Preparation of High-Performance 2D Si₃N₄f/SiBN Ceramic Matrix Composites by Precursor Infiltration Pyrolysis

X Ma¹², YY Liang¹², H P Qiu¹², L Wang¹², S H Liu¹²
¹ AVIC Composite Technology Center, AVIC Manufacturing Technology Institute, Beijing 101300, China
² AVIC Composite Corporation Ltd, Beijing 101300, China

Corresponding author. E-mail address: ustmaxin@163.com (Xin Ma)

Abstract. Continuous nitride fiber reinforced nitride matrix composite has been recognized as a promising microwave transparent radome material. The preparation of 2D silicon nitride fibers fabric reinforced silicon boronitride ceramic composites through polyborosilazane precursor infiltration pyrolysis routine is reported. The effects of thermal molding process on the properties and microstructure of the Si₃N₄f/SiBN composites were studied. The results show that the optimal molding pressure was 6 MPa due to the fine interfacial bonding between fiber and matrix. The Si₃N₄f/SiBN composites exhibits brittle fracture characteristic, the flexural strength and elastic modulus182.7 MPa and 51.1 GPa respectively, and the dielectric constant and dielectric loss are 4.12 and 8.82×10⁻³, respectively. The Si₃N₄f/SiBN composites get the best comprehensive performance.

1. Introduction

A radome is a structural, weatherproof enclosure in hyper-sonic aircrafts or re-entry vehicles that protects radar antenna from outside environmental erosion and high aerodynamic load [1]. During the high velocity re-entry stage, the harsh environment would induce extreme high aerodynamic pressure and thermal flux on the radome surface [2]. Thus, to avoid rough ablation surface or even shape deformation, the radar protective component must be strong enough to sustain the thermal shock while maintaining its structural integrity [3].

Continuous fiber reinforced ceramic matrix composites (CMCs) are designed to have a tough and predictable fracture, and thereby are superior in damage tolerance than bulk ceramics [4]. However, the high temperature performance of the CMCs depends largely on the properties of the reinforcing fiber. For instance, the heat resistance and oxidation resistance of the reinforcing fiber generally determine the application temperature of the CMCs; and the chemical activity of the fiber greatly influences the fiber/matrix bonding state and leads to different fracture behaviors [5].

Presently, quartz fiber, Al₂O₃fiber, BN fiber, SiBN fiber and Si₃N₄fiber are several popular wave-transparent fibers available for the BN based composites [6]. Quartz fiber is one of the most commonly used reinforcement in radome materials due to its outstanding thermal shock resistance and dielectric properties. However, the crystallization-prone nature of quartz fiber often leads to a low preparation temperature of the composites, typically 800 °C [7], which in turn generates unstable matrix structure and causes rapid strength reduction at higher temperatures [8]. Al₂O₃ fiber is a well-established oxide fiber with its mechanical strength being stable up to 1300 °C within air, whereas its
high dielectric constant (9~13) restricts it from many practical applications [9]. BN fiber also displays excellent high-temperature resistance and dielectric properties. However, the relative low oxidation temperature (~900 °C) of the fiber makes it unsuitable for longtime use at elevated temperatures, especially for those BNf/BN composites [10]. In comparison, those polymer pyrolysis derived SiBN fiber, Si3N4 fiber are particularly attractive because of their designable composition, fine flexibility as well as excellent high-temperature properties [11, 12]. Among them, the SiBN fiber is now laboratory available while the Si3N4 fiber can already be industrially produced [13, 14].

Amorphous SiBN ceramics are currently being developed as new ultrahigh temperature materials that can be alternatives to the established crystalline binary system of BN and Si3N4 [15]. This quaternary inorganic network composed of silicon, boron and nitrogen shows an excellent resistance towards crystallization since it is based on strong covalent bonds, and no grain boundaries are present [16]. Thus, SiBN ceramics are promising candidates as matrix in ceramic composites for high temperature microwave-transparent applications. The intended homogeneous ceramic has been previously obtained with molecular and polymeric precursors through the use of preceramic polymer pyrolysis. But to our knowledge, there are few reports and little research about such Si3N4f/SiBN composites.

The precursor infiltration and pyrolysis (PIP) route has been proved to be an effective way to fabricate high performance continuous fiber-reinforced ceramic matrix composites. In this work, Si3N4f/SiBN composites fabricated by PIP process with polyborosilazane (PBSZ) precursor. The effects of thermal molding process on the properties and microstructure of the Si3N4f/SiBN composites were investigated.

2. Experimental procedures

2.1. Raw materials

Polyborosilazane (PBSZ), provided by Institute of Chemistry Chinese Academy of Sciences, was used as the precursor. The precursor is a pale yellow solid and the ceramic yield of precursor is 55%. The average molecular weight and softening point of the PBSZ precursor are 6272 and 100 °C.

Si3N4 fibers used in this study were provided by the Xiamen University and were fabricated by the nitridation of electron beam irradiation cured polycarbosilane fibers. The Si3N4 fibers are amorphous in phase, with a density of 2.3 g cm-3 and a diameter of 12-14 μm.

2.2. Preparation of the composites

Si3N4f/SiBN substrates were prepared as follows. Firstly, Si3N4 fiber clothes were stacked, Z-stitching Si3N4 fibers (by 5 mm × 5 mm space) to an integral preform (40% volume fiber percent), with a thickness of 3 mm. Then BN interphase was deposited by CVD process with BCl3-NH3-H2-N2 system. Secondly, all of the preforms were vacuum-infiltrated with the precursor (50 wt.% PBSZ solution in xylene), stacked into a graphite mold, cured at 200 °C, and finally pyrolyzed at up to 1200 °C under flowing NH3 atmosphere. Finally, the process of infiltration, curing and pyrolysis was repeated until the Si3N4f/SiBN composites became compact.

2.3. Characterization of the composites

The apparent density and open porosity of the Si3N4f/SiBN composites were measured by the Archimedes' method with kerosene as medium. The monofilaments of as-received and treated Si3N4 fibers were tested at room temperature with a single yarn strength tester (YG-002, China). For each value, a batch of more than 25 monofilaments was tested with a gauge length of 25 mm and the data were used to determine the mean ultimate tensile strength.

Flexural strength was tested by using the three-point bending test (WDW-100, China)(ASTM C1341-06) on specimens of 3 × 4 × 40 mm with a span of 30 mm and a crosshead speed of 0.5 mm·min⁻¹. Over five samples were measured for the mechanical tests.
The fracture surfaces and polished sections of the composites were characterized by scanning electron microscopy (SEM) (Hitachi S-4800 and JSM-5600, JEOL).

3. Results and discussion

3.1. Continuous Si₃N₄ Fibers

The BN interphase was employed to provide a proper bond between the fiber and matrix, and protect fiber in oxidative environments, giving excellent mechanical properties of composites. The microstructures of the original Si₃N₄ fiber and BN interface modified Si₃N₄ fiber were shown in Fig. 1. The main properties of high-performance Si₃N₄ Fibers were shown in Tab. 1. Before and after the interface modification process, the surface of both fibers was smooth without obvious drawbacks. As well, the monofilament tensile strength of both fibers remained the same. The effect of CVD BN interface on the strength of Si₃N₄ fibers was negligible.

Table 1. Main properties of high-performance Si₃N₄ fiber

| Sample                  | Si₃N₄ fiber | modified Si₃N₄ fiber |
|-------------------------|-------------|---------------------|
| Tensile strength (MPa)  | 1530 ± 60   | 1495 ± 50           |
| Elastic modulus (GPa)   | 140         | 140                 |

3.2. Densification process of Si₃N₄/SiBN composites

The performance parameters of the Si₃N₄/SiBN composites under different molding pressure were listed in Tab. 2. Weight increase-cycle curves of the specimens under different pressure were shown in Fig. 2. The density of Si₃N₄/SiBN/SiBN composites increased first and then decreased with the increase of the pressure. The weight increase of 1# was much more than the other three specimens at the first three cycles. It was indicated that a large number of precursors are extruded out of the preforms. Thus, the weight increases of 2-4# were always lower than the 1# during the whole PIP process. The main reason was that too much pressure led to the internal stress concentration and volume rebound. The porosity was reduced and the fiber volume fraction was increased respectively.

Table 2. Performance parameters of Si₃N₄/SiBN composites at different molding pressure

| Specimen | Molding pressure /MPa | Fiber fraction /% | Density /g·cm⁻³ | Porosity /% |
|----------|------------------------|-------------------|------------------|-------------|
| 1#       | 0                      | 37                | 1.83             | 13.5        |
| 2#       | 2                      | 43                | 1.88             | 9.6         |
| 3#       | 4                      | 48                | 1.91             | 7.1         |
| 4#       | 6                      | 46                | 1.89             | 8.3         |
3.3. Properties of Si$_3$N$_4$/SiBN composites

The mechanical property and dielectric property of the Si$_3$N$_4$/SiBN composites were shown in Tab.3. The effects of molding pressure on the dielectric properties of Si$_3$N$_4$/SiBN composites were not apparently, the dielectric constant and dielectric loss were 4.12 and 8.82×$10^{-3}$ respectively. The typical flexural load-displacement curves are illustrated in Fig. 3. All of the Si$_3$N$_4$/SiBN composites failed in brittle modes, and the strength of the composite without the thermal molding process was the lowest than the other three composites. The mechanical properties of the Si$_3$N$_4$/SiBN composites increased rapidly at 0-4 MPa, and then decreased at above 4 MPa. Therefore, molding pressure exerted evident effects on mechanical properties. The maximum flexure strength and elastic modulus are 182.7 MPa and 51.1 GPa respectively.

| Specimen | Flexure strength /MPa | Elastic modulus /GPa | Dielectric constant | Dielectric loss /% |
|----------|-----------------------|----------------------|--------------------|-------------------|
| 1#       | 114.8                 | 37.5                 | 4.12               | 9.23×$10^{-3}$    |
| 2#       | 142.2                 | 45.4                 | 4.11               | 8.82×$10^{-3}$    |
| 3#       | 182.7                 | 51.1                 | 4.13               | 8.94×$10^{-3}$    |
| 4#       | 147.3                 | 44.1                 | 4.12               | 8.76×$10^{-3}$    |
It is well-demonstrated that the mechanical property of ceramic matrix composites is strongly dependent on the interfacial bonding strength, which can be evaluated by the average fiber pull-out length of the composites according to predictions of the classical shear-lag model [17]:

$$l_c = \frac{d\delta_f}{2\tau}$$  \hspace{1cm} (1)

where $\delta_f$ and $d$ are the tensile strength and diameter of the fiber respectively. $l_c$ is the fiber pullout length. The fracture surfaces of the Si$_3$N$_4$/SiBN composites are displayed in Fig. 4. All of the composites were highly dense, but a few long pulled-out fibers could be seen on the fracture surfaces. The composites exhibited flat fracture surfaces in accordance with the brittle fracture behavior. It indicated that the SiBN matrix and Si$_3$N$_4$ fiber react easily.

Figure 4. SEM micrographs of fracture surfaces: (a) 1#; (b)2#; (c) 3#; (d) 4#.

Figure 5. Morphology of fibers and interfaces of Si$_3$N$_4$/SiBN composites: (a) 1#; (b) 2#; (c) 3#; (d) 4#.
Morphology of the fibers and interfaces of the composites under different molding pressure were shown in Fig. 5. In Fig. 5(a), the fibers were bonded together with the matrix which indicated the strong interfacial bonding. In Fig. 5(c, d), the fiber pullouts on the fracture surface in some regions were short, illustrating the fast propagation of cracks through the specimens with little crack deflection or arrest at the fibers. This indicated the stress concentration in the composites. Fiber pullouts on the fracture surface of 3# were longer than the other specimens. Crack arresting, deflecting and branching behavior was beneficial to improve the strength of the composites. Accordingly, high molding pressure led to the fiber volume fraction increased, and the mechanical property of composite enhanced.

4. Conclusions
2D Si₃N₄/SiBN composites were successfully fabricated through PBSZ infiltration and pyrolysis method. Influences of thermal molding process on the properties of Si₃N₄/SiBN composites were systematically studied. Molding pressure exerted evident effects on the fiber volume fraction and density of the composites. Excessive molding pressure caused the strong interfacial bond and performance degradation of the composites. When the molding pressure was 6MPa, the composites own the optimal comprehensive performance. Density and open porosity of the Si₃N₄/SiBN composites were 1.91 g·cm⁻³ and 7.1%, respectively. The dielectric constant and dielectric loss were 4.12 and 8.82×10⁻³, respectively. The flexure strength and elastic modulus are 182.7 MPa and 51.1 GPa respectively.

References
[1] Gongjin Q, Changrui Z, Haifeng H 2006 J. Non-Cryst. Solids. 352 3794–3798.
[2] Bin L, Kun L, Changrui Z, Siqing W 2014 J. Eur. Ceram. Soc. 34 3591–3595.
[3] Bin L, Changrui Z, Feng C, Siqing W, Yingbin C, Gongjin Q 2008 J. Mater. Eng. Perform. 17 111-114.
[4] Naslain R 2004 Compos. Sci. Technol. 64 155–170.
[5] Xin M, Si’an C, Min M, Yong L, Guangde L, Haifeng H, Xinbo H, Xuanhui Q 2016 Mater. Sci. Eng. A. 666 238–244.
[6] Yu Z, Shubin W 2012 Appl. Surf. Sci. 258 4698–4701.
[7] Bin L, Changrui Z, Siqing W, et al. 2007 Refrac. Indust.Ceram. 48 280–283.
[8] Cooke F 1991 J. Am. Ceram. Soc.74 2959–2978.
[9] Toutois P, Miele P, Jacques S, et al. 2006 J. Am. Ceram. Soc. 89 42–49.
[10] Duan L, ChangriúZ, Bin L, et al. 2012 Mater. Lett. 68 222–224.
[11] Bansal P, Dickerson M 1997 Mater. Sci. Eng. A. 222 149–157.
[12] Yokoyama Y, Nanba T, Nishi I, et al. 1991 J. Am. Ceram. Soc.74 654–657.
[13] Wenhua L, Jun W, Zhengfang, X, Hao W, Yun T 2012 Mater. Lett. 78 1–3.
[14] Yun T, Jun W, Xiaodong L, Zhengfang X, et al. 2010 Chem. A Eur. J. 16 6158-6462.
[15] Riedel R,Kienzle A, Dressler W, Ruwisch L, Bill J, Aldinger F 1996 Nature. 382 796–798.
[16] Jansen M, Jäschke B, Jäschke T 2002 Struct. Bond. 101 137–191.
[17] Xiaoyu C, Xiaowei Y, Xiaoming F, Laifei C, Litong Z 2014 Carbon. 77 886–895.