Boron Nitride Matrices and Coatings Obtained from Tris(methylamino)borane. Application to the Protection of Graphite against Oxidation

B. Bonnetot,* F. Guilhon, J. C. Viala, and H. Mongeot

Laboratoire de Physico-chimie Minérale Ib, CNRS 116, U.C.B. LYON I,
43, Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

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Tris(methylamino)borane ($B(CH_3NH)_3$) partially converted into 1,3,5-tris(methylamino)-2,4,6-trimethylborazine ($[(CH_3H)NBNCH_3]_3$) used as a boron nitride precursor leads to an amorphous BN preceramic when pyrolyzed up to 1000 °C. Further annealing at 1700 °C is required to obtain a product free from organic residues and to achieve the crystallization of h-BN. A microcomposite consisting of a h-BN matrix reinforced with carbon fibers has been obtained by pyrolyzing bundles of fibers previously dipped into the precursor. Characterization of this microcomposite has shown that the BN matrix was compact and free of bubbles, although the theoretical ceramic yield was only 26%. Compact h-BN coatings with a thickness of 4–10 μm have also been deposited by an impregnation–pyrolysis treatment on graphite substrates. Penetration of the precursor into the open micropores of the substrates to a depth of about 5 μm resulted in strong BN–graphite interfacial bonding. Oxidation tests conducted on these coated graphite substrates have revealed the efficiency of the h-BN coating for protecting graphite. Compared with uncoated specimens, the oxidation resistance of BN-coated substrates was 10 times higher at 650 °C and 5 times higher at 750 °C.

Introduction

Due to its special properties, boron nitride has been widely used in high-temperature technology.[1–3] Its chemical inertness and oxidation resistance has led to consideration of this nitride as one of the best coating materials for protection of substrates from oxidation or corrosion.

Several techniques can be used for the coating of substrates or thin film preparation. The chemical vapor deposition of h-BN from various volatile boron compounds and ammonia has been studied for specific applications such as ceramic membranes.[4–7] However, the development of this technique in a large plant poses difficult problems and, although many promising results have been obtained, no industrial application has yet been described.[4–10] Coating of substrates by means of precursor impregnation followed by thermolysis has been intensively studied during the past 10 years using different boron–nitrogen compounds as precursors. These precursors are not numerous[1–3,11] because prior to their conversion to boron nitride, they must form a nonvolatile polymer. Moreover, although several BN precursors currently exist, all the requirements for the ideal precursor (be liquid or have good solubility in organic solvents, decompose with a high ceramic yield, and be easy to prepare) are never fulfilled in only one compound. Several papers reviewing the preparation of BN as a powder or coating have been recently published.[12–14] Apart from a few precursors based either on simple molecules[15,16] or complex boron clusters,[17,18] most of the research concerns borazine and its derivatives[19–39] whose structure possesses a B–N ring similar to that of boron nitride. Coatings are usually

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prepared from cross-linked polyborazine obtained by reaction of a B substituted borazine with an appropriate reactant[19−35] or, in the case of *B*-aminoborazines, simply by thermolysis.[36−3] Recently borazine-precursors utilization for fibers and composites preparations have been reported, and the thermal and mechanical properties of the materials have been described.[20,24,40] Owing to their volatility,[13,21] aminoboranes have not attracted the attention given to borazines except for tris(phenylamino)borane.[15,21,37] However aminoboranes can also lead to polymers when the amino group is suitably chosen,[41−48] the first step of the condensation reaction being the formation of 1,3,5-tris(alkylamino)-2,4,6-trialkylborazine:

$$3B(NHR)_3 \rightarrow (RHNBNR)_3 + 3RNH_2$$

In recent investigations[39,51] we have shown that the tris(methylamino)borane (**I**) presented interesting features as a precursor of boron nitride: its preparation was relatively easy, its conversion to 1,3,5-tris(methylamino)-2,4,6-trimethylborazine (**II**) occurred at a temperature as low as 150 °C, and heating at temperatures higher than 1000 °C led to boron nitride as a final product.

In the present work, boron trichloride has been reacted with methylamine at −70 °C which has yielded (**I**) as major product with (**II**) in low concentration. When heated at 100 °C for 1 h, the **I**:**II** molar ratio reached 80:20, rendering the product less volatile and then easier to use as precursor. After having observed that this precursor was a mobile liquid exhibiting the property of wetting graphite, attempts were made to prepare from it BN/carbon fiber microcomposites. This work was then extended in order to protect graphite against oxidation. The characterization of the BN microcomposite matrix was achieved by chemical analysis, X-ray diffraction, electron probe microanalysis, optical microscopy, and scanning electron microscopy. Oxidation tests of BN coated graphite substrates were carried out by isothermal gravimetry in air at 650 and 750 °C.

Experimental Section

General Procedure. The impregnation operations were carried out in an inert-atmosphere glovebox, under argon. All the solvents were dried on active molecular sieve before use. To remove moisture from the graphite and the carbon fibers, the samples have been degassed under vacuum for 3 h at room temperature before impregnation.

Materials. Methylamine, purchased from Fluka (97% purity), and boron trichloride from Alphagas were used as received. High-purity ammonia from Alphagas used as reducing atmosphere during the pyrolysis needed no special purification. Graphite ELLOR 10 type was provided from Carbone Lorraine. The unsized high-modulus P 55 carbon fibres were supplied by Union Carbide.

Experimental Measurements. The infrared spectra (IR) of liquids were recorded without addition of solvent and those of solids as Nujol mull on a Perkin-Elmer 842 infrared spectrometer. ^{1}H,^{13}C, and ^{11}B NMR spectra were recorded on a Brüker AM 300. Spectral standards were TMS (^{1}H, ^{13}C) and Et_2OBF_3 (^{11}B, positive values downfield). X-ray powder diffraction (XRD) were obtained with Cu Kα radiation using a Philips PW 3710/3020 diffractometer equipped with a monochromator. The morphologies of the BN fiber microcomposites and of the BN-coated graphite substrates were examined on diamond-polished sections, using an Olympus Vanox 1 optical microscope. Further characterization was performed by electron probe microanalysis (EPMA), using a Cameca Camebax microprobe equipped with a wavelength-dispersive spectrometer and an energy-dispersive Tracor Northern 2000 analyzer. An accelarating voltage of 5 kV, a regulated beam current of about 35 nA and a counting time of 10s were selected as operating conditions.[53] After background correction, the counting rates obtained for boron, carbon and oxygen were referred to pure standards of BN, C or B_4C and B_2O_3, respectively; the nitrogen content was evaluated by difference. The thermogravimetric analyses (TGA) were performed under a nitrogen or a dry ammonia atmosphere from room temperature up to 1000 °C, using different heating rates (Setaram B70 system). Chemical analyses were performed by the Centre de Microanalyse du CNRS, Vernaison, France.

Precursor Synthesis. Tris(methylamino)borane (**I**) was prepared by reaction of boron trichloride with methylamine[39,41] in pentane at −70 °C, with a yield of 65%. The ^{11}B NMR of the crude product clearly shows that **I** ($\delta^{11}B = 24.5$ ppm) is not pure. When compared with literature data,[41,44,46] 5−9% of the aminoborazine **II** ($\delta^{11}B = 27.5$ ppm) is present. The obtained product is a very mobile and volatile liquid (bp 140 °C) which evolves methylamine when heated.

Impregnation−Pyrolysis Treatment. The general procedure for the precursor handling has been utilized for the graphite and fiber impregnation. The bundles of fibres or cubic graphite samples of about 400 mg of edge about 6 mm were coated by dipping into pure precursor and then draining the excess liquid. The wetting properties of the precursor are very interesting: when a drop of **P** is deposited on graphite, the penetration of the liquid into the substrate is so fast that no

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Table 1. Composition and Properties of the Precursor

	% of species			
compound	direct synthesis	100 °C, 1 h	150 °C, 1 h	200 °C, 1 h
$B(CH_3NH)_3$	95	78	30	0
$(CH_3NHBNCH_3)_3$	5	20	65	80
dimer	traces	2	5	20
ceramic yield	24.5	26.5	32.3	35.7
physical properties	volatile	mobile	mobile	sticky
carbon interface	penetrate	wet	wet	cover slowly

angle could be measured between the drop and the graphite, whatever its porosity. The samples, placed in a quartz boat, were then transferred using a tightly closed container from the drybox to a quartz tube fitted into an oven. During the sample introduction into the pyrolysis tube, an argon flow was used to prevent the precursor oxidation. To avoid **I** stripping, a 0.5 °C min^{-1} heating rate up to 500 °C followed by a 5 °C min^{-1} heating rate up to 1000 °C were used. Then an exposure at 1000 °C for 3 h completed the pyrolysis. All these operations were performed under a 0.5 L h^{-1} NH_3 flow. The sample was then allowed to cool under vacuum.

High-Temperature BN Crystallization. Boron nitride obtained under the above experimental conditions is only a preceramic material,[24,51] and a high-temperature treatment is needed to obtain h-BN free of organic containing moities.[52] To achieve the pyrolysis, the coated graphite or fibers were heated under high vacuum (10^{-3} Pa) using a high-frequency furnace equipped with a BN-protected graphite susceptor. The temperature was ramped from ambient to 1700 °C in 1 h, held at 1700 °C for 3 h, and then returned to ambient under vacuum.

Oxidation Tests. The oxidation tests have been performed by isothermal TGA under air. The coated samples were first heated under vacuum (10^{-3} Pa) from room temperature up to the test temperature, then an air flow was introduced onto the hot samples while the weight loss was recorded.

Results and Discussion

Precursor Properties. When the proportion of **I** to **II** changes, the physical properties of the precursor are modified. However the polymerization does not stop when **II** is formed, and further heating produces the formation of a diborazine species. The composition and properties of the precursor are given in Table 1 for different values of the **I** versus **II** ratio. When the proportions of **II** and the dimer increase, the ceramic yield increases and the precursor becomes less volatile but the carbon wetting properties are lowered. The composition can be adjusted to the required properties.

The pyrolysis of the pure precursor has been studied[39,51] and the ^1H, ^{13}C NMR correlation spectra of the dimer are consistent with a structure consisting of two borazine rings bonded through a $-N(CH_3)-$ bridge[41,42,47,48] and not through a direct B−N link.[36,43,44] This type of bonding in polyborazines implies an important angular distortion between consecutive borazine rings. The polyborazines are converted to a disordered preceramic by pyrolysis at 800−1000 °C and a higher temperature treatment is required to obtain pure crystalline boron nitride. A choice has to be made between the volatility, wetting property, and the ceramic yield of the precursor and in the present work, a 1 h heated precursor composed of 80% of **I** and 20% of **II** has been used and called P.

BN/Carbon Fiber Microcomposites. Bundles of high-modulus carbon fibers were dipped in the standard precusor P and submitted to a two-step pyrolysis treatment, i.e., up to 1000 °C under NH_3 and then up to 1700 °C under vacuum, as described in the Experimental Section. The impregnated bundles were laid down on graphite holders to allow the draining of the excess precursor while being pyrolyzed. At the end of this treatment, compact composite rods consisting of carbon filaments embedded in a ceramic matrix were obtained.

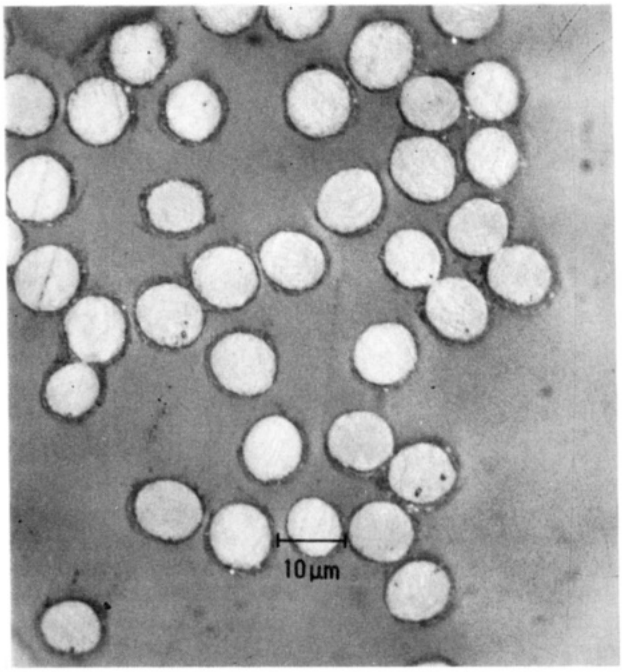

Figure 1. Optical micrograph of a cross section of a coated fiber bundle.

An optical micrograph of a transverse section of such a microcomposite is presented in Figure 1. It is obvious that the precursor has already wetted each carbon filament of the bundle during impregnation and has been retained between the filaments during pyrolysis. Moreover, the ceramic matrix appears dense and free of bubbles in places where the fiber volume fraction was sufficient to retain the liquid precursor by capillarity. This means that in spite of a low ceramic yield, the polyborazine preceramic is fluid enough to allow the amine evolving without formation of bubbles while the polymerization progresses. The specific properties of precursor P to wet a carbon surface, to be retained on it during pyrolysis, and to yield a dense ceramic free of bubbles must be emphasized. They make this precursor very attractive for ceramic−ceramic composite applications.

Attempts were then made to determine by EPMA the elemental bulk composition of the ceramic matrix of the microcomposites discussed. Due to the insulating character of the ceramic, it was not possible to obtain very precise results. However, the values determined by EPMA (B 37, N 45, C 8, O 10 wt %) can be compared with those obtained by chemical microanalysis on BN bulk powders formerly prepared by the same route[51] (B 40.3, N 58.0, C 0.4; H 0.8, O, 4.0 wt %) and with the theoretical elemental composition of pure BN (B 43.55, N 56.45 wt %). From these comparisons, it is confirmed that B and N are the major constituents of the matrix of the microcomposites, but it also appears that this matrix contains greater amounts of carbon and oxygen than the massive BN samples.

To characterize further the matrix−fiber interface, an EPMA line-scan profile has been recorded along the diameter of a carbon filament embedded in the ceramic

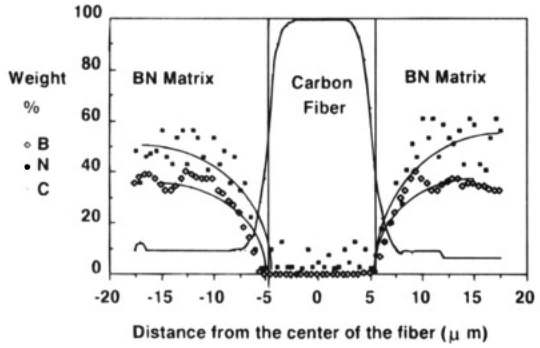

Figure 2. B, N, and C concentration profile through a cross section of a fiber of the composite.

matrix. Results obtained for boron, carbon, and nitrogen are reported in Figure 2. Concerning carbon, it is observed that the content of this element rises very quickly at the crossing of the matrix–fiber interface. In effect, it changes from 8 to 95 wt % over a distance of less than 2 μm. As the lateral resolution of the analytical technique is about ±1 μm under the operating conditions used, it can be concluded that no apparent diffusion has occured during pyrolysis from the fiber toward the matrix. In other words, the carbon fibers appear unaffected by the impregnation–pyrolysis process. Consequently, it can be assumed that the high carbon content found in the matrix of the microcomposites compared to that of massive BN samples mainly originates from slight differences in the pyrolysis procedure followed in the preparation of these two types of specimens. In contrast to carbon, the contents of boron and nitrogen decrease over a distance of about 5 μm at the crossing of the matrix–fiber interface. The oxygen content, not reported due to the poor quality of the recording, has been found to increase near the ceramic–fiber interface. From these observations, one can suppose that the high oxygen content found in the matrix of the microcomposite, compared to that of bulk powder BN,[51] is closely related to the presence of the fibers. This oxygen contamination could result either from the decomposition of oxygen-rich species that were present at the surface of the fibers before impregnation or from the migration of oxygen atoms along the BN/C interface during pyrolysis.

BN Coatings of Graphite Substates. Graphite substrates were dip-coated in the standard precusor P and pyrolyzed under NH_3 to 1000 °C and then under vacuum up to 1700 °C, as previously described. A photomicrograph of a polished section of a thus-coated graphite substrate is shown in Figure 3. Besides the thick overlayer of about 20 μm that coats the graphite surface, boron nitride is visible in the largest pores and cracks of the substrate. This observation confirms the excellent ability of the liquid precursor to wet the graphite surface. As in the case of microcomposites, this precursor has been retained at the surface and in the pores of the graphite substrate during pyrolysis and has been converted into dense boron nitride, in spite of the evolution of large amounts of methylamine. Under the microscope light, the appearance of the graphite substrate has also changed: treated samples look more bright than untreated ones.

Further analysis of the coating–substrate interface has been performed using EPMA. The variations of the concentrations of boron and carbon have been determined point by point along a straight line perpendicular to the BN–C interface and crossing it in a homogeneous area free of pores or cracks. Due to the great difference in the conducting properties of BN (insulator) and graphite (conductor) absorbed current corrections were needed to refer the recorded counting rates to pure carbon and BN standards. Results reported in Figure 4 clearly show that boron is present in the graphite substrate several microns under its physical surface. This means that infiltration of the precursor during impregnation has not been limited to the largest pores and cracks of the graphite substrate but has also entered micropores, leading to a strong coating–substrate bonding. In fact, the BN layer cannot be scraped from the graphite surface.

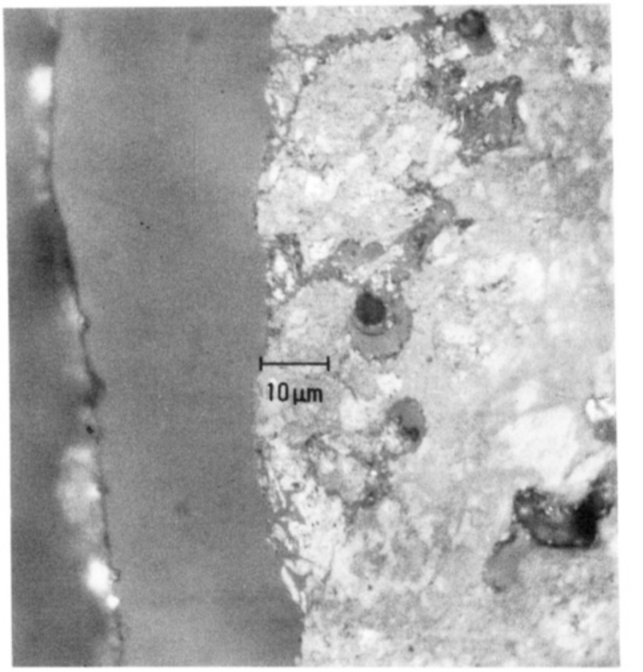

Figure 3. Optical micrograph of a cross section of a coated graphite sample.

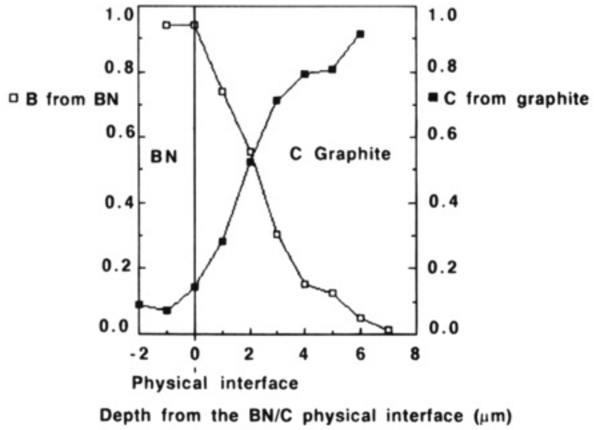

Figure 4. EPMA depth profile of the cross section of a coated graphite. Values reported on the ordinate are the ratios of the counting rate recorded for B and C at the crossing of the interface, to those measured on pure BN and C standards, respectively.

The impregnation–pyrolysis process being not optimized, the thickness of the BN coating is not uniform. During the sample heating, the precursor tends to ooze through the substrate into the crucible leading to a thicker deposit on the dipped part of the sample than

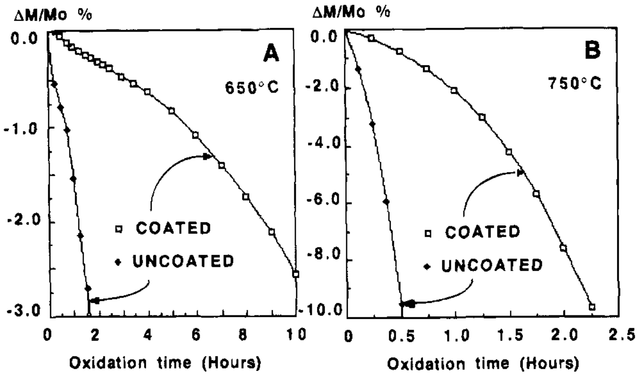

Figure 5. Isothermal oxidation weight loss of uncoated and coated graphite: (A) 650 °C; (B) 750 °C.

on the other faces. In fact, with this precursor composition, a 5−20 μm BN layer is usually obtained after one impregnation−pyrolysis cycle, BN being infiltrated to a depth of about 5 μm below the physical surface of the graphite substrate.

Oxidation Resistance of BN Coated Graphite. For many industrial applications of graphite, its protection against chemical attack, and more especially oxidation, is a major problem. With this aim in mind, graphite susbtrates were coated using the precursor P according to the standard impregnation−pyrolysis method previously described. To evaluate the efficiency of the BN coatings thus prepared, oxidation tests were performed in air. The coated substrates were as far as possible similar in shape and weight to permit comparison. The thickness of the BN coatings was irregular and difficult to measure. The weight of boron nitride deposited could not be directly determined because the weight loss of the graphite substrate during the impregnation pyrolysis treatment was similar to the weight of the BN coating. However with regard to the sample area and the average thickness of the coating, the total amount of deposited boron nitride should be 10−20 mg, i.e., 0.6−1.2 wt % of the sample.

The oxidation tests were carried out by thermogravimetric analysis (TGA) at 650 and 750 °C. Heating the samples to the testing temperature was conducted under vacuum: it was verified that no change in their weight occurred during this pretreatment. When the testing temperature was reached, an air flow was admitted and the weight losses of coated and uncoated graphite substrates were recorded as a function of time (Figure 5). At 650 °C (Figure 5 A), a 2% weight loss was reached after 530 min for a coated substrate compared with 70 min for an uncoated one. At this temperature, the oxidation resistance of the coated substrates is very good. At 750 °C (Figure 5 B), oxidation of coated and uncoated substrates proceeds at a faster rate than at 650 °C, but the BN coating still protects the graphite substrate: in effect, an 8% weight loss occured after 25 min for an uncoated substrate, whereas the coated one took 130 min to lose this much weight. These results are consistent with those recently published[40] on a different type of samples: in the literature, the oxidation tests were performed on BN/C composites (50 wt % BN); in this work, the graphite substrates were protected only by a thin BN coating (less than 5 wt %). However, the conclusions of these two works show the ability of the BN coatings to prevent carbon of oxidation. After oxidation, optical microscopy of the samples showed a very weak BN attack limited to the defects of the coating. The graphite appeared as black holes bounded by white BN coated areas, and no glassy boron oxide due to nitride oxidation was detected. Despite the presence of defects, the efficiency of the BN coating for protecting graphite against oxidation remains very attractive, especially in the temperature range 650−750 °C.

Conclusion

Tris(methylamino)borane (**I**) partially converted into 1,3,5-tris(methylamino)-2,4,6-trimethylborazine (**II**) constitutes a simple precursor for the preparation of boron nitride matrices and coatings. With its favorable impregnation and pyrolysis properties, it offers a number of advantages over other routes described to date.

Synthesis of this precursor from methylamine and boron trichloride is a high-yield one-step operation. The physical properties of the precursor can easily be adjusted to the required use by varying the **I**:**II** ratio. Owing to its very good wetting properties, the precursor can penetrate within the filaments of a carbon fiber bundle or infiltrate the open macro- and micropores of a massive graphite substrate. After pyrolysis, dense ceramic matrices or coatings can be obtained. The low ceramic yield of the precursor is balanced by the great fluidity of the polyborazine prepolymer allowing evolution of the volatile species without the formation of bubbles.

As demonstrated above, dense BN coatings with a thickness of 5−10 μm can readily be formed on graphite substrates by impregnation−pyrolysis. Penetration of the precursor into the open pores of the substrate results in a BN−C graduate interface leading to strong and durable interfacial bonding. In fact, the BN coating was unscalable and comparative oxidation tests carried out on coated and uncoated graphite samples have demonstrated the efficiency of the BN coating for protecting a graphite substrate at the 650−700 °C temperatures showing a special interest for industrial utilization. These results show clearly that BN can efficiently protect carbon against oxidation not only as a matrix in a BN/C fibers composite, as recently shown by Economy,[40] but also as a thin BN coating deposited on a graphite substrate.

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