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Synthesis of a powder precursor in the form of hydroxyhydrogel for reaction sintering of BN–mullite composite

A.K. Basu, A. Mitra, S. Ghatak *

Central Glass and Ceramic Research Institute, 196 Raja S.C. Mullick Road, Jadavpur, Kolkata 700032, India

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Abstract

A powder precursor in the form of hydroxyhydrogel was prepared for the reaction sintering in the h-BN–mullite composite system. The powder precursor contains all the essential elements for the formation of the composite. Characterization of the powder precursor indicated the presence of Al^{3+} in predominantly hexacoordinated state. The powder precursor yielded consolidated BN–mullite composite formed during heat treatment of pressed compact in ambient gas atmosphere.

Keywords: Boron nitride–mullite composite; Hydroxy hydrogel intermediate

1. Introduction

h-BN is an excellent material for its application in various engineering and refractory areas for its good thermal shock resistance, chemical inertness, stability at high temperature and machinability [1,2]. Alumina and mullite matrix–BN toughened composites is also a suggested material for radome application [3–6]. Major difficulty for successful application of these materials lies in the difficulty of sintering boron nitride. Hexagonal structure of BN consists of [13–15] layers of flat or nearly flat network of B_3N_3 hexagons. These hexagons are packed in the direction with alternating B and N atoms: cohesion between the sheets occurs primarily as the result of weak inter molecular interaction. Linking of the particles at the central faces is the only possibility in such type of structure and linking at an angle to the hexagon does not in practice occur [15].

Production of a self-bonded ceramic in this system has become possible as a result of development of methods of synthesis of turbostratic boron nitride [16], which has semi amorphous structure. This structure may be defined as B_3N_3 hexagonal layers stacked roughly parallel to each other with a random rotation and translation about the layer normal [17]. Turbostratic structure of boron nitride has been proposed [18–22] as solution for pressure less sintering of h-BN. However with its two dimensional structure and the absence of strong interlayer bonds, t-BN is not a stable modification of the boron nitride which is reported [23] to dissolve even in water. It is established [15] that the existence of packing defects in the stacking of the sheets is caused by the presence of oxygen between the sheets which in turn forms boric anhydride during sintering which is difficult to remove. Considerable densification is achievable only by uniaxial hot pressing of mechanically mixed powders of Al_2O_3, SiO_2 and h-BN [3]. Uniaxial hot pressing in addition being costlier, impart anisotropy to the sintered material due mainly to flakey structure of hexagonal boron nitride. An alternative method was attempted [6], where same composition was prepared by in situ reaction of B_2O_3 with AlN, Si_3N_4 and compositions thereof [24]. In this system B_2O_3 based transient liquid phase allowed densification of the materials bellow 1000 °C with the reaction to form hexagonal boron nitride and the matrix phase occurring around 1600 °C. The resulting material was nearly isotropic. It was suggested that the isotropy in the above system results from the formation by the reaction of BN in an already dense

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* Corresponding author. Tel.: +91 033 2473 5829;
fax: +91 033 2473 0957.
E-mail address: sghatak@cgcri.res.in (S. Ghatak).

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composite. The homogeneity results from the same process and is limited by the degree of mixing of the initial reactions. An important factor that makes the sintering process economically hard to sustain is the requirement of inert gas atmosphere during sintering in the above system.

To over come the above difficulties BN–mullite composite was prepared first by preparing a powder precursor in which BN particles were embedded in Al–O–SiO hydroxyhydrogel network followed by densification carried out in an ambient gas atmosphere.

2. Experimental[1]

2.1. Preparation of h-BN

h-BN powder was prepared in the laboratory by following the boric acid ammonia route [25]. Aluminium nitrate hydrate of purity 99% (E Mark, India) and reactive silica were used as the sources of alumina and silica respectively. Analysis of the prepared material showed the presence of B_2O_3 (1%) and traces of iron and calcium with 98.5% h-BN.

2.2. Preparation of powder precursor

Required amount of h-BN powder and Al $(NO_3)_3$, $9H_2O$ were mixed with distilled water and stirred to obtain a slurry. BN: H_2O ratio was maintained between 15 and 85 by weight. Calculated amount of reactive silica was mixed with the slurry in such a proportion that maintains a ratio of BN:mullite as 40:60, 30:70, 20:80, and 10:90 in molar ratio in the final product. Exact amount taken is tabulated in Table 1. The mixture was ammoniated with NH_3 solution to attain a pH between 3.5 and 5.5 with constant stirring. The formed gel like mass was equilibrated for 24 h. The equilibrated mass was filtered and washed with hot water to remove soluble salts. The washed material was dried at 110 ± 5°C in an air oven. A portion of the dried material was kept separately for characterization and the rest amount was calcined at 650 °C for two hours. Calcined material was ground in a hard polythene bottle with alumina balls as grinding media. This powder precursor was used during subsequent experiment (Table 2).

2.3. Preparation of samples for sintering

Powder precursors were isostatically pressed at 200 MPa to prepare pellets. These pellets were heated at the rate of 5 °C per min up to 1000 °C and 50 °C/min upto 1350 °C.

2.4. Characterization of powder precursors

2.4.1. I. R. spectroscopy

A small amount of powdered sample (0.2 gm) was thoroughly mixed with ground KBr in an agate mortar and disc of 2.5 mm diameter was prepared under vacuum at a pressure of 30 kg/m^2. IR spectra was taken for those discs by FTIR spectrometer (Perkin-Elmer model1615) in the range of 400–4000 cm^{-1}.

Table 1
Chemical analysis of BN powder

Boron nitride	98.5 (%)
Boric oxide	1 (%)
Calcium	Trace
Iron	Trace

Table 2
Composition of the prepared samples

Sl. no.	Percentage of h-BN	Percentage of SiO_2	Percentage of Al_2O_3	mBN:Mullite
1	90	02.82	7.18	90:10
2	80	05.64	14.37	80:20
3	70	08.46	21.54	70:30
4	60	11.28	28.72	60:40
5	50	14.10	35.90	50:50
6	40	16.92	43.08	40:60

2.4.2. DTA TGA analysis

DTA and TGA analysis were performed (Netzsch: Greatebau Gmbh, model: STA 409C) by taking approximately 80 g of powdered sample with Al_2O_3 as reference material. Temperature was raised at the rate of 10 °C/min in static atmosphere.

2.4.3. Characterization of sintered materials

A. *XRD analysis*: Crystalline phases were identified by XRD (CPW-1730Xray crystallographic unit) provided with a proportional counter (PW-1050/70) Goniometer camera (Phillips) using Cu Kα radiation and Ni filter.
B. Micro structural analysis
C. Micro structural analysis was done by SEM (LEO S4301). Energy dispersing X-ray spectroscopy was carried out to enable chemical and mineralogical identification.

3. Results and discussion

The process of making BN–mullite composite as followed in the present work essentially consist of three different steps viz.

(1) Preparation of preparing a suspension of BN, $Al(NO_3)_3$ $9H_2O$, and SiO_2 in aqueous medium.
(2) Preparation of a reactive powder precursor in the hydroxy hydrogel form.
(3) Conversion of the precursor to sintered BN–mullite composite.

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[1] A part of the preparation is applied for IPR protection in India.

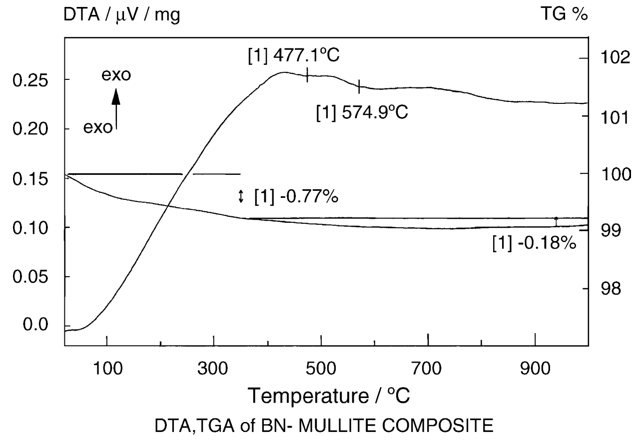

Fig. 1. DTA and TGA of powder precursor.

3.1. Characterization of powder precursor

Both thermo gravimetric and thermal analysis was performed on the powder precursors. DTA/TGA curves are shown in Fig. 1. For comparison similar curve for alumina gel prepared under same conditions is also shown (Fig. 2).

Total loss of water from pure alumina gel sample is 48.59% of which 14.32% was due to weakly bonded water molecules. Major loss of water in the temperature range of 200–400 °C (26.58%) was due to the removal of hydroxylated water. 6.695 wt.% loss was recorded in the range 400–750 °C, which was due to the removal of hydroxylated water.

FTIR confirms the existence of various OH bonds in the powder precursor (Fig. 3). Stretching modes of OH groups and H_2O molecules is indicated by the absorption band in the range 3462–3546 cm^{-1}. Bending mode of H_2O molecules is indicated by the band at 1631 and 1365 cm^{-1}. Peak at 1385 cm^{-1} is due to the presence of remnant ammonium salt in the precursor. Absorption band at 1100 and 977 cm^{-1} is due to Si–O stretch in SiO_4. Presence of predominantly octahedral form of Al_2O_3 is indicated by the band at 531 and 731 cm^{-1} [11,12].

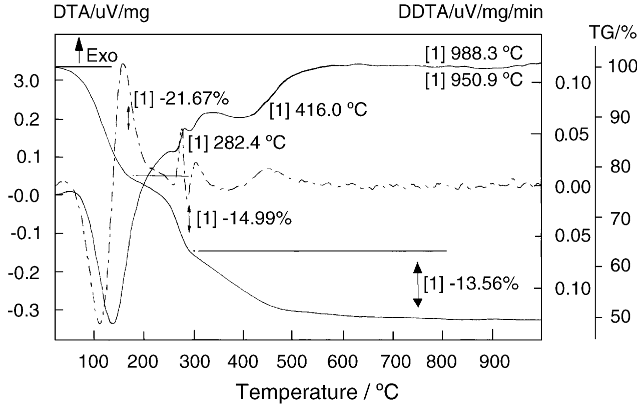

Fig. 2. DTA and TGA of alumina gel.

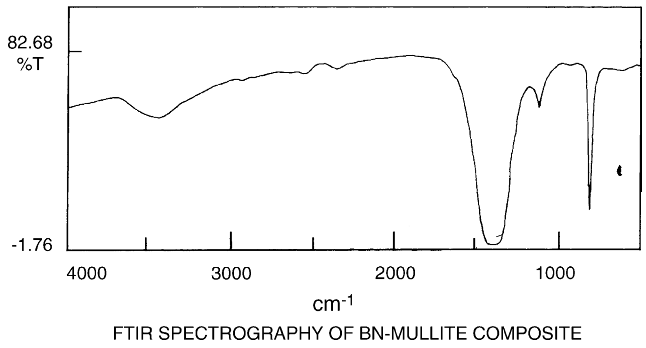

Fig. 3. FTIR of powder precursor.

In h-BN boron is in sp^2 hybridized state forming a planar configuration that leads to a layered structure and is difficult to convert it to a suspension. But in the present system the active silica hydrolyses to form silicic acid and aluminium nitrate dissociates in to Al^{3+} and NO_3^-. In addition to this B_2O_3 present in the material as an unconverted species as well as oxidation layer over the surfaces of BN, hydrolyses to orthoboric acid in aqueous solution. The presence of all the above species constituted a complex system as described below.

(a) B_2O_3 in aqueous solution form orthoboric acid.

$$B_2O_3 + 3H^- + 3OH^- \rightarrow 2H_3BO_3 \qquad (1)$$

The orthoboric acid, more correctly represented as $B(OH)_3$, act as Lewis acid by attachment with OH^- ion as shown in the Eq. (2)

$$B(OH)_3 + HOH \leftrightarrow [B(OH)_4]^- + H^+ \qquad (2)$$

Formed H_3BO_3 molecules are joined by hydrogen bond forming polymeric network in layered structure (Fig. 4). Each layers are linked to other above and below it through inter molecular forces.

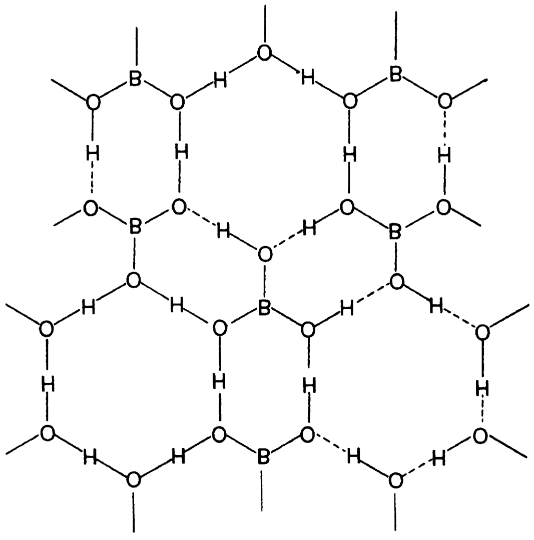

Fig. 4. Molecular structure of hydrolyzed boric acid.

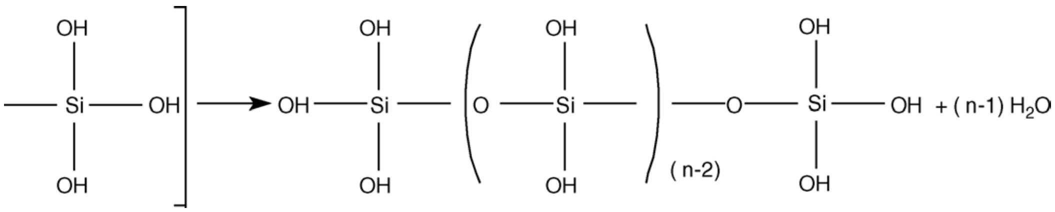

Fig. 5. Molecular structure hydrolyzed silicic acid.

(b) The reactive silica in aqueous solution forms silicic acid. It polymerizes as shown in the Fig. 5. The middle OH groups can interact in the same way forming extended network.

(c) Al^{3+} forms complexes $[Al(OH_2)_6]^{3+}$ water of which is gradually replaced by OH^- ions during reaction with hydroxides more or less in the following sequence:

$$\begin{tikzcd}
{[Al(OH_2)_6]^{+2}} \arrow[r] & {[Al(OH)(OH_2)_6]^{+2}} \arrow[r] & {[Al(OH)_2(OH_2)_4]^{+1}} \arrow[d] \\
 & & {[Al(OH)_3(OH_2)_3]^{0}}
\end{tikzcd}$$

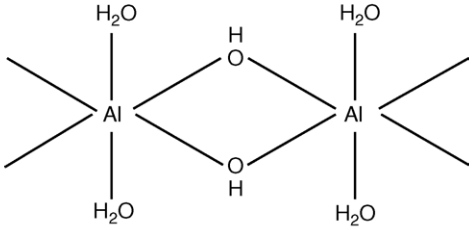

Fig. 6. Hydrolyzed structure of Al^{3+}.

Polymerization proceeded with the formation of polynuclear complexes as shown in Fig. 6 [7–10].

The overall scheme of the reaction that leads into a polynuclear hydroxy hydrogel complex is proposed in Fig. 7.

The net reaction between a mixture containing $Al(NO_3)_3$, reactive SiO_2 and h-BN in suspension and ammonium hydroxide solution leads to a gel like mass. The gel like mass consisting of polynuclear complex containing Al^{3+}, B^{3+} and Si^{4+} in the hydroxy hydrogel form in which h-BN particles are embedded. Therefore, the powder precursor for preparing BN–mullite composite consist of Al^{3+}, B^{3+} and Si^{4+} in hydroxy, hydro and oxo bonds forming polymeric structures.

3.1.1. Reaction sintering of BN–mullite composite

Weight of specimens were found to decrease continuously with increasing amount of the second phase materials i.e. alumina and silica (Fig. 8). The weight loss was due to the removal of different types of water- coordinated and physically bonded- from second phase materials only because oxidation of BN leads to weight increase. Specimens were also found to contract progressively with

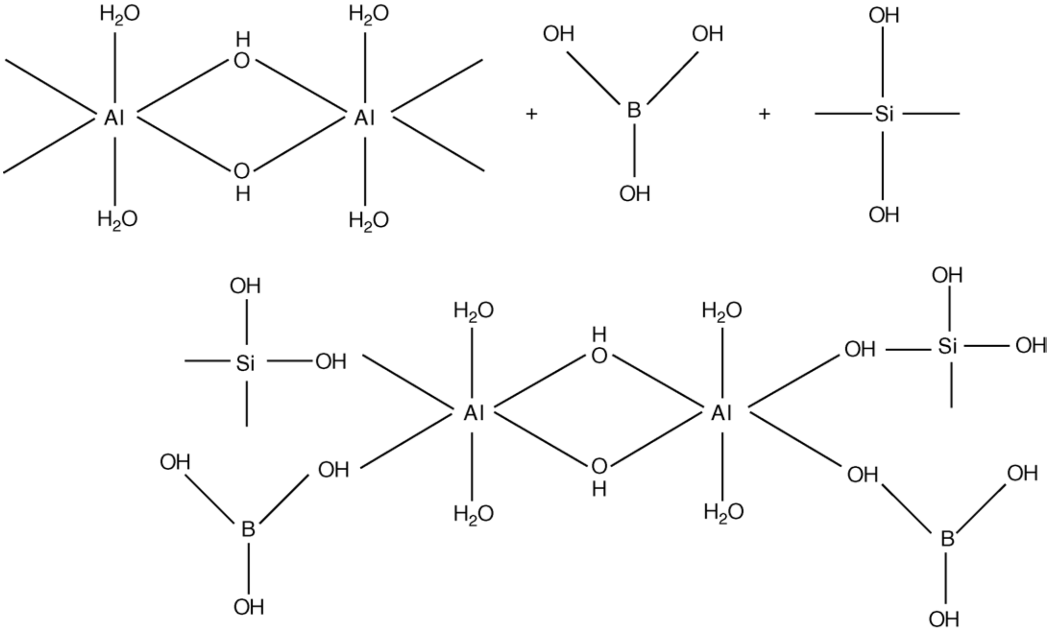

Fig. 7. Polynuclear complex formation—a generalized view.

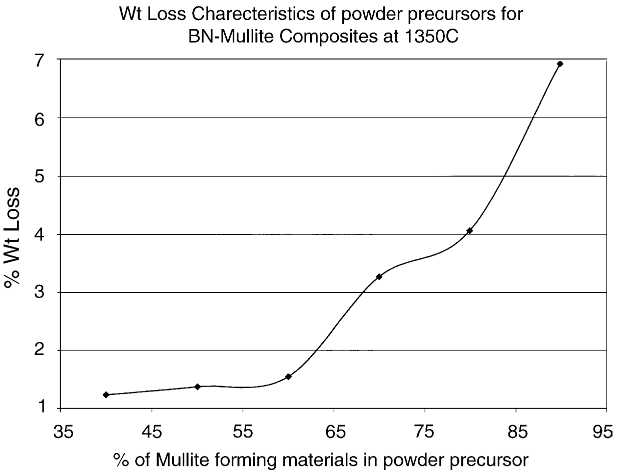

Fig. 8. Weight loss of specimens during heat treatment.

Table 3
Weight change characteristics of samples during heat treatment

Temperture (°C)	Weight change (%)
1000	1.17
1330	7.55
1350	7.42
1400	7.416

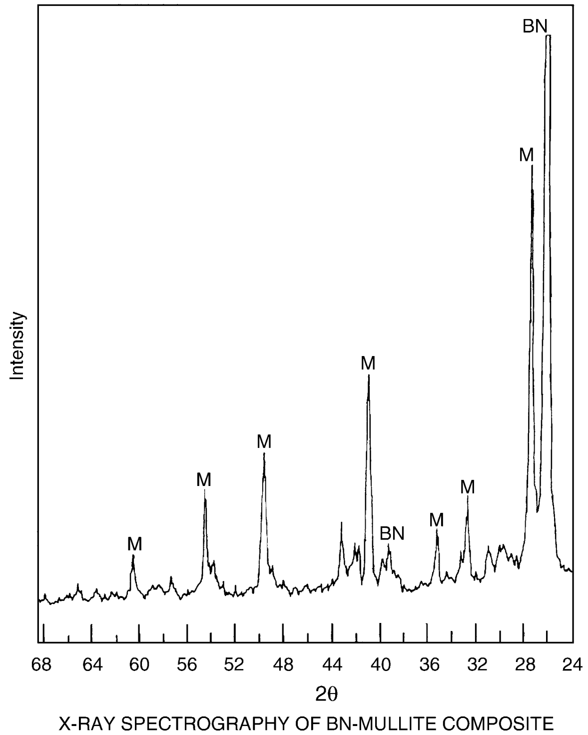

Fig. 9. XRD analysis of BN–mullite composite.

increasing amount of second phase material. Thus the second phase materials, i.e. Al_2O_3 and SiO_2 in the hydroxy hydrogel form were found to contribute in both weight loss and shrinkages of the sintered specimens.

XRD analysis of the sintered specimens indicated the presence of h-BN and mullite as major phases (Fig. 9). Precursor material in the hydroxy hydrogel form produces reactive aluminium oxide and silicon oxide during sintering. In situ formed Al_2O_3 and SiO_2 in the system took part in a series of chemical reactions forming mullite and aluminium borate.

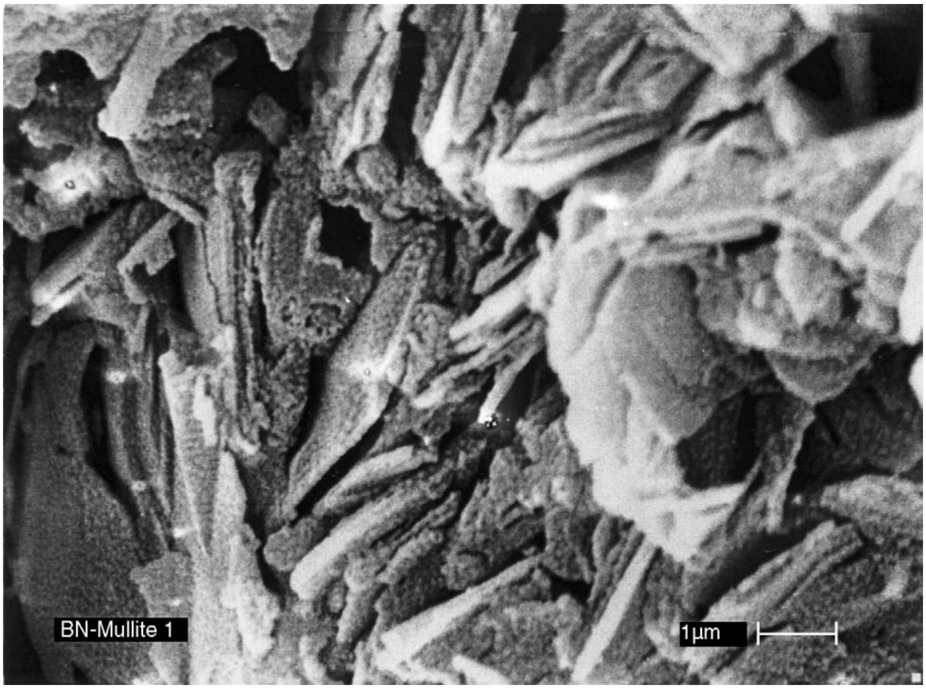

Fig. 10. SEM micro photograph of 80% h-BN and 20% Mullite.

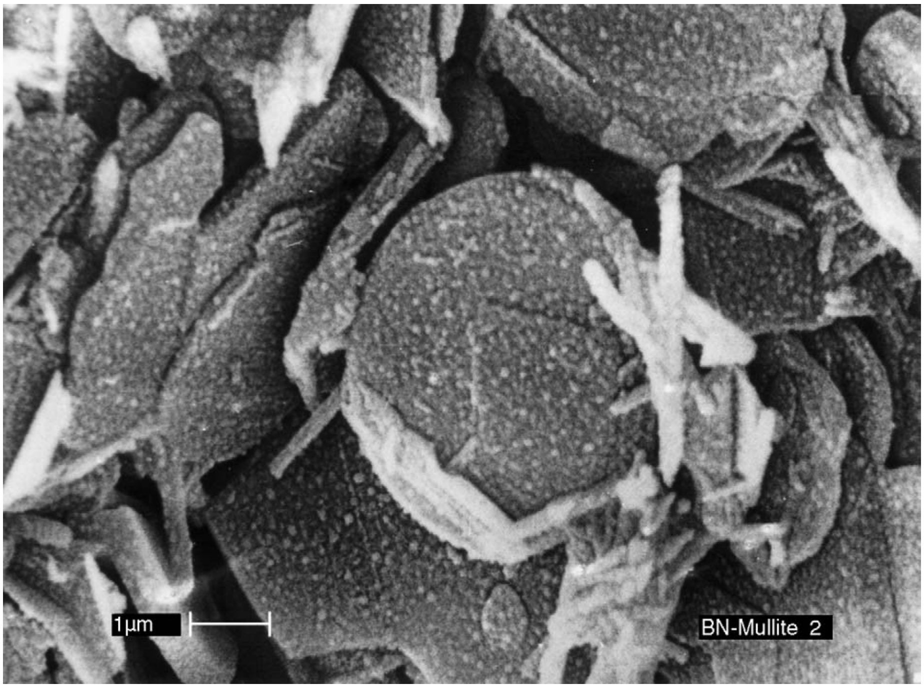

Fig. 11. SEM micro photograph of 95% h-BN and 5% Mullite.

Aluminium borate is formed by reaction of Al_2O_3 and B_2O_3 present in the system.

$$Al(OH)_3 \rightarrow Al_2O_3 + H_2O \tag{3}$$

$$H_2SiO_3 \rightarrow SiO_2 + H_2O \tag{4}$$

$$2BN + \tfrac{3}{2}O_2 \rightarrow B_2O_3 + N_2 \tag{5}$$

$$3Al_2O_3 + 9Al_2O_3 \rightarrow 3Al_2O_3{\cdot}2SiO_2 \tag{6}$$

$$2B_2O_3 + 9Al_2O_3 \rightarrow 9Al_2O_3{\cdot}2B_2O_3 \tag{7}$$

The overall weight change is due to the combined effect of loss of weight through reaction (3) and (4) and gain in weight by reaction (5). This phenomenon continues till sufficient mullite is formed that produces an impervious layer over the surface of BN particles impeding oxygen transport from surrounding to the bulk as shown in Table 3. Thus, the oxidation of BN is progressively reduced with the progress of densification of the specimen as was observed in the case of SiC–mullite composites (9).

Alumina borate ($9Al_2O_3{\cdot}2B_2O_3$) forms during the sintering of BN–Al_2O_3 compacts when B_2O_3 is made available by the oxidation of BN and crystallizes in the shape of needle [1]. Since aluminium borate is iso-structural with mullite it forms a solid solution with it.

3.2. *Microstructure*

Microstructures indicate interwoven BN grains with needle shaped crystals. EDX analysis indicate mullite but the formation of A_9B_2 is not ruled out as A_9B_2 and A_3Si_2 are iso-structural, they form solid solution and elongated crystals. Fig. 10 indicate the formation of elongated crystals formed from the surfaces of h-BN crystals in the specimen containing 95% h-BN. Fig. 11 shows the initiation of formation of the second phase from the surfaces of h-BN in the specimen containing 80% h-BN.

4. Conclusion

1. Powder precursor containing Al, B, O and N were synthesized in the hydroxy hydrogel form in which BN particles are embedded in the polynuclear hydroxyhydrogel network structure.
2. In the powder precursor Al^{3+} was present predominantly in the hexa-coordinated form.
3. Powder precursor could be easily processed to prepare BN–mullite sintered compacts.
4. Sintering could be done in an ambient gas atmosphere.

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