

Synthesis, Ceramic Conversion and High-temperature Behavior of Polymer-derived SiBCN Ceramic

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Abstract: SiBCN preceramic polymer was synthesized by hexamethyldisilazane simultaneously reacting with dichloromethylsilane and trichloroborane in one pot. The prepared precursors were investigated with respect to their chemical and phase composition, by means of FT-IR and XPS. The random arrangement of planar B-N units and Si-N bonds formed the desired polymer precursors with -Si-N-B- framework. The precursor was converted into multinary ceramics when heated above 800 °C with the yields of 50.1wt%. Under N₂, the obtained SiBCN ceramic remained amorphous up to 1700 °C and formed crystallization of Si₃N₄ at 1800 °C. But under Ar atmosphere, the sample showed obvious crystallization of β-SiC and BNC₂ at 1800 °C.

Key words: polyborosilazane; SiBCN ceramic; crystallization; atmosphere

Challenging the crystalline binary system of SiC or Si₃N₄, amorphous SiBCN ceramic has currently been developed as a new ultrahigh temperature material^[1]. The quaternary inorganic network composed of silicon, boron, nitrogen and carbon shows an excellent resistance towards crystallization since no grain boundaries are present^[2]. Resorting to preceramic polymer pyrolysis, the intended homogeneous ceramic has been obtained via molecular and polymeric precursors^[3-6].

The chemical component and synthetic procedure play an important role in the performance of the amorphous SiBCN ceramics. Modification of silicon containing polymer with an appropriate boron compound is a widely-used method for polymer precursors. Via the dehydrogenation of hydridopoly-silazane and (HBNH)₃ and pyrolysis, SiBCN ceramics were obtained by E. Remsen et al. All the ceramics remained amorphous up to 1400 °C; however, Si₃N₄ and SiC crystalline phase were formed at 1500 °C^[7,8].

Single source precursor route could obtain homogeneous SiBCN ceramics^[3]. The obtained Si₂BN_{4.3}C_{3.3} and Si₂BN_{4.1}C_{3.3} could resist crystallization up to 1565 °C^[9]. The SiB_{1.3}N_{2.1}C and SiBN_{2.8}C_{1.7} could remain amorphous up to 1600 °C, whereas SiB_{3.8}N_{4.6}C_{3.3} and SiB_{2.3}N_{3.4} crystallized at this temperature^[10]. Thus, it can be seen that the different high temperature stabilities and crystallization resistance are related to the different synthesis routes.

Recently, one-pot synthesis of polymer precursor for

SiBCN ceramic was realized by trichloroborane and dichloromethylsilane simultaneously reacting with hexamethyldisilazane^[11,12]. In this research, SiBCN ceramic will be prepared by pyrolysis of the one-pot synthesis polyborosilazane. The high-temperature crystallization behaviour will be investigated.

1 Experiment

All reactions were conducted under purified N₂ using Schlenk techniques. Boron trichloride (BTC) was obtained from Guangming Special Gas Corporation and dissolved in n-hexane at a concentration of 5.0 mol/L. Dichloromethylsilane (DCMS) and hexamethyldisilazane (HxMDZ) were purchased from Xinghuo Chemical Corporation and Guibao Chemical Corporation, and were each distilled before use. The as-prepared polyborosilazane (PBSZ) precursors were stored in an Ar glove box.

Synthesis of polymers: Synthesis of the PBSZ precursor was carried out in a 1000 mL Schlenk reactor with a mechanical stirrer, a thermocouple and a N₂ inlet. Firstly, 100 mL of BTC solution (0.5 mol) and 54 mL (0.51 mol) DCMS were added to the flask at -40 °C. Next, 640 mL (3.1 mol) HxMDZ was added to this mixture. As this reaction is a highly exothermic neutralization process, the temperature should be held less than -10 °C by controlling the rate of HxMDZ addition. Then, n-hexane and the by-product were then distilled off by slowly heating the mixture up to 150 °C to

Received date: August 25, 2017

Foundation item: National Natural Science Foundation of China (51403233); Fund of Science and Technology on Advanced Ceramic Fibres and Composites Laboratory (61429070102162907002)

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yield the product as a transparent viscous liquid. Finally, subsequent thermal treatment up to a temperature of 250 °C increased the viscosity of the polymer due to further cross-linking in the skeletal network. The hot polymeric product formed a highly viscous mass, which solidified into brittle chunks at ambient temperatures.

Pyrolysis of polymers: At pyrolysis temperatures below 1000 °C, samples were put into an alumina boat and heated in a quartz tube furnace under N₂ flow. The as-prepared ceramics were put in a graphite crucible and heated in a graphite furnace under N₂ and Ar atmosphere at 1600, 1700 and 1800 °C and held for an additional 2 h, to investigate the phase evolution.

2 Result and Discussion

2.1 Structure of the polyborosilazane precursor

Fig.1a shows the FT-IR spectrum of PBSZ. Asymmetric stretching vibrations of N-H and Si-H units are observed at 3400 and 2156 cm⁻¹, respectively^[13,14]. The sharp peak at 2950 cm⁻¹ for the formation of C-H bonds, and the symmetric deformation vibration of Si-CH₃ at 1260 cm⁻¹, both demonstrate that carbon exists in saturated Si-CH₃ groups from DCMS or HxMDZ. A broad and strong peak featuring overlapping C-H peaks at 1460 and 1360 cm⁻¹ reveals the planar B-N unit characteristic for a pure h-BN species^[15]. Finally, a Si-N-Si band signal was observed at 915 cm⁻¹ in all polymers.

The chemical bonding of polyborosilazane was also analyzed by X-ray photoelectron spectroscopy. Fig.2 reveals the existence of silicon, boron, carbon, nitrogen, and oxygen in the polymer. The formula of atomic composition is Si₁B_{1.6}C_{2.8}N_{2.4}O_{0.2} by semi-quantitative analysis of XPS

(omitting hydrogen atom). The existence of oxygen results from the hydrolysis of polyborosilazane during the storage and transfer, which was inevitable.

Fig.3 provides the XPS fine spectra by deconvolution

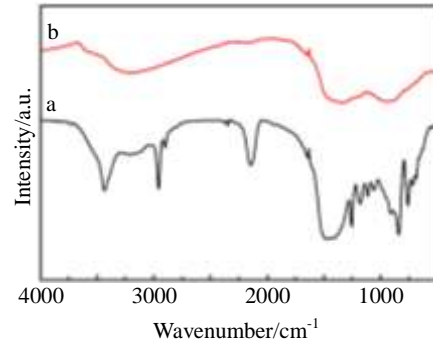


Fig.1 FTIR spectra of PBSZ (a) and SiBNC ceramic after pyrolysis at 1000 °C (b)

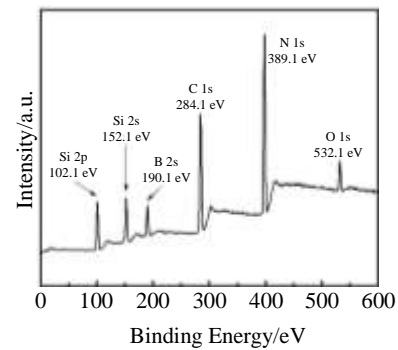


Fig.2 XPS full spectrum of PBSZ

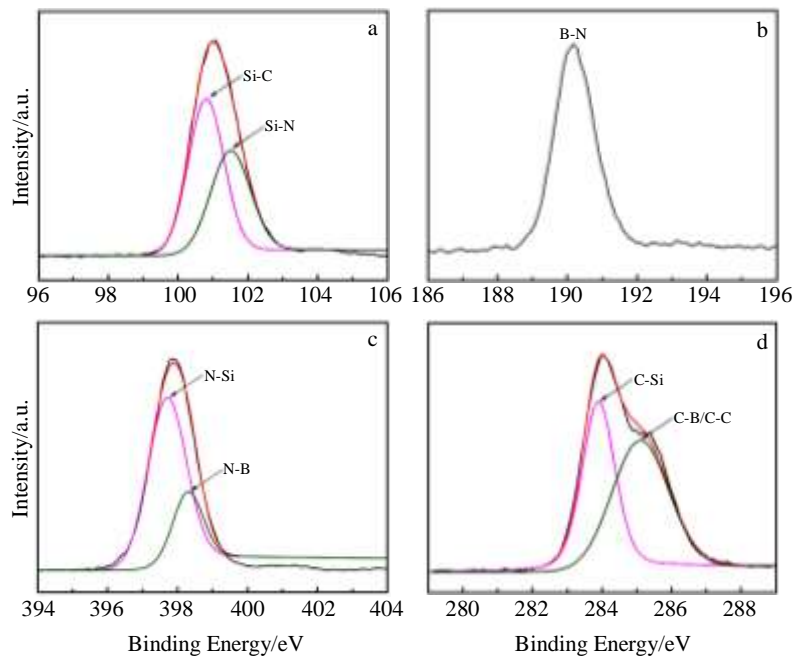


Fig.3 XPS fine spectra of PBSZ: (a) Si 2p, (b) B 1s, (c) N 1s, and (d) C 1s

procedure. In Fig.3b, the peak at 190.1 eV is assigned to B-N, which is consistent with the FTIR analysis. Peaks at 283.9 and 285.1 eV (Fig.3d) are assigned to the C 1s of C-Si bond and the C-C or C-B bond, and the C-Si bond is also identified with a Si 2p binding energy of 100.8 eV (Fig.3a). Si-N bond is formed with Si 2p binding energy of 102.1 eV (Fig.3a) and N1s binding energy of 397.6 eV (Fig.3c).

2.2 Ceramization process

To understand the thermal behavior during the pyrolysis of the PBSZ precursor, TGA was measured (Fig.4). In a temperature range from room temperature to 350~400 °C, dramatic mass loss was detected, which was mainly caused by the evolution of low molecular weight oligomers and cross-linking processes in the skeletal network. In the temperature range of 400~800 °C, mass loss was detected which was slower than when going from ambient temperature to 350~400 °C, and it was attributed to the ceramization process of PBSZ to yield SiBNC ceramics. The ceramization process was completed at approximately 800 °C as no mass change was observed at higher temperatures.

The ceramic yield of PBSZ after pyrolysis at 1000 °C is 50.1wt%. The structure of pyrolyzed ceramic was also determined by FT-IR spectrum. As shown in Fig.1b, compared with PBSZ, the peak intensity of N-H, Si-H, aliphatic C-H and -Si(CH₃)₃ almost vanish after pyrolysis. Meanwhile, the signals of B-N and Si-N are remained.

2.3 High-temperature behavior

As is known, SiBNC ceramics are X-ray amorphous and their thermal stabilities are impressively high, which can keep the absolutely amorphous state at least up to 1600 °C without any significant microstructural changes^[3,16]. To further investigate the high-temperature behaviour, the ceramic prepared by pyrolysis at 1000 °C was annealed at 1600, 1700 and 1800 °C under N₂ for 2 h. The crystallization behavior is observed by XRD patterns and shown in Fig.5^[11]. The as-prepared sample is shown to be X-ray amorphous and remains amorphous, remarkably, up to annealing at 1700 °C, indicating the high temperature stability of the SiBNC ceramic. Upon annealing at 1800 °C, the sample obviously shows crystallization of Si₃N₄. In addition, a slight crystallization of

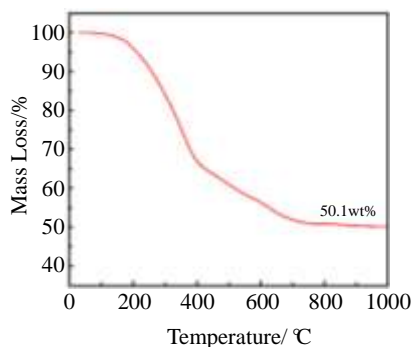


Fig.4 TGA curve of PBSZ pyrolysed under N₂

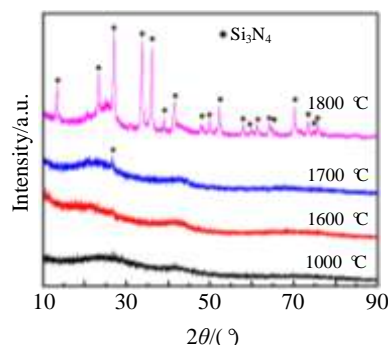


Fig.5 XRD patterns for SiBNC ceramics annealed at different temperatures under N₂

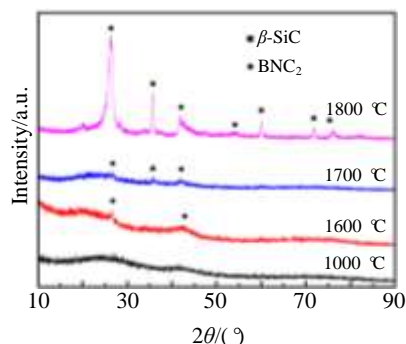


Fig.6 XRD patterns for SiBNC ceramics annealed at different temperatures under Ar

already visible at this temperature.

However, the crystallization behavior of as-prepared ceramic shows evident difference when annealing at Ar atmosphere (Fig.6). After annealing at 1600 °C, BNC₂ crystallites were detected and with the temperature increasing to 1700 °C, β-SiC crystallites were also detected. Upon annealing at 1800 °C, the sample shows obvious crystallization of β-SiC and BNC₂.

3 Conclusions

- 1) The random arrangement of planar B-N units and Si-N bonds forms the desired polymer precursors with -Si-N-B-framework.
- 2) The ceramization process is completed at approximately 800 °C with the ceramic yield of 50.1%.
- 3) The as-prepared ceramic could remain amorphous up to annealing at 1700 °C under N₂ and perform crystallites at this temperature under Ar, indicating the high temperature stability of the SiBNC ceramic.
- 4) Under N₂, the as-prepared ceramic forms Si₃N₄ crystallization at 1800 °C whereas generates crystallization of β-SiC and BNC₂ in Ar atmosphere.

References

- 1 Ji X, Wang S, Shao C et al. *ACS Applied Materials & Interfaces*[J], 2018, 10: 19 712
- 2 Ichikawa H. *Annual Review of Materials Research*[J], 2016, 46: 335
- 3 Baldus P, Jansen M, Sporn D. *Science*[J], 1999, 285: 699
- 4 Riedel R, Kienzle A, Dressler W et al. *Nature*[J], 1996, 382: 796
- 5 Tang B, Zhang Y, Hu S et al. *Ceramics International*[J], 2016, 42: 5238
- 6 Li W, Wang J, Xie Z et al. *Ceramics International*[J], 2012, 38: 6321
- 7 Lee J, Butt D, Baney R et al. *Journal of Non-Crystalline Solids* [J], 2005, 351: 2995
- 8 Widgeon S, Mera G, Gao Y et al. *Journal of the American Ceramic Society*[J], 2013, 96: 1651
- 9 Wüllen L, Jansen M. *Journal of Materials Chemistry*[J], 2000, 11: 223
- 10 Müller U, Weinmann M, Jansen M. *Journal of Materials Chemistry*[J], 2008, 18: 3671
- 11 Ji X, Shao C, Wang H et al. *Ceramics International*[J], 2017, 43: 7469
- 12 Ji X, Shao C, Wang H et al. *Ceramics International*[J], 2017, 43: 11218
- 13 Chen J, Wang X, Wang H et al. *Journal of the American Ceramic Society*[J], 2017, 100: 5044
- 14 Chen J, Wang J, Wang X et al. *Ceramics International*[J], 2017, 43: 7159
- 15 Jaschke T, Jansen M. *Journal of Materials Chemistry*[J], 2006, 16: 2792
- 16 Liang B, Yang Z, Chen Q et al. *Journal of the American Ceramic Society*[J], 2015, 98: 3788

SiBNC 陶瓷的制备与高温行为

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摘要: 通过六甲基二硅氮烷与二氯甲基硅烷和三氯化硼共聚缩合的方法, 合成了 SiBNC 陶瓷先驱体。通过 FT-IR 与 XPS 对先驱体的化学组成与结构进行了表征, 平面 B-N 单元与 Si-N 单元的随机排列形成了以-Si-N-B-为骨架的理想先驱体结构。先驱体在氮气气氛下加热到 800 °C 后转化成多元的 SiBNC 陶瓷, 1000 °C 裂解后的陶瓷产率为 50.1% (质量分数)。在氮气气氛下, 得到的 SiBNC 陶瓷在 1700 °C 下保持无定形, 在 1800 °C 下形成 Si₃N₄ 结晶。但在氩气气氛中, 得到的 SiBNC 陶瓷在 1800 °C 形成明显的 β-SiC 与 BNC₂ 结晶。

关键词: 聚硼硅氮烷; SiBNC 陶瓷; 结晶; 气氛

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