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Short communication

Preparation of a novel BN/SiC composite porous structure

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Abstract

A kind of BN/SiC open cell ceramic foams were fabricated from complex co-polymeric precursors of polycarbosilane and tris(methylamino)borane [$B(NHCH_3)_3$] using a high pressure pyrolysis foaming technique. The as-fabricated foams exhibit cell sizes ranging from 1 to 5 mm with bulk densities varying from 0.44 to 0.73 g/cm^3, depending on the proportion of the starting materials. Studies on microstructure and properties of the porous material shown that addition of BN into SiC can improve dramatically its oxidation resistance during 800–1100 °C and compression strength which was generally about a 5–10 times higher than that of a pure SiC foam.

Keywords: Silicon carbide; Boron nitride; Porous ceramics; Microstructure

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1. Introduction

Silicon carbide (SiC) porous ceramics or foams has been used as one of the best candidate materials for a wide range of technological applications, including filters of molten metals, hot gas for turbo engine and diesel engine exhaust; thermal and acoustic insulation; catalysts support and reinforcement for the polymer or metal composites, etc. [1,2]. This is because porous SiC possesses some advanced properties of high permeability, structural uniformity, resistance to chemical attack, excellent thermal shock resistance, low thermal conductivity and expansion coefficient [3,4]. The shortcomings of this ceramic foam are of its brittleness and heavily oxidation in air especially at most using temperatures ranging from 800 to 1100 °C, in which the formation of a dense protective pure silica layer is impossible [5].

Preparation of SiC porous ceramics involves synthesis and formation of pores [6,7]. Direct foaming technique using preceramic polymers under high gas pressure has been developed to produce macro-cellular ceramic foams with advanced application [8,9], because the production of ceramic components from pre-ceramic precursors offers unique opportunities, especially from a processing point of view, since it is possible to apply conventional plastic forming technologies, generally with low processing costs to achieve foams with high purity and less material/energy consumption because of avoiding solid phase sintering and template removing. BN layers have been used as interphase materials to improve the oxidation resistance and mechanical properties of SiC/SiC composites [10–12]. Hexagonal BN, which is isoelectronic with graphite and also has a similar layered structure to graphite, has been proposed as a very promising antioxidant because of its excellent oxidation resistance at temperatures from 600 to 1000 °C. Moreover, the formation of B_2O_3–SiO_2 borosilicate glass from a simultaneously oxidation of BN and SiC is considered as an antioxidant protection layer in a very broad temperatures ranges up to 1200 °C. In this study we present a novel BN/SiC composite porous structure for manufacturing cellular ceramic components from pre-ceramic polymers and investigations of their microstructure and properties.

2. Experimental procedure

2.1. Preparation of the materials

Three kinds of SiC/BN precursors with various compositions (wt.%) were prepared (Table 1). Commercially available polycarbosilane precursor (mean molecule weight = 1250,

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Table 1
Composition of the prepared samples of precursors.

Samples	PCS	PBN	PCS:PBN (mass ratio)
PCS	100%	0%	1:0
PB1	67%	33%	1:0.5
PB2	50%	50%	1:1
PB3	33%	67%	1:2

Table 2
Comparison of the properties of porous SiC–BN ceramics with different content of BN in the starting mixture.

PBN content (wt.%)	Porosity (%)	Bulk density (g/cm^3)	Compressing strength (MPa)
0	62.4	0.73	3.63
33	69.5	0.53	17.70
50	70.0	0.44	39.97
67	86.6	0.30	35.91

melting point = 180–240 °C) and self-made h-BN precursor (PBN) derived from tris(methylamino)borane [$B(NHCH_3)_3$] (average molecule weight = 900, melting point = 80 °C) were dissolved completely according a certain ratio into toluene and the solvent was then removed using a rotary evaporator. The dried precursor mixtures were directly foamed in a high-press vessel under an argon atmosphere at a heating rate of 2 °C/min to 500 °C and finally held at a constant pressure of 2.0 MPa for 1 h. The formed green foams were put into an alundum tube furnace and treated at 1500 °C for 2 h under flowing Ar to obtain the finial ceramic foams.

2.2. Characterizations of the materials

The ceramic foams were machined into cuboids of 1.5 mm × 1.5 mm × 2 mm for compressing tests (Model HVS-5, Lanzhou Huayin Experimental Instrument Limited Company, China) with a speed of 0.5 mm/min and a support span of 30 mm. Five specimens were tested to obtain the average strength value. Open porosity and bulk density of the porous structure were measured by the Archimedes method. Phase composition was identified by X-ray diffraction (XRD; Rigaku, Dmax-rb) using Cu K_α radiation. The microstructure was characterized by field emission scanning electron microscopy (SEM; S4700, Hitachi, Tokyo, Japan).

2.3. Oxidation tests of the porous material

Specimens were cleaned with acetone in an ultrasonic bath and weighed after drying, then laid in an electrical furnace and heated up to temperatures of 800 and 1100 °C in Ar for the following isothermal static oxidation tests, which were conducted in air with interruptions in the tests in order to measure mass change with oxidation time. The specific weight changes were calculated according to the mass change per surface area.

The non-isothermal oxidation resistance of specimen was tested using a Netzsch STA449C thermo-gravimetric analyzer. The tests were carried out at a heating rate of 5°/min from the room temperature to 1200 °C with a 1 h isothermal hold in a flowing air (50 ml/min).

3. Results and discussions

3.1. Composition and mechanical properties

Table 2 shows the porosity, bulk density and compression strength of the obtained SiC/BN porous ceramics with various contents of PBN. The influence of PBN content was apparent and interesting from these figures. On one side, higher content of PBN resulted in higher porosity and lower bulk density. As the cellular structure micrographs of the foams shown in Fig. 1(a)–(d), large open-cell pores (as indicated by the arrows) were observed, and compared with that of pure SiC foam, the morphologies of the pores in SiC foams with addition of BN changed greatly in cell size and shape. The foaming process involved the controlled heating of the precursors under pressure in an inert atmosphere. As the temperature increased during heating, the material first softened and then became fluid. At the temperature up to 400–450 °C, foam cells were formed with decomposition of the polymeric precursors producing thermally decomposed fractions which served as foaming agents in the highly viscous precursor material, and the volume of foaming precursor increased because of a large number of gas molecules evolved from the pyrolysis of the precursor. Further heating resulted in a cross-linking conversion of thermoplastic resin to thermosetting resin, which fixed the foam matrix. Volatiles continued evolving even after the solidification of the precursor material, which kept the cell-window open. Therefore, the resultant foam was an open-cell structure [13]. Changes in the morphologies of the pores in SiC/BN foams may due to more volatiles produced during the pyrolysis of the polymeric precursors.

The compression strength of the SiC/BN composite foams, on the other side, was greatly improved with the addition of BN. Fig. 2 shows the XRD results of the composite ceramics containing various contents of BN. Only broad peaks assigned to β-SiC are observed on the pure PCS sample. The small peaks at 2θ of 25° appears on the PB2 and PB3 samples which can be assigned to h-BN with a turbostratic microstructures. The soft h-BN layer could relax stress and absorb energy at the crack tip through microcracking or crack-particle interactions, and therefore preventing the main crack from extending, which should be propitious to improve compressing strength [14–16]. Furthermore, these peaks were observed to shift from that of pure BN, which suggested the formation of chemical bond between SiC and the h-BN layer, leading into the formation of weak SiC–BN interface in the composite. This should be caused by a coupling of co-pyrolysis of PCS and PBN, and may be the main reason for the improved compression strength of the composites. When PBN content was increased in the starting mixture, the interface areas between SiC particles and h-BN layer became larger, so an upward trend of compression strength appeared after the first rising with increasing contents of BN. In addition, decrease in the compression strength of PB3 may be caused by too much weight loss of the precursor during the foaming stage.

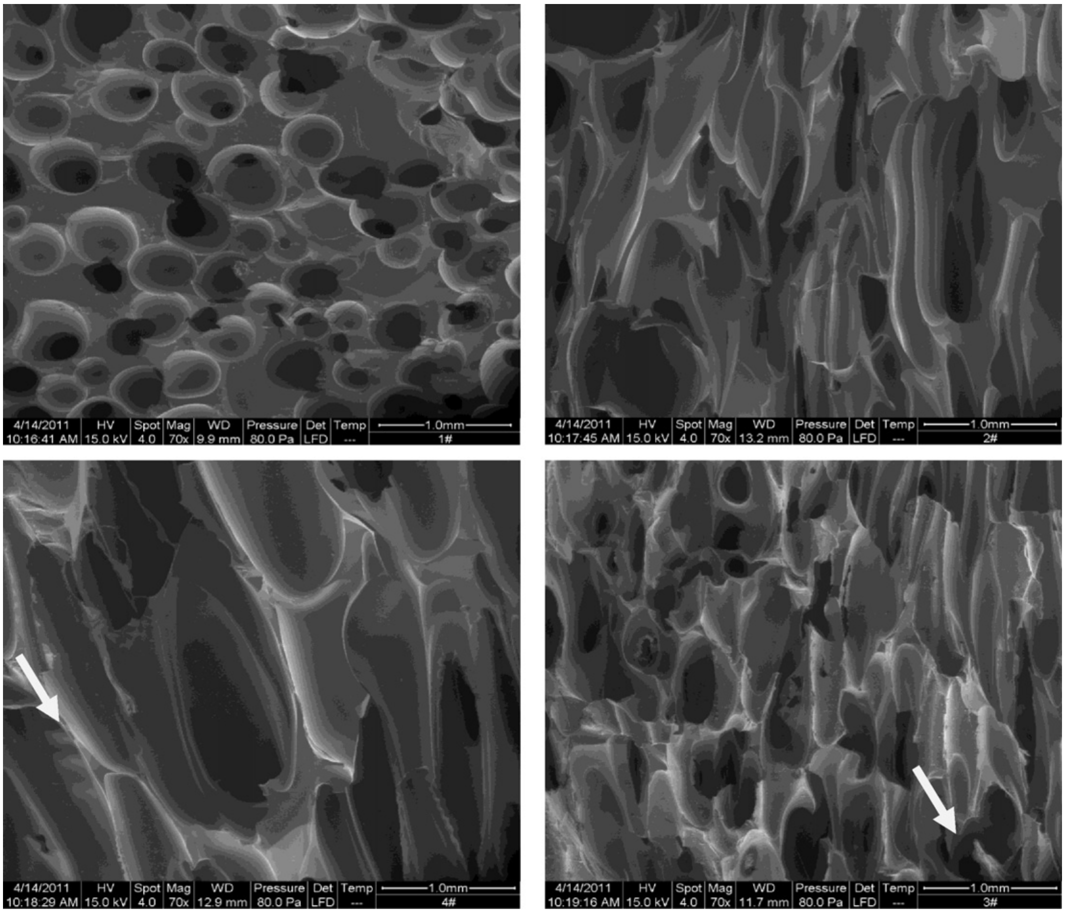

Fig. 1. SEM morphologies of the fabricated porous SiC/BN ceramics. (a) Pure SiC and with BN contents of 67% (b), 50% (c), 33% (d).

3.2. Oxidation resistance

3.2.1. Non-isothermal oxidation in air

Mass changes of the porous structures with and without BN during non-isothermal oxidation were shown in Fig. 3. No significant weight gain was observed during the temperature below 650 °C for all the four specimens. Weight loss, however, was observed separately as the temperature further increased, which indicated the beginning of oxidation of residue free carbon in the composites [17–19]. Moreover, the weight loss of PB2 was the slightest among the four samples. The formed oxide film actually acted as a barrier for further diffusion of oxygen into the fresh interface of the ceramics.

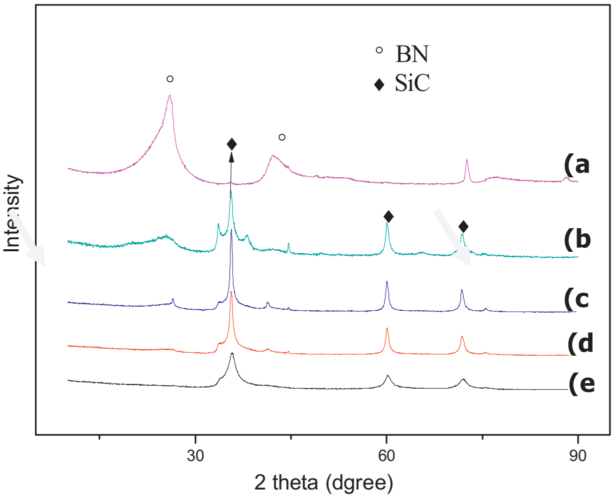

Fig. 2. XRD patterns of the synthesized SiC/BN ceramic foams. (a) Pure BN, (b) with BN contents of 67% (b), 50% (c), 33% (d) and 0% (e).

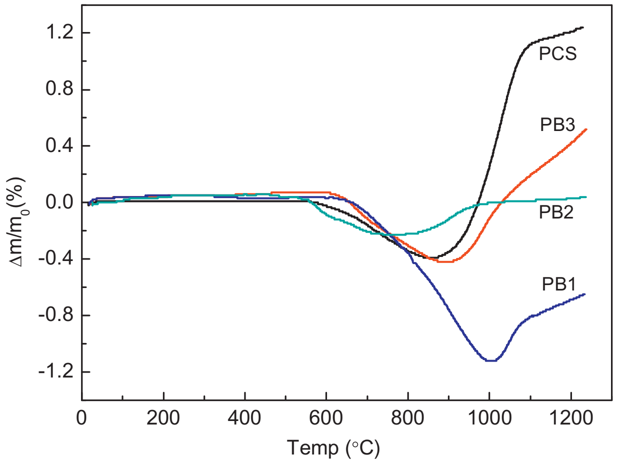

Fig. 3. Non-isothermal oxidation of the as-fabricated porous SiC/BN ceramics in air up to 1300 °C.

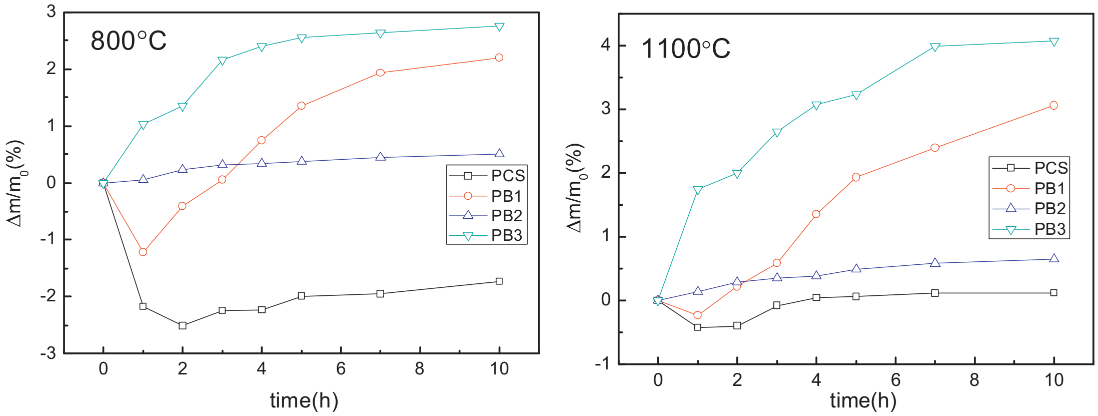

Fig. 4. Weight change of porous structures during oxidation in air for various durations and temperatures. (a) 800 °C and (b) 1100 °C.

3.2.2. *Isothermal oxidation in air*

The isothermal oxidation resistances for all the specimens were studied at 800 °C and 1100 °C with durations up to 10 h. The specific weight changes versus oxidation time are given in Fig. 4(a) and (b).

In general, except the mass loss of PCS and PB1 in the beginning of oxidation, the weight gain rates of all samples increased with the increase of temperatures, the specific weight change with time basically followed a parabolic oxidation law. The latter implied that the oxidation kinetics was controlled by transport of oxidized gaseous products diffusion through the growing oxide scale.

At the initial stage of oxidation the gasification of residual carbon resulted in mass loss. Meanwhile, B_2O_3 and SiO_2 derived from the oxidation of SiC and BN forms led into the mass gain [20,21]. At elevated temperatures above 800 °C, due to the formation of H_3BO_3 with lower melting point, the generated liquid B_2O_3 reacted with SiO_2 to form a stable borosilicate glass which acted as a protective layer to reduce oxidation rate more effectively than B_2O_3 due to its lower volatility and smaller oxygen diffusivity [22–24]. The sample PB3 got the highest rate of specific weight gain, which was attributed to the largest content of BN because the formation of B_2O_3 from the oxidation of BN brought obvious weight gain. For the sample PB2, it contained an appropriate amount of BN compared with the sample PB1, so more B_2O_3 was generated, which more easily spread in the material surface as oxide film. Moreover, the sample PB2 contained a higher proportion of silicon carbide than PB3, therefore more silicon oxide formed in PB2 than that in PB3. The higher SiO_2 content in borosilicate glass resulted in the higher viscosity and melting point, which can more effectively cover and protect the surface of the material [25]. Therefore, the oxidation resistance of PB2 with a suitable amount of BN additive was better than other samples.

4. Conclusions

In summary, a SiC/BN porous ceramics were successfully prepared from complex co-polymeric precursors of polycarbosilane and tris(methylamino)borane [$B(NHCH_3)_3$] using a high pressure pyrolysis foaming technique. With the addition of BN, the compression strength of the foams was improved. Below 1100 °C, the addition of BN significantly improved the oxidation resistance of SiC ceramics due to the formation of borosilicate. The composite started with components of 50% PCS and 50% PBN showed excellent oxidation resistance up to 1100 °C, and a very low weight gain after oxidation at 1100 °C for 10 h was observed. The addition of BN in the appropriate amount can be implied as an effective method to simultaneously improve the compression strength and the oxidation resistance of SiC porous ceramics.

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