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Wurtzitic Boron Nitride—A Review

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SUMMARY

Boron nitride exists in four main crystalline forms. These have graphitic, cubic, rhombohedral and wurtzitic crystal structures. Wurtzitic boron nitride is formed at relatively low temperatures above 12 GPa pressure. It is a hard ceramic with properties closely resembling those of cubic boron nitride, and has found application in composite cutting tools containing cubic boron nitride as the second phase. Earlier suggestions that the excellent performance of these cutting tools may be due to the wurtzitic boron nitride undergoing a stress-induced transformation to graphitic boron nitride appear to be incorrect.

1. INTRODUCTION

Boron nitride exists in several crystalline forms of which the graphitic (g-BN) and cubic (c-BN) forms are the best known because of their similarity to the graphite and diamond forms of carbon. The wurtzitic form (w-BN) has found use in composite cutting tools containing cubic boron nitride as the other phase. These cutting tools, called Geksanit-R or Hexanit-R in the Soviet Union, perform better in certain applications than tool bits composed only of c-BN.[1,2] The reason for this is not clear since the properties of w-BN are not well known. In this paper, the properties of w-BN are discussed primarily with respect to the graphitic and cubic forms of boron nitride. Efforts are also made to understand the fracture behavior of the composite materials consisting of c-BN and w-BN. In particular, the possibility that w-BN toughens the c-BN matrix[3] through a stress-induced transformation toughening mechanism is examined.

While the exact details of the transformation toughening mechanism are

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still uncertain it is well known that a martensitic phase transformation involving a stress-induced shear transformation is responsible for toughening. Shear transformations are exhibited by several ceramics[4] including zirconia and boron nitride. In zirconia ceramics the transformation is from the tetragonal phase to the monoclinic phase, whereas the shear transformation in boron nitride is between the graphitic and wurtzitic forms. The possibility of using the wurtzitic form of boron nitride as a means of toughening ceramics is intriguing because it is metastable at all temperatures and a large volume expansion (51 %) occurs on conversion of the wurtzitic form to the hexagonal form. Thus, the use of the wurtzitic form of boron nitride could produce substantial toughening of a ceramic matrix over a wide temperature range.

2. CRYSTAL STRUCTURES

The wurtzitic form (w-BN) was originally prepared by Bundy and Wentorf[5] by applying high static pressures to g-BN powder. The transformation occurred above 12·5 GPa at low temperature. Figure 1[5] shows that, with

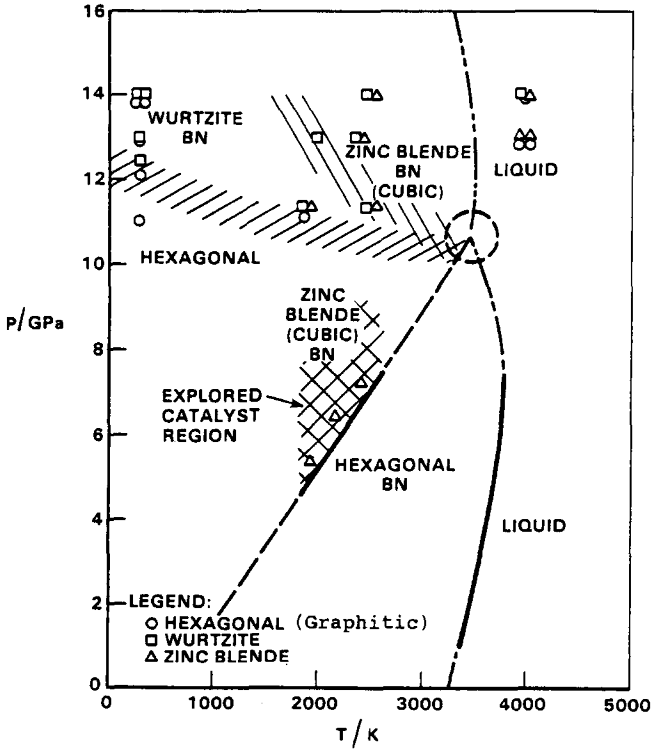

Fig. 1. Boron nitride pressure–temperature diagram.[5]

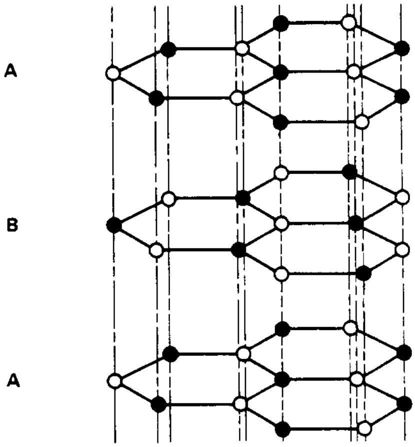

Fig. 2. Crystal structure of graphitic boron nitride.

increasing temperature at the same pressure, the cubic or zinc blende form is usually formed. The crystal structures of g-BN and w-BN are shown in Figs 2 and 3. The graphitic form consists of alternating AB layers, the boron and nitrogen atoms exchanging places in these layers, which are separated by half the length of the *c*-axis (333 pm). Boron nitride hexagons are nonplanar and form a 'chair' configuration.

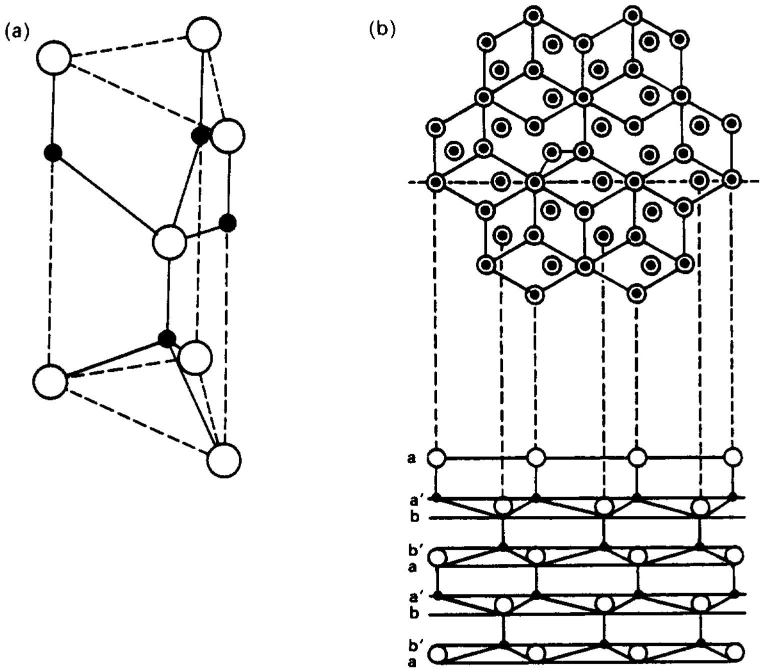

Fig. 3. (a) Hexagonal lattice of wurtzite; (b) schematic representation of the structure of wurtzitic boron nitride.

In the ideal wurtzitic structure (see Fig. 3(a)) each atom is tetrahedrally coordinated with a B—N bond length of 157 pm and a bond angle of 109·5°. The actual coordination tetrahedron in w-BN is distorted, being elongated along the *c*-axis and compressed along the *a*-axis. The distortion also depends upon whether the material was prepared by static or dynamic compaction. The structure consists of a series of close-packed layers alternating all boron and all nitrogen, aa′bb′aa′ (see Fig. 3(b)). The '*a*' unit cell dimension is similar to that found in the graphitic form, but the '*c*' dimension is approximately 35% shorter. The distinct difference in bond length and bond strength in these two crystallographic directions in g-BN is responsible for the large anisotropy in physical and thermal properties. The properties of w-BN are not expected to be as directionally dependent.

Kurdyumov and co-workers[6–16] have studied the substructures of both these forms of boron nitride extensively, using X-ray diffraction and electron diffraction techniques. Twins, stacking faults, and dislocations were found in g-BN. Whole or partial dislocations lie in the [0001] basal planes. Their Burger's vectors are $1/3a$ $[11\bar{2}0]$ and $1/3a$ $[10\bar{1}0]$, respectively. Stacking faults were characterized as being either polytypic or random. In the first type some hexagonal layers are shifted to positions equivalent to positions in the graphite structure. In the second type there is no correlation between neighboring layers in the defect region. Kurdyumov found the concentration of these defects to increase during shock compression[11] and concluded that the g-BN to w-BN transformation would not occur in regions containing these random or 'turbostratic' stacking faults.

In examining lattice defects in w-BN prepared by both shock and static compaction, Kurdyumov[7] found them to be independent of the preparation method. The crystallographic relations found within the boundaries of individual crystallites in two-phase particles were (001)w‖(001)g and $(1\bar{1}\bar{2}0)$w‖$(1\bar{1}\bar{2}0)$g. The lattice parameters of the w-BN samples prepared by the two methods were identical (within the error limits). Considerable comminution[8] occurs during the shock process so that the resulting w-BN particles are less than 0·3 μm in size and consist of 0·05-μm crystallites orientated primarily in the (001) direction normal to the main particle surface. These crystallites are under considerable strain (0·3%).

3. THE GRAPHITIC TO WURTZITIC BORON NITRIDE TRANSFORMATION

At pressures above 12 GPa, g-BN converts to the wurtzitic form.[5] Coleman and Forbes[17] calculated that the temperature at which this occurs is 230°C. The amount of w-BN formed depends upon the synthesis conditions and upon the nature of the boron nitride powder, but does not exceed 80% by weight. In particular, it has been shown that the crystallinity is an important factor controlling the transformation. Pyrolytic boron nitride shows very little conversion to w-BN unless it is first converted to g-BN. This is because a crystallographic correspondence exists between g-BN and w-BN. The basal planes of the wurtzitic phase are parallel to the basal planes of the graphitic form. Complete conversion to w-BN presumably does not occur because, in the early stages of compaction, random stacking faults are generated in a fraction of the material. These prevent w-BN formation, as discussed earlier. In addition, adiabatic heating of the powder compact during shock loading probably provides sufficient energy to reconvert some of the w-BN back to g-BN. The shear mechanism proposed for the transformation by Kurdyumov is similar to that proposed earlier by Lonsdale[18] for the graphite to wurtzite transformation in both graphite and boron nitride. Figure 4 illustrates the structure change which arises from shear in the basal plane by a B—N bond distance. The differences in stacking sequence in these two structures are shown more clearly in Figs 2 and 3(b). Kurdyumov explained the transformation in terms of a martensitic transformation, proceeding athermally under the influence of pressure. This does not appear to be correct since, if shock loading is carried out in such a way that the compact does not heat during shock loading,[19] then the conversion from g-BN to the wurtzitic form does not occur at room temperature. Under the same shock loading conditions maximum conversion to w-BN occurs on heating to 200 °C. This temperature is very close to the conversion temperature calculated by Coleman and Forbes[17] for normal shock loading of g-BN at room temperature. Thus both temperature and pressure are required to convert g-BN to w-BN.

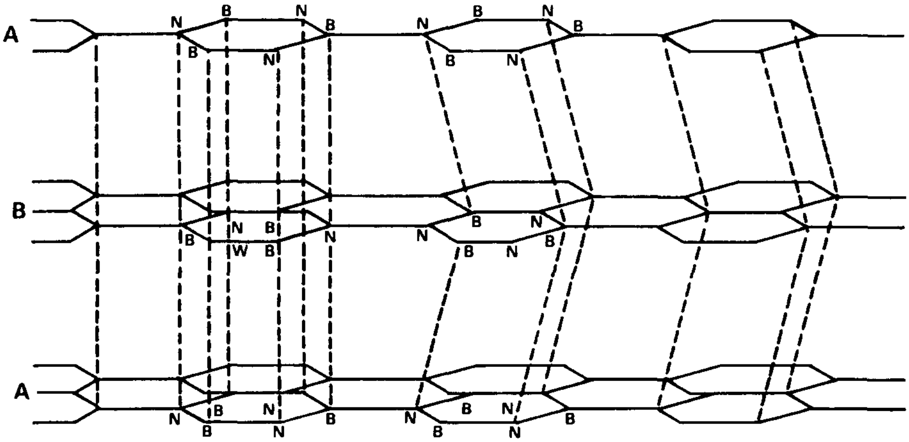

Fig. 4. Graphite → wurtzite orientation relation for boron nitride.[4] The (0001) planes straighten and shear by a B—N bond distance.

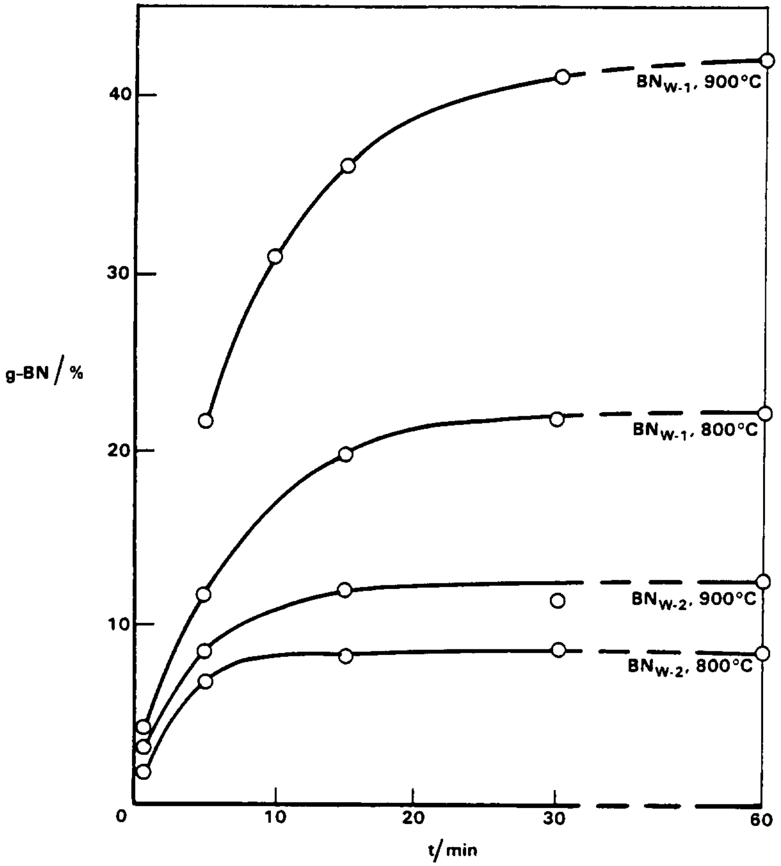

Fig. 5. Transformation of two wurtzitic boron nitride powders to graphitic boron nitride in flowing nitrogen at 800 °C and 900 °C.

The reverse transformation is of particular interest in preparing ceramic composites. On heating, w-BN reverts to a highly defective form of g-BN. There is evidence to suggest that the ambient conditions determine whether the transformation is truly reversible. At normal pressures the relation [0001]g⊥[0001]w was observed,[20] but at high pressures and temperatures the transformation is crystallographically reversible.[21]

Kinetic studies of the transformation at normal pressures have shown that the transformation is rapid, and depends upon both the temperature and the nature of the powder. Figure 5[22] shows the volume fraction of g-BN formed as a function of time at 800 °C and 900 °C for two different w-BN powders. The transformation consists of two stages: an initial rapid stage and a subsequent slow stage in which very little additional g-BN is formed. Kurdyumov *et al.*[20] interpreted the data in terms of a nucleation and growth mechanism and also observed this phenomenon in samples examined under the electron beam. The reaction kinetics obey an equation of the first order with an activation energy of 21 kJ mol^{-1}. It was concluded that the transformation was determined by the number of nucleation sites rather than by the growth of the nuclei, and that the transformation was of a diffusionless martensitic type. The exact experimental conditions used to obtain the data in Fig. 5 are not given in Ref. 22, but the factors which would affect the transformation rate would be expected to include powder compact density, particle size, the strain energy in the particles, and impurity content. Table 1[22] shows that there are some differences between the characteristics of these powders in terms of their impurity or second-phase content, but their surface areas are identical. Since it is likely that the surface energy of the powder plays a significant role in the transformation, it is somewhat surprising that the powders labeled $BN_{w\text{-}1}$ and $BN_{w\text{-}2}$ in Fig. 5 exhibit different transformation rates but possess identical surface areas. A difference in the respective strain energies of these powders might be expected because of the threefold difference in loading rates used to produce these powders. Yet if this were the reason for the observed difference in transformation rates, the powder labeled $BN_{w\text{-}2}$ should transform at a higher rate, not a lower rate, as shown in Fig. 5. The explanation offered by Pechentkovskaya and Savvakin[22] is that the extremely high loading rate conditions give rise to a new form of w-BN in which some changes in the fine structure of the valence band and conduction band exist. It is difficult to envisage why this modification of w-BN should be more stable if it is in some kind of excited state. Their explanation, therefore, cannot be considered to be very plausible.

The experimental data indicate that the transformation is both temperature and stress dependent. Both temperature and pressure are necessary to convert g-BN to w-BN, but the reverse transformation occurs at atmospheric pressure with a low activation energy typical of a displacive or diffusionless transformation mechanism. It does not, however, appear to be a martensitic transformation. This is in agreement with Kriven[4] who concluded that claims for a martensite mechanism in terms of an invariant plane strain model were not justified.

TABLE 1
Characteristics of Two Wurtzitic Boron Nitride Powders[22]

Material	*Average loading rate/ GPa s^{-1}*	*Content of the basic phase and impurities/%*				*Surface area/ m^{2} g^{-1}*
		w-BN	*g-BN*	*B_2O_3*	*O_2*	
$BN_{w\text{-}1}$	10^{7}	97·2	0·8	0·15	0·7	15
$BN_{w\text{-}2}$	10^{10}	95·6	2·4	0·10	1·6	15

4. PROPERTIES OF WURTZITIC BORON NITRIDE

The thermal and mechanical properties of w-BN are given in Tables 2 to 5. It should be noted that measurements were frequently made on impure samples or multiphase specimens such as the cutting tool material Geksanit-R (a two-phase boron nitride ceramic containing principally w-BN and c-BN). Some of the materials also contained residual stresses or were

TABLE 2

Thermal Properties of the Wurtzitic, Graphitic and Cubic Forms of Boron Nitride

Property	*Temperature (K)*	*w-BN*	*g-BN*	*c-BN*
Specific heat/J kg^{-1} K^{-1} at constant pressure	300	810 (Ref. 23)	800 (Ref. 24)	270 (Ref. 25)
Thermal conductivity/ W m^{-1} K^{-1}	1 150	60 (Ref. 26)	15–30 (Ref. 24)	26 (Ref. 26)
Linear coefficient of	300–530	3·7[a] (Ref. 38)		2·8 (Ref. 38)
thermal expansion/	300–550	2·7[b] (Ref. 38)		
M K^{-1}	270–1 070		40·5[a] (Ref. 39)	
	270–370		−2·9[b] (Ref. 39)	

Note: Temperatures given represent those for which data have been found for w-BN. More extensive data are available for g-BN and c-BN.

[a] Value in the '*c*' direction.

[b] Value in the '*a*' direction.

TABLE 3

Room Temperature Hardness Values for w-BN and c-BN Specimens

Material	*Measurement method*[a]	*Hardness/GPa*	*Reference*
c-BN	Vickers	>66·7	29
w-BN	Vickers	22·3	29
w+c-BN	Vickers	67·7	29
w+c-BN	Vickers	87·3	30
w-BN	Vickers	52·5	31
c-BN	Vickers	58·7	31
w-BN	Knoop	35·6	31
c-BN	Knoop	48·9	31
w+c-BN	Vickers	48·9–71·2[b]	32, 34
c-BN	Vickers	38·3	34

[a] Vickers hardness measurements were made at a load of 0·5 kg, Knoop at a load of 0·4 kg.

[b] Specimens were heat treated prior to testing.

TABLE 4
Young's Modulus, Fracture Toughness, and Fracture Surface Energy Values for Wurtzitic Boron Nitride Materials

Property	*Material*	*Value*	*Reference*
Young's modulus/GPa	50 % c-BN, 50 % w-BN	890	32
Fracture toughness/MPa m$^{1/2}$	Mixed w-BN/c-BN	15–17·05	34
	100 % c-BN	14·57–17·05	34
	Mixed c-BN/w-BN containing 2–7 % g-BN	5·89–6·20	34
	100 % c-BN	16–18	33
	Mixed c-BN/w-BN	16–18	33
	Mixed c-BN/w-BN after annealing	10–14	33
Fracture surface energy/J m^{-2}	Mixed w-BN/c-BN	62–75	33, 34
	100 % c-BN	62–75	

microcracked. Comparisons are made with the corresponding data for the cubic and graphitic forms of boron nitride (see Tables 2 and 3) and with several other ceramics (Tables 5 and 6).

The specific heat data at 300 K and the thermal conductivity data at 1150 K are shown in Table 2. The specific heat of the wurtzitic form (810 J kg^{-1} K^{-1}) is similar to that for the graphitic form (800 J kg^{-1} K^{-1}). The range of values for the thermal conductivity of g-BN reflects the anisotropy of this material, the higher value being for the '*a*' axis or basal plane in which the atoms are closer together. Even if the w-BN specimens used by Fedoseev *et al.*[26] were textured so that conduction was measured only along the '*a*' direction, this would still not explain the very high thermal conductivity found for this form of boron nitride. The specimen contained 15 % c-BN, so that if the appropriate correction is made using the data in

TABLE 5
Room Temperature Fracture Toughness Values for Boron Nitride and Other Ceramics

Material	*Fracture toughness*[a]/ *MPa m*$^{1/2}$	*Reference*
c-BN/w-BN	15·5–17·05	34
100 % c-BN	14·47–17·05	34
Silicon nitride	4·96	35
Cobalt-bonded tungsten carbide	16·75	35
Diamond	9·61	34
Sapphire (single crystal)	2·1	35

[a] Determined by the indentation technique of Evans and Charles.[35]

TABLE 6

Room Temperature Fracture Surface Energies for Alumina, Silicon Nitride and Wurtzitic Boron Nitride

Material	*Fracture surface energy/ $J m^{-2}$*	*Reference*
c-BN/w-BN	70	34
Hot pressed alumina	42[a]	36
	21[b]	36
Sintered alumina	23	36
Hot pressed silicon nitride	61[a]	36
	42[b]	36

[a] Flaw moving perpendicular to hot pressing direction.
[b] Flaw moving parallel to hot pressing direction.

Table 2, the thermal conductivity of w-BN is actually nearer 70 W m^{-1} K^{-1}. This is a very high value for a ceramic at this temperature and may be one reason that the cutting tools consisting of both c-BN and w-BN perform better than those composed of only c-BN. The higher thermal conductivity of w-BN is difficult to explain in terms of its crystal structure. Slack *et al.*[27,28] concluded that ceramics with high thermal conductivities possessed four characteristics: (1) low atomic mass, (2) strong bonding, (3) a simple crystal structure, and (4) low anharmonicity. On this basis, the simpler crystal structure of c-BN should result in the highest thermal conductivity value for any of the allotropes of boron nitride. Single-crystal c-BN has the highest thermal conductivity after diamond; thus, the high value for w-BN (60 W m^{-1} K^{-1} (Ref. 26)) is surprising, more so because it is not just slightly higher, but twice that for the c-BN specimen. The samples used by Fedoseev *et al.* were polycrystalline. Consequently, a likely explanation for the disparity in thermal conductivities is that it is due to differences in porosity and impurity content of the two specimens. The single-crystal value for w-BN should be lower than that for c-BN.

There is a marked difference in the thermal expansion coefficients of the wurtzitic and graphitic forms of boron nitride (see Table 2). The weak van der Waals forces between the layers of atoms in the '*c*' direction of g-BN are responsible for the high expansion coefficient in this direction. Stronger bonding exists between the layers of atoms in w-BN. Consequently, it has a lower expansion coefficient and exhibits only moderate anisotropy in expansion values. The thermal expansion coefficient of w-BN (average 3·2 M K^{-1}) is close to that of c-BN (2·8 M K^{-1} (Ref. 38)) and silicon nitride (2·9 M K^{-1} (Ref. 24)).

Hardness values for various specimens of w-BN and c-BN, shown in Table 3, exhibit considerable scatter for several reasons. First, most of the materials examined by Bochko and co-workers[31-33] were made by a process that gave rise to a temperature distribution in the samples during processing. Furthermore, many of the materials contained residual stresses arising from their multiphase composition. Stresses arise from the thermal expansion mismatch between w-BN and c-BN ($1{\cdot}0\ \mathrm{M\,K^{-1}}$, see Table 2) on cool-down, and from the formation of g-BN from either w-BN or c-BN during processing. Secondly, some of the samples listed in Table 3 were not fully dense. Annealing[31-33] to eliminate these stresses resulted in higher hardness values,[34] and a smaller scatter in values was obtained for the Geksanit-R materials. The hardness of w-BN is similar to that of c-BN.

The Young's modulus and fracture toughness values[32-34] for the mixed phase Geksanit-R materials and c-BN are shown in Table 4. The Young's modulus of 890 GPa is high for a ceramic and only about 15% lower than that for diamond (1033 GPa[32]). The data in Table 4 are not strictly accurate since all samples contained residual stresses unless they were annealed out. This is the reason for the differences in values for c-BN in Refs 33 and 34 and for the Geksanit-R material in Ref. 34 (Table 4 shows that annealing causes the fracture toughness of the mixed phase Geksanit-R to decrease from 16–18 $\mathrm{MPa\,m^{1/2}}$ to 10–14 $\mathrm{MPa\,m^{1/2}}$). The fracture toughness drops drastically if the material contains more than a small amount of g-BN. For example, Geksanit-R materials containing 2–7% g-BN exhibit a much lower fracture toughness (6 $\mathrm{MPa\,m^{1/2}}$ (Ref. 34)). This decrease in fracture toughness can be only partly explained by the lower Young's modulus (90 GPa[24]) of g-BN. These materials exhibit both intergranular and transgranular fracture, whereas Geksanit-R fractures only intergranularly. It thus appears that the main reason for the substantial decrease in fracture toughness is that the g-BN provides a lower resistance crack path. Toughening through a crack deflection mechanism is reduced since the advancing crack moves through the g-BN particles.

The fracture toughness values for c-BN and the mixed Geksanit materials are similar (approximately 16 $\mathrm{MPa\,m^{1/2}}$). Table 5 shows that this is higher than that for any other known monophase ceramic material and comparable to that for cobalt-bonded tungsten carbide. This is partly due to its high Young's modulus, but not entirely, since diamond also has a high Young's modulus but possesses a lower fracture surface energy. In Table 6 the fracture surface energies of several ceramics are given. The boron nitride materials have a high fracture surface energy in spite of their very fine grain size ($< 3\ \mu$m). This is difficult to explain in terms of conventional fracture behavior since fine-grained, polycrystalline ceramics do not generally have a high fracture surface energy. For example, in both hot-pressed alumina and silicon nitride crack propagation around the high aspect grains is responsible for their relatively high fracture energies in the direction perpendicular to the hot-pressing direction (see Table 6). In fine-grained, sintered alumina the fracture surface energy is 50 % lower. Complicating the issue also is the fact that the 100 % c-BN samples and Geksanit-R materials have different grain sizes and fracture modes, but possess similar fracture toughness values. Geksanit-R has a grain size of approximately 0·5 μm and an intergranular fracture mode, whereas c-BN has a slightly higher grain size (1–2 μm), and exhibits both intergranular and transgranular fracture.[34]

A fracture surface energy of 70 J m^{-2} is high for a fine-grained structure. One mechanism that might explain these data is transformation toughening. Following the method of Evans *et al.*,[37] the contribution to toughening by the transformation can be estimated:

$$\Delta K_{\mathrm{Ic}} = 0{\cdot}34\ V_{\mathrm{f}} E\,(\Delta V/V) r_0^{1/2}$$

where ΔK_{Ic} = the contribution to toughening due to the transformation; V_{f} = the volume fraction of transformable particles; E = Young's modulus; $(\Delta V/V)$ = the transformation volume strain; and r_0 = the width of the transformation zone.

Although this equation ignores any contribution due to shear strains, it enables an estimate of the amount of toughening due to volumetric changes. Assuming that r_0 is equal to the grain size (0·1 μm), the effect of 50 % w-BN in a matrix of c-BN would be to increase its fracture toughness by 25 MPa m$^{1/2}$. Table 4 shows very little difference in the fracture toughness values for the cubic and mixed-phase boron nitrides. Furthermore, Claussen[40] was unable to detect any stress-induced transformation toughening in silicon nitride and cordierite composites containing w-BN. Transformation toughening can, therefore, be ruled out as the mechanism responsible for the high fracture energy. It seems more likely that microcracking is the toughening mechanism, particularly since these boron nitride materials were formed under non-uniform temperature conditions and usually contain residual stresses. In view of the similarity in the properties of w-BN and c-BN it is difficult to explain, using the available information, why the Geksanit-R cutting tools perform better than the c-BN materials.

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