Fabrication of porous boron nitride by using polyborazylene as precursor, polymethylmeth-acrylate as reaction agent

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Abstract. A novel process for the production of micro-molecular boron nitride foams has been developed through foaming of boron nitride preceramic polymer with the help of sacrificial microbeads of polymethylmethacrylate (PMMA), followed by pyrolysis under inert atmosphere. The process parameters of porous BN ceramics were studied by thermo gravimetric analysis, thermo mechanical analysis, X-ray diffraction, scanning electron microscopy, mercury porosimetry and elemental analysis. The microstructure and element composition of the porous ceramics were also studied by the above methods. The results showed that: when using polyborazylene from thermolization of borazine at 60°C as boron nitride precursor, PMMA microbeads with pore size of 25μm as sacrificial microbeads, adding into polyborazylene powder with 80 wt% in the foaming mixture. After warm-pressing the powders under 74MPa at 60°C, subsequently pyrolyzing the powders under ammonia to 1000°C then to 1450°C under nitrogen atmosphere, we can obtain boron nitride foams. Through scanning electron microscopy observation, X-ray diffraction analysis and porosity measurement, it was confirmed that the obtained boron nitride pieces were microcellular foams with homogeneous distributed pore size average at ~19.15μm and had a mostly interconnected porosity of 79.06 vol%. The temperature should be increased to 1700-1800°C to prepare porous BN ceramic with a certain degree of crystallinity (layer spacing d002 = 0.335-0.333 nm)

Keywords: Boron nitride; foams; polyborazylene; polymethylmethacrylate; porosity

1. Introduction
Porous materials are an emerging material system, the most notable feature of which is a well-regulated pore structure, as well as a high specific surface area and porosity. With excellent properties, porous materials have broad application prospects in the fields of structure and optoelectronic materials, aerospace and other fields. Since its inception, it has attracted the attention of scholars from many international disciplines and has quickly become the focus and hotspot of interdisciplinary research [1-4].
h-BN exhibits a combination of particular attractive physical and chemical properties, including low density (2.34 g/cm³), low dielectric constant, high melting point, high thermal conductivity, outstanding thermal shock resistance, superior chemical inertness and above all, good resistance to corrosion and oxidation at relatively high temperature (800°C). This material has enjoyed widespread use, particularly in the range of steel mills and foundries, crucibles in furnace construction, the semiconductor industry and in protective and optical coatings. Furthermore, it can be used as films or fillers in the processing of composite materials, also in a variety of electronic devices too, such as field emitters and ultraviolet or radiation detectors[5-6].

Balmain et al[7] prepared hexagonal boron nitride for the first time in 1842 by reaction of molten boric acid with potassium cyanide. More than 100 years later, the commercial production of BN was established. Since that time, there have been many routes to synthesize BN, principally three methods are used: conventional high-temperature powder technology[8], chemical vapor deposition method[9], polymer derived ceramics(PDCs)[10]. The PDCs procedure has many innovative advantages[11]: it allows the chemistry of starting precursors to be precisely controlled and tailored which could be benefit to optimize ceramic properties.

The preparation of porous BN ceramics by PDCs route is a hot subject because it can control the atomic level of ceramic structure and morphology by adjusting the composition and percentage of precursors and pore formers[12]. It is reported in the literature that the precursors for preparing porous BN ceramics are borazine, trichloroborazine, ammonia borane and so on; The foaming agent includes CMK-3 template, three-dimensional mesoporous CMK-8 template, and mesoporous silica SBA-15 template[13-14].

The PDCs method has been applied to the preparation of SiC[15], Si3N4[16-17] porous ceramics, and there are few reports on the preparation of porous BN ceramics. Therefore, this paper explores the process of preparing porous BN ceramics by using polymethyl methacrylate as organic foaming agent and polyborazane as precursors, and studies its microstructure, structure and composition characteristics, which provides a new idea for the preparation of porous boron nitride.

2. Experimental part

2.1. Raw materials and equipments

The raw materials used in the experiment included polymethyl methacrylate powder (PMMA, particle size 25 μm), (NH₄)₂SO₄, (>99.0%, Sigma-Aldrich), NaBH₄ (>98.5%, Sigma-Aldrich), CH₃O(CH₂)₄CH₃ (>99%, Sigma-Aldrich). The synthesis of borazine was carried out in a Schlenk bench and its synthesis was carried out under argon with a purity of >99.995%. The polymerization of borazine was carried out in a 75 ml autoclave (Equilabo, France). Since both borazine and its polymer prepared during the experiment were sensitive to air and humidity, all of the experimental procedures were carried out in an argon-filled dry box (Jacomex BS521; Dagneux, France).

2.2. The preparation of porous BN

A flow diagram for the proposed fabrication method of porous BN materials by polymethyl methacrylate (PMMA) microbeads is shown in Fig. 1. Initially a controlled mixture consisting of a polyborazylene (PB) and the polymer microbead (PMMA) is used as feed materials for shaping by an uniaxial warm-pressing, while the polymer cross-linked. The resulting composite body was converted into porous ceramic materials via pyrolysis while the PMMA beads burned out.
Figure 1. Processing procedures for the fabrication of porous BN materials components from preceramic polymer (PB60) and sacrificial processing aids (PMMA)

The experiment used NaBH₄ and (NH₄)₂SO₄ as raw materials to synthesize B₃N₃H₆, and the reaction equation is shown in the following formula:

\[
3(NH_2)_2SO_4 + 6NaBH_4 \rightarrow 2B_3N_3H_6 + 3Na_2SO_4 + 18H_2
\]

Formula 1 Synthesis equation of B₃N₃H₆

During the polymerization, under the argon atmosphere, 20 ml of borazine was transferred to a 75 ml pressure reactor at 0 °C, and the temperature was raised to 60 °C for 240 h to obtain polyborazane white solid powder, which was recorded as PB60. The specific process flow and characterization results can be referred to the literature [18-19], and will not be described in detail here.

The synthesized PB60 powder was pulverized in a dry box to a particle size of ≤80 μm, and then mixed with PMMA powder at a certain mass percentage, and then the mixture (~300 mg) was heated to 60 °C for 30 minutes under a pressure of 75 MPa. A precursor mixture body (size ∅13 mm × 2 mm) was obtained. The green body was heated to 1000°C under NH₃ and kept for 2 h. Then, the temperature was raised to 1450°C under N2 atmosphere and kept for 2 hours. After cooling to room temperature, porous BN foam ceramic was obtained.

2.3. Characterization

2.3.1 TGA-DTG. Thermogravimetric analysis (TGA) of PB60 and PMMA as well as PB/PMMA mixture were recorded on a Setaram TGA 92 16.18. Experiments were performed in an nitrogen atmosphere at 5 oC min⁻¹ from RT to 1000 oC by using silica crucibles (sample weight of 80 mg) at ambient atmospheric pressure. Experimental differential thermogravimetric (DTG) data was generated from TGA measurements.

2.3.2 DSC. Thermal properties of PMMA was studied by differential scanning calorimetry (DSC, Mettler Toledo DSC TA 8000) in an argon atmosphere between 20 and 200 oC at a heating rate of 5 oC min⁻¹ in alumina crucibles.

2.3.3 XRD. X-Ray Diffractions (XRDs) were achieved using a Philips PW 3040/60 X’Pert PRO X-ray diffraction system operating at 30 mA and 40 kV from 10 to 900 with a step size of 0.0167°.

2.3.4 SEM-EDX. Samples were mounted on copper tape to determine the composition by energy-dispersive X-ray spectroscopy (EDX, EDAX for observation by scanning electron microscopy (SEM,
Hitachi S-800)). Samples were sputtered with (10 Å of a Pd/Au mixture) to prevent charging during observation.

2.3.5 Mercury porosimetry. A Micromeritics Autopore IV 9500 penetrometer was used to investigate mercury porosimetry.

2.3.6 TMA. Thermomechanical analysis (TMA) of the uniaxially pressed polyborazylene powders (Mold diameter 5 mm) has been investigated in an nitrogen atmosphere (Mettler Toledo TMA/SDTA 840) using a compressive load (0.8 N) upon heating to 400 oC.

3. Results and discussion

When manufacturing porous BN materials using sacrificial processing aids (PMMA), the following points need to be considered: the viscosity of the preceramic precursor should be kept sufficiently low to cover the sacrificial beads completely and homogeneously in the warm pressing procedure; furthermore, the polymer should not be excessively pre-crosslinked which leads cracking during the PMMA burning-out process.

3.1. Determination of process parameters for preparing porous BN ceramics

It is reported in the literature that in the preparation of porous ceramics, the mass percentage of organic precursors and PMMA is generally controlled between 30/70 or 20/80[20]. In the course of this experiment, we used PB/PMMA with a mass percentage of 20/80, PMMA with a particle size of 25 μm, and a sample of PB60-20@PMMA25-80. It is worth mentioning that in order to ensure the homogeneity of the mixture, the PB60 powder was pulverized in a hand dryer to a particle size of ≤ 80 μm before the start of the experiment.

The first thing to consider is the exothermic process of the PB60. During the experiment, the PB60 powder was pressed into a block having a diameter of 5 mm, and then the temperature was changed to 400 °C under the pressure of 0.8 N to examine the dimensional change. Figure 2 shows the TMA curve of PB60.

![Figure 2. TMA curve of PB60 (N2, heating rate: 5oC min⁻¹)](image-url)

From the TMA curve (Fig.2), it is observed that the PB60 slightly shrinks in thickness starting from 85 °C and the low dimensional change (2.5 %), reflecting the plastic deformation of the polymer, extends over 45 oC from 85 to 130 °C. Above 130 °C, PB60 swells most probably because of the occurrence of the polymer decomposition. The latter showed that PB60 transforms into a softened compound through
a glass transition that extended over 30 °C going from 88 to 120 °C, whereas an exothermic peak due to the polymer decomposition was observed between 120 and 170 °C.

These results prove that PB60 contains a sufficient amount of peripheral single-bound borazine groups and displays a tailored cross-linking degree allowing it to be deformable upon heating through the application of uniaxial pressure for grain bonding and specimen consolidation. Such results showed that a maximum temperature of 130 °C is required to press PB60. However, there are two aspects to consider. Firstly, the warm-pressing is performed under a pressure of 74 MPa which is considerably higher than the pressure used for TMA (P=0.04 MPa). Therefore, PB60 can be compacted at lower temperature, typically from 60 to 110 °C. Secondly, it is required to take into account the melting of PMMA.

We have investigated DSC and TGA of PMMA microbeads under nitrogen. According to the DSC analysis of PMMA microbeads (Fig. 3), we can identify the glass transition from 95 to 115 °C with an averaged temperature of 111 °C. Considering the results, the warm-pressing temperature of PB60/PMMA mixture has been tested at 60-110 °C. Another aspect to be considered for warm-pressing is the PB/PMMA ratio which is discussed later.

The pyrolysis step is also a key step of the processing of PDCs porous materials. We have investigated TGA to identify the weight loss profile of PMMA under nitrogen which is the atmosphere used to convert PB60 into BN.

The TGA-DTG curves of the PMMA (25 µm) microbeads (Fig.4) show that PMMA starts to decompose at around 277 °C and its decomposition finishes at 400 °C, which is in accordance with the literature[21]. Therefore, the heating rate of the pyrolysis step should not be too fast in the temperature range 275-400 °C in order to avoid collapsing during the template burning-out procedure. We deliberately fixed a heating rate during the whole pyrolysis of 0.5 oC min-1 from RT to 1000 °C. Above 1000 °C, heating rate was fixed at 1 °C min-1, the sample was kept 2 h at 1450 °C and cooling rate was fixed at 1 °C min-1.
Based on former study, the preceramic polymer/PMMA weight ratio is usually fixed at 30/70 or 20/80[20]. Here, we report the study on a PB/PMMA weight ratio of 20/80 based on PMMA bead size of 25 µm. We labeled this sample PB60-20@PMMA25-80.

The TGA curve of the sample PB60-20@PMMA25-80 (Fig. 5) shows a shift of the decomposition to lower temperature (starting at \( \sim 250 ^\circ C \)) in comparison to that of pure PMMA (\( \sim 278 ^\circ C \)) with a total weight loss of 79 % that corresponds to the theoretical calculation data (81.8 %). Since it is not possible to extrapolate a linear behavior in accordance with the rule of mixtures, it can be inferred that the PMMA beads and PB60 have a mutual influence on their thermal stability.
After the complete decomposition of PMMA, no further weight loss is detected. Based on TGA, an adequate pyrolysis procedure can be considered: a low heating rate from RT to 230 °C and between 410 to 1000 °C (1 °C min-1), combined with an extremely low heating rate during the weight loss of 0.5 °C min-1 from 250 to 410 °C. Further heat-treatment is required to stabilize BN and therefore, we applied a heating rate of 1.5 °C min-1 from RT to 1450 °C with a dwelling time of 2 h followed by a cooling rate of 2 °C min-1 to lead to a sample labeled PB60dBN20/80 (25) with 20:80 the PB60/PMMA weight ratio and 25 the size in µm of the PMMA beads.

3.2. Characterization of morphological composition of porous BN ceramics

Based on all attempts to optimize the warm-pressing procedure, we found that a temperature of 60 °C combined with a pressure of 74 MPa is required to generate a green compact then porous BN materials and a limited volume shrinkage (~20 %). The materials produced after pyrolysis at 1450 °C under nitrogen have excellent shape retention properties and they are obtained in an excellent reproducibility (Fig. 6).

![Figure 6. Pictures of the samples PB60dBN20/80(25) with the corresponding SEM images at different magnifications](image)

By keeping a PB60/PMMA ratio of 20/80 and warm-pressing parameters constant (T = 60 °C, P = 74 MPa) and using PMMA bead size of 50 µm, the disk-shape is maintained but the high porosity leads to a material which is extremely brittle (Fig. 7).

![Figure 7. Pictures of the sample PB60dBN20/80(50) with the corresponding SEM micrographs at different magnifications](image)
The PB60/PMMA weight ratio is also key factors. A too high PB60/PMMA ratio leads to dense materials, whereas a too low PB60/PMMA ratio results in a high porous material which is not able to retain the shape and the integrity of the morphology during the ceramic conversion. Based on all attempts, we found that a PB60/PMMA weight ratio of 20/80 is ideal to obtain porous BN labeled PB60dBN20/80(25) after warm-pressing and pyrolysis at 1450°C in a nitrogen atmosphere.

The SEM images in Fig.6 of the ideal samples PB60dBN20/80(25) show that it displays an homogeneous porosity with roughly spherical shaped cells. Cells are homogeneously distributed throughout the entire volume of the pyrolyzed materials. Through SEM images with higher magnification (Fig.8), we confirmed the presence of roughly spherical shaped cells with size close to that of the PMMA templating beads. EDX analysis revealed characteristic peaks for boron (0.18 keV), carbon (0.28 keV), nitrogen (0.39 keV) and oxygen (0.523 keV) leading to an empirical formula of B1.0N1.2O0.1 (Fig. 9) with 2 at% of carbon.

EDX experiments give evidence that the bulk composition of powders is close to stoichiometric boron nitride. According to these results, the presence of a small amount of carbon most probably results from PMMA burning. The result also points to the incorporation of a very weak amount of oxygen in
the final material. Oxygen could be attributed to the combined effects of physisorbed/chemisorbed water and oxygen impurities in PMMA beads that contaminated PB60 (despite the fact that PMMA were dried at 90 oC overnight before use) during warm-pressing.

3.3. Structural characterization of porous BN ceramics

The term “porosimetry” is often used to include the measurements of pore size, volume, distribution, density and other porosity-related characterizations of a porous material. Mercury porosimetry provides information related to the macroporosity and the features that control the mercury impregnation (connection between two adjacent macropores). Firstly, it is noteworthy to mention that porous BN materials have mechanical robustness to endure mercury porosity measurements, which is of great importance for application as catalyst supports or as host matrices to form hybrid materials. Also, we have to bear in mind that mercury porosimetry measurements are providing diameters of the void spaces limiting the mercury impregnation; this is to say the windows that connect adjacent cells and not the cells themselves. In Fig. 10, we can notice that cell windows are rather polydisperse, ranging from 0.1 μm to 338 μm, and with a mean pore size at ~22 μm which is consisted with the size of PMMA microbeads (25 μm).

![Figure.10. Pore size distribution for PB60dBN20/80(25) by mercury intrusion porosimetry](image)

Both mercury intrusion volume and the macroscopic porosity are reported in Table.1. Porous BN samples are associated with an intrusion volume, i.e., pore volume, of 1.97 cm3 g-1 and the porosity was calculated to be 79.06 %. The bulk and skeletal densities are 0.40 g cm-3 and 1.91 g cm-3, respectively. The median pore diameter of the material is 19.15 μm, consistent with the pore size distribution curve and also with the PMMA bead size.

| Total Intrusion Volume (ml g⁻¹) | 1.97 |
|---------------------------------|------|
| Median Pore Diameter (μm)      | 19.15|
| Bulk Density (g cm⁻³)          | 0.40 |
| Skeletal Density (g cm⁻³)      | 1.91 |
| Porosity (%)                   | 79.06|

Table 1. Mercury-intrusion porosimetry data of the porous boron nitride materials (PB60dBN20/80(25)).
3.4. Crystalline properties of porous BN materials

XRD can well characterize the layer spacing d002 and average crystal size of the obtained BN ceramics, which can reveal the crystallinity of the obtained BN. The diffraction peaks of h-BN with good crystallinity are 26.76° (002), 41.60° (100), 43.87°(101), 50.15°(102), 55.16°(004), 75.93°(110), 82.18°(112) and 85.52°(105) crystal faces[22]. There are three peaks in the X-ray pattern of BN ceramics (Fig. 11a) after pyrolysis at 1450°C: The (002) peak (2θ=25.35°, d002=0.352 nm) is shifted to lower angles in comparison to the h-BN (002) reflection (2θ=26.76°, d002=0.333 nm). It gives evidence of the disordered structure in the sample PB60dBN20/80(25). More precisely, the asymmetric shape of the (002) peak and the absence of the (102) and (112) peaks suggests in a coherent way the presence of turbostratic boron nitride, which is characterized by a random stacking sequence of the (002) layers and a disorientation of these layers around the c-axis.

Fig 11. XRD curve of porous BN ceramic: (a) 1450 oC; (b) 1700oC (N2, 2h)

In order to study the effect of temperature on the crystallinity of BN, the experiment was carried out by increasing the cracking temperature to 1700 °C for X-ray analysis of the obtained porous ceramics, as shown in Fig.(11b). From Fig.(11b) we can see all characteristic peaks of h-BN, which proves that as the temperature increases, the crystallinity of the prepared porous ceramic increases. Specifically, the curve exhibits a high intensity and a sharper (002) characteristic peak (2θ = 26.57°), and the layer spacing is calculated to be d002 = 0.335 nm.

4. Conclusion

Warm-pressing followed by pyrolysis of a mixture of polyborazylene (PB) and poly(methylmethacrylate) PMMA microbeads was investigated with the objective to prepare porous BN materials. Porous materials with a porosity of ~79 % could be obtained by applying a ratio between PB and PMMA of 20/80 with PMMA microbead size of 25 μm. The mixture has been warm-pressed under 74 MPa at 60 °C to generate a green composite compact that underwent a pyrolysis to 1450 oC under nitrogen atmosphere. SEM and mercury porosimetry measurement revealed that the pores in the material were homogeneous distributed with the average pore diameter 19.15 μm which has a good replication of the pore size of PMMA (25 μm). The volume porosity is 79.06 vol%, and the obtained materials have certain application prospects in the fields of catalysis, hydrogen storage, gas adsorption and separation.

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