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Boron nitride nanotubes: Pronounced resistance to oxidation

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Boron nitride (BN) nanotubes have the same nanostructure as carbon nanotubes but are found to exhibit significant resistance to oxidation at high temperatures. Our systematic study has revealed that BN nanotubes are stable at 700 °C in air and that some thin nanotubes (diameter less than 20 nm) with perfect multiwalled cylindrical structure can survive up to 900 °C. Thermogravimetric analysis reveals an onset temperature for oxidation of BN nanotubes of 800 °C compared with only 400 °C for carbon nanotubes under the same conditions. This more pronounced resistance of BN nanotubes to oxidation is inherited from the hexagonal BN and also depends on the nanocrystalline structure. This high level of resistance to oxidation allows promising BN nanotube applications at high temperatures. © 2004 American Institute of Physics. [DOI: 10.1063/1.1667278]

Carbon nanotubes, nanometer-sized cylinders of graphitic sheets, have many properties that are superior to those of graphite. An exception is the weak resistance of carbon nanotubes to oxidation.¹ This is mainly due to their large surface area and defects (pentagons) at tips. Carbon nanotubes readily oxidize in air (400 °C)^{2,3} and burn completely at 700 °C when sufficient oxygen is supplied, thus limiting their applications at high temperatures. Boron nitride (BN) nanotubes have the same nanostructures as C nanotubes^{4,5} and exhibit many similar properties such as a high Young's modulus.⁶ Recently, Han *et al.*⁷ transformed BCN nanotubes to BN nanotubes by heating in oxygen atmosphere; this suggests that BN nanotubes may be more stable than carbon nanotubes at high temperatures. Here we report the findings of a systematic study of oxidizing pure boron nitride nanotubes of different nanostructures in air by both isothermal annealing and thermogravimetric analysis. Compared with multiwalled C nanotubes, the results demonstrate a more pronounced resistance to oxidation for boron nitride nanotubes; this may allow BN nanotubes to replace carbon nanotubes for high temperature applications.

The oxidation of BN nanotubes was first conducted by heating in a tube furnace in an atmosphere of air. The BN nanotube samples were prepared using the mechano-thermal process in which boron powders were first mechanically milled in ammonia gas at room temperature and subsequently heated at 1200 °C for 6 h in nitrogen atmosphere.^{8,9} Transmission electron microscopy (TEM) with a Philips CM300 instrument revealed that the nanotube yield is about

70% and the rest is nanosized BN particles. About 40% of the nanotubes observed have an outer diameter less than 20 nm and about 60% are coarse nanotubes of diameter between 20 and 200 nm. Most nanotubes have the typical cylindrical structures, but some coarse nanotubes (about 20%) have bamboo-like or cone shaped structures.^{9–11} Electron energy-loss spectroscopy (EELS) analysis, which was attached to a VG601UX field emission electron microscope, confirmed the complete nitridation of B with an average B/N ratio of 1.0. Pure B particle was not detected. Both C and O contents are less than 0.1 at. %. The sample also contains about 10.5 wt % of Fe catalysts that initially came from the milling apparatus.⁶ 200 mg of the BN nanotube sample was loaded in an open-end ceramic tube with a large diameter of 50 mm so that sufficient oxygen was available for oxidation, and then the furnace was heated from the ambient temperature up to 700 °C with a slow rate of 10 °C/min and held for 2 h before cooling down. TEM examination of the heated samples revealed that the BN nanotubes were stable after heating to 700 °C. The TEM micrograph in Fig. 1 shows three different nanotubes. Nanotubes 1 and 2 have large diameters of 38 and 52 nm, respectively, and typical cone-like structures. The high-magnification image (insert 1) taken from nanotube 1 shows partial cone-shaped atomic layers ending on the wall of the nanotube. Nanotube 3 has a small diameter of 8 nm. The multiwalled cylindrical structure of nanotube 3 is demonstrated by the presence of fringes on the high-magnification image (insert 3). Disordered coating materials are observed on the external surface of tube 3. EELS reveals that the coating is most likely to be boron oxide as one of the end products of BN oxidation. After heating to 900 °C in air, severe damage was observed to the coarse nanotubes but not to the thin nanotubes. The TEM image in Fig. 2(a) shows a coarse tube with broken walls and an open

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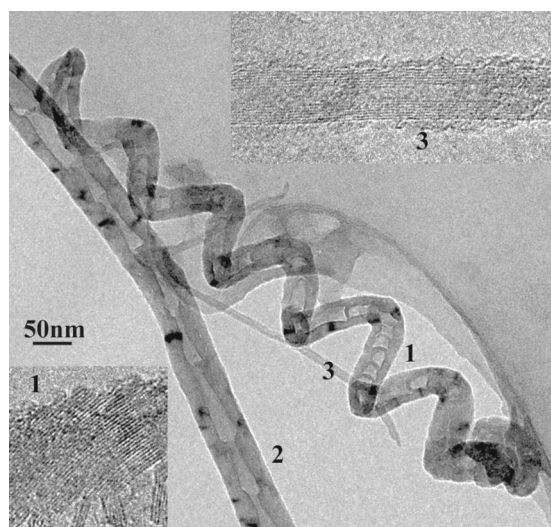


FIG. 1. TEM micrograph of BN nanotubes heated at 700 °C for 2 h in air. The insert image 1 (lower left) is a high magnification image taken from nanotube 1 and shows partial cone-like structures. The insert image 3 (upper right) was taken from nanotube 3 and shows a multiwalled cylindrical structure.

end, while the two thin nanotubes in Fig. 2(b) still maintain multiwalled structures. Some of them lose their capes. These results clearly demonstrate the dependence of oxidation of BN nanotubes on their nanostructures.

Thermogravimetric analysis (TGA) using a Shimadzu 50 instrument revealed that BN nanotubes have a stronger resistance to oxidation compared with carbon nanotubes. BN nanotube samples were heated up to 1200 °C at a rate of 20 °C/min under an air flow of 10 ml min⁻¹. The change in sample weight as a function of temperature is shown in Fig. 3(a). A sharp weight increase (12.5 wt %) occurred from 800 °C as a result of BN oxidation and formation of B₂O₃ was detected by EELS. The weight loss (8 wt %) observed at the beginning of the heating (<200 °C) is caused by vaporization of moisture and desorption of gases as reported by several authors.^{12,13} Indeed, the same weight loss was also found on heating in Ar gas. The slight weight increase of 1.9 wt % in the intermediate temperature range (500–800 °C) was mainly induced by oxidation of some iron (or steel) particles, resulting in the formation of Fe₂O₃. The presence

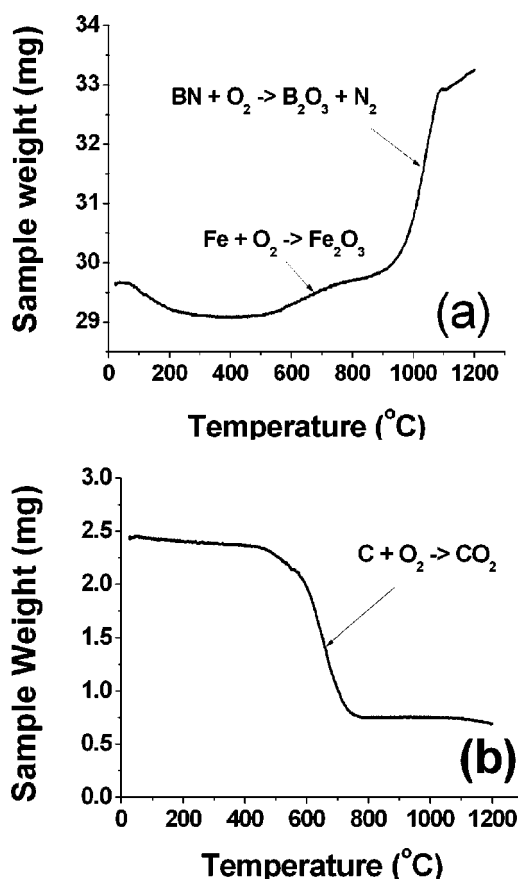


FIG. 3. Weight changes of (a) BN and (b) C nanotube samples vs temperature during heating in TGA at 20 °C min⁻¹ in an air flow of 10 cm³ min⁻¹.

of iron in the BN nanotube sample before oxidation and the formation of iron oxides after the treatment were confirmed by both x-ray diffraction (XRD) analysis (Fig. 4) and Mössbauer spectroscopy.¹⁴ For comparison, hexagonal BN powder of particle sizes in the micrometer range was also analyzed with significant weight increase found to take place above 1100 °C and weight loss of 10.2% recorded up to 1200 °C. Multiwalled carbon nanotubes prepared by chemical vapor deposition methods were also analyzed under the same conditions with the weight loss during heating shown in Fig. 3(b). It is clear from the rapid weight loss that oxidation starts at 400 °C and is complete at 700 °C. Compared with carbon nanotubes, BN nanotubes have stronger resistance to oxidation at high temperatures.

The oxidation process was investigated using XRD on samples before and after oxidation. The XRD spectra in Fig. 4(a) show that the BN nanotube sample has dominant hexagonal BN structure and some Fe, pure B was not found. The XRD spectra of the sample oxidized at 700 °C are shown in Fig. 4(b). The pronounced BN diffraction peak indicates that most BN phase is still stable, although oxidation starts as suggested by the newly formed B₂O₃. The low diffraction intensity of the BN peaks in the XRD spectra shown in Fig. 4(c) suggests that significant amount of BN was oxidized at 900 °C. These results are consistent with the TEM observation. The XRD spectra also clearly show the Fe oxidation.

Hexagonal boron nitride compounds have better resistance to oxidation than graphite. As a result boron nitride layers have been used to increase resistance to oxidation of

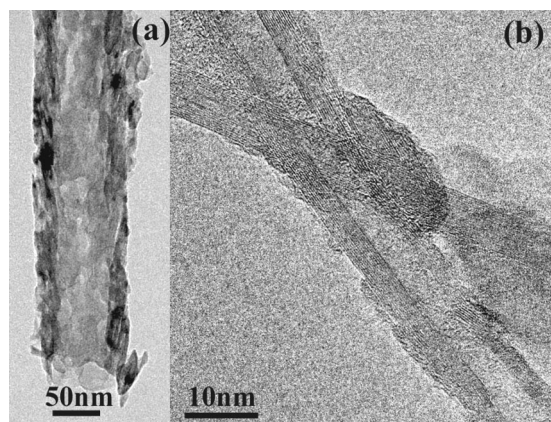


FIG. 2. TEM micrograph of BN nanotubes heated in air in a tube furnace up to 900 °C at a rate of 10 °C min⁻¹: (a) a coarse nanotube; (b) two thin nanotubes.

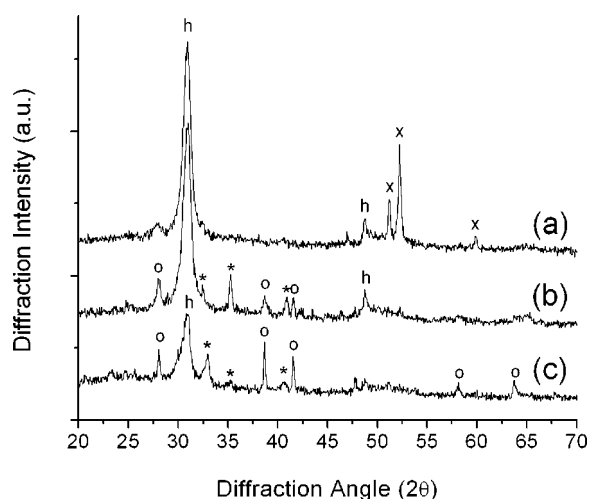


FIG. 4. X-ray diffraction spectra of BN nanotubes (a) before oxidation; (b) after heating to 700 °C in air; (c) after heating to 900 °C in air. h: hex-BN; x: Fe(steel); o: Fe_2O_3 ; *: B_2O_3 .

carbon fibers.¹⁵ BN nanotubes appear to inherit this property although their nanometer size and large number of structural defects (pentagons) make BN nanotubes less resistant to oxidation than hexagonal BN that oxidizes above 1100 °C.¹⁶ The TGA curves in Fig. 3 show that, under the conditions used, the onset temperature of oxidation for BN nanotubes is around 800 °C compared with only 400 °C for carbon nanotubes. These results are in agreement with the oxidation temperature of the BN nanotubes purified from BCN composite nanotubes.⁷ BN nanotubes in different structures and sizes are stable at 700 °C in air while carbon nanotubes burn off completely under the same condition. The sample weight increase induced by oxidation of BN nanotubes or particles is around 12%, which is significantly lower than the value expected from the oxidation reaction: $4\text{BN} + 3\text{O}_2 \rightarrow 2\text{B}_2\text{O}_3 + 2\text{N}_2$. TEM observation and XRD analysis [low intensity of B_2O_3 peaks in Figs. 4(b) and 4(c)] suggest that B_2O_3 is most likely released as vapor from the sample at high temperature range.

TEM reveals similar oxidation mechanisms for both BN and C nanotubes. For thin BN nanotubes with well-crystallized structures, oxidation starts from the tip (and possibly the outer layers) in agreement with the observation by Han *et al.*,⁷ who found reduced nanotube layers after an oxidation treatment. Although a B_2O_3 layer was formed on the external surface of BN nanotubes (Fig. 2), this oxide layer is not expected to slow down the oxidation processes as it does not form a homogeneous coating over the whole external

surfaces. In the case of coarse nanotubes, oxidation appears to progress from the tips and also along the broken atomic planes on the walls—the newly formed oxides fall off the tubes, resulting in many holes (or windows) on the walls. Clearly, structural defects (such as pentagons and dislocations) are critical to the resistance to oxidation. As a result, coarse tubes especially those with bamboo and cone-like structures have lower resistance to oxidation than thin cylindrical tubes.

We have demonstrated clearly that BN nanotubes have a stronger resistance to oxidation compared with carbon nanotubes. Most BN nanotubes are stable up to 700 °C in air and thin nanotubes with perfect cylindrical structures can survive up to 900 °C. Owing to their strong stability at high temperature in air, BN nanotubes are better candidates for composite materials, for example, ceramic/polymer-nanotube composite, designed for high temperature applications.

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