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Synthesis of Amorphous Boron Nitride by Pressure Pyrolysis of Borazine

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Amorphous BN that contains hydrogen could be synthesized by pressure pyrolysis of borazine below 700°C at 100 MPa. The fraction of B and N bonded to H in the pyrolysis product could be controlled by changing the pressure pyrolysis condition. The pyrolysis product at 700°C and 100 MPa showed formation of B–N–B bonds of the hexagonal structure in the amorphous state with some B–H and N–H bonding remaining. Spherulitic BN could be prepared only by pyrolysis below 400°C and 100 MPa. The yield of amorphous BN from borazine was as high as about 60% by this pressure pyrolysis. Amorphous BN formed from borazine could be readily converted to cubic BN by reacting it with AlN at 1200°C and 6.5 GPa. [Key words: boron nitride, synthesis, pyrolysis, phase transformations, bonding.]

I. Introduction

Borazine ($B_3N_3H_6$) consists of a six-membered planar ring of alternating borons and nitrogens and is isoelectronic and isostructural with benzene. Borazine, a liquid at room temperature, undergoes thermal decomposition by condensation reaction to produce polycyclic BN compounds, such as the B–N analogues of naphthalene and biphenyl.[1]

Since borazine itself has the same stoichiometric ratio of boron and nitrogen as boron nitride (BN), several workers have used borazine as a starting material for the preparation of high-purity BN. Adams synthesized BN films from borazine and compared their properties with those of films prepared from diborane and ammonia.[2] Savel'ev *et al.* reported the properties of BN films formed from borazine in a high-frequency plasma.[3] Shanfield and Wolfson demonstrated the synthesis of films containing the cubic BN phase from borazine, using an ion-beam technique.[4] Because borazine is a volatile compound, the yield by ordinary pyrolysis is quite low.

Cubic BN has normally been synthesized from crystalline BN under high-pressure and high-temperature conditions using various catalysts. Hirano *et al.* reported that AlN was an effective catalyst for the reduction synthesis of cubic BN and simultaneously acted as a sintering agent during conversion.[5] In this series of studies, both the control of the crystallinity of the starting BN and the selection of reductive conditions at high temperature and pressure were found to be important in the synthesis of sintered cubic BN–AlN composites. Borazine might exhibit a high yield of amorphous BN powders by pressure pyrolysis (similar to the synthesis of carbon with controlled morphology and bond nature), which are synthesized by the pressure pyrolysis of organic compounds.[6,7]

This paper describes the synthesis of amorphous BN by pressure pyrolysis of borazine with high yield below 700°C at 100 MPa. Amorphous BN, including hydrogen as B–H and N–H bonds, was synthesized from borazine and was converted to a cubic BN–AlN sintered compact without any intended addition of reducing agents.

II. Experimental Procedure

Borazine (bp 55°C/10^5 Pa) was prepared by the reduction of B-trichloroborazine as described.[8] B-trichloroborazine was prepared according to the methods described by Rothgery and Hohnstedt.[9]

Pressure pyrolysis was performed within a hydrothermal apparatus of the cold-seal type. Borazine was sealed under nitrogen in a thin-walled gold capsule of 3.0- or 5.0-mm diameter and 50-mm length. The pressure and the temperature of the specimen were transmitted through the gold capsule, which was set in a cold-seal-type pressure vessel.

Borazine was pyrolyzed at temperatures between 250° and 700°C under 100 MPa in a gold capsule. The heating rate was $10°C \cdot \mathrm{min}^{-1}$ at a constant pressure of 100 MPa. The pyrolysis was conducted at the given temperature for 5 min, 1 h, and 3 h. Pressure was measured with a calibrated Heise gage, and temperature was measured with a calibrated sheathed thermocouple set inside the pressure vessel. The sample was quenched after each experimental run.

Yields of pyrolysis product were about 60% of the starting borazine in weight. The infrared (IR) spectra of borazine itself and the pyrolysis product were measured by a liquid-film method using an NaCl plate and by a KBr disk method, respectively. The pyrolysis product was characterized by X-ray diffraction (XRD) analysis and electron diffraction. A combustion analysis method was used to analyze the amount of hydrogen in the pyrolysis product. The morphology of the pyrolysis product was analyzed by scanning electron microscopy (SEM).

The high-pressure treatment was performed using a girdle-type apparatus[5] to elucidate the features of the pyrolysis products used as the starting material for cubic BN synthesis. The sample arrangement in the pressure apparatus was the same as that reported,[5] except that the specimen was placed directly into the graphite crucible without using a platinum capsule. The crucible serves as a heating element by passing the electrical current through it under pressure. The calibration method of temperature and pressure was the same as described.[5] The specimen prepared by pressure pyrolysis of borazine was mixed with aluminum nitride powder (>99%)[‡] under nitrogen atmosphere, and then placed in a graphite crucible. The products were analyzed by XRD after treatment at 1200° and 1800°C under 6.5 GPa. The yield of cubic BN was determined using the same calibration curve as reported.[5]

III. Results and Discussion

(1) Characterization of Pyrolyzed Borazine

White solid particles of BN could be synthesized by pressure pyrolysis of borazine with a yield of about 60% in weight. The pyrolysis product formed at 250°C and 100 MPa was found to react with atmospheric moisture, yielding boric acid and ammonia after

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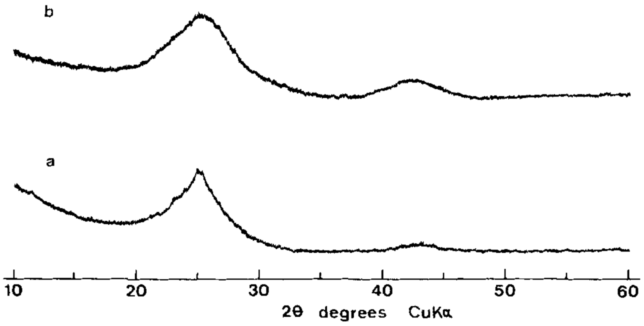

Fig. 1. X-ray diffraction profiles of pyrolysis products of borazine (a) at 250°C and 100 MPa and (b) at 700°C and 100 MPa.

a few weeks. However, the pyrolysis product synthesized at a higher temperature and 100 MPa is much more stable to oxidation than that formed at 250°C.

XRD profiles of pyrolysis products synthesized at 250° and 700°C under 100 MPa for 3 h are shown in Figs. 1(a) and (b), respectively. No characteristic sharp reflections of hexagonal BN can be observed in either profile. The pyrolysis product at 250°C shows a broad diffraction with a maximum at about $2\theta = 25.0°$ (Cu*Kα*), whereas the diffraction profile of the product pyrolyzed at 700°C is composed of two diffractions centered at $2\theta = 25.5°$ and 42.5°. The former is ascribed to the [002] diffraction of hexagonal BN; the latter corresponds to the [100] and [101] diffraction of hexagonal BN.

The selected area diffraction of the product pyrolyzed at 600°C and 100 MPa has diffuse rings, as shown in Fig. 2, which reveals that the product is turbostratic BN of hexagonal symmetry.

The degree of order of B_3N_3 layers in the pyrolyzed products apparently increases with increasing pyrolysis temperature from 250° to 700°C as in the carbonization process, although both products have low crystallinity.

(2) *Features of Chemical Bonds of Pyrolyzed Borazine*

The pyrolysis process of borazine under 100 MPa was followed by IR spectroscopy.

Borazine itself shows absorption bands at 3440, 2490, 1430, 890, and 700 cm^{-1} (Fig. 3), which are in good agreement with those reported.[10]

The IR spectra of pyrolyzed products, formed at various temperatures under 100 MPa for 1 h, are shown in Fig. 4(A). As the pyrolysis temperature increases, the absorptions assigned to NH groups at 3440 and 700 cm^{-1} noticeably decrease in intensity. In addition, B–H absorptions at 2490 and 890 cm^{-1} decrease in intensity with an increase of pyrolysis temperature. However, the bands due to N–H and B–H stretching at 3440 and 2520 cm^{-1} still remain after a pyrolysis at 700°C and 100 MPa for 1 h.

The sharp and strong B–N absorption of borazine at 1430 cm^{-1} changes to a broad absorption at 1400 cm^{-1} at 250°C. This change corresponds to cleavage of the borazine ring and the subsequent condensation and polymerization reaction of a B–N bond. With increasing pyrolysis temperature from 250° to 600°C, the intensity ratio of the B–N absorption at 1400 cm^{-1} to the N–H at 3440 cm^{-1} increases. This fact indicates the formation of polymeric BN that contains hydrogen and its concurrent dehydrogenation. At the final stage of the pyrolysis, an absorption band at 800 cm^{-1} appears in the pyrolysis product at 700°C. This agrees well with the value of the out-of-plane B–N–B resonance of hexagonal BN.[11,12]

Changes in the IR spectra with reaction time at 250° and 700°C under 100 MPa are shown in Figs. 4(B) and (C), respectively.

The product formed at 250°C and 100 MPa for 5 min contains sharp B–H and N–H absorptions at 2520 and 3440 cm^{-1}, respectively. The intensities of these bands decrease as the pyrolysis time increases from 5 min to 3 h. The disappearance of the 1400-cm^{-1} band at 250°C for 3 h indicates that the cyclic $(BN)_3$ ring disappears because of the ring cleavage of borazine. However, no absorption ascribed to B–N–B resonance is observed in the product pyrolyzed at 250°C for 3 h.

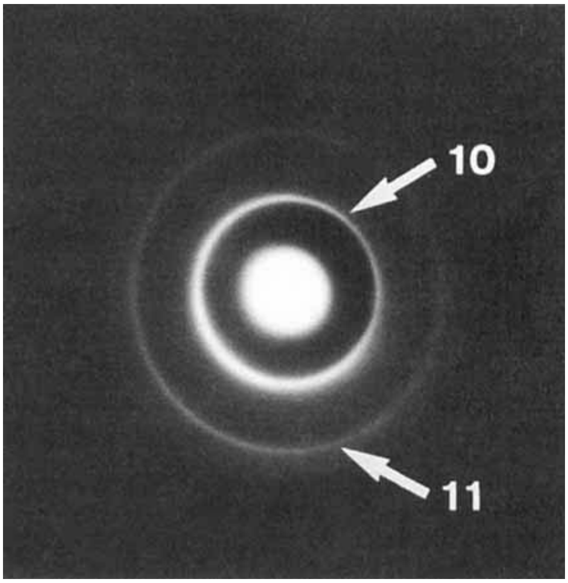

Fig. 2. Selected area diffraction of BN formed from borazine at 600°C and 100 MPa for 3 h.

On the other hand, polycondensation and dehydrogenation of borazine proceed more rapidly at 700°C than at 250°C. Moreover, the B–N–B absorption band at 800 cm^{-1} appears in the product pyrolyzed at 700°C for 1 h and then increases in intensity as the pyrolysis time is increased to 3 h. The spectrum of the product formed at 700°C is similar to that of a crystalline hexagonal BN.[13] The degree of alignment of B_3N_3 hexagonal layers increases at 700°C with an increase of pyrolysis time.

The amount of hydrogen in the pyrolysis product decreases with increase of both temperature and time. The elemental analysis showed that the product formed at 700°C for 1 h contains 2.8 wt% of hydrogen.

The formation and growth of B_3N_3 hexagonal layers depend mainly upon the pyrolysis temperature, and the growth proceeds rapidly at 700°C. The pyrolysis product formed at 700°C is amorphous BN which includes B_3N_3-layer structures having a residual amount of terminal B–H and N–H bonds.

(3) *Morphology of Prepared Amorphous BN*

The pyrolysis product of borazine at 300°C and 100 MPa for 3 h is a porous solid, which comprises a smooth surface of coalescing spherulites as shown in Fig. 5(A). The diameter of pores

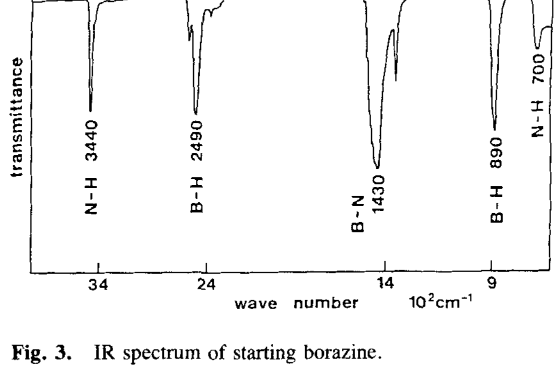

Fig. 3. IR spectrum of starting borazine.

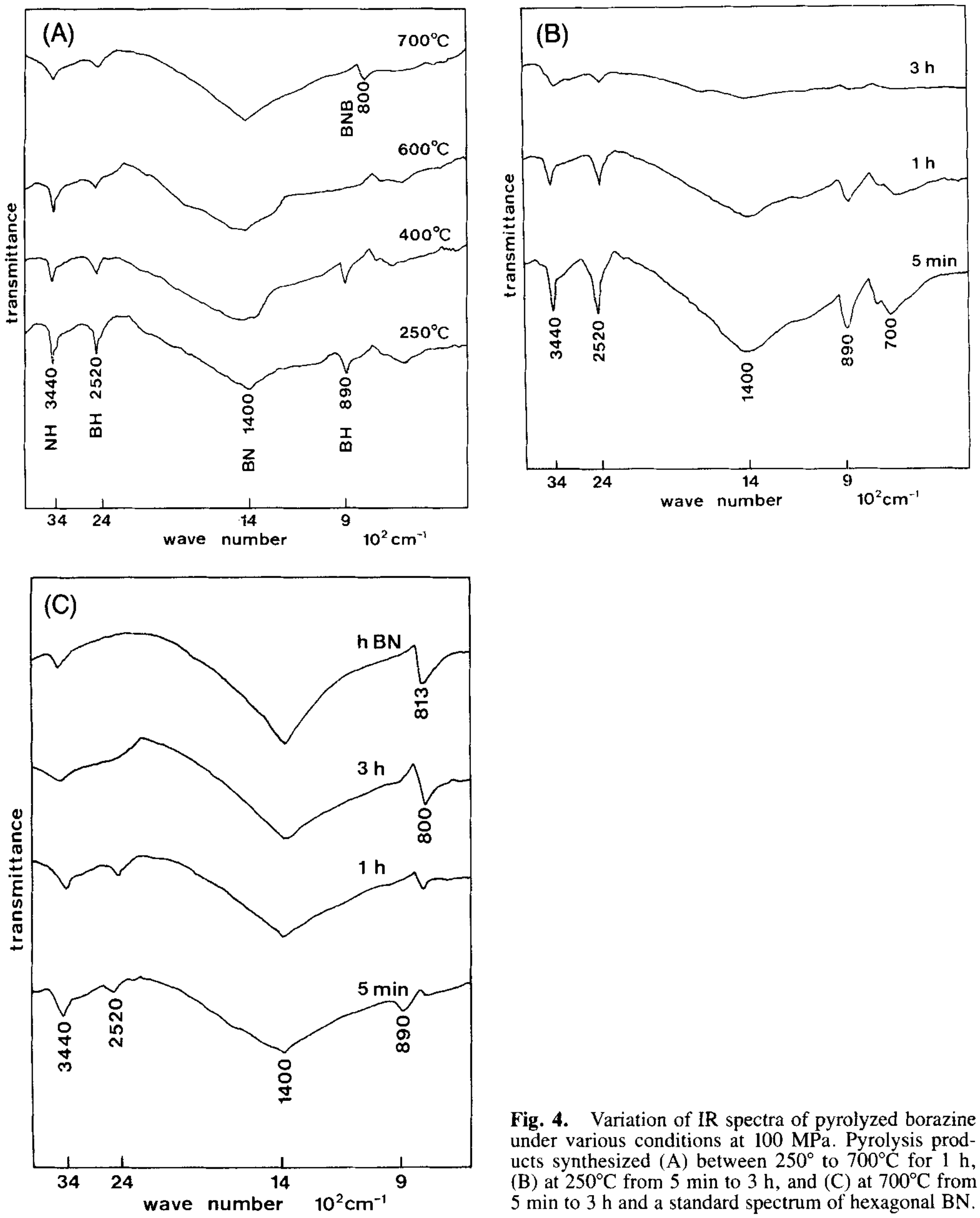

Fig. 4. Variation of IR spectra of pyrolyzed borazine under various conditions at 100 MPa. Pyrolysis products synthesized (A) between 250° to 700°C for 1 h, (B) at 250°C from 5 min to 3 h, and (C) at 700°C from 5 min to 3 h and a standard spectrum of hexagonal BN.

ranges from 50 to 100 μm. A variety of BN morphologies can be observed on the inside wall of pores. BN spherulites synthesized at 400°C and 100 MPa for 1 h have diameters of 1.0 to 3.0 μm as shown in Fig. 5(B). The pyrolysis of borazine at 400°C and 100 MPa for 5 min gives fibrous BN, with sizes near 1.0 μm in diameter and 5.0 μm in length (Fig. 5(C)).

The relationship between the morphology of BN and its pyrolysis conditions is summarized in Fig. 6. Only coalescing spherulites are observed in the product pyrolyzed for 3 h; however, various morphologies such as spherulites and fibrils were found in products pyrolyzed for 1 h or less. The morphology of BN formed by pyrolysis for 1 h or less tends to change from spherulite to fibril as the temperature increases from 250° to 700°C.

The formation of carbon spherulites from poly(divinylbenzene) could be explained by the decomposition of the polymer to oligomers and subsequent homogeneous liquid–liquid microphase separation between higher and lower molecular weight components.[7]

Borazine can be considered to undergo ring cleavage and polymerization to yield liquid phases of different molecular weight components. Gaseous components composed mainly of high hydrogen content seem to participate in phase separation with increasing pyrolysis temperatures, although pressure suppresses the generation of gases during phase separation. Therefore, the various morphologies of BN could be formed at the interfaces of gas–liquid and liquid–liquid phases at the initial stage of pyrolysis. Spherulitic and fibrous BN enriched with active N–H and B–H bonds appear to release hydrogen and aggregate to yield the coalescing spherulitic morphology at higher temperatures and for longer reaction times.

(4) Synthesis of Cubic BN–AlN Sintered Compacts

Amorphous BN synthesized from borazine by pyrolysis at 400°C and 100 MPa for 3 h was mixed with 20 mol% AlN and then placed in a graphite crucible under nitrogen.

The specimen was heat-treated at 1200°C and 6.5 GPa for 10 min to yield cubic BN in a 90% molar conversion. On the other hand, hexagonal BN was converted to cubic BN in a 66% yield in the presence of 20 mol% of AlN treated at a higher temperature of 1600°C and 6.5 GPa.[5] Amorphous BN synthesized from borazine was transformed to cubic BN at a lower temperature and at a higher conversion ratio than that found for hexagonal BN. In addition, high-pressure treatment of the speci-

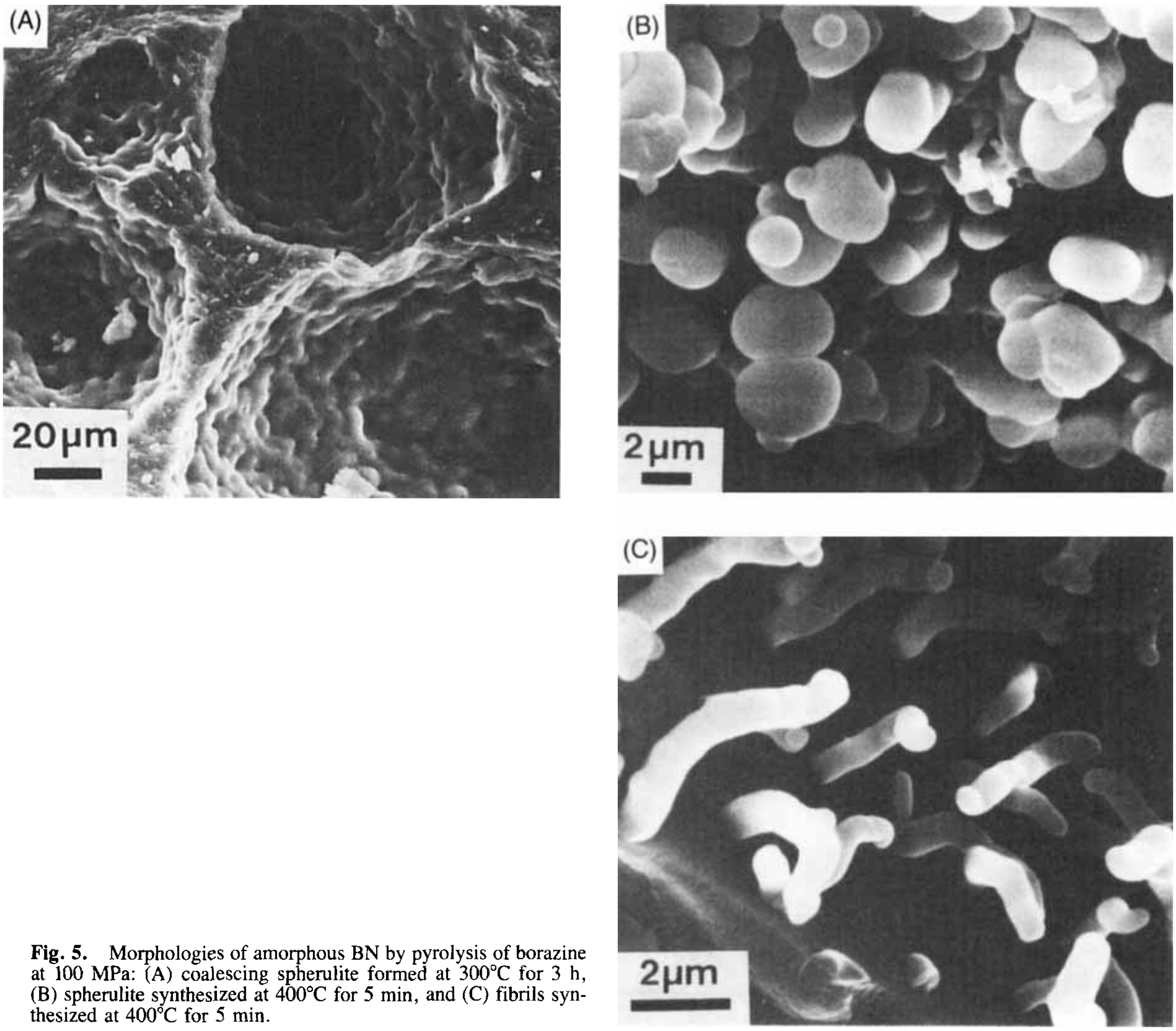

Fig. 5. Morphologies of amorphous BN by pyrolysis of borazine at 100 MPa: (A) coalescing spherulite formed at 300°C for 3 h, (B) spherulite synthesized at 400°C for 5 min, and (C) fibrils synthesized at 400°C for 5 min.

men at 1800°C and 6.5 GPa for 1 h yielded a cubic BN–AlN sintered body. The XRD analysis showed that the product was composed of cubic BN and AlN phases without hexagonal BN. The starting amorphous BN was transformed to cubic BN in a 100% yield.

Amorphous BN produced by this study was found to be superior to well-crystallized BN as a precursor of cubic BN. Amorphous BN is also more effective at maintaining the reducing conditions necessary for cubic BN formation with AlN because the reducing condition can be realized by the breakage of residual B–H and N–H bonds. The high-pressure and high-temperature treatment removes hydrogens bonded to amorphous BN to yield the cubic BN–AlN sintered body. A detailed study of the preparation of cubic BN sintered bodies prepared from borazine is in progress.

IV. Conclusions

Borazine was pyrolyzed under pressure to synthesize amorphous BN with some hydrogen remaining as B–H and N–H bonds. The pyrolysis process of borazine and the morphology of amorphous BN were studied. The results are summarized as follows:

(1) Amorphous BN was synthesized successfully by pressure pyrolysis of borazine below 700°C at 100 MPa with a yield of about 60%.

(2) The decomposition of borazine started with polycondensation and polymerization of B–N bonds, followed by dehydrogenation. The extent of dehydrogenation of the pyrolyzed product depended upon pyrolysis temperature and time.

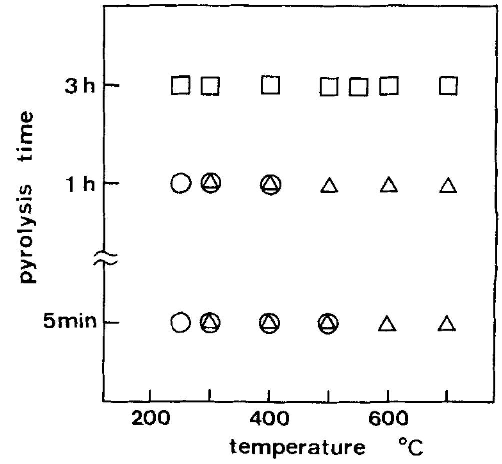

Fig. 6. Pyrolysis conditions of borazine and morphology of amorphous BN: (□) coalescing spherulite, (○) spherulite, and (△) fibril.

(3) The B_3N_3 hexagonal structure was formed locally in amorphous BN at 700°C and 100 MPa, and increased in size with an increase of reaction time at 700°C.

(4) Pyrolysis temperature also influenced the morphology of amorphous BN. Liquid–liquid and gas–liquid phase separation between pyrolyzed polymeric components having different molecular weights seemed to result in the formation of spherulitic and fibrous BN.

(5) The prepared amorphous BN could be converted completely to cubic BN with AlN addition at 1800°C and 6.5 GPa. Amorphous BN formed from borazine contained some amount of hydrogen, which produced a reducing atmosphere necessary for the formation of cubic BN during the subsequent high-pressure sintering to cubic BN in the presence of AlN.

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Micromechanical Stresses in SiC-Reinforced Al_2O_3 Composites

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Applying an Eshelby approach, the internal micromechanical stresses within an SiC-inclusion-reinforced (platelet to whisker geometries) polycrystalline alumina matrix composite were calculated. The results are compared to the experimental residual stress measurements of a SiC-whisker-reinforced Al_2O_3 by Predecki, Abuhasan, and Barrett and found to be in excellent agreement. The calculations are then extended to SiC-reinforced composites with polycrystalline mullite, silicon nitride, and cordierite matrices. It is concluded that the internal stresses are significantly influenced by the inclusion geometry as well as the thermoelastic differences between the inclusion and the matrix and also the volume fraction. [Key words: composites, silicon carbide, alumina, mechanical properties, stress.]

I. Introduction

The use of multiphase microstructures to enhance the mechanical properties of ceramic materials has been applied in physical ceramics almost since the time that ceramists have consolidated ceramics for utilitarian purposes. One of the earliest examples is that of the crystalline quartz and mullite phases in porcelains.[1] Recently, there has been increased interest in strengthening and toughening polycrystalline ceramics by the incorporation of particulate dispersions or whiskers within the microstructure. Conventional wisdom that is based on composite theory has usually suggested that the particle or whisker additions should have a high elastic modulus.[2] For that reason there has been substantial interest in utilizing silicon carbide (SiC) particles and whiskers as the reinforcing phase.[3] The most commercially successful of these structures appears to be that of SiC whiskers within a polycrystalline alumina (Al_2O_3) matrix,[4,5] although SiC whiskers have also been considered and utilized as additions to the matrices of mullite ($3Al_2O_3 \cdot 2SiO_2$),[6] silicon nitride (Si_3N_4),[7,8] and cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$).[9]

Whenever a multiphase microstructure experiences processing at elevated temperatures, the differences in the thermal expansions and the elastic constants of the phases result in residual

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