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Boron Nitride Obtained from Molecular Precursors: Aminoboranes Used as a BN Source for Coatings, Matrix, and Si_3N_4–BN Composite Ceramic Preparation

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Aminoboranes, pure or partially converted into aminoborazines using thermal or aminolysis polymerization, have been used as boron nitride precursors. An amorphous BN preceramic is obtained when pyrolysed up to 1000°C that can be stabilized using further annealing up to 1400°C or crystallized into h-BN above 1700°C. These molecular precursors have been used to prepare carbon fiber/BN matrix microcomposites to get an efficient BN coating on graphite and as a BN source in Si_3N_4/BN composite ceramic. The properties of these new types of samples have been compared with those obtained by classical processes. The boron nitride obtained from these precursors is a good sintering agent during the hot-pressing of the samples. However, the crystallinity of BN, even sintered up to 1800°C, remains poor. In fact, most of the mechanical properties of the composite ceramic (density, porosity, hardness) are clearly improved and the aminoboranes can be considered as convenient boron nitride sources and helpful sintering agents in hot-pressing technology. © 1997 Academic Press

INTRODUCTION

Boron nitride, in view of its unique properties, especially the absence of electrical conductivity, oxidation resistance, and optical transparency, offers advantages over other ceramics. Until recently, the main part of ceramics have been prepared as powders and made into articles via classical high-temperature techniques. However, their unreliable processing and sintering characteristics make it difficult to obtain high performance products (1, 2). The need for more processible boron nitride has opened new routes of obtaining BN coatings, matrix and fibers. The transformation of organoelement polymers to inorganic solids by polymer thermolysis gives novel ceramic materials which can be processed to fibrous or bulk materials. Polymers that contain boron and nitrogen offer an attractive approach (3–5). Two classes of these compounds have been known for many years: the borazines, six-membered ring B_3N_3 benzene like molecules, and the more simple aminoboranes $B(NHR)_3$. The aminoborane chemistry was developed in the early 1960s but no further attention was given to material science applications (6–8). In regard to their simple and high yield preparation through a one step reaction using BCl_3 and a primary amine, RNH_2, the aminoboranes have been used in order to obtain boron nitride. Previously reported works have described the polymerization of tris(methylamino) borane and the ability of this compound to provide turbostratic and then h-BN when thermolysed up to 1700°C (9–11). The influence of the organic part of the aminoborane has been studied and the conversion of bulky aminoborane into boron nitride through an aminolysis reaction performed (12). This reaction proceeds through an exchange of the bulky amine for ammonia. The aminoborane obtained is highly reactive and a polymerization occurs as soon as the ammonia treatment is performed. This aminolysis reaction, if run to completion, leads to a carbon free precursor, where the borazine rings are bonded through a NH bridge (13). The lowering of the carbon ratio of the precursor allows the preparation of as pure boron nitride as prepared from borazine polymers. However, as described for borazine precursors, the wetting properties of carbon-free precursors are low, especially toward carbon fibers and graphite. The composites or coatings obtained exhibit poor interface adherence or require hot-pressing techniques to infiltrate the precursor into the carbon fiber bundles (14, 15).

In the present work, several types of polymerization treatments have been performed to get graphite coatings using

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tris(methylamino)borane or tris(isopropylamino)borane. The efficiency of the protection was determined using oxidation tests performed on coated graphite. In the same way, the preparation of a BN matrix from aminoboranes have been realized.

Boron nitride addition to silicon nitride, Si_3N_4, leads to composite ceramics which combine the mechanical properties of Si_3N_4 and the superior resistance of BN to the thermal shock and to the erosion of molten metals. In order to prepare the composites Si_3N_4–BN, several attempts have been made to evaluate the efficiency of aminoboranes as a boron nitride source and as a sintering agent when used with silicon nitride and BN platelets.

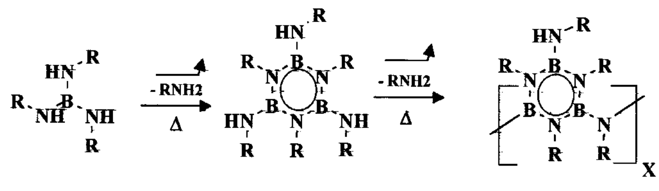
RESULTS

Precursors preparation. The aminoboranes have been prepared according to Reaction I. The synthesis is performed at low temperature to reduce side reactions leading to aminoborazines. The yield is high in regard to the more expensive reactive, the boron trichloride. The crude product is related to the nature of the amine. Using methylamine a polymerization of the aminoborane occurs as soon as the reaction is started and a mixture of tris(methylamino) borane **A** and 1,3,5-tris(methylamino)-2,4,6-trimethylborazine **B** is obtained. **B** is the first step of the polymerization of **A** as shown in the general polymerization reaction shown in the Scheme 1.

Using the bulky amine, Pr^iNH_2, no polymerization occurs and the pure aminoborane is recovered. The polymerization can be improved using ammonia treatment of the crude product of the synthesis as shown in Scheme 2.

$BCl_3 + 6\,RNH_2$ ------> $B(RNH)_3 + 3\,RNH_3Cl$

REACTION I



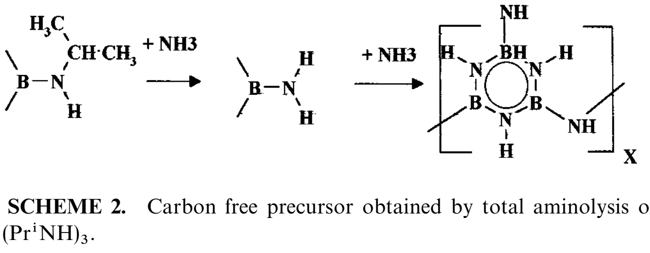
A **B**

SCHEME 1. Thermal polymerization of $B(MeNH)_3$.

Usually the tris(methylamino)borane used as precursor for ceramic preparation is a mixture of aminoborane (85 wt%) and aminoborazine (15 wt%). When the borazine proportion increases, the precursor viscosity is raised and the wetting properties toward the reinforcing substrate are lowered. The aminolysis prepolymerization of the precursor also increases the ceramic yield by decreasing the amount of the hydrocarbon part of the precursor. This pretreatment is especially efficient when tris(isopropylamino)borane is used but to maintain the physical properties of the precursor, the ammonia exchange must not exceed 20 to 25% molar of aminoborane when used for impregnation. When pyrolysed up to 1400°C the elemental composition of the BN matrix obtained is related to the thermolysis conditions. Under an inert gas flow, the tris(methylamino)borane precursor thermolysis leads to a black ceramic containing a large amount of carbon (B, 33.4; C, 15.4; N, 45.5; H, 0.6; O, 5.3; Anal Calcd for BN: B, 43.6; N, 56.4). When the thermolysis is performed in two steps, the first under an ammonia flow up to 500°C and the second under inert gas up to 1400°C, white BN is obtained and the carbon amount is drastically lowered (B, 40.3; C, 0.4; N, 58.0; H, 0.8; O, 4.0). Comparable results are obtained from $B(Pr^iNH)_3$. The thermolysis under an inert gas does not lead to a ceramic because the stripping of the aminoborane prevails over its polymerization however the aminolysis followed by the thermolysis leads to white BN (B, 38.3; N, 53.2; C, 0.7; H, 1.8; O, 6.4).

BN/C microcomposites and graphite coating. These precursors have been tested in a microcomposite preparation using a dip coating technique. The bundles of PAN fibers or graphite samples were dipped into the precursor and then thermolysed following different conditions. The more efficient thermal program is based on a two-step thermolysis used for bulk precursors. From room temperature up to 500°C the heating rate is $0.5\,K\,mn^{-1}$ while ammonia is added to pure nitrogen. Then the temperature is raised to 1000°C with a $5\,K\,mn^{-1}$ heating rate under nitrogen. The samples obtained are then stabilized up to 1400°C under vacuum and a compact composite rod composed of carbon filaments embedded in a BN ceramic matrixis obtained. An optical micrograph of a cross section of this rod shows a compact BN matrix obtained including very few bubbles that is consistent with the thermolytic procedure favoring the liquid or waxy form of the preceramic polymer allowing the evolution of the gas formed during the polymerization.

The dip-coating technique has been used to protect graphite samples. The usual thermolysis and stabilization process has been employed to coat standard graphite cubic samples of 6 mm edge and about 400 mg weight in order to



SCHEME 2. Carbon free precursor obtained by total aminolysis of $B(Pr^iNH)_3$.

compare the results of the oxidation tests. When the optimized process is used a tightly adherent coating is formed. The optical surface micrography shown in Fig. 1 exhibits large boron nitride chips separated by microcracks. Using the same technique, a section of treated samples (Fig. 2) shows that an irregular overlayer of about 10 μm coats the surface (A) and infiltrates the larger pores (B). If the aminolysis of the precursor is complete, a carbon free precursor is obtained particularly with $B(Pr^{i}NH)_3$. Unfortunately in this case, the BN coating obtained is not adherent to the substrate. These results are comparable with those of the literature obtained using other precursors (13–15). To evaluate the BN coating efficiency toward the graphite oxidation, treated and untreated samples have been heated up to 650 or 750°C under high vacuum and then placed abruptly in air while their weight changes were recorded. Figure 3 shows the results obtained using a monoimpregnated-pyrolyse cycle of the samples. The weight loss rate of the untreated sample at 650°C is comparable to the results obtained using a coated sample but at a temperature of 750°C. At 650°C the oxidation rate of coated samples is 10 times lower than with uncoated graphite. These results show the great efficiency of the impregnation thermolysis treatment to cover graphite with a boron nitride thin overlay using aminoboranes as BN precursors.

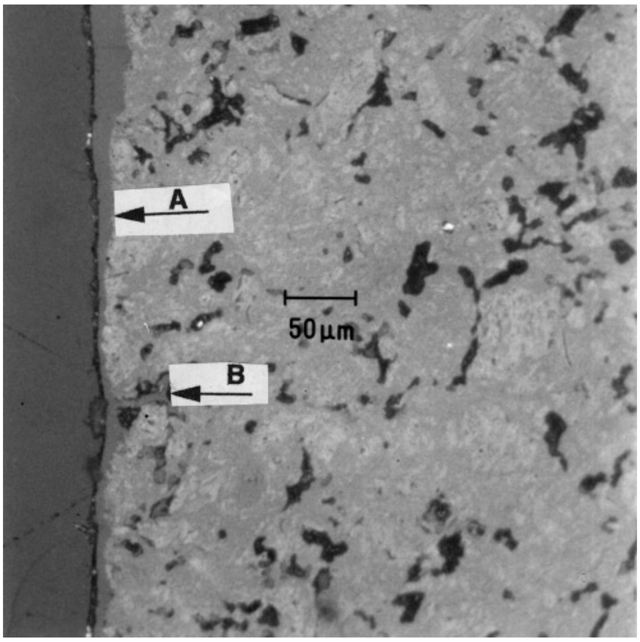


FIG. 2. Optical micrograph of a cross section of the BN-coating on graphite.

Si_3N_4/BN composite ceramic preparation. Hot-pressing techniques have been used for many years to prepare Si_3N_4/BN composite ceramics (16). New trends in nanostructured ceramics have led to the development of new syntheses involving complex molecular precursors reacted to obtain polymers or gel whose thermolysis leads to composite ceramics (17–19). In previous work (20), composite Si_3N_4/BN ceramic using classical sintering aids (5 wt% Y_2O_3, 2 wt% Al_2O_3) and hot-pressing preparation has been prepared and studied. In order to compare the properties of the new synthetic routes, the composite ceramics have been synthetized by mixing the molecular BN precursor with fine powders of Si_3N_4 or with a mixture of Si_3N_4 and h-BN

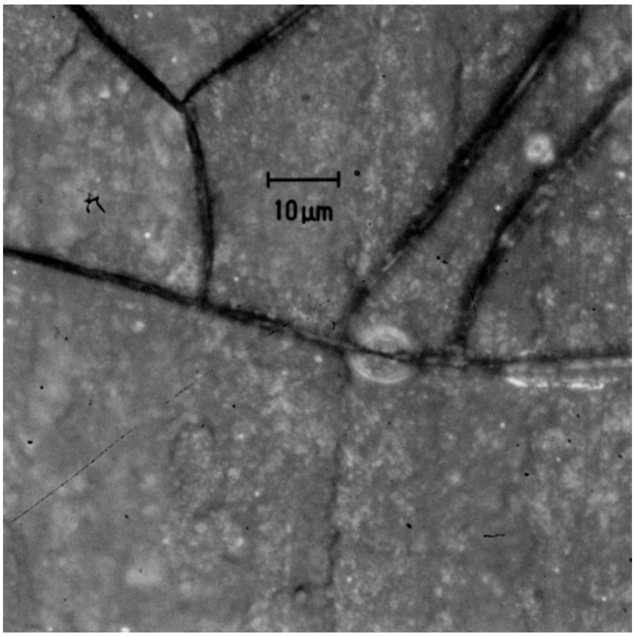


FIG. 1. Micrograph of the graphite coated surface.

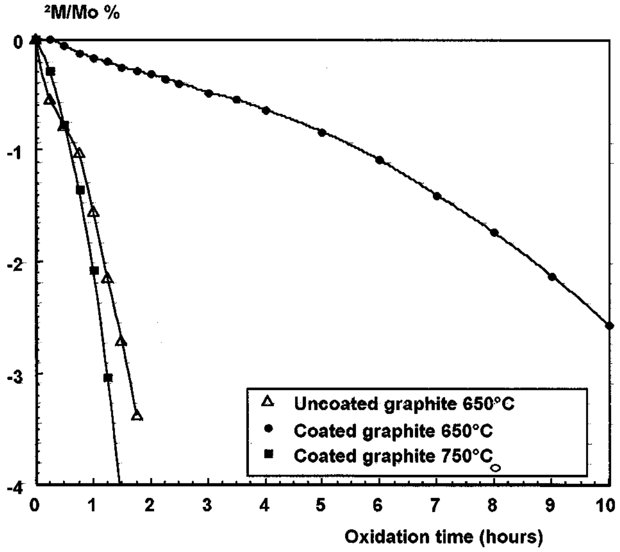


FIG. 3. Efficiency of the coating protection of graphite against oxidation.

platelets according to a described procedure (21), an homogeneous paste-like mixture is obtained. Two pyrolysis temperatures, 700 and 1050°C, have been used for the preceramic, while the heating rate and the ammonia flow are kept the same as for the bulky precursor thermolysis. A preceramic white residue was obtained and introduced, under controlled atmosphere, into graphite dies to be submitted to a uniaxial hot-pressing up to 40 MPa and 1800°C under a nitrogen atmosphere. Two Si_3N_4/BN ratios, 21.3 and 27.7 wt%, have been obtained directly from Si_3N_4 and the precursor mixture and from the mixture Si_3N_4, h-BN, and the precursor to estimate the ability of the system and the properties of the ceramics produced. Figure 4 shows the shrinkage rate change during the hot-pressing of a 10% BN prepared using the classical method and a 21.3% BN sample (sample III) prepared with molecular precursor. The evidence of the shrinkage aid afforded by the precursor during the hot-pressing is very important and the compaction of the powder is more efficient. Figures 5 and 6 show two characteristic properties of composite ceramic: density and hardness. The porosity is also lowered from 4.8% for a 20% BN classical sample to 1.9% for a 21.3% BN sample obtained from precursor thermolysis. These measurements are indicators of an important increase of the qualities of the ceramics and the samples obtained exhibit very good properties. No difference can be seen between the two temperatures used for the pyrolysis of the preceramics. The SEM fractographic observation exhibits a very fine and isotropic texture of the precursor made samples consistently with the high density observed. BN obtained from molecular precursors leads to good quality Si_3N_4–BN composites under the experimental conditions. The density, porosity and Vickers hardness of the samples are clearly improved and the increase in the density of the sample is easier than with classical sintering aids. The aminoborane molecular precursor can be considered as a sintering activator and as a boron nitride source for Si_3N_4–BN composites preparation.

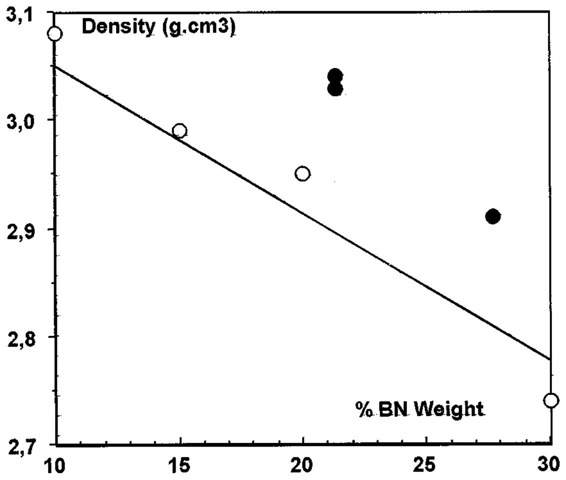


FIG. 5. Density of the samples obtained. ○, Classical obtained samples; ●, samples obtained from preceramics.

CONCLUSION

New trends in composite ceramics have rekindled interest in inorganic polymers. Some recent findings are making researchers look again at the potential of inorganic polymers that can develop through sol–gel or copolymerization technique, giving new access to nanostuctured ceramic. The intimate structure realized directly from the precursor seems to be able to enhance the composite ceramic properties. In fact, early chemistry of aminoboranes can lead to an attractive development because these compounds are among the most easily available and less expensive of the boron nitride molecular precursors.

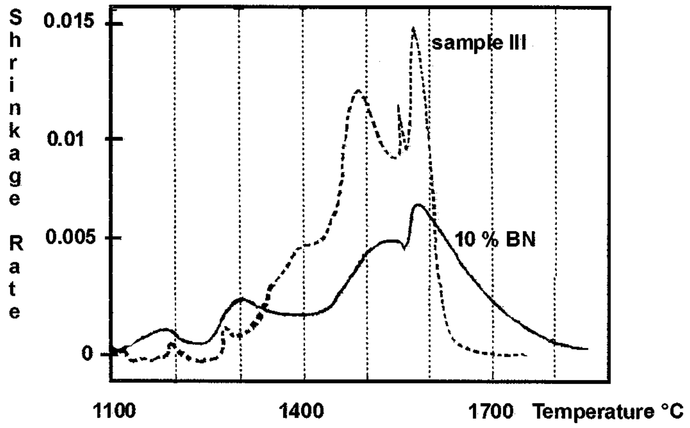


FIG. 4. Shrinkage rate change during the hot pressing for a 10% BN sample and a 21.3% BN sample prepared from molecular precursor (sample III).

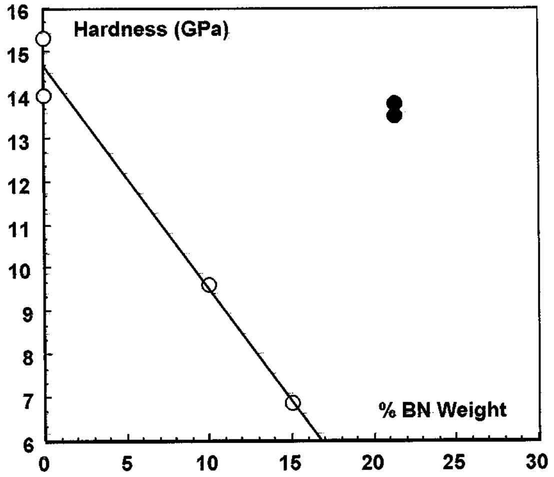


FIG. 6. Hardness change of the composite ceramics obtained.

As it has been shown, the aminoboranes can be employed for various purposes. The compounds or mixtures of precursors used in the examples described can be modified in regard to the special properties of the precursor required. In the field of composite ceramics the preliminary results obtained seem to be attractive, especially taking in account the great difficulty in BN sintering. Preparation of coatings, reinforced composites, and composite ceramics from organometallic precursors are new possibilities for development in material science but also in solid state science, especially in the determination of microstructures related to nanostructured composites.

REFERENCES

1. R. T. Paine, J. F. Janick, and M. Fan, *Polyhedron* **13,** 1225 (1994).
2. R. Reidel, *Naturwissenchaften* **82,** 12 (1995).
3. R. T. Paine and C. K. Narula, *Chem. Rev.* **30,** 71 (1990).
4. R. T. Paine and L. G. Sneddon, *CHEMTECH* **7,** 29 (1994), and references therein.
5. J. J. Pouch and S. A. Alterovitz, "Synthesis and Properties of Boron Nitrides," Mater. Sci. Forum, Vols. 54 and 55. Trans. Tech., Zürich, Switzerland, 1990.
6. M. F Lappert and M. K. Majunder, *Proc. Chem. Soc.* 425 (1961).
7. R. H. Toeniskoetter and F. R. Hall, *Inorg. Chem.* **2,** 29 (1963).
8. W. Maringgele, *in* "The Chemistry of Inorganic Homo- and Heterocycles" (I. Haiduc and D. B. Sowerby, Eds.), Vol. 1. Academic Press, London, 1987.
9. B. Bonnetot, B. Frange, F. Guilhon, and H. Mongeot, *Main Group Mater. Chem.* **17,** 583 (1994).
10. B. Bonnetot, J. Atchekzai, B. Frange, F. Guilhon, and H. Mongeot, *Jpn. J. Appl. Phys.*, Series **10,** 178 (1994).
11. B. Bonnetot, F. Guilhon, J. C. Viala, and H. Mongeot, *Chem. Mater.* **7,** 299 (1995).
12. F. Guilhon, B. Bonnetot, D. Cornu, and H. Mongeot, *Polyhedron* **15,** 851 (1996).
13. Y. Kimura, Y. Kubo, and N. Hayashi, *J. Inorg. and Organometallic Poly.* **2,** 231 (1992).
14. T. T. Borek, X. Qui, L. Rayfuse, A. K. Datye, R. T. Paine, and L. F. Allard, *J. Am. Chem. Soc.* **74,** 2587 (1991).
15. D. Kim and J. Economy, *J. Chem. Mater.* **5,** 1216 (1993).
16. K. Isomura, T. Fukuda, K. Ogasahara, T. Funahashi, and R. Uchimura, *Proc. UNITECR. 89*, L. S. Trosel, Ed, *J. Am. Ceram. Soc.* 624 (1989).
17. L. V. Interrante, W. R. Schmidt, W. J. Hurley, V. Sukumar, and R. H. Doremus, *Mater. Res. Soc. Symp. Proc.* **171,** 79 (1990).
18. H. P. Baldus, M. Jansen, and O. Wagner, "Key Engineering Materials," p. 89. Trans Tech Publi. Eds, Switzerland, 1994.
19. R. Schmidt, D. Sporn, and W. Schubert, *cfi/ber. D.K.G.* **73,** 182 (1996).
20. C. Doche and F. Thevenot, *Jpn. J. Appl. Phys.* **10,** 212 (1994).
21. C. Doche, F. Guilhon, B. Bonnetot, F. Thevenot, and H. Mongeot, *J. Mater Sci. Lett.* **14,** 847 (1995).