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REVIEW

Boron Nitride Precursors—A Perspective

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Research efforts conducted in the Chemistry Division of the Oak Ridge National Laboratory on the preparation of polymeric precursors to boron nitride are reviewed. They evolved from the preparation of powders, which contained significant amounts of residual carbon, derived from the pyrolysis of aminoborane polymers to relatively pure films produced by chemical vapor deposition using polymeric cyanoborane as a single source. Interesting C/B/N films were produced from the pyrolyses of volatile borazine derivatives, and a polymeric borazine intermediate produced denser boron nitride (BN) compact bodies when used as a binder as opposed to bulk BN compressed without a binder. The challenges of producing boron nitride fibers have been defined.

Keywords: boron nitride; pyrolysis; chemical vapor deposition; aminoborane; borazine

INTRODUCTION

A marked upsurge in research efforts took place about 15 years ago to find new synthetic routes to ceramic materials, both oxide and non-oxide compounds, that departed from the conventional 'heat and beat' approach which had proven adequate for many years in the production of oxide-based ceramics. The driving force behind this trend was the need to fulfill the more stringent requirements that advances in technology have placed on materials. The physical and chemical properties, such as mechanical strength and chemical resistance, at ever-high temperatures that are now required of materials are no longer being met by conventional metal alloys and ceramics. A new category of materials is making its way from research laboratories, both industrial and academic, into the market place. These are known as 'advanced ceramic materials'; they consist mainly of simple combinations of the lighter elements of the Periodic Table and have as distinguishing characteristics higher strength and higher chemical and thermal stability. Examples of advanced ceramic materials are boron nitride (BN), silicon carbide, silicon nitride and aluminium nitride, as well as composites of two or more ceramic phases. The synthetic challenges for the preparation of advanced ceramic materials are compounded because these materials are used as bulk materials, as composites or as coatings; thus specific morphologies such as powders, fibers, whiskers or films are required.

Much of the impetus for the new trends in the development of advanced ceramic materials was initially prompted by the pioneering work of Yajima[1] on the production of silicon carbide fibers from organosilicon polymers, as well as the vision expressed by Rice[2] of the research opportunities and needs at an early stage of that area of research.

Research efforts on advanced ceramic materials conducted at this Laboratory covered diverse materials, but a great deal of those efforts were concentrated on the preparation of boron nitride in different morphologies. This review is a description of that work from the perspective of a few years after its completion, from which one can glean a vision of the significance of past accomplishments and future research requirements.

AMINOBORANE POLYMERS AS PRECURSORS OF BORON NITRIDE

Aminoborane polymers were prepared via condensation reactions between polyfunctional amines and either triethylborane or tris(dimethylamino)borane.[3] The thermal degradation of the products was studied to establish pyrolytic pathways so that a rational synthetic approach could be obtained in order to design better precursors, specifically those that would produce the desired ceramic product in high yield

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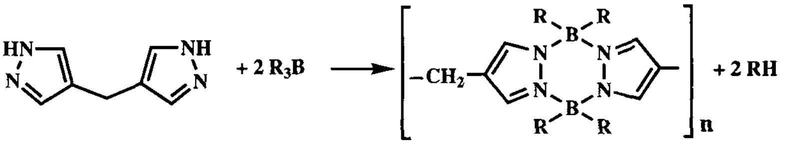


[1]

and ideally preserve the morphology of the precursor. The different products prepared in this study will be discussed in turn, according to the starting amine used for the condensation reaction.

4,4-Methylenedipyrazole

Trofimenko[4] described the preparation of pyrazabole polymers by the reaction of 4,4′-methylenedipyrazole and triethylborane according to Eqn [1], where R = ethyl.

The product was described as being soluble in toluene, but it was not fully characterized other than by chemical analysis and thermal treatment under mild conditions. This polymer seemed attractive since it was soluble, suggesting that it could be cast as a film or spun into fibers. The material prepared in the course of our study was toluene-soluble and consisted of a polymer with nine repeat units on the basis of chemical analysis and a molecular weight determined to be 2704. Pyrolysis under dynamic vacuum to 800 °C left a residue containing 51.5 wt% of the initial amount. The volatiles condensed in a trap held at −196 °C consisted of ethylene, hydrogen cyanide, ammonia and triethylborane. A material balance showed that the condensable fraction accounted for 83 wt% of the volatile evolved; the remainder, detected in a separate experiment, was hydrogen and methane. It is significant that the triethylborane evolved in the pyrolysis was only 10 wt% of the total boron content; thus the residue contained the bulk of the initial boron in the polymer. The polmer was also subjected to thermal analysis by thermogravimetric analysis—differential thermal analysis (TGA–DTA), heated under a stream of argon to 1200 °C. The results of the analysis, illustrated in Fig. 1, showed a sharp exothermic event at 432 °C that coincided with a significant weight loss. Cumulative weight losses amounted to 53% at 700 °C and 76.7 at 1200 °C. The X-ray pattern of the residue showed some faint lines suggestive of graphite. A sample of the vacuum pyrolysis residue was hot-pressed at 1600 °C and 44 MPa. The

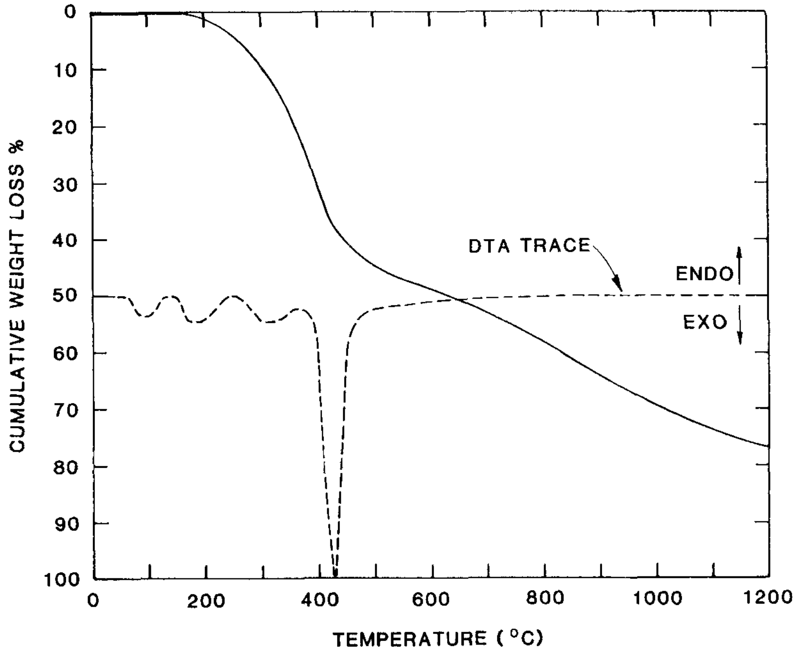
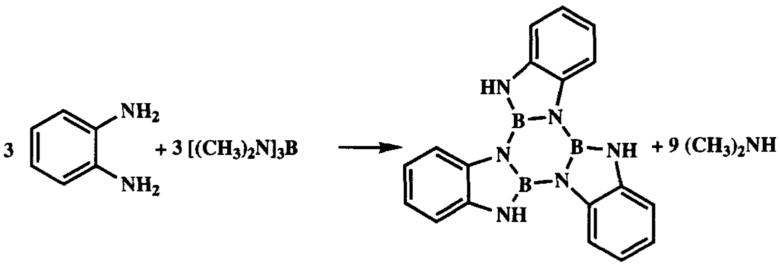


Figure 1 TGA–DTA of pyrazabole polymer.



[2]

overall yield of the compact was 25 wt% and it had a density of 1.41 g cm^{-3}, considerably lower than that of graphite or pure boron nitride. The chemical analysis of the 1600 °C residue showed, in wt%: C, 51.85; H, 0.16; N, 21.59; B, 20.51; O, 1.73. The electrical conductivity of this material was 1.1 S cm^{-1}, similar to that of pyrolyzed organic polymers. It was observed that the residue contained significant amounts of carbon but it was not until a later stage that it became established among different groups conducting research on the preparation of ceramic materials from polymeric precursors that residual carbon could be eliminated by heating in ammonia to ≥700 °C. In any event, ceramic materials containing composites of carbon and boron nitride are attractive in their own right, given the differences in electrical conductivity between the two materials.

The pyrazabole polymer could not be formed as fibers or as a film that would remain intact after pyrolysis to 800 °C. The polymer failed to form viscous solutions and it did not melt as it was heated.

o-Phenylenediamine

The reaction between tris(dimethylamino)borane (TMADB) and *o*-phenylenediamine was previously studied by Beyer *et al.*[5] It produces an interesting fused-ring system with an inner core of a borazine ring. The reaction is described by Eqn [2].

The pyrolysis of this borazine derivative had to be conducted in a closed system,[6] given its extraordinary thermal stability and tendency to sublime in an open system. Pyrolyses were conducted in sealed quartz ampules at 800 °C, which produced a residue with an 85% yield in the form of adherent coatings. Volatiles generated in the pyrolysis were methane and hydrogen as well as small amounts of ammonia, hydrogen cyanide and benzene. A variety of substrates such as silicon, steel, titanium or quartz were coated within the confined volume of the sealed ampule. The coatings appeared as smooth, highly reflective metallic films which were characterized by a variety of physicochemical means. A material balance showed that the residue would have an idealized composition corresponding to, in wt%: C, 64.8; N, 23.4; H, 0.8; B, 11.0. Actual analysis of the residue proved to be somewhat difficult, since it is deposited as a tenaciously adhering coating. Material scraped from the inner wall of the ampule was analyzed as, in wt%: C, 55.69; H, 1.69; N, 19.24; B, 9.6; O, 10.3. This accounts for 96.58%. The unaccounted balance might be due to silicon from the substrate which would also account for the oxygen present. Alternative interpretations for the presence of oxygen are moisture incorporation or as a result of diffusion and chemical attack on the quartz. The density of the films was 2.07 g cm^{-3}, and the electrical resistivity measured 2.34 Ω cm at room temperature. Attempts were made to measure the microhardness but the film behaved elastically in a fashion similar to vitreous carbon, showing Young's modulus of 20 GPa. In common with vitreous carbon, the films proved to be quite resistant to chemical attack according to an empirical test[7] that measures oxidation resistance to a sulfuric–nitric acid mixture. The thermal band gaps derived from the temperature dependence of the electrical conductivity were 0.02 eV for the as-deposited film and 0.46 eV for the oxidized film. Examination by transmission electron microscopy (TEM) revealed that the material was for the most part amorphous, but there were a few spots containing crystallites of cubic BN, as well as another modification of boron nitride observed by Russian workers[8] on materials subjected to explosive shock compression. It is interesting to note the presence of high-pressure modifications in films deposited under conditions close to atmospheric pressure; evidently, high compressive forces may develop on a microscopic scale on the film as it is being deposited and cooled to room temperature. The Raman spectrum of the film was similar to that of other carbonaceous materials;[9] no confirmation was found, using this technique, for the presence of cubic boron nitride, which evidently is present in relatively small amounts.

3,3′Diaminobenzidine

The condensation product between 3,3′-diaminobenzidine and TMADB produced a polymeric product, having an approximate molecular weight of 2600. An idealized structure of this polymer is shown below.

Pyrolysis of this polymeric material produced a residue containing 59 wt% of the initial material. The residue appeared as a tan-colored solid that did not undergo carbonization unless maintained at 800 °C for a few hours. The initial residue retained a considerable amount of hydrogen as C—H and N—H moieties as observed in the IR and confirmed by chemical analysis, in wt%: C, 61.75; H, 3.29; N, 22.24; B, 8.84. It is interesting to note the marked contrast in the nature of the condensation products from TMADB and from the two aromatic amines; one amine, *o*-phenylenediamine, led to a cyclic product while the other, diaminobenzidine, led to a polymeric material. Apparently steric effects and the presence of two reaction sites in the benzidine favor polymerization for the latter instead of ring closure.

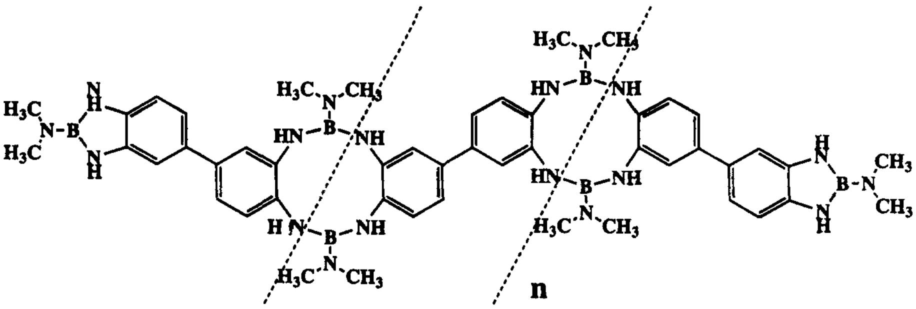
Diethylenetriamine

Given the higher initial nitrogen content, this amine was used in an attempt to increase also the boron content of the resulting condensation product. Indeed, the chemical analysis of the condensation product showed relatively high nitrogen and boron contents of 36.3 and 11.74 wt%, respectively; the balance is accounted for by 42.4 C wt% and 7.39 H wt%. Removal of toluene from the initial polymer solution led to additional crosslinking and loss of solubility. Pyrolysis of this material to 800 °C generated volatile oligomers and small amounts of acetylene, ammonia and hydrogen cyanide, leaving a residue of 12% of the initial weight.

This initial study on the thermal stability of a variety of aminoborane polymers pointed to the fact that borazine-based polymers were in all probability better precursors to boron nitride since the aminoboranes have a relatively low initial boron content and, in spite of the fact that very little boron is evolved in the pyrolysis, the retention of significant amounts of carbon leads to C–B–N composites. Additional work was conducted[10] on the deposition of carbon films containing nitrogen and/or boron using pyrolysis of a variety of precursors in sealed systems. These films are not readily accessible by means other than chemical vapor deposition (CVD) that involve mixtures of gases as the source for the films.

BORAZINE POLYMERS AS PRECURSORS OF BORON NITRIDE

An attempt was made to produce polymeric precursors having borazine as the main building block through the condensation of trichloro- or dichloro-borazine with bis(trimethylsilyl)-acetylene.[11] The reactions were conducted in sealed ampules at 100 °C and required the presence of anhydrous aluminum chloride as catalyst. The condensation reaction produced trimethylchlorosilane and borazine linked through acetylene moieties. The reactions had to be stopped at about 60% conversion, as determined by the amount of chlorosilane released, in order to preserve solubility in organic solvents.



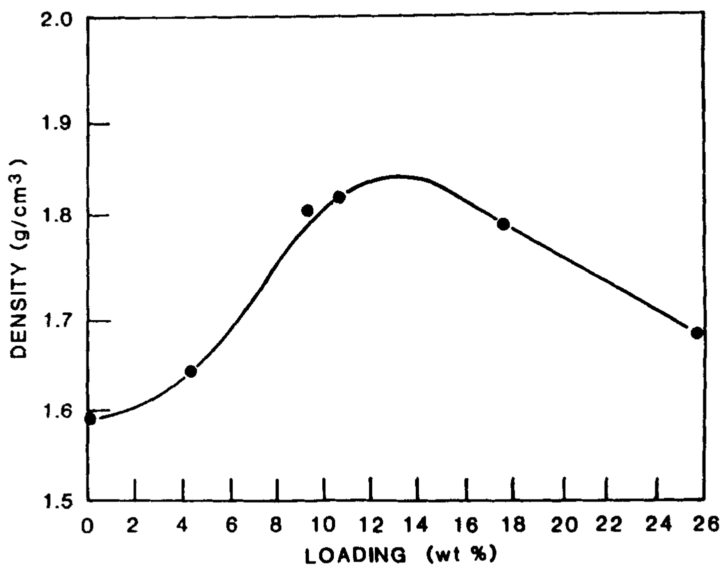


Figure 2 Effect of binder-derived residue on the density of hot-pressed BN–binder composite.

Dichloroborazine was examined with the expectation that it would produce a tractable linear polymer, but it behaved in a similar manner to the trichloroborazine. The partially converted products did not produce viscous solutions appropriate to draw fibers; this fact limited the use of these intermediates to ceramic binders, which also comprise a valuable application for ceramic precursors. The development of SiC fibers from polymeric precursors by Yajima and his colleagues, mentioned in the introduction, brought the realization that precursors of ceramic materials could be used as binders of bulk ceramic powders.[12,13] This concept is of importance in forming nonoxide ceramic materials which sinter only at very high temperatures. Use of a ceramic precursor as a binder offers the advantage that, during processing, a residue derived from the binder is deposited within the pores of the form being processed to produce a denser and stronger product.

The precursor derived from the trichloroborazine condensation appeared to be a good candidate as a binder of bulk boron nitride powder because of its relatively high ceramic yield and the straightforward nature of the pyrolysis that produced a small volume of volatiles. The pyrolysis of the precursor, conducted under dynamic vacuum to 800 °C, produced a weight loss of 46% which was accounted for by the amount of chlorosilane collected. The chemical analysis of the residue showed, in wt%: C, 30.7; N, 30.7; B, 23.5; Cl, 4.9; Si, 3.8. It is significant that the pyrolysis does not release any nitrogen- or boron-containing species. Use of the precursor as a binder involved mixing a solution of the precursor dissolved in toluene with different proportions of boron nitride powder. The solvent in the suspension was evaporated under dynamic vacuum while holding the mixture in an ultrasonic bath. The resulting free-flowing powder was hot-pressed under vacuum at 27.6 MPa and 800 °C in a graphite die. The apparent density of the resulting pellets is plotted in Fig. 2 as a function of the relative proportion of residue derived from the initial precursor load. The figure shows that loading to the extent of 13 wt% produces a maximum in density of about 81% of theoretical for pure BN. Higher loadings produce a decrease in density. This phenomenon was also observed by Yajima *et al.*[13] and relates to the optimum filling of voids.

An extensive microstructural analysis was conducted on the hot-pressed specimens. It was possible to distinguish the initial boron nitride from that derived from the precursor because of the presence of minor impurities such as the aluminum used as catalyst. The microscopic observations revealed the fact that the boron nitride derived from the precursor underwent crystallization to produce a material with acicular morphology, in contrast with the initial bulk boron nitride that had a platelike morphology, being subjected to densification. This is illustrated in Figs 3 and 4.

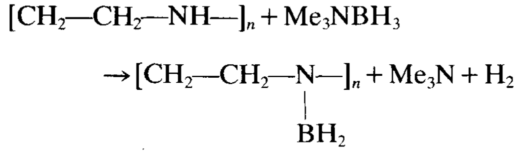
Figure 3 TEM micrograph of an area of hot-pressed BN–binder showing acicular crystals.

Figure 4 Micrograph of fracture surface of a hot-pressed BN–binder composite showing intergranular fracture and platelike grains.

These observations were rather unexpected, given the relatively low processing temperature: it was found in independent tests that this temperature was not sufficient to crystallize the precursor in the absence of the bulk boron nitride present in the composite.

DERIVATIZATION OF PREFORMED POLYMERS

An attempt was made to use the derivatization of preformed polymers as an alternative synthetic approach to ceramic precursors,[14] given the fact that most polymeric ceramic precursors are prepared from moisture- or air-sensitive starting materials and the condensation reactions are difficult to manipulate in such a way that tractable products are obtained. In this study polyethyleneimine (PEI), $[\text{—HN—CH}_2\text{—CH}_2\text{—}]_n$, a commercial product available in different degrees of polymerization, provided a convenient material to test the concept that derivatization could afford processable precursors. The derivatization reactions examined involved transamination with trimethylamine borane (Eqn [3]) or trimethylamine triborane.



$$[\text{CH}_2\text{—CH}_2\text{—NH—}]_n + \text{Me}_3\text{NBH}_3 \rightarrow [\text{CH}_2\text{—CH}_2\text{—}\underset{\substack{|\\ \text{BH}_2}}{\text{N}}\text{—}]_n + \text{Me}_3\text{N} + \text{H}_2 \qquad [3]$$

Equation [3] shows the formation of an aminoborane and hydrogen elimination instead of the simpler borane transfer to form an amine–borane ($\text{R}_2\text{NH}\cdot\text{BH}_3$) moiety. This assignment was based on the observation of hydrogen evolution during solvent elimination as well as analytical results from the determination of hydridic hydrogen in the final product.

An alternative derivatization strategy involved conversion of the polymeric amine to the corresponding hydrochloride followed by reaction with sodium cyanotrihydroborate. The insertion of the —CNBH_2 moiety is useful because the nitrogen on the cyano functionality may be further derivatized with additional boron-containing reactants. Transamination of PEI with trimethylamine borane produced boron incorporation corresponding to 56% derivatization. No clear advantage was found in using the triborane derivative for loading additional boron. The cyanoborane reactions proceeded as expected, but it proved difficult to eliminate the sodium chloride by-product of the derivatization. The derivatized PEI products were pyrolyzed at 800 °C under vacuum, resulting in powders with yields ranging from 30 to 60%. A typical analysis of these products shows, in wt%: C, 38.1; H, 0.4; N, 35.2; B, 26.3. The preparation of films was also examined by spin-coating quartz disks with derivatized polymer solutions followed by vacuum pyrolysis to 800 °C. The films contained residual carbon after the pyrolysis treatment, but this impurity could be significantly reduced by an additional thermal treatment in the presence of ammonia.

BORON NITRIDE FILM DEPOSITION

A search of the literature for potential polymeric precursors to boron nitride identified polymeric cyanoborane, $(CNBH_2)_n$, as a reasonable choice, given the relatively high boron and nitrogen content. The preparation and chemistry of this material was first described by Spielvogel *et al.*[15] It is obtained by treating a suspension of sodium cyanotrihydroborate in ether with hydrogen chloride. The sodium chloride by-product is readily separated to leave a solution of the polymer, which is actually a mixture of oligomers. Preliminary pyrolyses experiments of the polymer under dynamic vacuum showed little ceramic yield but there was distinct film deposition on the cooler portions of the pyrolysis tube, just beyond the furnace. This finding clearly suggested the potential of the cyanoborane as a single-source precursor for the chemical vapor deposition (CVD) of boron nitride, and additional experiments proved that this was indeed an appropriate use. The CVD procedure consisted of a two-zone furnace containing the source at 150 °C and the substrate at 600 °C. The resulting films contained mostly boron nitride with a residual carbon content of 18 wt% which would be lowered to 2 wt% by treatment with ammonia at 800 °C. The films were adherent to a variety of substrates, including steel, silicon, quartz and sapphire as well as silicon carbide fibers. The electrical resistivity of the films, both the crude deposit and the ammonia-treated material, was extremely high, of the order of 10^{15} Ω cm in accordance with the anticipated characteristics of boron nitride. The Knoop hardness of the pure boron nitride film was 88, which is comparable with hot isostatically pressed BN with a Knoop hardness of 29, and quite short of cubic BN with a hardness in the 1000–3000 range.

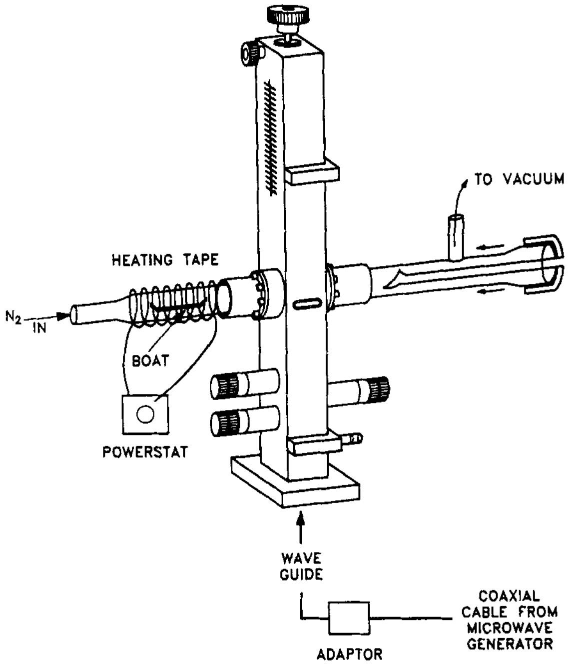


Figure 5 Apparatus for the plasma-enhanced chemical vapor deposition of boron nitride films.

Additional work was conducted with a cyanoborane as a source for the deposition of BN films. In this case the process was activated with a nitrogen plasma generated with microwaves and using 100 W net power in the apparatus illustrated in Fig. 5. No additional external heating of the substrates was supplied. Film deposition took place at about 400 °C to generate adherent coatings on a variety of substrates. The films deposited by plasma-enhanced CVD contained paracyanogen as an impurity to the extent of about 20 wt%. Paracyanogen is a polymeric form of cyanogen;[17] it is generated by sputtering carbon in a nitrogen plasma or it can also be generated by chemical means. The paracyanogen impurity in the boron nitride films could be eliminated by a thermal treatment at 800 °C in vacuum, given the susceptibility of paracyanogen to depolymerization at that temperature. In any event, the elimination of paracyanogen is not required if the intended application of the boron nitride does not involve high temperatures. Paracyanogen is an electrical insulator so that the electrical properties of boron nitride films would not be degraded by its presence.

CONCLUSIONS

Synthesis of boron nitride from a variety of precursors, particularly those with pre-existing boron nitrogen bonds, is simplified by the favorable thermodynamic driving force resulting from the stability of BN. The challenges reside in attempting to obtain a given morphology. The preparation of boron nitride fibers is by far the most demanding task, requiring a well-defined set of characteristics so that crosslinking takes place as the pyrolysis progresses in order that the fiber morphology might be preserved. A few groups achieved the goal of producing boron nitride fibers using polymers based on the borazine structural unit.[18] An alternative to the preparation of pure boron nitride fibers for use in ceramic composites is to coat other more accessible fibers already in commercial production. This approach is much less demanding since CVD processes are simpler to control.

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