Aerosol Assisted Vapor Synthesis of Spherical Boron Nitride Powders

Eugene A. Pruss,[1] Gary L. Wood,[2]
William J. Kroenke,[1] and Robert T. Paine*,[1]

*Departments of Chemistry and Chemical Engineering
and the University of New Mexico/National Science
Foundation Center for Micro-Engineered Materials,
University of New Mexico,
Albuquerque, New Mexico, 87131, and Department of
Chemistry, Valdosta State University,
Valdosta, Georgia 31698*

Boron nitride (BN) is refractory, electrically insulating, relatively inert, and crystallizes in a graphite-like structure that promotes lubricity. Consequently, its primary applications are found in the formation of crucibles, insulators, and mold release liners. Since BN is also an excellent thermal conductor,[3,4] the microelectronics industry is interested in using it as a filler in polymer/ceramic composites for thermal management applications. These include IC molding compounds, liquid-based encapsulent systems, and underfills for printed circuit boards, where high resistivity and heat dissipation are critical design requirements. Unfortunately, commercially produced BN powders have a platelet morphology that results in low filler loadings and poor composite processability. As a result, there is a need to develop a procedure for synthesizing boron nitride with a spherical morphology that may permit higher filler loadings in standard thermoset polymers and improved composite processing characteristics.

The aerosol synthesis of spherical metal oxide powders has been widely reported.[5−7] This is due to the ease of formation of metal oxides from inexpensive water-soluble precursors, such as metal acetates or nitrates, that are readily converted to their oxides when sprayed and heated in air. The aerosol formation of non-oxide materials, such as, nitrides, carbides, or sulfides, has been less actively pursued in part due to the need to employ more reactive atmospheres. The syntheses of AlN,[8,9] Si_3N_4,[10] and Si_3N_4/SiC[11] powders by gas-to-particle conversion have been reported and fine particles with diameters less than 100 nm have been obtained. Two reports of the formation of spherical boron nitride have appeared. Paine et al. described the formation of spherical BN particles by spray pyrolysis of a poly-(borazinylamine) precursor dissolved in liquid ammonia (NH_3),[12] and a European Patent claimed the reaction of boron trichloride (BCl_3) and gaseous NH_3 at low temperatures results in the formation of spherical BN particles.[13] Neither of these routes is particularly convenient or economically viable.

In this communication we describe an inexpensive, easily practiced method for the formation of spherical boron nitride powders. The vapor phase method, aerosol assisted vapor synthesis (AAVS), relies on the reaction of aerosol droplets containing water-soluble boric acid (H_3BO_3) with ammonia gas at elevated temperatures in an ammonia/nitrogen mixed gas atmosphere. This technique produces smooth, featureless spherical particles with an average diameter of 1−2 μm.

The particles are formed by first using an ultrasonic transducer, operating at ∼1.7 kHz, to generate an aerosol from an aqueous solution containing boric acid (∼3 wt %) (99+%, Aldrich) and distilled water. The aerosol droplets are then transported by N_2 (99.99%) carrier gas (3 L/min) into a mullite tube (3.5 in. × 60 in.) inside a Lindberg three-zone tube furnace. Anhydrous ammonia (99.995%) is fed simultaneously into the tube furnace (2 L/min). The resulting white powder is collected on a nylon filter at the reactor outlet. The residence time of the powder in the reactor is ∼30 s. Reactions are conducted at furnace temperatures of 600, 800, 1000, and 1200 °C. The powder produced at 1000 °C is subsequently annealed (1200 °C for 12 h) in an ammonia atmosphere.

The products produced at each temperature are white powders. The morphology, particle size distribution and the degree of crystallinity of the samples were investigated by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and powder X-ray diffraction (XRD). The SEM analyses (Hitachi S-800) indicate that each sample consists of spherical particles with diameters ranging from 0.5 to 5.0 μm, with an average particle size of 1−2 μm. All the particles, regardless of reaction temperature, have a smooth, featureless surface as is evident in Figure 1. Particles with platelet morphology are totally absent. HRTEM analysis (JEOL JEM 2010, 200 keV) reveals that both hollow and dense particles are present in each sample. A TEM image of the powder obtained at 1000 °C is shown in Figure 2. SAED analysis of the samples indicates that all are relatively amorphous. The XRD patterns (Siemens D5000 diffractometer configured with a position sensitive detector (PSD) and a Cu Kα source) for powders formed at 600, 800, 1000, and 1200 °C are

(1) University of New Mexico.
(2) Valdosta State University.
(3) Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73 and references therein.
(4) Duclaus, L.; Nystue, B.; Issi, J. P. *Phys. Rev. B* **1992**, *46*, 3362.
(5) Gurav, A.; Pluym, T.; Xiong, Y.; Kodas, T. T. *Aerosol Sci. Technol.* **1993**, *19*, 411 and references therein.
(6) Chandler, C.; Powell, Q.; Hampden-Smith, M. J.; Kodas, T. T. *J. Mater. Chem.* **1993**, *3*, 775.
(7) Kodas, T. T.; Hampden-Smith, M. J. *Aerosol Processing of Materials*; Wiley: New York, 1999. Hines, W. C. *Aerosol Technology, Properties, Behavior and Measurements of Airborne Particles*; Wiley-Interscience, New York, 1999.
(8) Pratsinis, S. E.; Wang, G.; Panda, S. *J. Mater. Res.* **1995**, *10*, 512−520.
(9) Adjaottor, A. A.; Griffin, G. L. *J. Am. Ceram. Soc.* **1992**, *75*, 3209−3214.
(10) Mizutani, N.; Lui, T. Q. In *Ceramic Powder Science III*; Hirano, S. I., Messing, G. L., Hausner, H., Eds.; American Ceramic Society: Westerville, OH, 1990; pp 59.
(11) Xiao, T. D.; Strutt, P. R.; Gonsalves, K. E.; Shankar, V. *Mat. Res. Soc. Symp. Proc.* **1992**, *249*, 127−132.
(12) Lindquist, D. A.; Kodas, T. T.; Smith, D. M.; Xiu, X.; Hietala, S. L.; Paine, R. T. *J. Am. Ceram. Soc.* **1991**, *74*, 3126−3128.
(13) A. Iltis, A.; C. Magnier, C. (assignors to Rhone Poulenc Chimie) Procedure for Preparing Amorphous or Turbostratic Boron Nitride with a Spherical Morphology. European Patent 396 ,448, 11 July 1990.
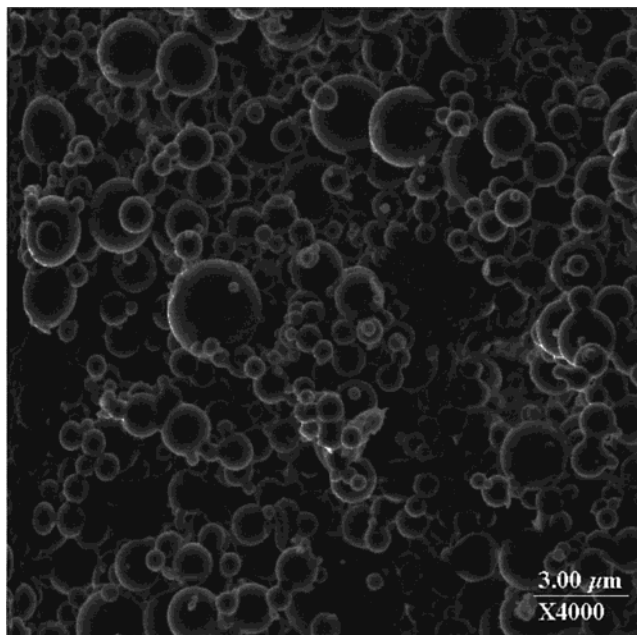
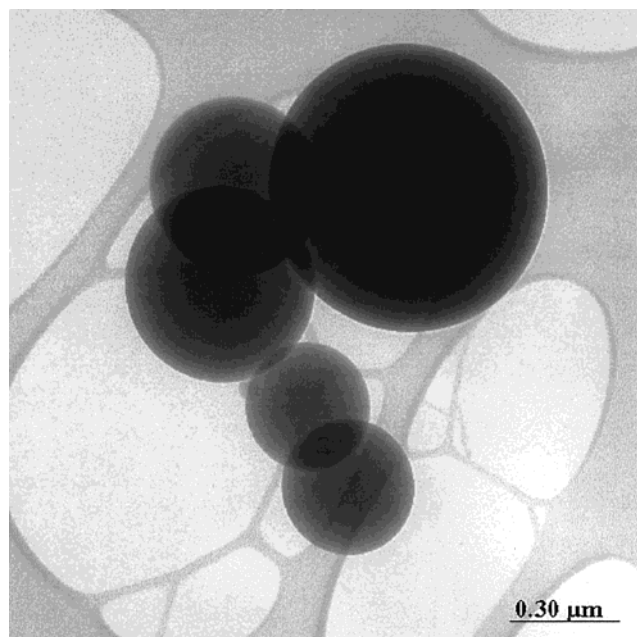**Figure 1.** SEM of aerosol particles produced at 1000 °C.

Figure 2. TEM of aerosol particles produced at 1000 °C.

shown in Figure 3. They contain broad reflections centered at the strongest diffraction peaks characteristic of crystalline h-BN,[14] and there is a trend toward increasing crystallinity with increasing reaction temperature. The low degree of crystallization and/or very small crystallite size is not surprising since the crystallization of h-BN typically requires temperatures above 1600 °C[3].

The chemical composition of the powders was determined by utilizing both surface (XPS, Kratos Analytical AXIS HSi) and bulk analytical techniques. The surface and near surface composition of the samples varies with reactor temperature as indicated by variation of the B/N
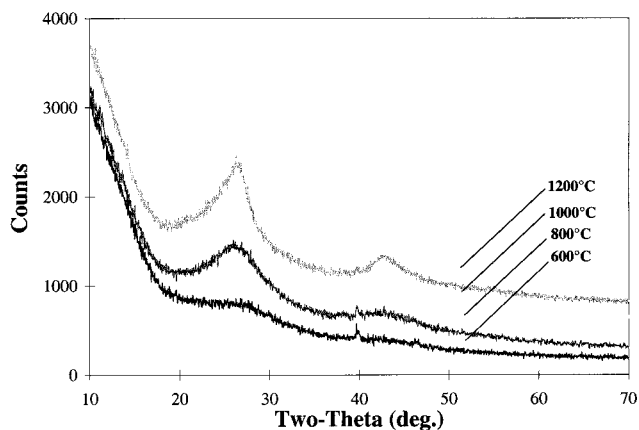

Figure 3. Powder X-ray diffraction patterns for aerosol particles formed at 600, 800, 1000, and 1200 °C.

Table 1. Bulk Compositional Analysis Data

sample	T (°C)	atomic %				
		B	N	O	H	C
aerosol	600	21	7	34	37	1
	800	26	12	30	31	1
	1000	30	16	27	26	1
	1200	33	18	25	22	2
	1700	50	50			
commercial sample		50	50			

(atomic % B/atomic % N) ratio with temperature: 4.6 (600 °C), 3.0 (800 °C), 1.8 (1000 °C), 1.6 (1200 °C). This decrease in the B/N ratio with increasing reaction temperature correlates with decreasing oxygen content at the surface. Therefore, at higher reaction temperatures, the powders contain less surface oxygen. Sputtering (Ar$^+$) of the powders indicates that oxygen content increases with increasing sputtering depth. This is consistent with the formation of the spherical particles by surface reaction of ammonia on initially generated BO-containing particles. The bulk boron, nitrogen, carbon, and hydrogen elemental compositions of each sample were measured directly by standard methods (INEOS, Moscow), while oxygen percentages were calculated by subtraction. These data also indicate that the bulk oxygen content decreases with increasing synthesis temperature (Table 1). Thermogravimetric analyses of the powders (Perkin-Elmer TGA/DTA 7) were conducted under an atmosphere of N_2. A single event weight loss occurs in all samples in the region of 50–400 °C. The total weight loss decreases with increasing reaction temperature: 28% (600 °C), 18% (800 °C), 10% (1000 °C), and 5% (1200 °C). These data correlate well with loss of oxygen primarily as H_2O (g) as would be expected in nitridation of B_2O_3 with NH_3[15].

Surface area measurements of the powders (Micromeritics Gemini 2360) were conducted by nitrogen gas adsorption. The surface areas were calculated utilizing both single and multipoint BET analysis methods. The measured surface areas of the powders produced at 600, 800, 1000, and 1200 °C show little variation and are ~1 m²/g. The densities of the powders, measured by helium pycnometry (Micromeritics AccuPyc 1330) increase slightly as the reactor temperature increases, and

(14) International Center for Diffraction Data (ICDD), Joint Committee on Powder Diffraction Studies (JCPDS) powder diffraction database, sets 1–42 (1994).

(15) Lindemanis, A. E. In *Emergent Process Methods for High Technology Ceramics*; Davis, R. F. Ed.; Plenum Press: New York, 1984; pp 111–121 and references therein.
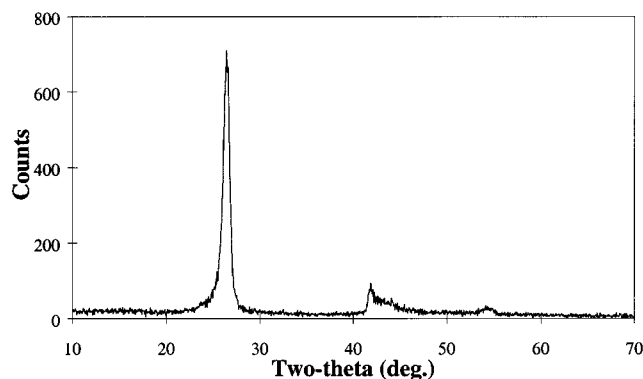
Communications

Chem. Mater., Vol. 12, No. 1, 2000 21

Figure 4. Powder X-ray diffraction pattern for boron nitride annealed at 1700 °C under NH_3.

Figure 5. SEM of boron nitride aerosol particles annealed at 1700 °C under NH_3.

they fall in the range $1.8-2.0$ g/cm^3. These values are higher than the density of vitreous B_2O_3 (1.8 g/cm^3),[16,17] but lower than the density of hexagonal BN (2.3 g/cm^3).[1,16,17]

Infrared spectra (Nicolet 600 FTIR) of the powders were collected from samples heated under vacuum at 60 °C to remove adsorbed oxygen and water. Bands at 1390 and 770 cm^{-1} are observed, consistent with the presence of BN. However, broad absorption bands in the region of $1100-900$ cm^{-1} also indicate the presence B$-$O bonds in the powders. These bands decrease in intensity with increasing reaction temperature.

On the basis of the above characterization data, it is clear that the aerosol-produced powders are not fully nitrided under the aerosol reactor conditions employed. Therefore, powder produced at 1000 °C was annealed in an ammonia atmosphere in a high-temperature tube furnace (Thermolyne 59300) fitted with an alumina tube. One gram of powder was contained in an open pyrolytic BN crucible that was heated to 1700 °C and held at this temperature for 8 h under an ammonia flow of 0.1 L/min. The resulting powder exhibits both increased crystallinity (Figure 4) and surface area (5.4 m^2/g) after annealing. SEM analysis indicates that the spherical morphology of the powder is retained (Figure 5), and HRTEM imaging indicates that the typical crystallite size is $5-10$ nm. Bulk chemical analysis of the powder shows a large reduction in oxygen content
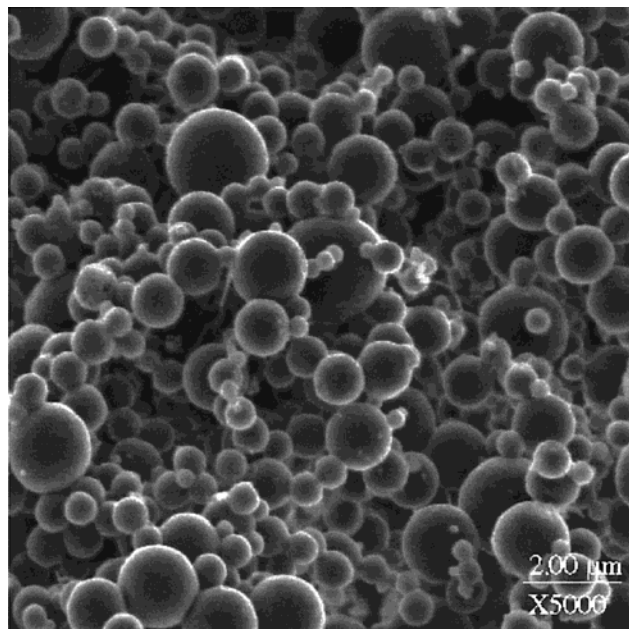
(Table 1). These results are consistent with observations made by Lindemanis[15] for the high temperature nitridation of boric oxide fibers, and it is likely that the reaction mechanisms for these two systems are identical.

These observations show that BN particles with a spherical morphology are easily produced in a two-stage nitridation of a boric acid/water aerosol. This unusual BN powder morphology has several potential applications, including use as a filler in polymer/ceramic composites. Further publications describing additional details of the synthesis and annealing of these spherical powders, in addition to the behavior of polymer/ceramic composites utilizing these powders, will be forthcoming.

CM990562L

(16) *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons, Inc.: New York, 1994; Vol. 1.

(17) *Handbook of Inorganic Compounds*; Perry, D. L., Philips, S. L., Eds., CRC Press, Inc.: Boca Raton, FL, 1995.