

Effect of Ambient Gas and Temperature on Crystallization of Boron Nitride Spheres Prepared by Vapor Phase Pyrolysis of Ammonia Borane

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Synthesis of boron nitride spheres (BNS) was achieved by vapor phase pyrolysis of ammonia borane (BH_3NH_3) using two independently temperature-controlled furnaces in a glove box filled with N_2 . The BNS were heated at $1300^\circ\text{--}1700^\circ\text{C}$ in flowing NH_3 , N_2 , or Ar by multistep heat treatment. The sizes of the BNS could be controlled by heating BH_3NH_3 at different rates ($1^\circ\text{C}/\text{min}$: 300–800 nm, $5^\circ\text{C}/\text{min}$: 300 nm–1.2 μm and $10^\circ\text{C}/\text{min}$: 300 nm–1.8 μm). The microstructures of BNS heated in different ambient gases were observed using transmission electron microscopy with selected area electron diffraction. NH_3 gas produced BNS with well-crystallized surface shells and amorphous cores whereas N_2 and Ar gases crystallized the entire BNS. It is evident that of these three ambient gases (NH_3 , N_2 , and Ar), N_2 gas significantly enhances the crystallization of BN with randomly oriented grains.

I. Introduction

HEXAGONAL boron nitride (h-BN) with a graphite-like structure is an interesting and significant material with many unique properties, such as a low dielectric constant, high thermal conductivity, high temperature stability, and high corrosion and oxidation resistance.^{1–3} The applications of BN in industry are limited to the fabrication of crucibles, electrical insulators, and mold-release liners. Recently, interest has arisen in a new application of h-BN, using small-scale BN as a selective gas sorbent or hydrogen storage medium.^{4–8}

Commercial h-BN powders are generally prepared at low cost by nitridation or carbothermal reduction of boric acid or boric oxide with melamine or urea.⁹ The powders thus produced are platelet shaped, providing a small packing factor, and also usually contain oxygen or carbon impurities, which makes it difficult to obtain high-purity BN with good crystallinity. On the other hand, spherical h-BN powder is considered to be a promising material because it can provide a large particle packing factor and a large specific area. To date, there have been only a few reports on the preparation of spherical BN powder. For example, boron nitride spheres (BNS) have been prepared by melting and subsequent quenching of the BN particles with a hot plasma-torch ($>3500\text{ K}$).¹⁰ Wood *et al.*¹¹ have prepared BN spherical powders by aerosol synthesis from guanidinium nonaborate $[\text{C}(\text{NH}_2)_3]_3[\text{B}_9\text{O}_{12}(\text{OH})_6]$ as an organoborate precursor. However, there are still problems in the production of BNS, such as high cost, oxygen and carbon impurities, or large size distributions of the spherical powder particles. Therefore, the selection of the starting material for the formation of high-purity BN is important and precursors without oxygen and carbon

should be used. In this respect, borazine ($\text{B}_3\text{N}_3\text{H}_6$) or ammonia borane (BH_3NH_3) are considered to be ideal precursors. We have reported the preparation of nanosized tube-, fiber-, and bamboo-type BN by template-aided wetting and thermal decomposition of borazine.¹² However, nanosized BNS could not be obtained from borazine using the template-aided method. BH_3NH_3 is expected to be a suitable precursor for the preparation of BNS through vapor phase pyrolysis because BH_3NH_3 has no toxicity and can be easily transformed from a stable solid to the gas phase through the formation of droplets by moderate temperature heating without the need for a catalyst.^{13–15} This paper describes the first simple and efficient approach to the preparation of high-purity BNS from BH_3NH_3 using vapor phase pyrolysis. This approach makes it possible to control the size of the spheres by a single heating of BH_3NH_3 . In addition, the effect of ambient gas (NH_3 , N_2 , and Ar) and temperature on the crystallization of BNS at high temperatures was investigated.

II. Experimental Procedure

(1) Preparation of BNS

BH_3NH_3 as the starting material was synthesized from sodium borohydride (NaBH_4) and ammonium sulfamate ($\text{NH}_4\text{NH}_2\text{SO}_3$), as described by Suenram and Thorne.¹⁶ ^1H -nuclear magnetic resonance analysis showed that the product BH_3NH_3 contained 97 wt% BH_3NH_3 and $\approx 3\text{ wt}\%$ $(\text{BH}_2\text{NH}_2)_x$ ($x < 3$). High-purity NH_3 , Ar, and N_2 (each purity: 99.999%) were used as ambient gases during further heat treatment.

The experimental apparatus for the preparation of BNS is shown in Fig. 1. Two independently temperature-controlled furnaces (I and II) were set vertically in a glove box filled with N_2 . A silica glass tube with one end closed, which functioned as the reaction chamber, was passed up through both furnaces. A porous anodic alumina membrane (Whatman Ltd., London, UK, Anodisc 13, nominal pore size = 100 nm) was fixed at the top end of the silica reaction tube in furnace (I) to control the flow rate of the gas and to prevent BNS from escaping from the reaction chamber. 0.3 g of BH_3NH_3 was introduced to the middle of the glass tube in furnace (II) and an alumina crucible was placed mid way up the silica reaction tube to collect the BNS in furnace (I). Furnace (I) was initially heated to 550°C and then furnace (II) was heated from room temperature to 250°C at a heating rate of 1° , 5° , and $10^\circ\text{C}/\text{min}$ and maintained at this temperature for 1 h, after which it was allowed to cool naturally, while furnace (I) was maintained at 550°C for another 24 h. During these operations, the BNS formed in the silica reaction tube fell down into the alumina crucible by the action of gravity. After removal from the alumina crucible, the BN samples were placed in an alumina boat and heated to a fixed temperature (from 1300° to 1700°C) at $10^\circ\text{C}/\text{min}$ in a horizontal tube furnace. Heat treatments were carried out under different schemes in flowing NH_3 , Ar, or N_2 at a rate of 100 mL/min, as presented in Table I.

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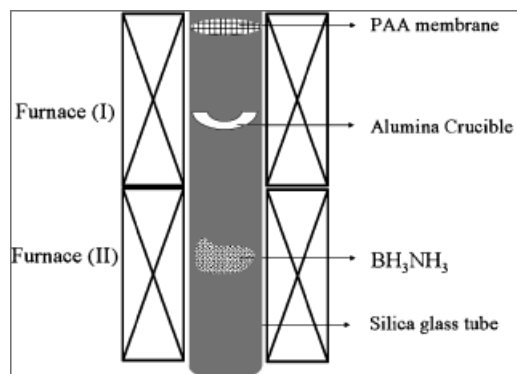


Fig. 1. Schematic diagram of the experimental apparatus.

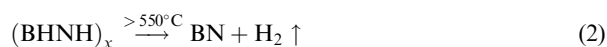
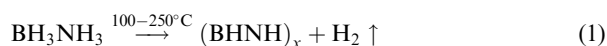
(2) Characterization

One hundred and fifty particles of BNS obtained at heating rates of 1°, 5° and 10°C/min to 250°C were chosen at random to determine the size distribution and the mean diameter by the scanning electron microscopy (SEM; JEOL Ltd., Tokyo, Japan, JSM 6500F) observation. The degree of crystallinity of the samples was investigated by high-resolution transmission electron microscopy (HRTEM; JEOL Ltd., Tokyo, Japan, JEM2000) with selected area electron diffraction (SAED) at an accelerating voltage of 200 kV and by powder X-ray diffraction (XRD; Rigaku Corp., Tokyo, Japan, RTNT2000). The samples were also examined using fourier transform infrared spectroscopy (FT-IR; Thermo Nicolet AVATAR 320, Thermo Fisher Scientific Inc., Waltham, MA).

III. Results and Discussion

(1) Formation of BNS with Controlled Diameter

Because BH_3NH_3 has a B/N mole ratio of 1:1, it is thought to be an ideal precursor for the formation of BN by decomposition. The formation of BN from BH_3NH_3 occurs in two steps^{13–15}:



When BH_3NH_3 is heated to 250°C in furnace (II), polymer $[(\text{BHNH})_x (x > 3)]$ droplets and H_2 gas are formed by the decomposition (Eq. (1)). These droplets are carried upward by the H_2 gas stream into furnace (I) at 550°C, at which temperature

Table I. Heating schemes for heat treatment of BNS in different ambient gases (NH_3 , N_2 , and Ar)

Sample No.	Step 1 (°C)	Step 2 (°C)	Step 3 (°C)
Group A: NH_3			
A-1	1300		
A-2	1300	1600	
A-3	1300	1700	
A-4	1300	1500	1600
Group B: N_2			
B-1	1300		
B-2	1300	1700	
Group C: Ar			
C-1	1300		
C-2	1300	1700	
C-3	1300	1500	1600

The heating rate between the steps was 10°C/min. The keeping time for each step was 1 h. BNS, boron nitride spheres.

the rapid pyrolysis and solidification of $(\text{BHNH})_x$ droplets occurs, forming amorphous BN (a-BN) (Eq. (2)). White powders were then collected in the alumina crucible.

Thermogravimetric analysis reported by Wolf *et al.*¹⁵ showed that BH_3NH_3 starts to decompose at approximately 100°C, with the release of H_2 , the decomposition rate being strongly dependent on the heating rate. For this reason, different heating rates were used to produce BNS, with the final temperature of 250°C being selected to ensure completion of the decomposition reaction. SEM images of the resulting powders are shown in Fig. 2. All the samples are white in color and exhibit good spherical morphology, with little agglomeration and smooth featureless surfaces. The spheres obtained by heating at a lower rate (1°C/

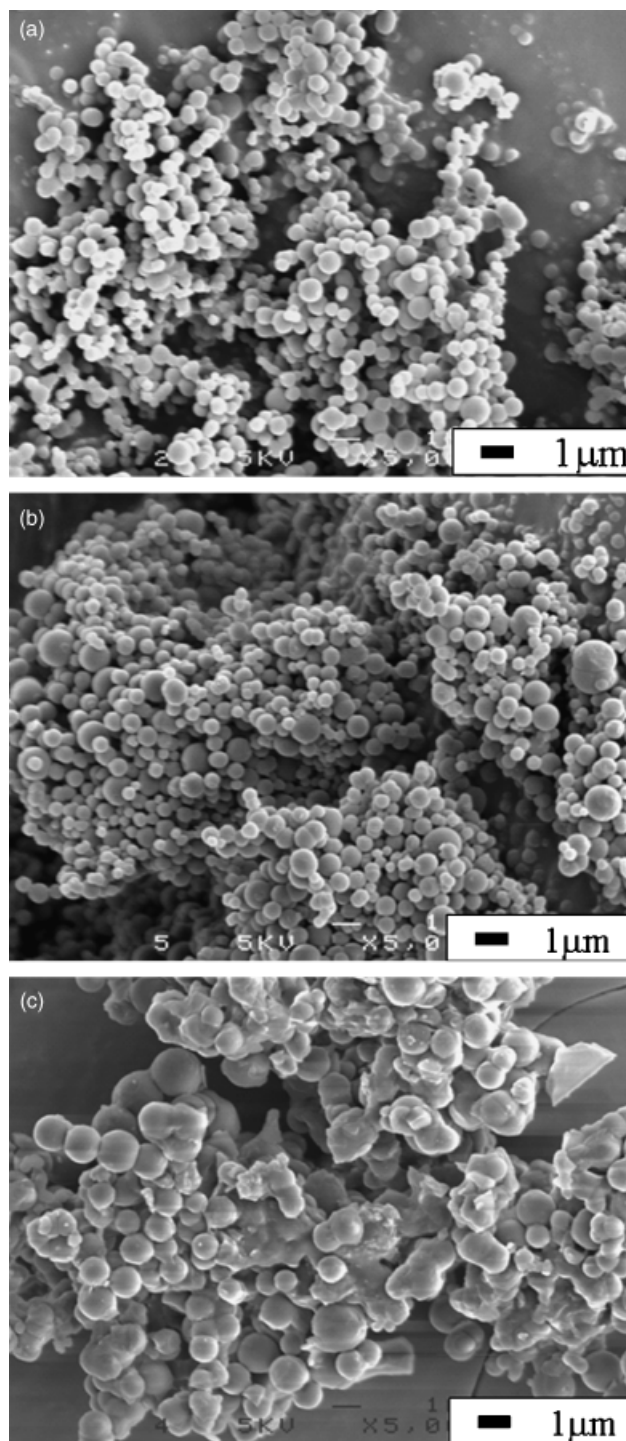


Fig. 2. Scanning electron microscopy images of spheres obtained at a heating rate of (a) 1°C/min, (b) 5°C/min, and (c) 10°C/min to 250°C.

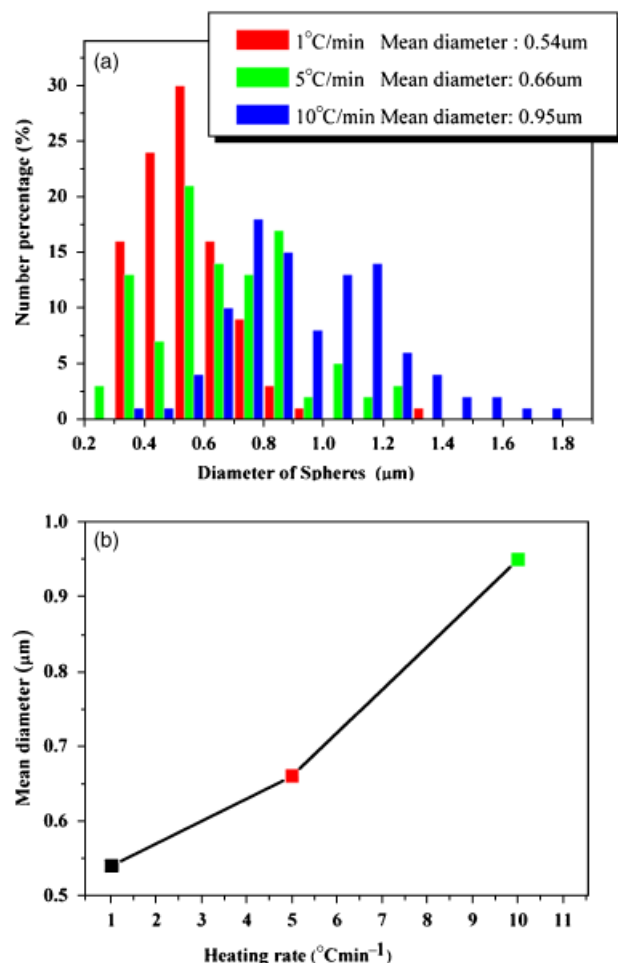


Fig. 3. (a) The size distribution of boron nitride spheres obtained at a heating rate of 1°, 5°, and 10°C/min and (b) the relationship between the mean diameter and the heating rate.

min) have small diameters with a narrow particle size distribution (300–800 nm) (Fig. 2(a)). Higher heating rates (5° and 10°C/min) yielded BNS with wider size distributions of 300 nm–1.2 μm and 300 nm–1.8 μm, respectively (Figs. 2(b) and (c)). The average diameter of the spheres prepared at heating rates of 1°, 5°, and 10°C/min was determined to be 0.54, 0.66, and 0.95 μm, respectively (Fig. 3(a)), which indicates that **higher heating rates increase the diameters of spheres** formed during the decomposition process (Fig. 3(b)). **It is assumed that a higher heating rate enhances the decomposition of BH_3NH_3 , releasing more H_2 gas in a shorter time and forming larger precursor droplets of high molecular weight.** Further heating experiments were confined to a heating rate of 5°C/min because this rate can produce powders of better spherical morphology and less agglomeration compared with the other heating rates, as shown by SEM (Fig. 2).

To confirm the formation of BNS from BH_3NH_3 , FT-IR spectra (Fig. 4) were obtained for BH_3NH_3 , spheres heated in the glove box at 550°C, and the three samples A-1, B-1, and C-1, which were heated in NH_3 , N_2 , and Ar at 1300°C, respectively. **The FT-IR spectrum of BH_3NH_3 shows N-H and B-H stretching peaks at 3280 and 2320 cm^{-1} , respectively, and a N-H deformation peak at 1560 cm^{-1} (Fig. 4(A)).**¹⁷ After heating at 550°C, the N-H and B-H peaks decrease due to dehydrogenation, with polymerization and condensation (Fig. 4(B)). The B-H peak appears at 2500 cm^{-1} , about 150 cm^{-1} higher than that of BH_3NH_3 (2320 cm^{-1}). The reason for the shift is not understood at present. However, the broad weak N-H stretching peak centered near 3300 cm^{-1} as well as the small B-H stretching peak at 2500 cm^{-1} remain, indicating that the dehydrogenation of BH_3NH_3 is incomplete. The XRD pattern of the samples heated at 550°C shows a broad weak hump, as shown later, in-

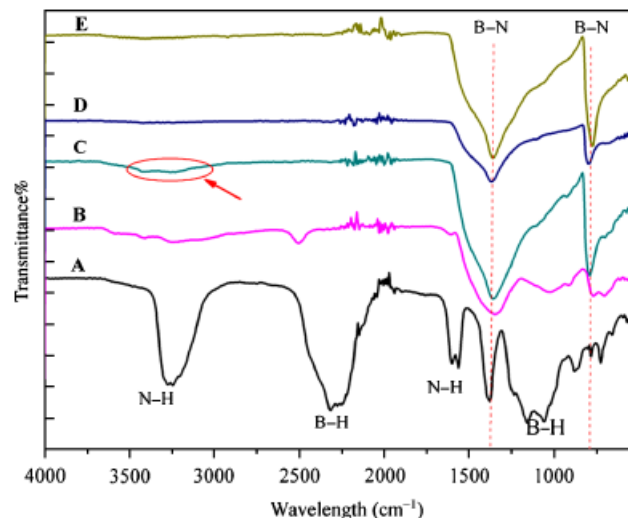


Fig. 4. Fourier transform infrared spectroscopy spectra of BH_3NH_3 and boron nitride spheres obtained by heating at different temperatures: (A) BH_3NH_3 , (B) 550°C in N_2 (glove box), (C) 1300°C in NH_3 , (D) 1300°C in N_2 , and (E) 1300°C in Ar.

dicating the presence of an amorphous phase. Therefore, after heat treatment at 550°C, the BN is considered to be amorphous, with a small amount of remnant B-N-H polymer. When the sample was subsequently heated at 1300°C in NH_3 , N_2 , and Ar, **broad B-N peaks appeared at about 1380 and 780 cm^{-1} in the three samples, these being the typical peaks of h-BN (Figs. 4(C)–(E)).**¹⁷ The samples heated in NH_3 display a broad weak peak centered at 3300 cm^{-1} (see arrow), which is assigned to N-H stretching, whereas this peak is not observed for the samples heated in N_2 and Ar (Figs. 4(D) and (E)).

(2) Crystallization of BNS

It is known that the final heating temperature and ambient gas are key factors affecting the crystallization of BN.¹ To examine the effect of heating temperature and ambient gas on the crystallinity of BNS, the a-BNS obtained at 550°C were further heated in different ambient gases of NH_3 , N_2 , and Ar according to the heating schemes with steps 1–3 (Fig. 5 and Table I). When a-BNS (550°C) were directly heated to $\geq 1500^\circ\text{C}$ in NH_3 , the spherical morphology was changed, with the formation of needles or plates protruding from the spherical surface, as shown by TEM images (Fig. 6). For this reason, multistep heat treatments were used to produce highly crystalline BNS in three different atmospheres (NH_3 , N_2 , and Ar).

(A) *The Effect of NH_3 : Group A:* The samples of group A (Table I) produced at final temperatures of 1300°, 1600°, and 1700°C in NH_3 were white in color. The XRD patterns of a-BNS obtained at 550°C and BNS heated in NH_3 at 1300°C, 1300°/

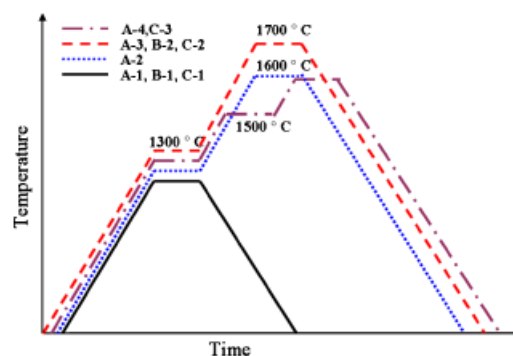


Fig. 5. Heat treatment schemes: heat treatments at high temperatures in NH_3 , N_2 , and Ar (groups A, B, and C in Table I).

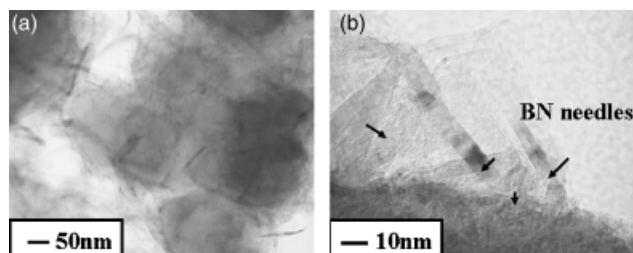


Fig. 6. Transmission electron microscopy images of boron nitride spheres by one-step heat treatment to 1500°C in NH_3 : (a) BNS with damaged surface, (b) high-resolution TEM images of BN needles protruding from the surface (see arrows).

1600°C and 1300°/1700°C are shown in Fig. 7. The patterns show broad reflections centered at the strong diffraction peaks (002) and (100) of crystalline h-BN and there is a trend toward increasing crystallinity with increasing heat treatment temperature.¹⁸ The two broad peaks imply that poorly crystalline or amorphous regions exist in BNS. TEM images of the BNS microstructures (group A in Table I) produced after one, two and three-step heat treatments are shown in Fig. 8. The images show that the spherical morphology of BNS is maintained after heat treatment (Figs. 8(a)–(d)). It is interesting that the BNS, subjected to multistep heat treatment, form a shell on their surface (Figs. 8(b') and (c')), while no shell is visible on the BNS surface heated by a one-step heat treatment at 1300°C (Fig. 8(a')). The thicknesses of the shells formed on the BNS surface obtained at final temperatures of 1600° and 1700°C (samples A-2 and A-3, Table I) were 40 and 60 nm, respectively, indicating that the thickness increases with the heating temperature. The BNS prepared by a three-step heat treatment at 1300°/1500°/1600°C (sample A-4, Table I) form a two-layered shell on the surface (Fig. 8(d')). The SAED patterns (insets of Fig. 8) of the shells on the BNS show strong (002) arcs with (100) and (110) rings, indicating the formation of a turbostratic layer structure on the surface of the BNS. On the other hand, the inside cores of the spheres should be amorphous, based on the results of the SAED ring patterns (insets of Fig. 8). Therefore, the BNS heated in NH_3 are considered to have h-BN shells with turbostratic layer structure and amorphous cores inside. Thus, the crystallization of BNS in NH_3 gas begins at the surface and slowly moves toward the interior of the sphere.

(B) *The Effect of N_2 : Group B:* Single- and multistep heat treatments of BNS were carried out in flowing N_2 (Table I). The BNS heated in N_2 were white. The XRD patterns of the BNS heated at 1300° and 1300°/1700°C in flowing N_2 are shown

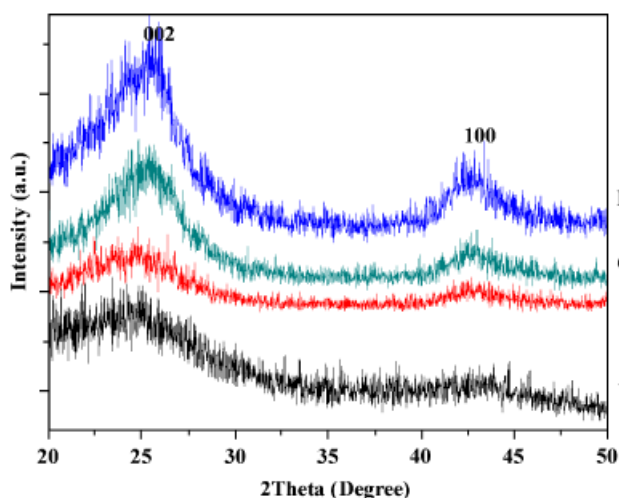


Fig. 7. X-ray diffraction patterns of (A) amorphous boron nitride spheres (BNS) obtained at 550°C and BNS after heating at (B) 1300°C, (C) 1300°/1600°C, and (D) 1300°/1700°C in NH_3 .

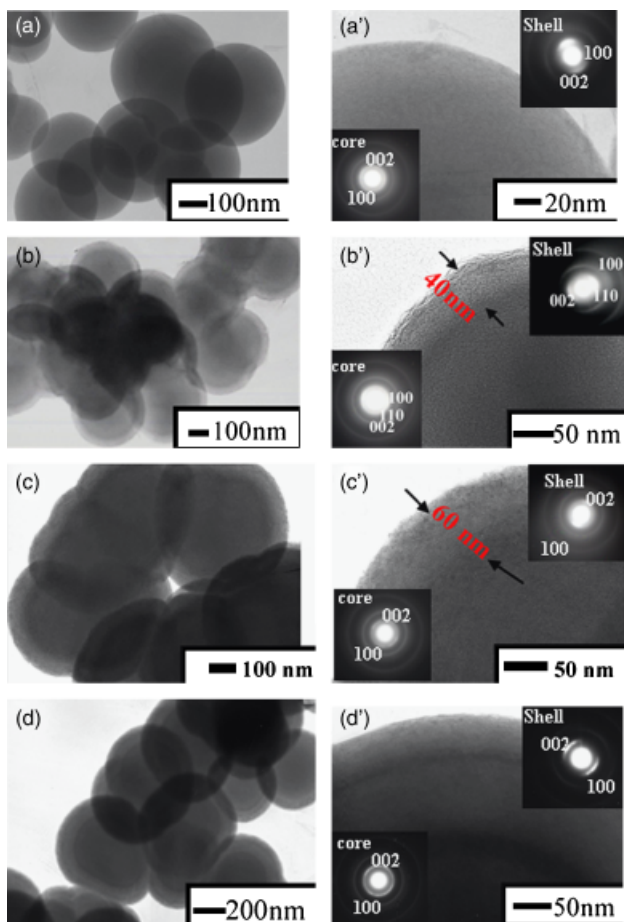


Fig. 8. Transmission electron microscopy images of boron nitride spheres prepared by different heat treatment schemes in NH_3 : (a, a') 1300°C, (b, b') 1300°/1600°C, (c, c') 1300°/1700°C, and (d, d') 1300°/1500°/1600°C. The insets are the selected area electron diffraction patterns of the surface and in the core of the samples.

in Fig. 9. The latter BNS show very sharp (002) and (100) peaks, indicating that the crystallinity of the BNS is greatly enhanced by heating in N_2 at 1700°C. Figures 10(a) and (b) show TEM images of BNS obtained at 1300° and 1300°/1700°C, respectively. The spherical morphology of these BNS is retained after heat treatment in N_2 without the formation of a shell on the surface. The SAED patterns (insets of Fig. 10) of the two kinds of BNS indicate the formation of a turbostratic layer structure,

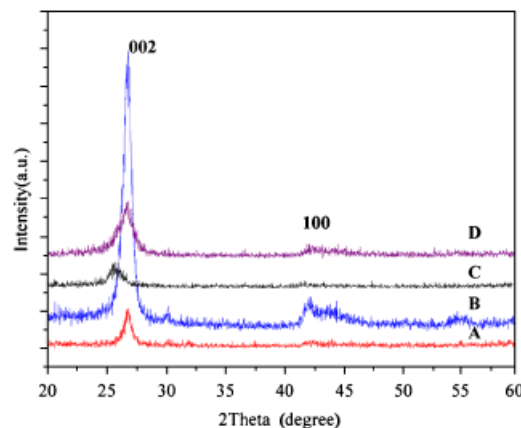


Fig. 9. X-ray diffraction patterns of boron nitride spheres prepared at (A) 1300°C and (B) 1300°/1700°C in N_2 and (C) 1300°C and (D) 1300°/1700°C in Ar.

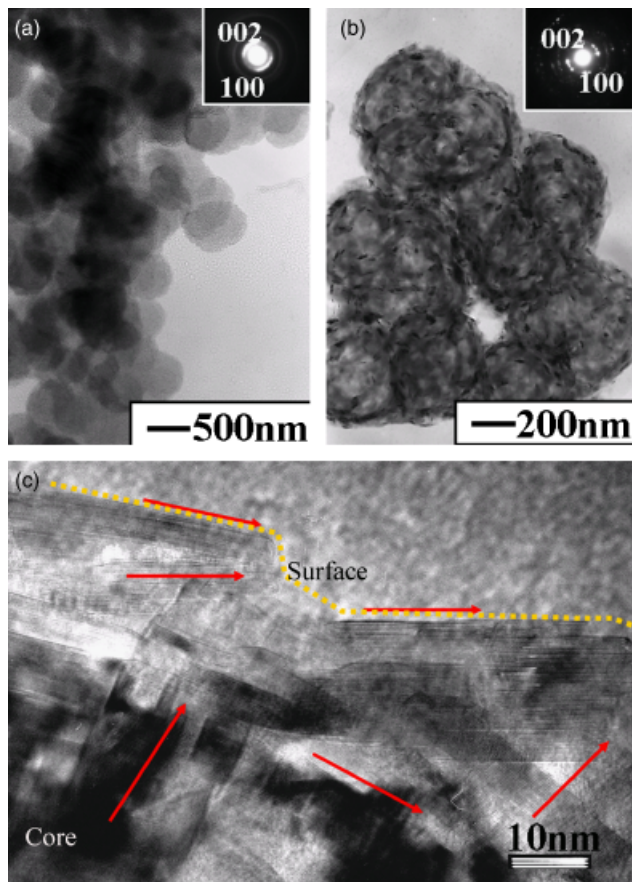


Fig. 10. Transmission electron microscopy (TEM) images of boron nitride (BN) spheres prepared by different heat treatment schemes in N_2 : (a) 1300°C, (b) 1300°/1700°C, and (c) high-resolution TEM image of a BN sphere surface (1300°/1700°C). The arrows show the orientation of the BN crystallites. The insets are the selected area electron diffraction patterns of the samples.

as shown by (002) arcs. The BNS obtained at 1300°/1700°C displayed a good crystallinity, as confirmed by the (002) spots of h-BN. Its HRTEM image (Fig. 10(c)) shows that the crystallographic orientation of BN grains in the spheres is randomly distributed, as indicated by red arrows. According to the XRD and TEM results, the BNS heated in N_2 are considered to be well-crystallized h-BN, with the existence of turbostratic layers.

(C) *The Effect of Ar: Group C:* BNS heated in Ar were also white in color. The XRD patterns of the BNS treated at 1300° and 1300°/1700°C in flowing Ar are shown in Figs. 9(C)

and (D), respectively. Compared with the BNS produced in NH_3 , the crystallinity of BNS is improved in Ar, as indicated by the distinct (002) peak. The microstructures of BNS obtained by heating at 1300°, 1300°/1700°, and 1300°/1500°/1600°C in Ar are shown in Fig. 11. The spherical morphology of the BNS is retained; however, the surfaces become rough with an increase in the heating temperature. A number of crystallites (black spots) can be observed over the entire sphere of each BNS. HRTEM images and SAED patterns (insets of Figs. 11(a) and (b)) show the formation of the crystal planes running parallel to the surface of the sphere. The BNS heated at 1300°/1700°C contain many platelet crystallites 20–50 nm long and 5–10 nm wide, meeting at an angle of approximately 130° (Fig. 10(b)). For the BNS treated in Ar, shells were not observed on the surface even when a-BNS were treated by two- or three-step heat treatments (Figs. 11(b) and (c)). Therefore, it can be concluded that the crystallization of BN in Ar occurs throughout the sphere and does not proceed from the surface toward the core, as is the case with NH_3 .

It is found that the ambient gases (NH_3 , N_2 , and Ar) used in heat treatment have different influences on the crystallization of BNS produced from BH_3NH_3 . Of these gases, N_2 gas promotes the crystallization of BNS in the whole sphere after heat treatment at 1700°C (Figs. 9(B) and 10(b)) and produces grains with randomly distributed orientations approximately 50-nm long (Fig. 10(c)). In Ar, well-crystallized BN grains are also present throughout the spheres, but the crystallographic orientation tends to run along the surface of the sphere (Figs. 11(a) and (b)). On the other hand, NH_3 gas produces BNS with well-crystallized layers on the surface, but with an amorphous core (Figs. 8(b) and (b')). A possible mechanism can be described as follow. It is known that NH_3 decomposes to H- and N-containing species (NH_2 , NH , H , H_2 , or N_2) at temperatures $\geq 700^\circ C$.¹⁹ It is assumed that such N-containing species work as a nitrogen source, which can enhance the crystallization of BN as N_2 (Figs. 9(A) and (B)), while H-containing species, probably H or H_2 , retard the crystallization of BN with formation of N-H bonding (Fig. 4(C)). Because it is thought that N_2 /N-containing species diffuse into a-BNS slower than H/H_2 , the crystallization of a-BNS occurs on the surface with formation of a crystallized shell that is 40–60-nm thick (Figs. 8(b) and (c)), while the core part of BNS remains amorphous due to the formation of N-H bonding. Therefore, BNS with shell-core structures are formed by heating in NH_3 at high temperatures.

IV. Conclusion

Synthesis of BNS with controllable size distributions was achieved by heating BH_3NH_3 in two independent temperature-controlled furnaces at different heating rates. The BNS were then heated by multistep heating schemes at high temperatures from

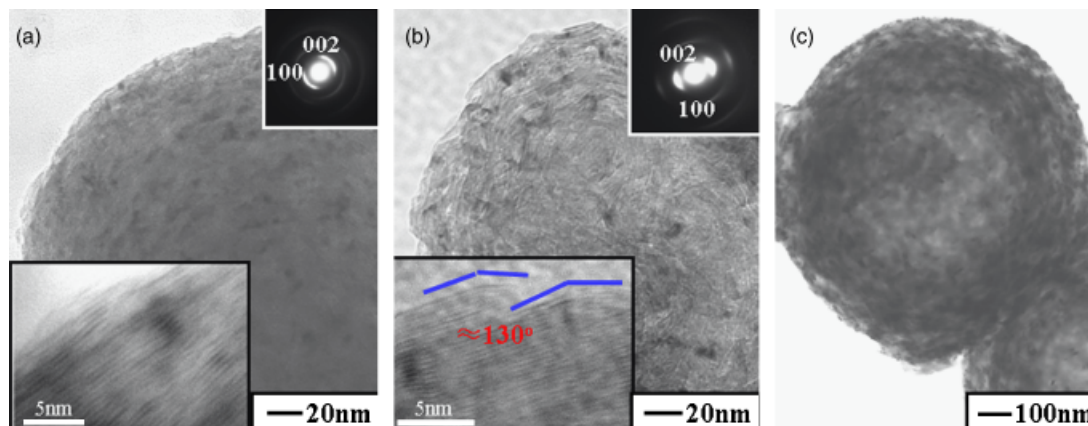


Fig. 11. Transmission electron microscopy (TEM) of boron nitride spheres prepared in Ar. (a) 1300°C, (b) 1300°/1700°C, and (c) 1300°/1500°/1600°C. The insets are high-resolution TEM images and the selected area electron diffraction patterns of the samples.

1300° to 1700°C in flowing NH₃, N₂, and Ar. The influence of different atmospheric gases on the crystallization of BNS was revealed by XRD, FT-IR, and HRTEM. BNS with well-crystallized surfaces and amorphous cores were produced by heating in NH₃. BNS heated in N₂ exhibited good crystallinity and the crystallographic orientation of the BN grains was randomly distributed in the spheres. The crystallographic orientation of grains in BN heated in Ar tended to run along the surface of the sphere. Mechanisms for the crystallization of BNS in different ambient gases were proposed. The coeffect of N- and H-containing species decomposed from NH₃ results in the formation of core-shell BNS. N₂ enhanced the crystallization of BNS. The crystallization of BNS heated in Ar resulted from the heat treatment.

References

- ¹R. T. Paine and C. K. Narula, "Synthetic Routes to Boron Nitride," *Chem. Rev.*, **90** [1] 73–91 (1990).
- ²R. S. Pease, "Crystal Structure of Boron Nitride," *Nature*, **165** [4201] 722–3 (1950).
- ³L. Pauling, "The Structure and Properties of Graphite and Boron Nitride," *Proc. Natl. Acad. Sci. USA*, **56** [6] 1646–52 (1966).
- ⁴R. J. Baierle, P. Piquini, T. M. Schmidt, and A. Fazzio, "Hydrogen Adsorption on Carbon-Doped Boron Nitride Nanotube," *J. Phys. Chem. B*, **110** [42] 21184–8 (2006).
- ⁵C. Tang, Y. Bando, X. Ding, S. Qi, and D. Golberg, "Catalyzed Collapse and Enhanced Hydrogen Storage of BN Nanotubes," *J. Am. Chem. Soc.*, **124** [49] 14550–1 (2002).
- ⁶H. J. Xiang, J. Yang, J. G. Hou, and Q. Zhu, "Linear Scaling Calculation of Band Edge States and Doped Semiconductors," *J. Chem. Phys.*, **126** [24] 244707 (2007).
- ⁷S. Hu, E. J. Kan, and J. Yang, "First-Principles Study of Interaction Between H₂ Molecules and BN Nanotubes with BN Divacancies," *J. Chem. Phys.*, **127** [16] 164718 (2007).
- ⁸X. Chen, X. P. Gao, H. Zhang, Z. Zhou, W. K. Hu, G. L. Pan, H. Y. Zhu, T. Y. Yan, and D. Y. Song, "Preparation and Electrochemical Hydrogen Storage of Boron Nitride Nanotubes," *J. Phys. Chem. B*, **109** [23] 11525–9 (2005).
- ⁹T. E. O'Connor, "Synthesis of Boron Nitride," *J. Am. Chem. Soc.*, **84**, 1753–4 (1962).
- ¹⁰J. Phillips, S. S. Gleiman, and C. C. Chen, "Spherical Boron Nitride Particles and Method for Preparing Them," US Patent No. 6652822, 2003.
- ¹¹G. L. Wood, J. F. Janik, M. Z. Visi, D. M. Schubert, and R. T. Paine, "New Borate Precursors for Boron Nitride Powder Synthesis," *Chem. Mater.*, **17** [7] 1855–9 (2005).
- ¹²Y. Wang, S. Shimada, Y. Yamamoto, and N. Miyaura, "Preparation of h-BN Nano-Tubes, -Bamboos, and -Fibers from Borazine Oligomer with Alumina Porous Template," *Mater. Res. Bull.*, **43** [2] 251–6 (2008).
- ¹³F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-Roler, and G. Leitner, "Thermal Decomposition of B-N-H Compounds Investigated by Using Combined Thermoanalytical Methods," *Thermochimica Acta*, **391** [1–2] 159–68 (2002).
- ¹⁴M. T. Nguyen, V. S. Nguyen, M. H. Matus, G. Gopakumar, and D. A. Dixon, "Molecular Mechanism for H₂ Release from BH₃NH₃, Including the Catalytic Role of the Lewis Acid BH₃," *J. Phys. Chem. A*, **111** [4] 679–90 (2007).
- ¹⁵G. Wolf, J. Baumann, F. Baitalow, and F. P. Hoffmann, "Calorimetric Process Monitoring of Thermal Decomposition of B-N-H Compounds," *Thermochimica Acta*, **343** [1–2] 19–25 (2000).
- ¹⁶R. D. Suenram and L. R. Thorne, "Microwave Spectrum and Dipole Moment of BH₃NH₃," *Chem. Phys. Lett.*, **78** [1] 157–60 (1981).
- ¹⁷D. P. Kim, C. G. Gofer, and J. Economy, "Fabrication and Properties of Ceramic Composites with a Boron Nitride Matrix," *J. Am. Ceram. Soc.*, **78** [6] 1546–52 (1995).
- ¹⁸Joint Committee on Powder Diffraction Standards (JCPDS) Card No.: 34-0421.
- ¹⁹W. Huang, W. Lai, and D. Xie, "First-Principles Study of Decomposition of NH₃ on Ir (100)," *Surf. Sci.*, **602** [6] 1288–94 (2008). □