

# Reactions of Aluminum Hydride Derivatives with Ammonia–Borane: A New Approach toward AlN/BN Materials

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Received July 3, 1996. Revised Manuscript Received August 27, 1996<sup>⊗</sup>

Pre ceramic precursors containing Al–N–B linkages were produced from the reactions of  $\text{Me}_3\text{NAIH}_3$  with  $\text{NH}_3\text{BH}_3$  in 1:1 and 1:2 ratios in toluene solutions followed by treatment with liquid ammonia. Both precursors were transformed into intimate ceramic mixtures of AlN and BN via pyrolysis under  $\text{NH}_3$  at 1000 °C. The AlN/BN ceramic composites were characterized by IR, XRD, and solid-state  $^{27}\text{Al}$  and  $^{11}\text{B}$  MAS NMR spectroscopies. SEM studies revealed that they were composed of nanosized composite particles of AlN and BN.

## Introduction

BN and AlN are two important non-oxide ceramics whose syntheses and properties have been extensively studied.<sup>1–7</sup> To a much lesser degree, dispersed-phase composite materials containing AlN and BN have been studied. These materials offer the promise of improved fracture toughness and resistance to wear and erosion by incorporation of a soft lubricating BN phase with a hard and wear resistant AlN phase.<sup>8</sup> In fact, in recent years high thermal- and shock-resistant windows made from AlN/BN composite materials have been used for the protection of communication and detection equipment on aircraft.<sup>9</sup> Performance of these materials is highly dependant on their uniformly dispersed microstructures. However, such microstructures are difficult to obtain through classical powder-processing techniques. Recently, several precursors were developed to prepare these materials. In one procedure,<sup>10</sup> intimate mixtures of AlN and BN powders were prepared from the reactions of alkylaluminum and borazine followed by pyrolysis. In another report,<sup>11</sup> a homogeneous composite of turbostratic BN and crystalline AlN was obtained by pyrolysis of a precursor from the reaction of  $\text{B}(\text{NEt}_2)_3$  with diethylaluminum amide. Mixtures of aluminum nitride and boron nitride were also prepared

by decomposition of aluminum ammoniate borohydrides<sup>12</sup> and by the pyrolysis of a precursor from the reaction of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  with  $\text{H}_3\text{BO}_3$  and  $(\text{NH}_2)_2\text{CO}$  in aqueous solution.<sup>13</sup> Here, we report a new method for the preparation of AlN/BN mixtures which employs the pyrolysis, under  $\text{NH}_3$ , of ceramic precursors prepared from the reaction of  $\text{Me}_3\text{NAIH}_3$  with  $\text{NH}_3\text{BH}_3$ .

## Experimental Section

**General Comments.** All manipulations were performed using standard high-vacuum-line techniques or in a glovebox under  $\text{N}_2$ . Toluene was dried over sodium metal and freshly distilled into reaction flasks prior to use. Liquid  $\text{NH}_3$  (Matheson) was dried over sodium metal and stored in a stainless steel cylinder at room temperature.  $\text{NH}_3\text{BH}_3$  and  $\text{Me}_3\text{NAIH}_3$  were prepared by literature procedures.<sup>14,15</sup>  $\text{Me}_3\text{NAIH}_3$  is a potential fire hazard when in contact with moisture. All IR spectra were recorded with  $2\text{-cm}^{-1}$  resolution using a Mattson-Polaris FT-IR spectrometer. Boron-11 NMR [ $\delta(\text{Et}_2\text{OBF}_3) = 0.00$  ppm],  $^{27}\text{Al}$  NMR [ $\delta[\text{Al}(\text{NO}_3)_3] = 0.00$  ppm], and proton NMR spectra [ $\delta(\text{tms}) = 0.00$  ppm] were obtained on either a Bruker MSL-300 NMR spectrometer operating at 96.3, 78.2, and 300 MHz or a Bruker AM-250 NMR spectrometer operating at 80.2, 65.2, and 250 MHz respectively. X-ray powder diffraction (XRD) spectra were recorded on a Rigaku Geigerflex powder diffractometer using  $\text{Cu K}\alpha$  radiation. Solid-state MAS  $^{27}\text{Al}$  NMR spectra were recorded on a 400 MHz Chemagnetics spectrometer operating at 104 MHz with a spinning rate of  $\sim 10$  kHz. Scanning electron microscopy was carried out using a JEOL JSM-820 instrument. Energy-dispersive X-ray spectroscopy (EDS) was carried out using a JEOL JSM-820 SEM with a Link Analytical Oxford Instruments eXL EDS utilizing a Be window. All pyrolyses under 1200 °C were performed in a Lindberg tube furnace under an anhydrous ammonia atmosphere. A trap system was designed such that any vapors produced during pyrolysis (other than  $\text{H}_2$  and  $\text{NH}_3$ ) were collected at  $-30$  °C. Pyrolyses above 1200 °C were done in an induction furnace with samples sealed in Ta metal tubes.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, October 1, 1996.

(1) Rice, R. W. *Bull. Ceram. Soc.* **1983**, *62*, 889.  
 (2) (a) Selvaduray G.; Sheet, L. *Mater. Sci. Technol.* **1993**, *9*(6), 463.  
 (b) Sheppard, L. M. *Am. Ceram. Soc. Bull.* **1990**, *69*, 1801. (c) Marhant, D. D.; Nemecek, T. E. *Adv. Ceram.* **1989**, *26*, 19.  
 (3) *Gmelin Handbuch der Anorganische Chemie, Boron Compounds*; Springer-Verlag: Berlin, 1983.  
 (4) Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73.  
 (5) Lewis, D. W. *J. Electrochem. Soc.* **1970**, *117*, 978.  
 (6) (a) Jiang, Z.; Interrante, L. V. *Chem. Mater.* **1990**, *2*, 439. (b) Interrante, L. V.; Lee, W.; McConnell, M.; Lewis, N.; Hall, E. J. *Electrochem. Soc.* **1989**, *136*, 472.  
 (7) Maya, L. *Adv. Ceram. Mater.* **1986**, *1*, 150–53.  
 (8) (a) Twait, D. J.; Lackey, W. J.; Smith, A. W.; Lee, W. Y.; Hanigofsky, J. A. *J. Am. Ceram. Soc.* **1990**, *73*, 1510. (b) Lee, W.; Lackey, W. J.; Freeman, G. B.; Angrawal, P. K.; Twait, D. J. *J. Am. Ceram. Soc.* **1991**, *74*, 2136. (c) Lee, W. Y.; Lackey, W. J.; Angrawal, P. K.; Freeman, G. B. *J. Am. Ceram. Soc.* **1991**, *74*, 2649.  
 (9) Morris, J. R. J.; Tanzilli, R. A. U.S. Patent No. 4,666,873, 1987.  
 (10) Bolt, J. D. U.S. Patent No. 4,764,489, 1988.  
 (11) Kwon, D.; Schmidt, W. R.; Interrante, L. V.; Marchetti, P.; Maciel, G. *Inorg. Organomet. Oligomers; Proc. IUPAC Symp. Marcomol., 33rd*, 191–7; Harrod, J. F.; Laine, R. M., Eds; Kluwer, Dordrecht, The Netherlands, 1991.

(12) Polushin, N. I.; Burdina, K. P. (USSR). *Deposited Doc.* **1983**, VINITI 7085–83, Pt 3, 379–82 (Russian).

(13) (a) Strutt, P. R.; Xiao, T. D.; Gonsalves, K. E.; Boland, R. *Nanostruct. Mater.* **1993**, *2*, 347–353. (b) Gonsalves, K. E.; Xiao, T. D.; Chow, G.-M. *Adv. Powder Metall. Part. Mater.* **1994**, *5*, 59–71.

(14) (a) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 6084. (b) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 8. (c) Shore, S. G.; Bøddeker, K. W. *Inorg. Chem.* **1964**, *3*, 914.

(15) Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 2141.

Elemental analysis was performed at Mikroanalytisches Labor Pascher (Remagen, Germany).

**Formation of the AlN/BN Composite.** A quantity of 0.357 g of  $\text{Me}_3\text{AlH}_3$  (4.00 mmol) was dissolved in 25 mL of toluene and then was combined with 0.123 g of  $\text{NH}_3\text{BH}_3$  (3.99 mmol) at room temperature. Hydrogen evolution started immediately. The reaction mixture was stirred at room temperature for 12 h and at 55 °C for an additional 12 h. A 4.7 mmol quantity of  $\text{H}_2$  was released. Toluene was pumped away from the system and the white solid (0.22 g) that remained was dissolved in 2 mL of liquid  $\text{NH}_3$  at -78 °C. Additional  $\text{H}_2$  (0.59 mmol) was released. The  $\text{NH}_3$  was pumped away leaving behind the ceramic precursor as a white solid (0.18 g) which is not soluble in common organic solvents. IR (KBr) 3310 (s, NH), 3261 (s, NH), 3185 (s), 2321 (vs, BH), 2245 (vs, BH), 1613 (w), 1560 (w), 1400 (w), 1297 (w), 1192 (m), 1121 (m), 983 (s), 879 (s), 697 (s)  $\text{cm}^{-1}$ .

Pyrolysis of this solid at 1000 °C for 5 h under  $\text{NH}_3$  flow produced 0.13 g of AlN/BN which is approximately a 72% yield (from ceramic precursor to the final ceramic). No volatile boron or aluminum containing materials were produced in the pyrolysis reaction.

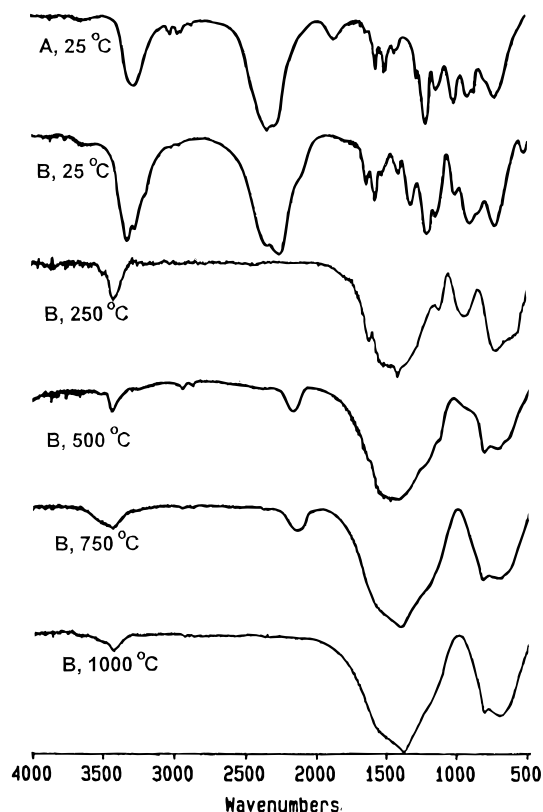
**Formation of the AlN/2BN Composite.** The procedure employed was like that described above. The reactants were 0.267 g (3.00 mmol) of  $\text{Me}_3\text{AlH}_3$  and 0.185 g (5.99 mmol) of  $\text{NH}_3\text{BH}_3$ . A total of 10.07 mmol of  $\text{H}_2$  gas was collected from the reactions in toluene (9.5 mmol  $\text{H}_2$ ) and  $\text{NH}_3$  (0.57 mmol  $\text{H}_2$ ). The ceramic precursor obtained after removal of ammonia is a white solid (0.24 g) that is insoluble in common organic solvents. IR (KBr) 3305 (m, NH), 3252 (m, NH), 2957 (w), 2928 (w), 2870 (w), 2320 (s, BH), 2266 (s), 1617 (w), 1560 (w), 1466 (w), 1400 (m), 1182 (m), 1119 (w), 974 (m), 873 (m), 703 (s)  $\text{cm}^{-1}$ .

Pyrolysis of this solid at 1000 °C for 5 h under  $\text{NH}_3$  flow produced 0.16 g of AlN/2BN which is approximately a 67% yield (from ceramic precursor to the final ceramic). No volatile boron- or aluminum-containing materials were produced in the pyrolysis reaction. Elemental anal. found: 29.05% Al, 21.80% B, 44.35% N, 1.05% C, 0.73% H, 3.00% O. Calcd: 29.77% Al, 23.86% B, 46.37% N.

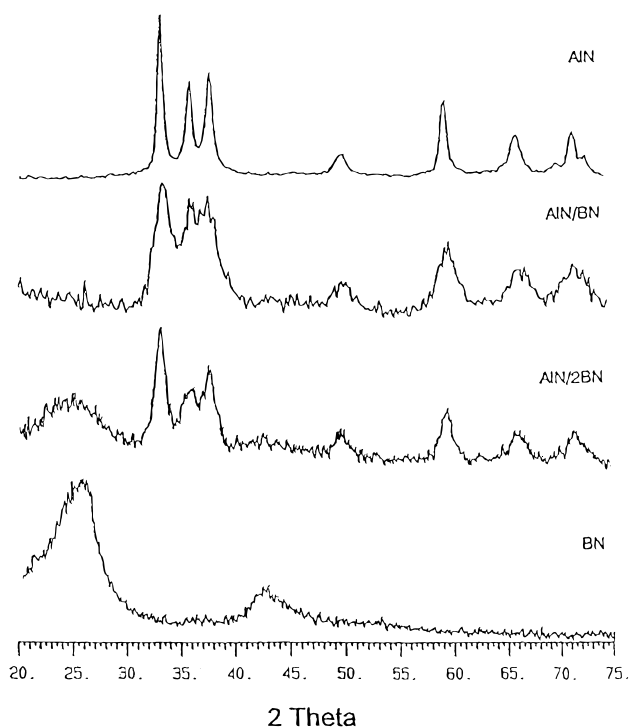
## Results

In the reaction of  $\text{Me}_3\text{AlH}_3$  with  $\text{H}_3\text{NBH}_3$  in a 1:1 molar ratio 1.32 equiv of  $\text{H}_2$  was eliminated in the formation of the precursor material. The displacement of  $\text{NMe}_3$  by  $\text{NH}_3$  (indicated by the absence of CH bands in the IR spectrum) yields a material that is a stable solid that is insoluble in common organic solvents. Pyrolysis of this solid under  $\text{NH}_3$  at 1000 °C produced the white powder AlN/BN. At no point was there any evidence for the loss of any Al- or B-containing species. The IR spectrum of this material (Figure 1) contains bands that are characteristic of BN and AlN: a strong absorption at 1400  $\text{cm}^{-1}$  ( $\text{BN}^{16}$ ), a broad band at 703  $\text{cm}^{-1}$  ( $\text{AlN}^{17}$ ), and a shoulder at 810  $\text{cm}^{-1}$  ( $\text{BN}^{16}$ ). The X-ray powder diffraction pattern of this material (Figure 2) indicates that it is mainly amorphous with weak peaks for AlN phases. Crystalline phases of BN were not observed. Annealing at 1100 °C for 3 days in a sealed quartz tube gave a crystalline material with an XRD powder pattern consistent with crystalline AlN wurtzite and amorphous BN phases (Figure 2).

In a second set of experiments, pyrolysis of the precursor to AlN/BN, under  $\text{NH}_3$  flow, was monitored by IR spectroscopy at 250, 500, 750, and 1000 °C. A



**Figure 1.** IR spectra of the 1:1 precursor material before treatment with liquid  $\text{NH}_3$  treatment (A, 25 °C), after treatment with liquid  $\text{NH}_3$  (B, 25 °C), and the pyrolysis of B at 250, 500, 750, and 1000 °C under an  $\text{NH}_3$  atmosphere.

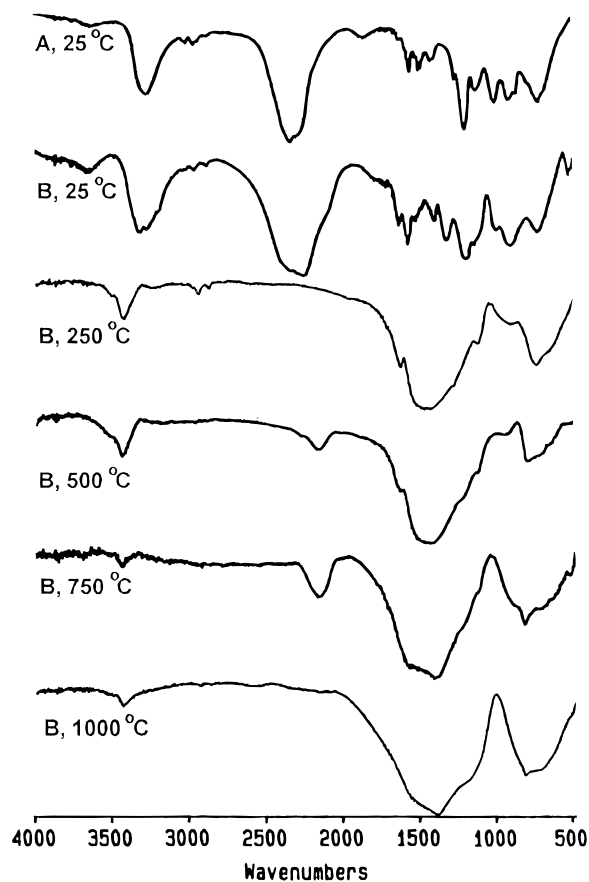


**Figure 2.** XRD patterns of the 1:1 AlN/BN, 1:2 AlN/BN, and BN (from the pyrolysis of  $\text{NH}_3\text{BH}_3$  under  $\text{NH}_3$ ) ceramic powders.

stacked display of these spectra is presented in Figure 1. At 250 °C, B-H stretching bands disappear and conversion of the precursor to AlN and BN was complete at 500 °C. At 500 °C, besides absorption bands expected for BN and AlN, a new band at 2139  $\text{cm}^{-1}$  grew in but

(16) Geick, R.; Perry, C. H.; Puppriechet, G. *Phys. Rev.* **1966**, *146*, 543.

(17) Makarenko, G. N.; Zyatkevich, D. P.; Arsenin, K. I. *Inorg. Mater.* **1979**, *15*, 535.

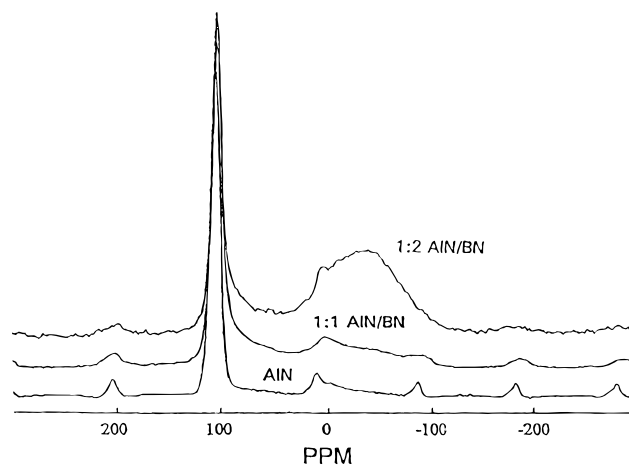


**Figure 3.** IR spectra of the 1:2 precursor material before treatment with liquid  $\text{NH}_3$  (A, 25 °C), after treatment with liquid  $\text{NH}_3$  (B, 25 °C), and pyrolysis of B at 250, 500, 750, and 1000 °C under an  $\text{NH}_3$  atmosphere.

its intensity decreased at higher temperatures and it eventually disappeared at 1000 °C.

In a third pyrolysis experiment, when the precursor material was heated to 1000 °C under vacuum, a black material was obtained. The IR spectrum of this material showed absorption bands for BN and AlN and an additional band at  $2120\text{ cm}^{-1}$ . The only volatile product from this pyrolysis was  $\text{H}_2$  (identified by mass spectrometry).

The reaction of  $\text{Me}_3\text{NAlH}_3$  with  $\text{H}_3\text{NBH}_3$  in a 1:2 molar ratio produced 3.36 equiv of  $\text{H}_2$ . The IR spectrum (Figure 3) of this precursor gave no evidence for Al–H bands. This material was pyrolyzed under  $\text{NH}_3$  at 1000 °C to yield the white powder AlN/2BN. After annealing the product at 1100 °C for 3 days, the X-ray powder diffraction pattern showed very weak peaks consistent with the formation of AlN wurtzite and h-BN phases (Figure 2). Annealing of the 1:2 ratio AlN/BN mixture at 1400 °C for 5 h had little impact on the crystallinity of the sample. It is likely that the crystallization process of either phase was hindered by the presence of the other phase. Similar findings were reported on AlN/BN nanocomposite materials,<sup>18</sup> and we found that when AlN/BN mixtures were maintained under similar conditions they also showed weak peak intensities for AlN wurtzite phases and h-BN phases. The IR spectra indicating conversion of the precursor into AlN/2BN at



**Figure 4.**  $^{27}\text{Al}$  MAS NMR spectra of the 1:1 ratio AlN/BN, 1:2 ratio AlN/BN, and AlN powders.

different pyrolysis temperatures are shown in Figure 3. Elemental analysis indicates a composition of  $\text{Al}_{1.08}\text{B}_{2.02}\text{N}_{3.17}$ , leading to an Al:B:N ratio of 1:(1.9):(3.2). These results are consistent with the initial Al:B ratio of the reactants and indicate that no Al or B has been lost during precursor formation and pyrolysis.

The solid-state  $^{27}\text{Al}$  MAS NMR spectrum for AlN/BN shows an  $^{27}\text{Al}$  resonance centered at 100 ppm for AlN phases. However, the spectrum for AlN/2BN shows one  $^{27}\text{Al}$  resonance centered at 100 ppm for AlN phases and an additional very broad resonance centered at  $-60$  ppm (Figure 4). Its shift and appearance suggest a high coordination and distorted aluminum environment; however, a survey of the current literature indicates that it does not match with any reported values for related compounds and we are unable to assign this resonance at this time. The solid-state  $^{11}\text{B}$  MAS NMR spectra of the AlN/BN composites obtained at 128.4 MHz show a broad resonance centered at 18.5 ppm which is identical with the resonance for pure BN samples and in agreement with the reported spectrum obtained at 115.5 MHz for BN.<sup>19</sup>

The morphology of the ceramic powders of the AlN/BN and the AlN/2BN composites was examined by SEM. At low magnification ( $\times 1000$ ), each sample shows composite particles about  $5\text{--}50\ \mu\text{m}$  in size with smaller fragments of random sizes. Similarly, large composite particles for the 1:1 and 1:2 ratio AlN/BN mixtures also appear to be composed of secondary and much smaller nanosized composite particles. The AlN/2BN composite shows an agglomeration of particles more so than in the AlN/BN composite. An in situ EDS study indicates that the large composite particles of both composites contain both AlN and BN. However, the AlN/2BN composite also contains only BN particles.

## Discussion and Summary

The preparation of the AlN/BN composites involved three discrete steps.

(1) The probability of preparing composites containing AlN and BN in intimate contact was maximized by generating Al–N–B linkages in the precursor material. In the formation of these precursors, the Al–N–B

(18) Kwon, D.; Schmidt, W. R.; Interrante, L. V. In *Inorganic and Organometallic Oligomers and Polymers*; Harrod, J. F., Laine, R. M., Eds.; Kluwer Academic, Dordrecht, 1991.

(19) Machetti, P. S.; Kwon, D.; Schmidt, W. R.; Interrante, L. V. *Chem. Mater.* **1991**, *3*, 482.

linkage is established through the reaction of a N–H proton of  $\text{BH}_3\text{NH}_3$  with a hydride atom of  $\text{Me}_3\text{NAlH}_3$  to eliminate  $\text{H}_2$ . In these reactions  $\text{H}_2$  given off was measured and identified. Some  $\text{NMe}_3$  also eliminated. No other volatile materials were produced.

(2) The isolated nonvolatile product of step 1, a solid, was treated with liquid  $\text{NH}_3$ , which displaced the remaining  $\text{NMe}_3$ . The solid that was isolated after  $\text{NH}_3$  was pumped away contained no  $\text{NMe}_3$  based upon the IR spectrum.

(3) The nonvolatile solid from step 2 was pyrolyzed under a slow stream of  $\text{NH}_3$  at  $1000^\circ\text{C}$ . In this step, a trap system was set up such that any volatile materials that would not have a significant vapor pressure at  $-30^\circ\text{C}$  would be caught in the trap. No material was collected in the trap. On the basis of these results, no Al or B has been lost during the reaction sequence. Therefore, the starting Al:B ratios of 1:1 and 1:2 have been preserved in both the precursors and the ceramics. As a further test that aluminum and boron are not removed from the reaction mixture, an elemental analysis was performed on the 1:2 ceramic. It shows that the 1:2 Al:B ratio is retained.

This study demonstrates that  $\text{Me}_3\text{NAlH}_3$  and  $\text{H}_3\text{NBH}_3$  can serve as starting materials for AlN/BN composites.

The reactions of  $\text{Me}_3\text{NAlH}_3$  with 1 or 2 mol equiv of  $\text{NH}_3\text{-BH}_3$  in hydrocarbon solvents produce precursors for ceramic mixtures of AlN/BN. AlN/BN mixtures are produced in good yield (60–75%). SEM studies reveal that the AlN/BN mixtures are composed of nanosized composite particles of AlN and BN. Solid-state MAS  $^{27}\text{Al}$  NMR spectra for the AlN/BN mixtures show expected resonances for AlN phases, and no oxide phases are detected. An interesting new resonance centered at  $-60$  ppm for the 1:2 ratio AlN/BN was observed. However, assignment of this signal could not be made due to limited references available in this area.

**Acknowledgment.** We want to thank John C. Mitchell in the Department of Geology for his help with the SEM studies and Chris R. Feger and Dr. R. P. Ziebarth on the induction furnace work. This work has been supported by the Army Research Office through Grant DAAL03-92-G-0199. NMR spectra were obtained at The Ohio State University Chemical Instrumentation Center (funded in part by NSF Grant No. 79-10019 and NIH Grant No. 1S10PR0140518-01A).

CM960355A