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BORON NITRIDE COMPOSITES BY CHEMICAL VAPOR DEPOSITION*

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ABSTRACT

Composites of boron nitride (BN) have been made by the chemical vapor deposition (CVD) of a BN matrix on a BN felt fiber substrate. Reactant gases were boron trifluoride and ammonia. The composites had a relatively high density (1.70 g/cm^3), a crystallite size L_c = 150 Å and an interlayer spacing d_{002} = 3.35 Å. Measurements of elastic modulus and thermal conductivity and expansion showed some anisotropy as a result of the preferred fiber orientation of the substrate.

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INTRODUCTION

Boron nitride prepared by chemical vapor deposition (CVD), also known as pyrolitic boron nitride (PBN), has been extensively investigated in the last few years. Due to its unusual structure and properties, it has caused a great deal of scientific and technological interest.[1] It is a crystalline material and, in its most common form and the one considered here, it is composed of layers of hexagonal pseudo cells of alternating atoms of boron and nitrogen with a basal plane lattice constant a = 2.504 $\mathring{A}$, a B-N bond length b = 1.446 $\mathring{A}$ and a spacing between layers d_{002} = 3.330 $\mathring{A}$ (Fig. 1).[2] Such a crystal structure is very similar to graphite with the difference that, in boron nitride, the hexagons are stacked directly on top of each other whereas, in graphite, the carbon atoms in one layer lie over the midpoint of the hexagons in the layer immediately above. The bonding energy between layers is low (reported at 4 kcal/mole)[3] and considerably less than the boron to nitrogen bond strength (reported a 152 kcal/mole).[4] This leads to a high degree of anisotropy in the properties of the polycrystalline material as shown in Table I.[5] The differences in thermal expansion cause large internal stresses that develop during cooling which in turn lead to delaminations between the ab planes.

A similar problem of microstructure anisotropy is found in pyrolytic carbon and has been successfully mitigated by depositing the carbon on a randomly oriented carbon fiber substrate such as felt.[6] Although the carbon deposit on each fiber is still anisotropic, the randomness of the substrate leads to a composite with

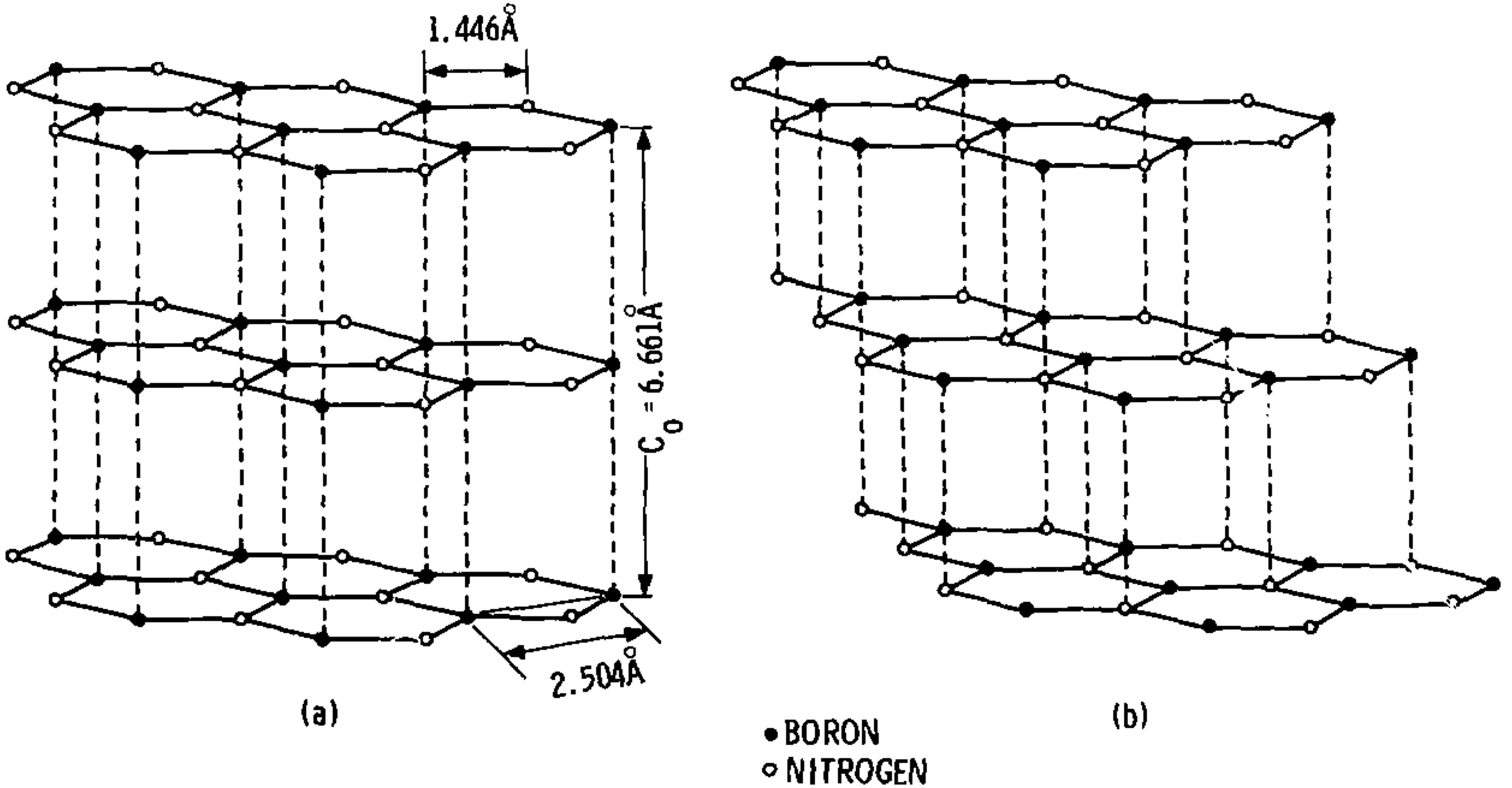

Fig. 1 Crystalline structures of boron nitride (a) and graphite (b).

TABLE I

Anisotropy of Crystalline Boron Nitride (Ref. 5 and 12)

	Direction of Measurement	
	ab	c
Flexural Strength MN/M^2	103	10
Flexural Modulus GN/m^2	24.8	---
Thermal Conductivity W/mK		
at 25°C	62.7	1.45
at 300°C ---	75	---
Coefficient of Thermal Expansion m/mK	3.24×10^{-6}	81×10^{-6}
Electrical resistivity at 437°C Ω-cm	3.0×10^{7}	3.0×10^{9}

essentially isotropic macroscopic characteristics. A similar approach has been taken in this study: boron nitride is chemically vapor deposited on a boron nitride felt with the intent of obtaining a composite with isotropic macroscopic properties.

Development of Boron Nitride Felt

The technique of felting can provide an essentially randomly oriented fiber array and can be applied to boron nitride fibers. This was demonstrated by the Carborundum Co. under contract to Sandia Laboratories.[7] Several felting methods were tried. The best was found to be 1) carding the boron nitride roving, 2) forming the web in a Tappi machine by means of a water slurry, 3) mechanically needling the webs. The felt obtained in this manner had an average bulk density of 0.04 to 0.05 g/cm^3, was uniform in appearance, could be handled without damage and was suitable for infiltration.

The fibers used in these felts were produced by a commercial process by nitriding a boron oxide fiber precursor.[8] Their properties are summarized in Table II.[9]

Chemical Vapor Deposition of Boron Nitride

Various chemical reactions have been used to deposit boron nitride. The major ones are:

1. Thermal decomposition of trichloroborazole ($B_3N_3Cl_3H_3$)[1,10]
2. Reaction of trimethyl borate ($B(OCH_3)_3$) and ammonia (NH_3)[11]
3. Reaction of boron trichloride (BCl_3) and ammonia (NH_3)[1,5,12]

These reactions were studied extensively by Dungan and Gilbert at Sandia Laboratories.[13] Their study showed that trichloroborazole

TABLE II

Properties of Boron Nitride Fibers[9]

Fiber Diameter	5-7 μm
Apparent Density	1.8-2.0 g/cm^3
Theoretical Density	2.25 g/cm^3
Color:	white
Tensile Strength	410-1300 MN/m^2
Modulus of Elasticity	up to 83 GN/m^2
Elongation	2-3%

would not be satisfactory for a bulk deposit due to the low deposition rate and the very high cost of the material. The trimethylborate and ammonia reaction produces a low density deposit in the range of 1.? to 1.5 g/cm^3 even at 1700°C deposition temperature. Because of the low densities, the strength of the material is not high and this system was ruled out.

Dungan and Gilbert found that the boron trichloride/ammonia reaction produces deposits with densities of 1.5 g/cm^3 at 1300°C deposition temperature increasing to 2.0 g/cm^3 at 1600°C. However, at these temperatures, solid intermediates are formed in the vapor phase which interfere with infiltration within the felt. This observation was also reported by Gebhardt.[10]

Yet another potential source of boron nitride comes from the reaction of boron trifluoride and ammonia.[13]

$$BF_3 + NH_3 \rightarrow BN + 3HF \quad .$$

Boron trifluoride are stable thermodynamically than boron trichloride and it is likely that the number of subsidiary reactions and the formation of intermediate products are fewer. These considerations led to the choice of BF_3 as a source of boron.

EXPERIMENTAL PROCEDURE

CVD Process

The CVD apparatus is shown schematically in Fig. 2. Heat was supplied by a 50 KW, 3000 cycle induction generator and a cylindrical graphite susceptor. Temperature was monitored with a type S thermocouple (Pt + Pt, 10% Rh) located in the center of the infil-

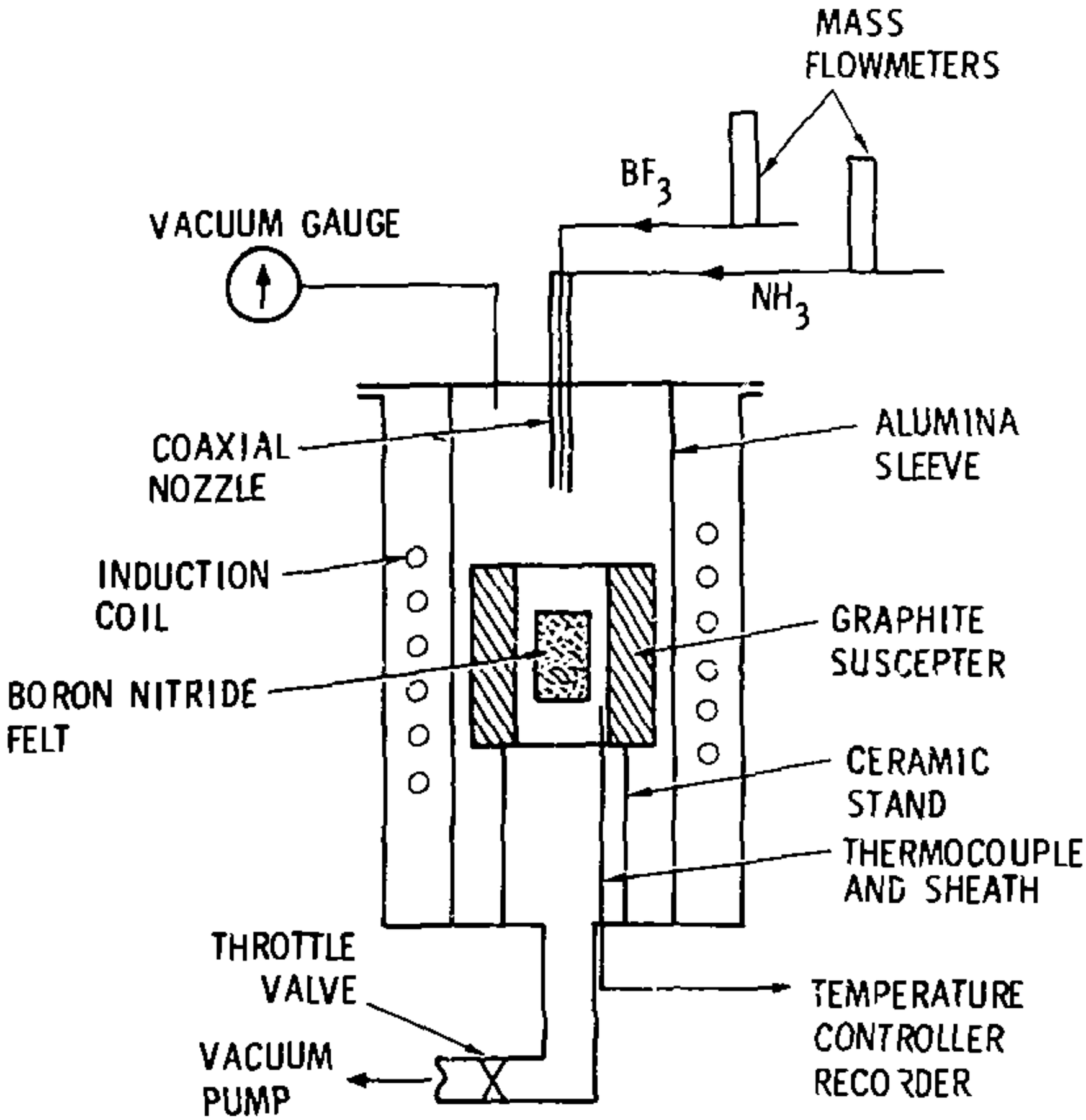

Fig. 2 Schematic of apparatus used for the chemical vapor deposition of boron nitride.

tration zone. The low pressure was obtained with a two stage water jet vacuum pump with an ultimate vacuum capability of less than 1 Torr. Ammonia and boron trifluoride were supplied from standard pressurized cylinders and metered through mass flowmeters. The gases were preheated and mixed in a coaxial nozzle.

A block of felt measuring 5 x 2.5 x 1 cm was placed with the long axis vertically inside the graphite susceptor. The infiltration then proceeded as follows: 1) Temperature was stabilized under vacuum, 2) The required gas flow was metered in, 3) and the pressure was stabilized. It was found that, after 6 to 8 hours of operation, a large quantity of solid intermediate would form consisting mostly of ammonium chloride, which would clog the exhaust line. It was, therefore, necessary to shut down, clean the furnace and start again several times during infiltration of the felt.

Parametric Study

Two deposition temperatures were investigated: 1100°C and 1200°C. These were automatically controlled to ± 10 C. On the basis of Dungan's work[13], it was expected that the deposition rate would be too low below 1100°C. Temperatures much above 1200°C on the other hand were expected to result in too high a deposition rate and a tendency to deposit mostly on the outside portion of the felt and crust over.[10,13]

Pressure was maintained between 30 and 40 Torr. The selection of this pressure level was based on the results obtained by Dungan[13].

A balanced reaction would require an essentially equal flow rate of the two reactants. The flows were arbitrarily fixed at 300 cm^3/min of ammonia and 230 cm^3/min of boron trifluoride, thereby, using an excess of ammonia to insure that most, if not all, of the boron trifluoride was reacted.

The duration of the infiltration experiments was usually over 100 hours to obtain satisfactory densification of the felt.

Material Characteristics

The properties of the boron nitride fibers and the infiltrated material were measured to determine the degree of anisotropy of the composite and compare it to bulk PBN.

Fiber density was determined by acetone displacement. Bulk density of the composite was determined by dimensional and weight measurements on machined samples. Porosity of machined samples of the composite was measured in a helium pycnometer (Beckman Instruments Model 130) and both true and apparent volumes and densities were recorded.

Metallographic examination was accomplished with a Bausch and Lomb Research Metallograph equipped with a xenon light source. Each sample, including samples of uninfiltrated felt, was encapsulated in epoxy and polished with silicon carbide to 600 grit followed by diamond paste. Some samples were then cathodically etched with argon. This treatment etched the fibers at a different rate than the matrix, thereby increasing visual contrast. The samples were then examined with an image analyzing computer (Quantimet, Metals Research Ltd.). This instrument is capable of discrim-

inating optically between fiber, matrix and void and, thus, establishes fiber volume content, total proosity and pore size distribution.

X-ray diffraction data were obtained from flat plate samples with a General Electric XRD-6 diffractometer using Ni-filtered Cu Kα radiation. The interlayer spacing d_{002} and apparent crystallite size L_c were obtained from the position and width of the (002) peak.

The thermal diffusivity was measured by the laser flash technique.[14] The thermal conductivity was calculated from the diffusivity by the relation.

$$\bar{\alpha} = K/\rho C_p$$

where $\bar{\alpha}$ is the thermal diffusivity, K the thermal conductivity, ρ the bulk density and C_p the specific heat.[5] The conductivity was determined in the direction parallel to the surface of the CVD felt plate and the direction perpendicular to the surface.

The linear thermal expansion was measured with a Brinkman dilatometer in the range of 0-600°C, in the directions parallel and perpendicular to the surface of the plate.

The sonic modulus at room temperature was obtained by standard ultrasonic through transmission by measuring the delay time of the ultrasonic wave to travel from one face of the sample to the other using two 1/4" diameter 5 MHz transducers. Measurements were made parallel and perpendicular to the surface of the plate. The sonic modulus was calculated from the delay time by the relation

$$E \cong \rho V^2$$

where E is the sonic modulus, ρ is the density and V the sonic velocity.

RESULTS AND DISCUSSION

Matrix Deposition

Under the conditions used in this study, a dense, low porosity composite was obtained. The densification of the felt vs. time is plotted in Fig. 3. Density increases rapidly at first then levels off as the size of the open pores decrease and an increasing amount of pores becomes closed. The densification is also a function of the thickness of the felt. A felt of less than 0.25 cm thick was infiltrated to a density of 1.75 g/cm^3 in 16 hours, while it took 150 hours to reach the same density with a 1 cm thick felt.

The chemical analysis of the composite is shown in Table III. It is essentially stoichiometric boron nitride (stoichiometry is 43.55% boron). The presence of carbon (0.21%) is probably due to reaction of the source gas with the graphite susceptor. This percentage is smaller than the percentage reported for hot pressed boron nitride (0.4% in a high grade commercial material[15]).

Microstructure

X-ray diffraction results are shown in Table III. The material has a crystallite size L_c = 150 Å, an interlayer spacing d_{002} = 3.35 Å, which is close to the theoretical value of 3.33 Å.[2] These findings contrast with those of Li[12] and Gebhardt[10] who report that, with other source gases such as BCl_3 or $B_3N_3H_3Cl_3$ and deposition temperatures of 1100°C to 1200°C, the deposits were essentially amorphous. Even for a 2000°C deposition temperature, Li reports a d_{002} 3% greater than theoretical which would be ~ 3.43 Å, considerably above the results of this study. Thus the use of BF_3 as

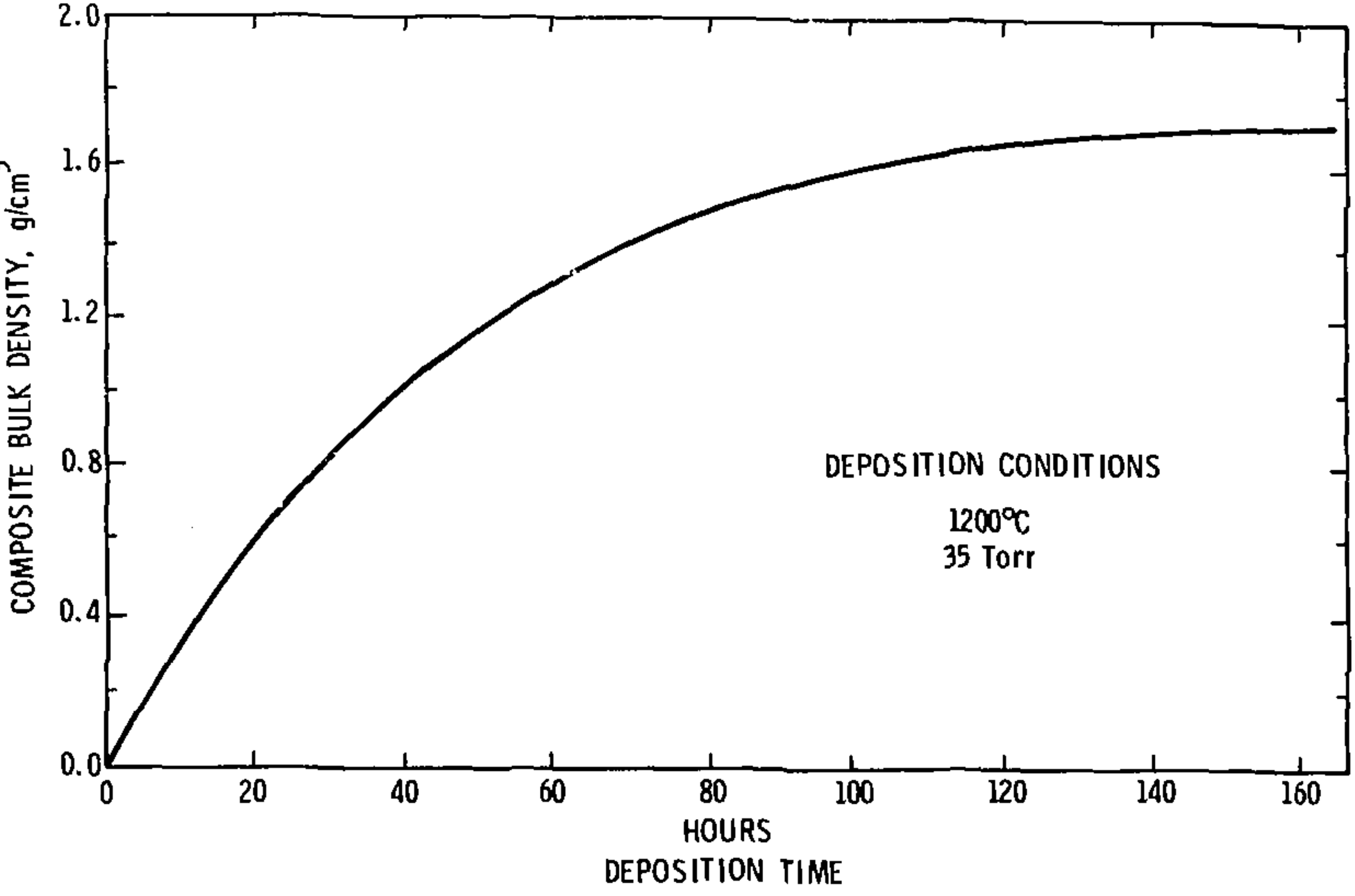

Fig. 3 Densification of BN felt as a function of deposition time.

TABLE III

Chemical Composition and X-ray

Diffraction Characteristics of BN Composites

Chemical Composition (weight percent)

B	43%	Al	80 ppm
O	0 -	Ti	25 -
C	0.21%	Cu	10 -
Na	250 ppm	Fe	25 -
Li	0.3 -	Mg	25 -
K	40 -	Si	250 -
Ca	160 -		

X-ray diffraction (3 samples)

$$d_{002} = 3.35 \text{ Å}$$

$$L_c = 150 \text{ Å}$$

a source gas seems to produce deposits with low interlayer spacing even at low deposition temperatures. Figure 4 is a photomicrograph of a typical section of the composite.

Physical Properties

Both Li[12] and Gebhardt[10] mention colors of the deposit varying from white to light yellow to brown; these colors were also noted in this study. They varied from run to run in a random way and could not be correlated with the deposition conditions.

The boron nitride fiber has a density of 1.76 g/cm^3 (4 measurements) as compared to a theoretical density of 2.25 g/cm^3. An average fiber diameter of 6.0 μm ± 5% (20 measurements) was obtained by measuring on 800 X photomicrographs of the metallography samples.

Table IV shows the results of the pycnometry and Quantimet studies. The Quantimet analyses of the felt prior to infiltration gives a fiber volume of 5%. As mentioned in the introduction, the role of the fiber is to act as a substrate for the deposition of the boron nitride matrix. The Quantimet was also used to measure the angle of each fiber with the surface of the sample (by measuring the area of each fiber cross section). Figure 5 plots the fiber population as a function of the angle of the fiber to the surface of the felt. It also plots the fiber population of a truly random fiber array. The plot shows that the felt is not truly isotropic and that the fibers tend to align themselves parallel to the surface.[16]

FIGURE 4. PHOTOMICROGRAPH OF BORON NITRIDE COMPOSITE

TABLE IV

Pycnometry and Quantimet Analysis

of BN Composite

Fiber Volume (Quantimet)	5%
Apparent Bulk Density (Dimensions and Weight) ρ_B	1.70 ± 0.03 g/cm^3
Helium Displacement Density (Pycnometer) ρ_{He} (1)	1.81 ± 0.02 g/cm^3
Open Porosity (2) (Pycnometer)	6.0%
Total Porosity (Quantimet)	11.0%
True Density ρ (Estimated)	1.90 K/cm^3

(1) 4 samples tested

(2) given by $100\ \frac{(\rho_{He}-\rho_B)}{\rho_{He}}$

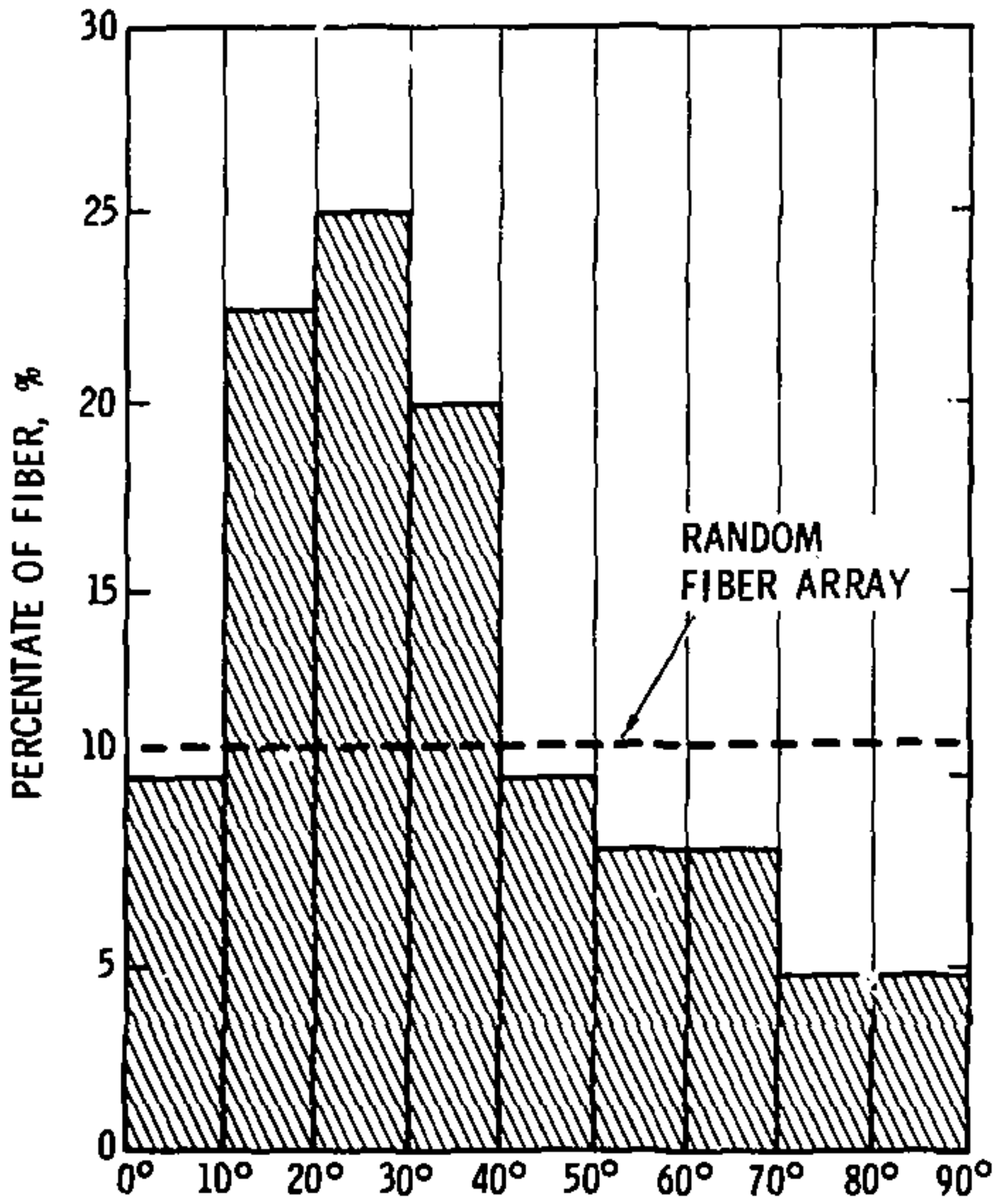

Fig. 5 Fiber population as a function of the angle of the fibers to the surface of the BN felt.

Table IV also gives the helium displacement density, the open porosity of the components as measured by pycnometry and the porosity measured by the Quantimet. The porosity measured on the Quantimet (11%) includes both open and closed pores as well as delaminations between layers of BN matrix and is thus higher than the porosity calculated from pycnometry (6.0%). Furthermore, optical contrast between fibers, matrix and voids is sometimes difficult to obtain and the porosity determination with the Quantimet is subject to interpretation. The porosity might be further reduced by additional infiltration.

The closed porosity of the composite (impermeable to helium) as seen on the Quantimet screen is estimated at 5%. Using this value the true density of the composite (matrix and fibers) from the measured helium density is estimated at 1.90 g/cm^3. This is high compared to the density obtained by other investigators using other source gases. With boron trichloride, Li reports true densities of ~ 1.35 g/cm^3 at 1100°C and 1.42 g/cm^3 at 1200°C deposition temperature.[12] Dungan and Gilbert[13] quote a true density of ~ 1.5 g/cm^3 with trimethyl borate over a wide range of temperature and 1.6 g/cm^3 for BCl_3 at 1200°C.

Mechanical Properties

Table V gives the sonic moduli of the BN composites. It shows that the modulus in the direction parallel to the surface is 39% higher than in the direction perpendicular to the surface. This anisotropy may be related to fiber orientation in the following manner.

The deposition of the BN matrix on the BN fiber produces a sheath around each fiber with the basal planes (ab direction) aligned parallel to its long axis. Since the strength and modulus of the PBN in the ab plane is considerably higher than in the c direction (Table I), it follows that the higher strength and modulus orientations of the matrix will be aligned with the fiber.

Therefore, the high strength and modulus of the matrix in the direction of the fiber mean the strength and modulus of the composite should be higher in the direction parallel to the surface since the majority of the fibers tend to be aligned in that direction. The observed trend in the sonic modulus measurements (Table V) is consistent with this fiber matrix orientation effect. It is expected that the strength of the composite would have the same directional dependence as the modulus.

Thermal Properties

Table VI gives the thermal conductivity of the BN composite at 300°C, 700°C and 1130°C. The conductivity measured in the direction parallel to the surface is 54% higher than in the direction perpendicular to it. Table VII gives the linear thermal expansion from 25°C to 600°C. The expansion measured in the direction parallel to the surface is 10% lower than in the direction perpendicular to it.

As in the case of the sonic modulus, this anisotropy may be realted to fiber orientations. The basal planes of pyrolytic BN (ab direction) have a much higher thermal conductivity than the

TABLE V

Sonic Modulus of BN Composites

	Direction	
Sonic Velocity[1]	Parallel to surface	0.401 cm/μsec
- -	Perpendicular to surface	0.315 -- --
Sonic Modulus[2]	Parallel to surface	25.56 GN/m^2 (3.71 M psi)
- -	Perpendicular to surface	15.77 -- (2.28 M psi)

(1) 4 measurements

(2) calculated by the relation $E = 93.55 \times V^2 \times \rho$ where E is in GN/m^2, V in cm/μsec and ρ in g/cm^3 (density of samples was 1.70 g/cm^3).

TABLE VI

Thermal Conductivity of BN Composite

Testing direction (3 samples)	Test Temperature °C	Average Thermal Conductivity W/m°C
Parallel to surface	300	11.51
	700	13.05
	1130	12.60
Perpendicular to surface	300	7.21
	700	7.92
	1130	8.91

Note: Estimated uncertainty 15 ± %

TABLE VII

Thermal Expansion of BN Composite

Testing Direction	Test Temperature	Coefficient of Thermal Expansion ppm ^{o}C
Parallel to surface	25-600	6.4
Perpendicular to surface	25-600	7.3

out of plane (c direction) (Table I); the anisotropy ratio is more than 40 to 1. These basal planes are aligned parallel to the fiber axis and the highest conductivity will therefore be along the fiber. Since the majority of the fibers tend to be aligned parallel to the surface, it follows th[illegible]he highest conductivity should be higher parallel to the surfa[illegible] lower perpendicular to it. The observed trend (Table VI) is consistent with this fiber matrix orientation effect. As might [illegible] expected, the thermal conductivity measurements of the composite in either direction, fall between the measurements for pyrolytic BN.

Likewise, the basal planes (ab direction) have a much lower thermal expansion than the out of plane (c direction) (Table I); the anisotropy ratio is 25 to 1. The lowest expansion will therefore be along the fiber and, in the composite, the lowest expansion will be parallel to the surface and the highest perpendicular to it. The observed trend (Table VII) is consistent with this fiber matrix orientation effect.

The failure to achieve an isotropic material can be attributed to the lack of isotropy of the fiber substrate. Since both mechanical and thermal properties appear to be related to fiber orientation, it may be assumed that, if a truly random felt substrate were used, a composite would be obtained with essentially isotropic mechanical and thermal properties.

SUMMARY

Boron nitride (BN) composites have been prepared by the chemical vapor deposition (CVD) of BN on a BN felt substrate. Boron

trifluoride and ammonia were reacted at low pressure (30 to 40 Torr) and at temperatures of 1100°C to 1200°C. Under these conditions a deposit was obtained which exhibited a higher degree of crystallinity than deposits obtained with other CVD reactions. Densification of the felt was achieved with only a relatively small amount of open residual porosity (6%) and an apparent bulk density of 1.70 g/cm^3. The orientation of the fibers in the felt showed a certain degree of anisotropy with the fibers tending to align themselves parallel to the surface of the felt. This anisotropy was reflected in the properties of the composite (sonic modulus, thermal conductivity, and thermal expansion). One may assume that, with a truly random BN felt, an essentially isotropic composite would be obtained.

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