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Formation of novel sintered composites by high-pressure crystallization of amorphous ceramics

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A combination of chemical vapour deposition (CVD) and high-pressure (HP) techniques has achieved the fabrication of the zincblende form of boron nitride (z-BN)-based ceramic composites. The CVD technique provides amorphous B–N–X (X = aluminium, silicon or titanium). The HP technique renders the amorphous samples crystalline and decomposition into z-BN plus the respective nitride (β-Si_3N_4 for instance) occurs. Compacts of the composites are obtained by *in situ* sintering under high pressure. The compacts exhibit peculiar microstructures composed of z-BN nano-crystals homogeneously dispersed in the nitride matrices.

1. Introduction

Recent progress in electronic as well as structural engineering materials has led to the requirement of very accurate, fine, and rapid machining of the materials of interest. For such machining, abrasive and cutting tools made, for example, of diamond are employed in many cases [1–5]. Because diamond is readily attacked by steels at high temperatures and the zincblende form of boron nitride (z-BN) is, on the other hand, chemically stable against steels, z-BN can be complementary to diamond [5]. In the case of z-BN, the tools employed have exclusively been compacts made of sintered polycrystals.

Sintering of z-BN is achieved at high pressure–high temperature conditions under which z-BN is thermodynamically stable. The sintering is categorized into two groups: sintering with [1, 6–8] or without [9–13] additives. Sintering without additives is a concurrent process with non-catalytic synthesis of z-BN from the graphite-type form (g-BN) [9, 10], wurtzitic form (w-BN) [11, 12], or rhombohedral form (r-BN) [13], and hence is referred to as reaction sintering.

Sintering with additives is a process whereby z-BN is mixed in most cases with elements, nitrides, borides, etc. [6–8]. Also categorized into this group is that starting with g-BN [14] or w-BN [7], each being mixed with an additive which also functions as a catalyst for the conversion of g-BN or w-BN into z-BN. After sintering, the resultant sintered body is simply a mixture of BN phase(s) (primarily z-BN) and the additive.

As a third category, we present here a new method for sintering of BN. This employs three component amorphous ceramics which decompose and crystallize at high pressure, spontaneously forming sintered compacts of z-BN-based composites. A description will be made of the underlying concept, experimental procedures, and characteristics of the sintered compacts.

2. Basic concept

Our starting samples were amorphous three-component materials, B–N–X in this case. The element X was chosen because of its ability to readily form a nitride. When heated under pressure, the starting amorphous sample is expected to undergo crystallization. The sample may also decompose into BN plus X–N if given pressure–temperature conditions are met. After decomposition, the product may either be simply a mixture of the two phases or be a composite having intimate bondings with nitrogen atoms in common. The phase of BN formed, whether g-BN or z-BN, is dependent on pressure–temperature conditions. For our purposes, however, the formation of z-BN is preferable and hence the samples should be exposed at conditions penetrating deep into the z-BN stability field.

For simplicity, our discussion is limited to the crystallization of z-BN from the amorphous state, pro-

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ceeding in this case apart from the thermodynamic equilibrium line between g-BN and z-BN [15]. The process involves nucleation and subsequent growth of z-BN crystals. For homogeneous nucleation [16], the critical size of the nuclei is given by

$$R^* = 2\sigma/\Delta G_v \qquad (1)$$

where σ is the amorphous-crystal specific surface free energy and ΔG_v is the difference in Gibbs free energy per unit volume between amorphous and crystalline samples. The change of the critical size with pressure is expressed as [17]

$$\left(\frac{\partial R^*}{\partial P}\right)_T = -R^*\left[\frac{\Gamma V^A}{\sigma} + \frac{V^A - V^C}{V^C(\Delta G_v)}\right] \qquad (2)$$

where V^A and V^C are the molar volumes of amorphous and crystalline samples, respectively, and Γ is surface excess mass. Because $V^A > V^C$ and ΔG_v itself is positive, then R^* decreases with pressure if Γ is positive, or negative but less than $\sigma(V^A - V^C)/V^A V^C(\Delta G_v)$.

The growth rate here is assumed to be interface-controlled, as often observed in recrystallization, precipitation, and phase transition. The rate, k, is given by [16]

$$k = \delta D\left[1 - \exp\left(-\Delta G_v/RT\right)\right] \qquad (3)$$

where δ includes geometrical terms as well as the fraction of active sites for a jump, and D is the diffusion coefficient for atomic (or molecular) transport across the amorphous–crystal interface. The coefficient, D, decreases with increasing pressure. On the other hand, δ and the term in the bracket in Equation 3 either increase or decrease with pressure. Thus the crystal growth rate may exhibit a maximum as pressure is applied across the equilibrium between g-BN and z-BN, and then the rate may become slower as the pressure is raised.

A simple expectation drawn from the above discussion is that the amorphous B–N–X exposed to conditions deep in the z-BN stability field would undergo crystallization, forming z-BN plus nitride. It is plausible that by crystallization small-sized nuclei may be formed and that the subsequent growth of crystals may be retarded. Consequently, the grown crystals could remain very tiny. A salient feature of the present technique is that fabrication of composites can be performed *in situ* under pressure from the decomposed microcrystalline z-BN plus nitride, without the presence of other material(s).

3. Experimental procedure

Amorphous B–N–X samples (where X = aluminium, silicon or titanium) were prepared by chemical vapour deposition (CVD) technique [18, 19]. The compositions of the samples studied are given in Table I. The X contents were known from wet chemical analysis. The samples prepared were in the form of platelets, approximately 20 × 10 × 1 mm^3. They were pulverized into powders for high-pressure experiments.

The powdered sample was enclosed in an octahedral sample cell (Fig. 1) and was pressurized in a high-pressure device of the octahedral anvil type [20, 21]. Pressures generated inside the cell were known from calibrations using fixed points [22, 23]. High temperature was attained by passing an alternating current through a graphite tube. The temperature was monitored using a Pt–Pt/Rh(13%) or W/Re(5%)–W/Re(26%) thermocouple.

After the high pressure–high temperature experiment, the sample was recovered to ambient conditions and was subjected to X-ray diffraction analysis, Vickers microhardness test, scanning electron microscopy (SEM) observation, and X-ray microanalysis as well.

4. Results

4.1. Pressure–temperature conditions

Table I gives the pressure–temperature–time conditions and the phases obtained from amorphous B–N–Al, B–N–Si, or B–N–Ti. Each of the starting amorphous samples decomposes under high pressure and high temperature, forming g-BN and/or z-BN. The formation of z-BN occurs at higher regimes of pressure and temperature. In the B–N–Si system, the crystallization is unequivocally accompanied by the formation of β-Si$_3$N$_4$. In Table I, the formation of AlN or TiN is not observed for the B–N–Al and B–N–Ti systems. This is attributed to the small

TABLE I Descriptions for B–N–X systems

System	High-pressure treatment			Phases	Hardness, H_v (GPa)
	Pressure (GPa)	Temperature (°C)	Time (min)		
B–N–Al	6	1000	10	g-BN	
(Al: 1.4 wt %)	7	1000	10	z-BN, g-BN	
	7	1000	10	z-BN, g-BN	
	7	1500	10	z-BN	
B–N–Si	6	2000	10	z-BN, g-BN, β-Si$_3$N$_4$	32–47
(Si: 32.5 wt %)	7	1000	10	amorphous	
	7	1200	10	amorphous	
	7	1500	10	amorphous	
	7	1800	10	z-BN, β-Si$_3$N$_4$	30–38
	7	2200	10	z-BN, β-Si$_3$N$_4$	29–40
B–N–Ti	6	1000	10	g-BN	
(Ti: 2.0 wt %)	7	800	10	g-BN	
	7	1000	10	z-BN	
	7	1200	10	z-BN	

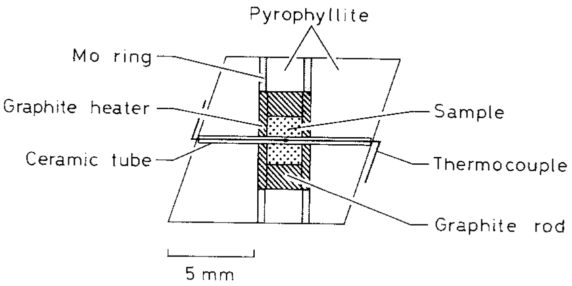


Figure 1 Cross-section of an octahedral sample cell.

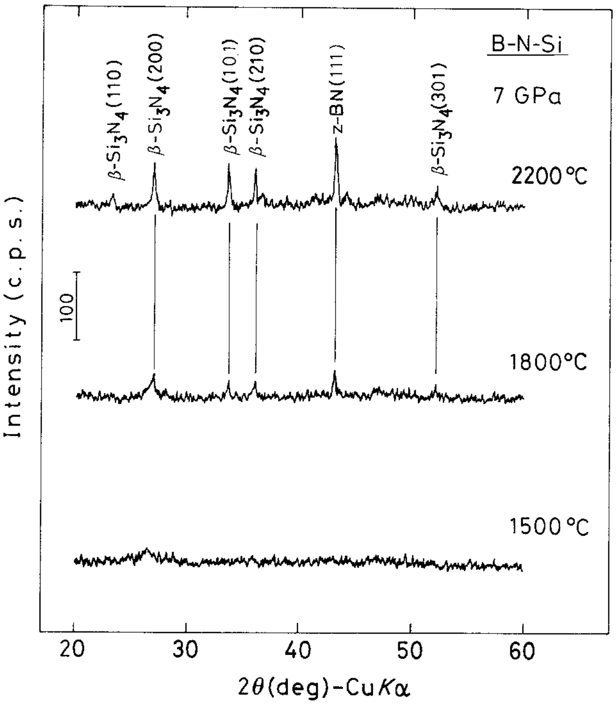


Figure 2 X-ray diffraction patterns for the B–N–Si system recovered after heat treatment at 7 GPa.

amounts of aluminium and titanium contained in the starting amorphous materials, or to the low temperatures in the heat treatments, or to a combination of these. The nitrides could be formed if the metal contents were increased to certain amounts and/or if the samples were heated to higher temperatures.

Fig. 2 shows X-ray diffraction patterns for the B–N–Si system recovered after heat treatment at 7 GPa. The sample remains amorphous at temperatures below 1500° C under this pressure. Crystallization accompanied by decomposition is observed at 1800° C as evinced from the appearance of z-BN and β-Si_3N_4. Upon increasing temperature to 2200° C, both the z-BN and β-Si_3N_4 peaks are strengthened further.

4.2. Hardness

Typical examples for Vickers microhardness, H_v, are given in Table I for the compacts obtained from B–N–Si samples. In Table I, the highest hardness for B–N–Si composites is recorded for the compact sintered at 6 GPa and 2000° C. For comparison, representative data are: H_K (Knoop hardness) $= 65$ GPa for z-BN [9], and $H_K = 25$ GPa for β-Si_3N_4 [24]. Also to be compared are $H_v = 45$ GPa for a z-BN/AlN compact [14] and $H_v = 30$ to 40 GPa for compacts obtained from mixtures of w-BN with AlN or with amorphous Si_3N_4 [7].

4.3. Microstructure

Fig. 3 shows scanning electron micrographs of fracture surfaces of the B–N–Si composite compacts sintered at 7 GPa. Similar grain morphologies are observed in Figs 3a and b; polyhedral grains are bonded to each other. These grains are, as expected from Fig. 2, composed of z-BN and β-Si_3N_4 crystals. Apparently, grains with smaller sizes stay on or are held with larger grains. A greater extent of grain growth is perceivable when the heat-treatment temperature is raised from 1800° C, Fig. 3a, to 2200° C, Fig. 3b.

A typical example of the microstructures is given in Fig. 4a, showing a scanning electron micrograph on and around a Vickers indent on a polished surface of the B–N–Si compact obtained at 7 GPa and 2200° C. The microstructure of this compact is basically made up of two phases, namely, black islands and a grey matrix. The islands, small in size of the order of 10 to 100 nm, are homogeneously dispersed in the matrix.

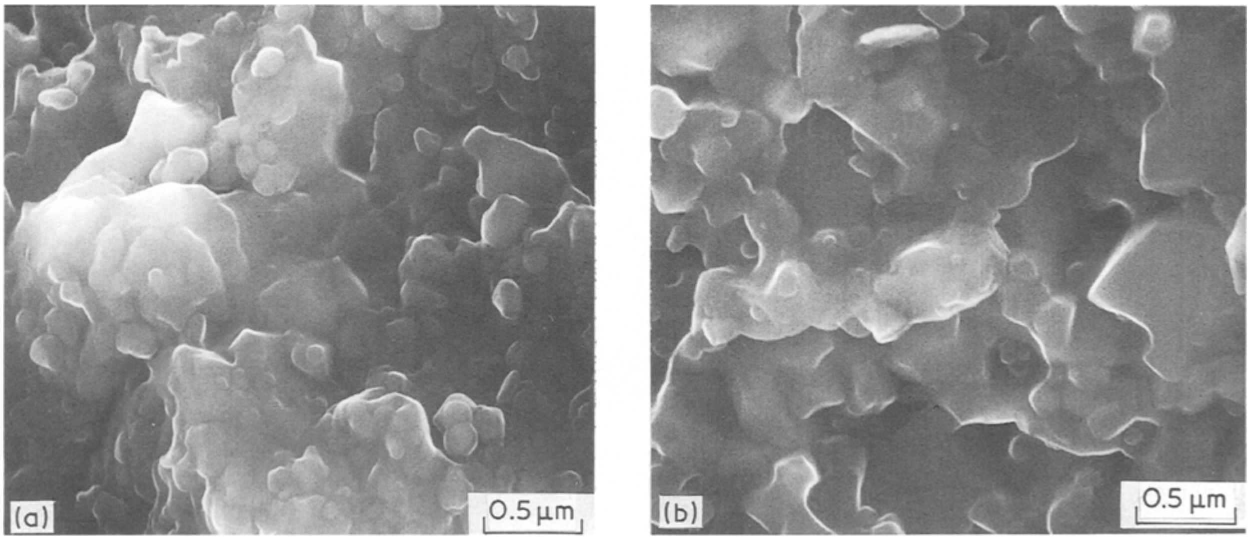


Figure 3 Scanning electron micrographs of fractured surfaces of composite compacts fabricated from B–N–Si at 7 GPa: (a) 1800° C, (b) 2200° C.

Fig. 4b is an enlarged view of such microstructure. For this area, X-ray microanalysis maps for silicon and boron are given in Figs 4c and d. It is apparent from the distribution of the two atoms, silicon and boron, that the black islands correspond to z-BN and the grey matrix to β-Si_3N_4. Thus the sintering has been achieved, forming nanocrystalline z-BN homogeneously dispersed among β-Si_3N_4 crystals.

5. Discussion

The present study has demonstrated that novel composites made up of nanocrystalline z-BN can be fabricated *in situ* under pressure from CVD amorphous B–N–X. The fabrication is associated with decomposition and crystallization of amorphous B–N–X followed by phase transition of BN. For these complex phenomena occurring either simultaneously or subsequently, the basic concept outlined in Section 2 still holds as evinced from the appearance of microcrystals of 10 to 100 nm in size. The crystals are homogeneously dispersed within the matrix, constituting composites.

The bonding between z-BN crystals seems to be complicated; if grains (the black islands in Figs 4a and b) of z-BN crystals were simply dispersed in the β-Si_3N_4 matrix, then the Vickers microhardness could not be as high as is given in Table I. Any linkage should be provided between the islands, forming strong networks. In this sense also, the composite compacts fabricated herein are different from those compacts made up of a mixture of z-BN and additive(s). Verification of such direct bonding as suggested in Section 2 between z-BN and β-Si_3N_4 has not, however, been performed and needs further investigation.

We have employed three-component amorphous samples prepared by the CVD technique as the starting material for fabricating composites. The preparation technique is not necessarily CVD. However, it is quite easy with CVD to prepare multi-component materials and even to control the amount of the components. Also, the starting sample is not necessarily amorphous; the sample may contain crystalline parts to some extent. In fact, we have studied samples containing β-Si_3N_4 [25].

For X in B–N–X, we chose the nitride-forming elements aluminium, silicon and titanium. Eventually, these elements react with boron, forming various borides. Dangling bonds existing in general in amorphous materials are chemically affinitive with H_2O, O_2, etc. In fact, z-BN compacts reaction-sintered from amorphous BN are attacked by water in some cases [26]. By forming nitrides (and also presumably borides), the elements aluminium, silicon and titanium can consume those dangling bonds which otherwise become origins of a hygroscopic nature for amorphous-bearing materials.

The CVD/HP technique presented here can also be extensively applied to the development of other novel composites with micro-crystalline structure. Systems to be studied can be alternative to B–N–X, and accordingly the pertinent pressure regime required for fabrication can be lowered to some extent.

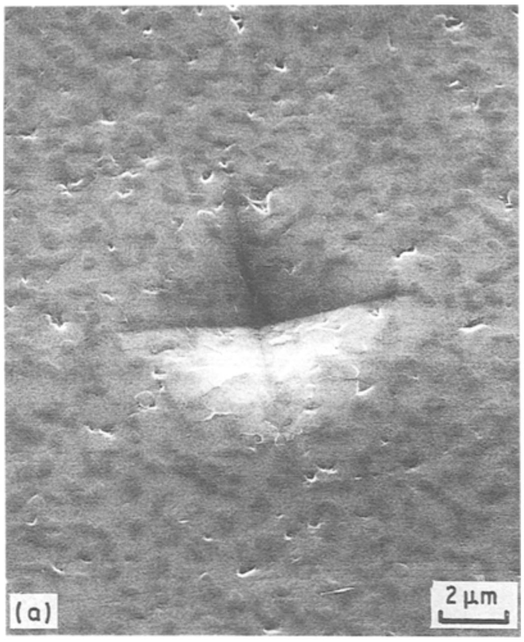
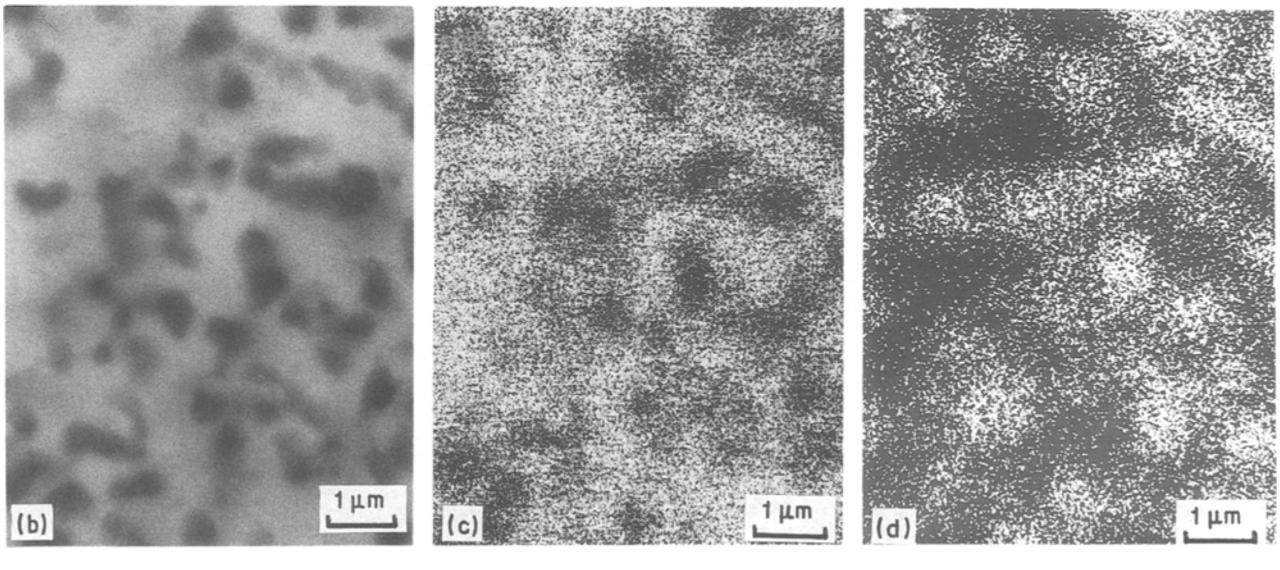


Figure 4 (a) Scanning electron micrograph of an indent on a B–N–Si composite compact fabricated at 7 GPa and 2200° C. (b) Enlarged view of (a). (c) X-ray microanalysis image for silicon. (d) X-ray microanalysis image for boron.



6. Conclusion

An application of the CVD/HP technique to the fabrication of z-BN-based ceramics composites has been proposed. The underlying basic concept for this application in terms of nucleation and growth of z-BN crystals under conditions penetrating deep in the z-BN stability field is shown.

One of the salient features of this technique is that the fabrication is performed *in situ* under pressure, through decomposition and crystallization of amorphous B–N–X, followed by phase transition.

Composites obtained from B–N–Si above 6 GPa and 1800° C were made up of z-BN nano-crystals homogeneously dispersed in a β-Si_3N_4 matrix, and were sintered to microhardness as high as 47 GPa on a Vickers scale.

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