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Fabrication and properties of precursor-derived SiBN ternary ceramic fibers

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ABSTRACT

In this paper, polymer precursor polyborosilazane (PBSZ) was synthesized from hexamethyldisilazane, $HSiCl_3$, BCl_3 and CH_3NH_2 using a multi-step polymerization process. Continuous PBSZ fibers were prepared by a laboratory scale melt-spinning machine. SiBN ceramic fibers were then obtained by the pyrolysis of PBSZ fibers. The chemical structure character and its ceramic conversion of the polymer precursor were presented. After high temperature pyrolysis process at 1100 °C, SiBN ceramic fibers were obtained with a diameter of about 14 μm. Those fibers showed average tensile strength of 0.87 GPa. The carbon content of the obtained SiBN ceramic fibers was less than 0.1 wt%. SiBN ceramic fibers revealed excellent dielectric properties and structural stability at high temperatures.

1. Introduction

Advanced wave-transparent composites are the key materials of hypersonic vehicles [1]. Quartz fibers, BN fibers, and Si_3N_4 whisker/fibers are the reinforcements available nowadays with practical applications in wave-transparent composites [2–5]. However, each of these reinforcements has its individual defects in properties. For instance, quartz fibers have poor mechanical properties at high temperatures (above 900 °C). BN fibers have low mechanical strength and ineffective high-temperature oxidation resistance. The dielectric properties of Si_3N_4 also need to be improved. Therefore, it is urgent to develop new types of ceramic fiber with good high-temperature oxidation resistance and wave-transparent property for hypersonic vehicles. Multinary Si-based nitride ceramics such as SiBN(C) have received considerable scientific attention because of their outstanding oxidation and creep resistance at extremely high temperatures [6–10]. More importantly, SiBN ceramics are expected to have the advantages of both Si_3N_4 and BN, thus it possess excellent dielectric properties and good mechanical properties. Since the self-diffusion coefficients of nitrides of Si and B are extremely low, it is difficult to prepare homogeneous SiBN ceramics by conventional preparation techniques such as powder-sintering method, particularly for SiBN ceramic fibers [11]. So far, the only feasible approach known for the preparation of SiBN fibers is the precursor-derived ceramics (PDCs) route. The preparation of precursor (polyborosilazane, PBSZ) is a key step in SiBN ceramic fiber production. However, synthetization of PBSZ without any carbon-containing organic groups is difficult to control since it has extreme high reactivity. After pyrolysis in an inert atmosphere, PBSZ can be converted into SiBNC ceramics, which have improved dielectric property and excellent electromagnetic wave absorbing property [12]. The carbon atoms in SiBNC ceramic agglomerate in domains with predominant carbon-carbon bonding, and present as free carbon [13,14]. The content of free carbon has a major influence on the wave-transparent property of SiBNC ceramics. It is known that lower content of free carbon leads to better the wave-transparent performance [15–17]. In addition, the free carbon tends to crystallize to form graphite phases which greatly impair the mechanical properties of the material [18]. Therefore, the pyrolysis process of PBSZ should be carried out under reactive atmosphere for decarburization.

Numerous researchers synthesized various kinds of PBSZ precursor for SiBNC ceramic (fiber). Typically, Jansen et al. synthesized several single-source precursors, such as $Cl_3Si{-}NH{-}BCl_2$, $(CH_3)Cl_2Si{-}NH{-}BCl_2$ and $(CH_3)_2ClSi{-}NH{-}BCl_2$, and they transformed them into borosilazane polymer by ammonolysis [19–22]. Boron-modified polysilazanes of the type $[B(C_2H_4SiRNCH_3)_3]_n$(1b, R = CH_3; 2b, R = H) were prepared via aminolysis of the tris(dichlorosilylethyl) boranes $B(C_2H_4SiRCl_2)_3$ by S. Bernard et al. [23,24]. For the extensive cross-linking of Si and N-bonded methyl groups, these PBSZ can be successfully processed into spun fibers by melt spinning. PBSZ spun fibers were cured in an ammonia(NH_3) atmosphere at 200 °C, and then pyrolyzed at 1400 °C in nitrogen(N_2) atmosphere resulting in SiBNC ceramic fibers. Wang et al. synthesized PBSZ from BCl_3, $MeSiCl_3$ and

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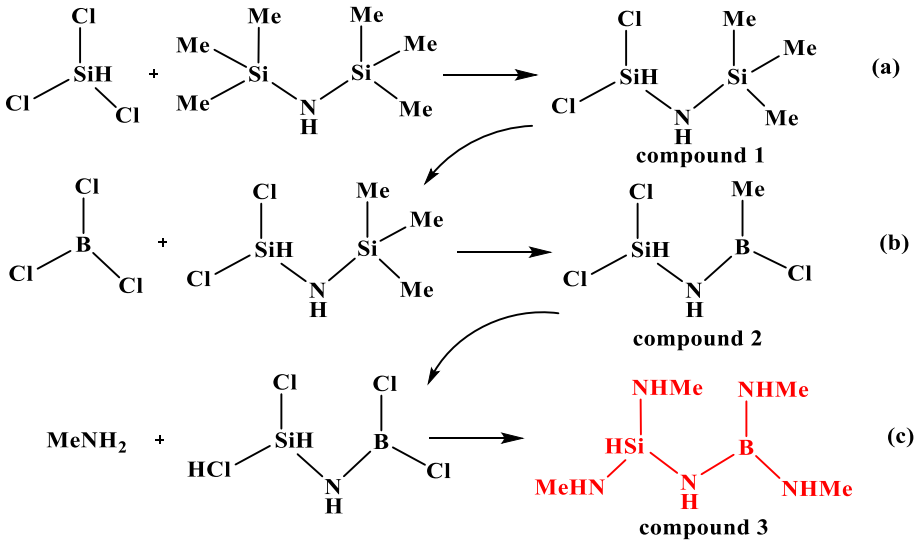

Fig. 1. Synthesis routes of SiBN(C) molecular precursor.

hexamethyldisilazane(HMDZ). The obtained polymer can be easily melt-spun into polymer fibers and then chemically cured by trichlorosilane ($HSiCl_3$) or BCl_3 vapor [25]. A great amount of research work focused on the preparation and high-temperature behavior of SiBNC ceramics, however, SiBN wave-transparent ceramics (fibers) were rarely reported in the literature. Ghalith et al. investigated the effects of BN composition on the thermal and mechanical properties of amorphous SiBN ceramic by computational modeling, and the model showed the potential of studying the composition-structure-properties relationship in more complex quaternary amorphous ceramics [26]. Ge et al. synthesized PBSZ by coammonolysis reaction of BCl_3, $MeSiHCl_2$ with HMDZ, after pyrolysis at 900 °C under NH_3, the carbon content of the obtained SiBN ceramics was only 0.29 wt% [27]. Tang et al. reported the preparation of SiBN fibers using methyl-containing polyborosilazane as the precursor polymer, and the decarburization of the fiber was carried out by pyrolysis under NH_3 atmosphere, the obtained SiBN fiber possessed excellent and thermally stable dielectric properties [28]. Li et al. reported the preparation of hollow SiBN fibers with composition of $Si_{0.3}BN_{1.4}$ by pyrolysis of polyborosilazane fibers, the obtained SiBN ceramic fibers were about 16 μm in diameter with inner hollow pore diameter of about 4 μm, and showed good average tensile strength of 1.03 GPa and excellent dielectric properties [29]. In the previous work of our group, PBSZ with suitable viscosity was synthesized by reaction of $(CH_3NH)_4Si$ and $(CH_3NH)_3B$, and then melt spun into green fibers having diameter of 50 μm, after thermolysis, the diameters of the fibers were reduced from 50 to 35 μm [30]. Recently, another kind of PBSZ was synthesized by HMDZ, $SiCl_4$, BCl_3 and CH_3NH_2, and then spun into fibers via melt-spinning techniques, and the as-spun fibers were cured in a pure NH_3 atmosphere to form SiBN ceramic fibers. The final SiBN ceramic fibers had a large diameter of 25–30 μm and had relatively low tensile strength of 0.5 GPa. The atomic ratio of Si:B:N in the resultant fibers was 1.5:1:3.1 [31]. It is generally known that the diameter of the ceramic fiber has a significant impact on its mechanical properties. To some extent, smaller fiber diameter gives better mechanical performance. The diameter of SiBN (C) fiber is directly related to the spinnability of PBSZ. The PBSZ has better spinnability, and its fiber has a smaller diameter. Referring to the literatures [32,33], the atomic ratio of Si:B:N had significant effects on the mechanical performances of SiBN ceramics. With the increase of B content, the BN-rich region tended to be larger and the SiN-rich region became smaller. If compared with Si_3BN_7 and $Si_3B_5N_7$, $Si_3B_3N_7$ had the largest ultimate stress and Young's modulus. Therefore, for improving the mechanical properties of SiBN ceramic fiber, the spinnability of the PBSZ need to be enhanced and the final ratio of Si:B:N need be regulated.

In this paper, a new kind of PBSZ was synthesized from HMDZ, $HSiCl_3$, BCl_3, and CH_3NH_2 using a multi-step polymerization. $HSiCl_3$ was used instead of $SiCl_4$ for the better linearization degree of PBSZ. As a result, the spinnability of PBSZ was enhanced. The as-spun SiBN fibers were prepared by the melt-spinning process. The chemical structure of the polymer precursor and its ceramic conversion were studied. The high-temperature performance and dielectric properties of SiBN ceramic fibers were also investigated.

2. Experimental details

2.1. Materials

BCl_3 was provided by Beijing Multi-Technology Co., and $SiHCl_3$ was purchased from Sigma-Aldrich Co. HMDZ was purchased from Acros Organics. CH_3NH_2 and N-Hexane were obtained from Zhejiang Jiangshan Chemical Co. Ltd. and Sinopharm Chemical Reagent Co. Ltd. respectively. N-hexane was used as the solvent which was purified from sodium by distillation under N_2 atmosphere.

2.2. Synthesis of PBSZ

Three tandem glass reaction vessels (V1, V2, and V3) were dried fully by high purity N_2. Firstly, HMDZ (20 mol) was dissolved in 25 L pre-dried n-hexane and was then pumped into V1 and was finally cooled down to − 20 °C. $SiHCl_3$ (20 mol) was gradually added to V1 with fully mechanical stirring. The resulting mixture was left for 12 h before the next experimental procedure. The chemical formula of the solute (Compound 1, $Si_2(CH_3)_3Cl_2NH_2$) in the upper clear liquid of V1 was showed in Fig. 1(a). The upper clear liquid in V1 was then pumped into V2. In the next step, BCl_3 (20 mol) was dropped in V2 slowly and reacted with $Si_2(CH_3)_3Cl_2NH_2$ for approximately 6 h with a fully mechanical stirring. The chemical formula of the solute (compound 2, $SiBNH_2Cl_4$) in the upper clear liquid of V2 was showed in Fig. 1(b). In the third step, excessive amounts of CH_3NH_2 (200 mol) was dissolved in 75 L pre-dried n-hexane. The liquid was pumped into V3 and then kept in the low temperature at − 40 °C. The upper clear liquid in V2 was added to react with CH_3NH_2 in V3. After 12 h without disturbance, the upper clear liquid in V3 was separated to a distillation till. Distillation was carried out at a temperature of 76 °C, and then the molecular precursor (compound 3) was obtained and was thus transferred to