectronic devices to reinforcing agents in polymers, ceramics or lightweight metals. Opposed to CNTs, which are metals or semiconductors depending on the type of graphene-like sheet wrapping along the tube axes, BNNTs always exhibit stable electrically insulating properties independent

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of morphologies and atomic structures [1]. In addition, these tubes are much more thermally and chemically stable compared to CNTs, while withstanding heating in air up to 900-1000°C. Similarly to CNTs, BNNTs demonstrate an ultimate tensile strength exceeding 30 GPa [2], huge values of vield stress (~1 TPa) [3], Young's modulus (1 TPa) [4], electrical resistance (~1 G Ω) [5], and thermal conductivity [6], i.e. all properties which look very attractive for many mechanical and functional applications. The bottleneck of BNNTs is their production technologies and the product yield. Many useful methods found appropriate for the CNTs synthesis do not properly work for BNNTs. In view of these arguments, a search of the new effective synthetic techniques for their fabrication is still a challenge.

To date, BNNTs have been synthesized via a number of various methods such as arc discharge [1], chemical vapor deposition (CVD) [7-10], laser ablation [11, 12], ball milling [13], extended-pressure inductively-coupled thermal plasma sintering (EPIC process) [14], self-propagation and post-annealing process [15]. These methods differ in yield and morphology of BNNTs. Most remarkable harvest of BNNTs was achieved in the EPIC process [14] and the annealing process of boron containing precursor [15]. The EPIC process produces a fibrous, cotton-candy web-like BN-material, which may find applications in the fields of filtration, adsorption, heat and chemical protection, but such material morphology may hardly be used as a reinforcing element for composites because of interconnection and irregular bundling of debris-like BNNTs. The boron precursor post-annealing process yields BNNTs of four types, i.e. wave-like, bamboo-like, bubble-chain and cylinder-like tubes with curved and curled morphology [15]. Although these BNNTs appear as individual structures having no interconnections (that is highly desired for the their application composite production), for reinforcement of metallic or polymer matrixes is rather questionable because of their structural imperfectness negatively affecting mechanical properties. During the boron oxide-assisted CVD straight process [10] and discrete **BNNTs** demonstrating an ultimate tensile strength of ~30 GPa can be grown [2]. Unfortunately this method

allows production of perfect BNNTs only in a gram-level amount. Increased yield of BNNTs in any process would be possible through detailed understanding of the growth mechanism and factors influencing the process kinetics. Usage of Li2O for the generation of a boron oxide vapor in the CVD process facilitated decreased BNNT diameters and increasing their yields [16]. It was proposed that BNNTs growth had occurred through redox reactions between Li₂O and B in different temperature zones of a CVD reactor in the presence of ammonia. In one temperature zone Li₂O oxidizes B, producing boron oxide vapor and lithium, which evaporates. Then in another temperature zone this reaction goes in reverse direction and lithium reduces boron oxide yielding active elemental boron reacting with ammonia and thus generating BNNTs [16].

Addition of lithium compounds such as LiOH, Li₂CO₃, and LiCl was demonstrated to enhance the yield, crystal size, and crystallinity of hexagonal BN during carbothermal synthesis [17]. It was suggested that lithium entering into the BN lattice had intensified reaction between layers promoting their ordering [17]. Since BNNTs have a hexagonal crystal structure it is reasonable to expect a positive effect of lithium compounds on the BNNTs growth process.

In the present study, the influence of LiNO₃ on the nucleation and growth of BNNTs during boron oxide-assisted CVD process was studied in detail.

2 Experimental

2.1 Experimental set-up

CVD synthesis of BNNTs using boron oxide vapor and flowing ammonia was realized in a horizontal tubular reactor. A schematic experimental set-up is shown in Fig. 1. The reactor consisted of an alumina tube with an inner diameter of 56 mm, equipped with water cooled tight flanges with inlet and outlet for the flowing ammonia gas. Temperature profiles along the reactor for set temperatures in a range of 1200-1400°C were measured using an additional external thermocouple before performing the regarded experiments.



Figure 1. A schematic view of an experimental set-up with a temperature profile outline inside the reactor.

2.2 Materials

Ammonia of 99.98% purity was used. A boron oxide vapor as a boron source for the CVD process was generated from a powdered mixture of B, FeO, and MgO upon its heating. The mixture was taken in a molar ratio of B:FeO:MgO = 3:1:0.2. Amorphous B of >99% purity and FeO of a chemical grade were utilized. Magnesia was obtained by calcination of a chemical grade Mg(OH)₂ powder at 500°C in air for 5 h. The mixture was grinded in a mechanical alumina mortar for 2 h; after this it was placed in an alumina boat in a reactor zone reaching 900-1150°C, when a set temperature of the reactor (T_{set}) 1400°C was fixed. LiNO₃x3H₂O of a chemical grade was used. 100 mg of LiNO3x3H2O were dissolved in 20 ml of distilled water; after this 200 µl of the solution were uniformly dripped onto one long (upper) face of a BN bar. The BN bar of 1.5x1.5x10 cm³ dimensions was machined from a hot pressed bulk BN. High water solubility of lithium nitrate ensures its smooth and homogeneous distribution along the BN face. The BN bar was then placed in the reactor in a temperature gradient zone of 1200-1360°C for Tset=1400°C. The reactor was evacuated up to 10⁻² mbar while heating to 400°C,

then ammonia was introduced into it and at 1 bar of ammonia pressure its flow of 100 cm³/min was maintained. The reactor was further heated up to a set temperature of 1400°C with a ramp of 275°C/h, kept at this temperature for 1 h and finally cooled down to room temperature naturally.

2.3 Characterization

The morphology of synthesized products was studied using a scanning electron microscope Jeol JSM-7600F. Transmission electron microscopy (TEM) including high resolution (HRTEM) and selected-area electron were diffraction (SAED) carried out using a Tecnay G2 30 UT microscope operated at 300 kV and having 0.17 nm point resolution. High resolution high angle annular dark field scanning TEM (HAADF-STEM) imaging and elemental mapping were performed on a JEM ARM-200F cold FEG double aberration corrected microscope operated at 200 kV and equipped with a solid-angle CENTURIO EDX detector. large Chemical and phase composition were analyzed by energy-dispersive X-ray (EDX) spectroscopy (using 80 mm² X-Max EDX detector (Oxford Instruments)), confocal Raman spectroscopy (using a NT-MDT NTEGRA Spectra instrument with an excitation wavelength of 473 nm) and X-ray diffraction analysis (using X-ray diffractometer Difrei-401 equipped with a coordinated CCD detector and operating with Cr K α radiation).

3 Results and discussion

After the experiments, a snow-white film was found

on the BN bar face treated with the lithium nitrate water solution (Fig. 2). The film was observed only in a temperature range of approximately 1280-1350°C. The probes of the synthesized material were taken from different temperature zones without any additional thermal or chemical treatments. SEM analysis revealed dramatic changes in the morphology of the formed material depending on the synthesis temperature (Fig. 2).



Figure 2. SEM images of a deposit from corresponding temperature zones. Optical image of the BN bar after exposure to a boron oxide vapor in a temperature gradient zone (as shown on the lower panel). A white deposit is seen on the BN face where LiNO₃·3H₂O was applied.

In the temperature range between 1280 and 1320°C

the material mainly consisted of discrete, long, thin,

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and straight nanotubes with an average diameter of 40-50 nm (Figs. 2, 3), whereas at higher temperatures thick curved fibers were observed (Fig. 2). Length of both the nanotubes and the fibers was at least 50 μ m. EDX analysis performed in the entire area of the SEM image in Fig. 3(a) shows almost stoichiometric BN composition. C and O are apparently from a carbon scotch tape used for fixing the sample to the holder. Trace amounts of Mg and Si are coming from a binder of the BN bar, also some Mg may come from the B:Fe:MgO mixture. Elemental mapping of the individual nanotubes presented in Fig. 3(b) also reveals spatially-matched coexistence of boron and nitrogen species within the nanotubes.

TEM images and corresponding SAED patterns of the BNNTs obtained from the temperature zone of 1280-1320°C are shown in Fig. 4. SAED ring pattern (the inset in Fig. 4(a)) can be indexed as a hexagonal BN structure. SAED pattern taken from a single multiwalled BNNT (the inset in Fig. 4(c)) basically evidences a preferential armchair type of the BN nanotube shells with a marked splitting of basic reflections due to a slight mismatch between the front and back tube wall portion orientations with respect to the incident electron beam. HRTEM image of the BNNT along nanotube axis (Fig. 4(c)) shows good crystallinity of all walls free of any defects. All nanotubes are long, straight, of good crystal quality, exhibiting almost uniform wall thickness of around 15 nm, and inner diameter in the range of 10-20 nm.

Different contrast intensities on various sides of the tube in Fig. 4(c) implies a characteristic polygonal cross-section of the nanostructure, rather than cylinder-like. Such peculiar feature of BNNT was well established in the previous HRTEM studies [18] and goes well along with the partially ionic-like character of BNNT (giving rise to insurmountable B-N-B-N stacking across the tube) compared to purely covalent bonding in standard CNTs which are typically cylindrical in cross-section.



Figure 3. SEM images of a deposit from the temperature zone of 1280-1320°C at different magnifications (the upper panel). EDX analysis and element mapping of the nanotubes from the same temperature zone (the lower panel). The EDX spectrum was taken from the entire area of the image (a).

X-ray analysis revealed a hexagonal phase with crystal lattice parameters of a= 2.50 Å and c= 6.69 Å,

which fit very well those of the standard BN nanotubes [19]. Small peak marked with an asterisk



Figure 4. (a) Low and (b) middle magnification bright field TEM images of the BNNTs collected from the temperature zone of 1280-1320°C and corresponding ring ED pattern given as an inset. (c) HRTEM image of a single multiwalled BN nanotube. The inset shows a typical SAED pattern of preferentially armchair BN nanotube shells revealing a marked splitting of the basic reflections due to a rotational mismatch between front and back nanotube portions with respect to the incident electron beam.

The quality of BNNTs was analyzed by Raman spectroscopy (Fig. 6). The sharp peak at 1365 cm⁻¹ can be assigned to the E_{2g} mode of the h-BN. FWHM of this band is about 21 cm⁻¹ being slightly wider compared with that of BNNTs synthesized at 1600°C [20], but narrower than the FWHM reported for BNNTs synthesized at 1000-1200°C [21]. It is well known that narrowing of the Raman peak with an increase in the synthesis temperature is due to the reduction of defects concentration caused by annealing. A broad and weak band observed at ~800

cm⁻¹ corresponds to traces of B₂O₃. Thus, the Raman data confirmed decent crystal quality of the synthesized BN product.



Figure 5. X-ray diffraction pattern of a deposit collected from the temperature zone of $1280-1320^{\circ}$ C. Indexes correspond to a hexagonal BN phase (Cr K α radiation was used).

The presented data provides evidence that in the temperature range of 1280-1320°C almost pure BNNTs have been grown on the BN bar face coated with LiNO₃. The nanotubes appeared as discrete and straight structures with a uniform external diameter of 40-50 nm and an inner channel of 10-20 nm. In the higher temperature zone, the amount of straight BNNTs decreased, while curved and thicker BN fibers appeared.



Figure 6. Raman spectrum of a deposit collected from the temperature zone of 1280-1320 °C.

Above 1345°C, only individual BNNTs were observed in a dominating mixture of curled BN fibers

of various diameters, up to ~1 µm (Fig. 7(a)). SEM analysis and ED studies of the fibers showed that they are polycrystalline in nature and consist of numerous faceted and well accreted BN single crystals (Fig. 7(b)). EDX analysis confirmed that the fibers consist of boron and nitrogen with a small amount of Mg and Si, apparently coming from a BN bar binder and from the B:MgO:FeO mixture generating a boron oxide vapor (Fig. 7(c)). HAADF-STEM images and elemental mapping of a single fiber grown in the temperature zone of ~1320-1340°C revealed that it consists of BN with Mg-Si-O inclusions dispersed irregularly in the fiber manifesting inner channel otherwise unobservable by SEM and TEM in the silicate free fibers because of their big thickness.



Figure 7. (a) SEM image of the fibers grown above 1345° C; (b) the enlarged SEM image of an individual thick BN fiber; (c) the EDX spectrum taken from the entire area of the image (a); (d) HAADF- STEM image and element mapping (e-j) of a thin fiber grown in the temperature zone of $1320-1340^{\circ}$ C. Notice bright contrast filled channel in HAADF –STEM image in (d) marked by white arrows.

Diameter of the channel estimated from a size of the

7

magnesia silicate particles is approximately 30 nm.

In discussing the results several important facts should be mentioned: (i) The growth of BNNTs occurred only on the BN surface coated with LiNO₃; (ii) BNNTs were observed to grow numerously in a very narrow temperature range between 1280°C and 1320°C; (iii) At higher temperatures, curled polycrystalline BN-fibers appeared along with the BNNTs; (iv) The fibers had an inner channel; (v) Diameter of the fibers and their quantity increased, whereas amount of BNNTs decreased above 1320°C.

There are two general growth processes of nanotubes: from their tips and from their roots. The former process is usually associated with a vapor-liquid-solid (VLS) growth mode. The VLS mode was proposed for the growth of BNNTs produced along with the boron oxide-assisted CVD process [22]. It was suggested that FeO and MgO had served as the catalysts for the formation of BN from a reaction of B_xO_y vapor with NH₃ gas. The regarded mechanism was described as follows. During the reaction within the precursor (B-FeO-MgO) powder the growth vapors containing both BN and catalyst species are generated. When the vapor pressure is sufficient, the catalyst vapors condense into liquid (or partially melted) particles. The BN species dissolve into the catalyst, cause supersaturation and lead to the precipitation of BNNTs, which diameter depends on the sizes of these catalyst particles and the partial pressure of BN growth species [22]. Thus a peculiar feature of the VLS process is the presence of catalyst particles on the tip of grown nanotubes. Since in our case we do not observe any particles terminating the BNNTs, we assume that their growth was realized via the root process, which briefly can be described as follows: after the nucleation stage the BNNT growth occurred via incorporation of B, N, or BN species into the nanotube base lifting it from a nucleation site; structural species (B, N, or BN) came from a vapor phase or from a liquid. The nucleus size determined the nanotube diameter.

Numerous well faceted and densely associated BN crystals composing the fiber (Fig. 7(b)) indicate that they were grown via crystallization from a melt-solution rather than through condensation from a vapor phase. We suppose that the melt appeared as a result of the reaction of LiNO₃ with the BN bar in the ammonia gas atmosphere. Though the reaction of

h-BN with a related compound, NaNO3, has been well known [23], nevertheless, we checked the possibility of formation of lithium borate upon heating of hexagonal BN with LiNO3 in ammonia. For this purpose a mixture of h-BN powder (1 g) with LiNO3·3H2O (1 g) was heated in a flowing ammonia at 850°C for 3 h. XRD of the quenched product revealed the existence of a Li₄B₂O₅ phase along with h-BN. Thus at high temperatures a lithium borate melt exists and its composition depends on temperature. Since the amount of the applied LiNO3 onto the BN bar was a fairly small and the BN bar had some porosity, the lithium borate melt appeared in tiny droplets but not as a continuous layer. Crystallization and growth of the BNNTs occurred from these droplets and each droplet served as the growth site for one nanotube (Fig. 8(a)). Taking into account the existence of the channels in the fibers we concluded that their growth was associated with the BNNTs. In this regard two possible scenarios could be proposed to explain formation of the hollow polycrystalline fibers: (i) the fibers appeared as a result of crystallization of the melt which had wetted the previously grown BNNTs. It is a three stage process: first BNNTs were grown, then, with increasing temperature the amount of the melt increased and it wetted the nanotubes due to capillary forces, and eventually a layer of the melt crystallized (Fig. 8(b)); (ii) the fibers appeared as a result of simultaneous growth of the BNNTs and BN crystals on the surface of growing nanotubes. This is a single stage process - the growth of a BNNT initiated crystallization of BN crystals on its surface. The BNNT covered with BN crystals moves out from the liquid and new BN crystals nucleate at the liquid/gas interface (Fig. 8(c)). In the latter scenario a denser polycrystalline somewhat BN layer is expected compared with а spontaneously crystallized liquid film in the former scenario. Also in a favor of the latter scenario is the fact that we did not observe the BNNTs partially covered with a polycrystalline BN shell, what would be expected for the former scenario. Fiber bending occurred because of intergranular stress arisen during simultaneous BN crystal growth. With increasing temperature the BNNTs' diameter increased, and also the droplets served as the growth sites spread out on the BN bar because of enhancement in their wettability, leading

to the increase in fiber diameters on heating.

Small amount of the liquid appeared after reaction of lithium nitrate and the BN substrate and correspondingly small amount of boron oxide dissolved in it is insufficient for the growth of long fibers and even for long BNNTs. Apparently, boron oxide depletion in the liquid is continuously replenished from the boron oxide vapor produced by the (B-FeO-MgO) mixture. Thus it appears that the lithium borate liquid acts as a promoter for the BN crystallization in the present boron oxide-assisted CVD transport process. It should be noted that in a test experiment when a boric acid was used instead of lithium borate, the BN formation went very slow denoting a crucial role of lithium oxide. Therefore we could conclude that lithium oxide dissolved in a boron oxide melt promotes BN formation during a reaction of boron oxide with ammonia. The underlying catalytic mechanism may be related to alteration of a borate liquid network structure, depending on concentration of lithium [24, 25]. This is an issue for the on-going study.

For deeper understanding of the BNNTs growth mechanism it is important to get insight into the nature of nuclei for BNNTs and BN crystals. Are they of the same origin or not? Whereas each BNNT was nucleated and grown as a single crystal from one nucleus, the nuclei of the BN crystals constantly appeared. This implies that nuclei initiated the growth of BNNTs have a longer lifetime in the liquid compared to the nuclei initiated the growth of BN crystals. This difference highlights a different nature of the BNNTs' and the BN crystals' nuclei. For the sake of clarity, in the following-up discussion we, however, will neglect this difference.

Reaction of alkaline-earth borate melts with nitrogen ions dissolved in the melt was suggested to explain a catalytic effect of the borates during the carbothermal synthesis of hexagonal BN [28-30]. The former model assumes that the lithium borate melt has appeared during the reaction of lithium nitrate with the BN bar, then dissolved boron nitride, and as a result, some (n·Li₂O + m·B₂O₃ + q·BN) liquid emerged. It should be noted that the formation of BN solution in molten lithium borate during the reaction of turbostratic BN with lithium carbonate was previously analyzed [31].



Figure 8. Schematic model for the nucleation and growth of BNNTs (a) and a hollow polycrystalline BN fiber (b, c) from (Li-B-N-O) liquid droplets on the BN bar substrate at various temperatures. (b) The first scenario of a fiber growth: wetting of the previously grown BNNT with the liquid; crystallization of the liquid. (c) The second scenario of a fiber growth: growth of the BNNT initiates nucleation and growth of the BN crystals. The size of the liquid droplets acting as the growth sites increases with temperature due to increase in their wettability (T1<T2).

The nucleation of BN structures started from the BN solution in a borate when BN oversaturation in the liquid had been reached. The oversaturation may arise as a result of the following processes: (i) evaporation of the lithium borate melt; and (ii) decreasing in BN solubility caused by a change in liquid composition, which may happen due to evaporation of lithium oxide, absorption of boron oxide vapor, or dissolution of ammonia (nitrogen) in the liquid. Solubility of h-BN in B2O3 bearing melts has been studied in a temperature range of 1273-1823 K [27]. It was shown that BN solubility in the melts has a maximum when the mole fraction of basic oxides, in particular Li₂O, is around 0.1-0.2. Deviation of Li₂O content from this value leads to a decline in BN solubility. Under conditions of our

experiments, composition of BN bearing liquid may change due to evaporation of Li₂O from the liquid during heating or due to absorbance of a boron oxide vapor when it arises from the (B-FeO-MgO) mixture. Dissolution of nitrogen in the lithium borate melt discussed above may affect the solubility of BN as well. At this stage it is not clear which model holds. Nevertheless we can certainly conclude that lithium borate-based melt promotes the growth of both BNNTs and polycrystalline BN fibers. Morphology of the growing BN structures is governed by the liquid composition, which in turn depends on the temperature. LiNO₃ on the surface of a BN substrate remarkably affected the growth of BNNTs in a boron-oxide CVD transport process. Lithium borate-based melt, formed during the reaction of LiNO₃ with the substrate in ammonia, promoted the synthesis of BN structures. The BN synthesis process depends on the melt composition. Its composition varied with temperature and affected the morphology of the growing BN structures. Straight and discrete multiwalled BNNTs formed in the temperature range of 1280-1320°C, above which the growth of thick polycrystalline BN fibers was dominant.

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