Oxidation Behavior of SiC/Si-B-C-N Ceramic Matrix Composites

Haipeng Qiu1,2*, Mingwei Chen1,2, Weijie Xie1,2, Bingyu Zhang1,2, Shanhua Liu1,2, Wendong Luo1,2, Xin Ma1,2
1 AVIC Composite Technology Center, Beijing, China, 101300
2 AVIC Composite Corporation Ltd., Beijing, China, 101300
* hpqiu@163.com

Abstract: Silicon carbide fiber reinforced Si-B-C-N (SiC/Si-B-C-N) ceramic matrix composites were manufactured through polymer impregnation pyrolysis (PIP) process with SiC fiber as disperse phase and Si-B-C-N ceramic as continuous phase. Thermal stability of Si-B-C-N ceramic and the high temperature oxidation behavior of SiC/Si-B-C-N ceramic matrix composites were studied. Results showed that the introduction of boron and nitrogen element restrained the growth of SiC grain and the formation of crystalline phase transformation effectively, and could help to keep the amorphous state up to 1400°C. In addition, SiC/Si-B-C-N ceramic matrix composites possessed excellent high temperature oxidation resistance with bending strength retention rate of 80.57% after oxidation test at 1200°C for 100 hours due to the formation B2O3 or borosilicate glass from the oxidation of boron element. Liquid B2O3 or borosilicate glass with suitable fluidity could fill the pores and cracks in the interior which acted as a protective layer and lowered oxygen diffusivity according to the morphology and component analysis. Therefore, SiC/Si-B-C-N ceramic matrix composites possessed excellent oxidation resistance for a wide temperature range.

1. Introduction
Silicon carbide fiber reinforced SiC (SiC/SiC) ceramic matrix composites were prepared with silicon carbide fiber as reinforcement and SiC ceramic as continuous matrix phase. So, SiC/ SiC ceramic matrix composites retained the excellent performance of SiC ceramic such as high temperature resistance, oxidation resistance and corrosion resistance, and possessed the properties of silicon carbide fiber for high strength and high toughness. Therefore, SiC/SiC ceramic matrix composites was identified as a novel and promising material with brilliant prospects in aero engine, aerospace vehicle and nuclear field, and much attention had been paid in Europe, America, Russia and other developed countries and regions. A large number of plans have been developed and implemented in order to improve the preparation technology and application scale of advanced structural materials, such as HITEMP(Advanced High Temperature Engine Materials Technology), IHPTET (Integrated High Performance Turbine Engine Technology), UEET(Ultra Efficient Engine Technology), VAATE (Versatile Affordable Advanced Turbine Engines), AMG (Advanced Material Gas-generator) and ESPR (Research and Development of Environmentally Compatible Propulsion System for Next-generation Supersonic Transport) project. Ceramic matrix composite had been applied in nozzle seals and flaps, combustor, turbine stator and other hot section components on M88-2, F100-PW-229, CFM56-5B, F-135, GEnx, LEAP-X and other aero engines. In particular, SiC/SiC ceramic matrix composite high pressure turbine shroud ring were successfully manufactured and tested on LEAP-X.
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2. Experiment

2.1. Preparation of Si-B-C-N multiphase ceramics
Si-B-C-N multiphase ceramics were prepared through pyrolysis process of mixture precursor with a certain proportion of polyborazine (PBN) and polycarbosilane (PCS). PBN with softening point around 90°C was obtained by Institute of Process Engineering, Chinese Academy of Sciences, and PCS with softening point around 210°C was provided by Suzhou Saifei Group Co., Ltd. All raw materials must undergo strict inspection before the preparation of Si-B-C-N multiphase ceramics, SiC/Si-B-C-N ceramic matrix composites and other products.

2.2. Preparation of SiC/Si-B-C-N multiphase ceramics
SiC/Si-B-C-N ceramic matrix composites were manufactured through polymer precursor impregnation pyrolysis (PIP) process with domestic second generation SiC fiber as disperse phase and Si-B-C-N multiphase ceramic as continuous phase. And the PIP process include fabrication of SiC fiber preforms, preparation of pyrolytic carbon interphase, vacuum impregnation, hot moulding and pyrolysis. Besides, SiC/SiC ceramic matrix composites were also prepared through the same process with PCS as impregnation solution as reference of SiC/Si-B-C-N ceramic matrix composites.

2.3. Detection and characterization
The solid phases of Si-B-C-N multiphase ceramic were analyzed by X-ray diffraction (XRD) (PANalytical X’Pert PRO). The morphology and microstructure of Si-B-C-N multiphase ceramic were characterized by scanning electron microscopy (SEM) (FEI Quanta 200 FEG). Furthermore, The bulk density of SiC/Si-B-C-N ceramic matrix composites was carried out by the Archimedes method based on the GB/T 21650.1-2008, and the chemical compositions were obtained by energy dispersive X-ray spectroscopy (EMAX-300, Horiba). The flexural strength was measured by three-point-bending test based on GB/T 6569-2006 and the fracture toughness was measured by a single-edge notched beam test based on GB/T 23806-2009.
3. Results and Discussion

3.1. Thermal stabilization of Si-B-C-N multiphase ceramic
Si-B-C-N multiphase ceramics were obtained at different temperatures through pyrolysis process of Si-B-C-N multiphase ceramic precursors with with PBN weight ratios of 50%. Moreover, SiC ceramics were also prepared as reference to in order to prove the modifying effect and mechanism of boron and nitrogen elements. According to the phase analysis of Si-B-C-N and SiC ceramic shown in Figure 1 and Figure 2, Si-B-C-N multiphase ceramic possessed obvious amorphous state at 800°C, no significant changes in phase structure emerged with the pyrolysis temperature increase to 1400°C. The crystal characteristics only appeared when the pyrolysis temperature rose to 1500°C based on the Strength changes of the diffraction peaks for Si-B-C-N multiphase ceramic. That is to say, SiC/Si-B-C-N composites could keep amorphous state up to 1400°C. SiC composite changed from amorphous
state to obvious $\beta$-SiC crystal characteristics with the pyrolysis temperature increase from 800°C to 1000°C. Then the diffraction peaks changed more sharper and stronger with the increase of pyrolysis temperature from 1000°C to 1550°C. That is to say, structural changes easily took place during the evolution of high temperature for SiC ceramic matrix [9,10].

So, we concluded that the introduction of B and N components effectively restrained the growth of SiC grain and hindered the formation of crystalline phases transformation, which might favor the structural stability of SiC ceramic matrix composites under high temperature [11].

3.2. Thermodynamic analysis of oxidation reaction

The chemical reaction of Si-B-C-N multiphase ceramic in oxidation environment can be obtained by thermodynamic calculation based on HSC Chemistry 5 software(Figure 3), and chemical reactions mainly includes the following parts.

$$
\begin{align}
\text{2/3SiC (s) + O}_2 (g) & = 2/3\text{SiO (g) + 2/3CO}_2 (g) \quad (1) \\
1/2 \text{SiC (s) + O}_2 (g) & = 1/2 \text{SiO}_2 (s) + 1/2 \text{CO}_2 (g) \quad (2) \\
2/3 \text{SiC (s) + O}_2 (g) & = 2/3 \text{SiO}_2 (s) + 2/3 \text{CO (g)} \quad (3) \\
\text{SiC (s) + O}_2 (g) & = \text{SiO (g) + CO (g)} \quad (4) \\
4/3 \text{BN (s) + O}_2 (g) & = 2/3 \text{B}_2\text{O}_3 (l) + 2/3 \text{N}_2 (g) \quad (5)
\end{align}
$$

Figure 3. Relation diagram of $\Delta G^0$-$T$.

According to the relationship of Gibbs free energy and reaction temperature during oxidation reaction, the values of Gibbs free energy for reaction (1), (2), (3), (4) and (5) were less than zero among room temperature to 1600°C which meant the oxidation reaction mentioned above could take place spontaneously in thermodynamics. Gibbs free energy value of reaction (2) reached the minimum among all the oxidation reaction of SiC. BN oxidation reaction (5) particularly had a low Gibbs free energy value.

This is to say, the oxidation reactions of Si-B-C-N multiphase ceramic in high temperature mainly consisted of two parts based on principle of minimum Gibbs free energy of reaction.

3.3. Basic properties analysis of SiC/Si-B-C-N ceramic matrix composites

Porosity, flexural strength and fracture toughness of SiC/Si-B-C-N and SiC/SiC ceramic matrix composites were tested by the Archimedes method, three-point-bending test method and single-edge notched beam test method respectively. Results showed that SiC/Si-B-C-N and SiC/SiC ceramic
matrix composites possessed similar porosity of 13.51% and 12.07% shown in Table 1. Furthermore, there is no obvious differences in flexural strength of 341MPa and 350MPa as well as fracture toughness of 20.93MPa·m$^{1/2}$ and 23.90MPa·m$^{1/2}$ for SiC/Si-B-C-N and SiC/SiC ceramic matrix composites. Previous research estimated that ceramic fibers was the primary structure for ceramic matrix composites and interphase was the key to the improvement of toughness, which implied that the mechanical properties of SiC/Si-B-C-N and SiC/SiC ceramic matrix composites prepared with the same SiC fiber and pyrolytic carbon interphase were similar.

| Material         | Porosity (%) | Flexural strength (MPa) | Fracture toughness (MPa·m$^{1/2}$) |
|------------------|--------------|-------------------------|-----------------------------------|
| SiC/SiC          | 12.07        | 341                     | 20.93                             |
| SiC/Si-B-C-N     | 13.51        | 350                     | 23.90                             |

Figure 4. Load/displacement curves of the SiC/SiC and SiC/Si-B-C-N ceramic matrix composites. (a)flexural strength,(b) fracture toughness.

It was worthwhile to note that the load-displacement curves were similar and possessed characteristic of pseudo-elastic fracture behaviors on the whole show in Figure 4. That is, the load increased nonlinearly in the primary stage of loading. After reaching the peak, the load remained...
mainly unchanged for a relatively wide range, and then declined in a ladder-like process rather than a drastic fall which effectively prevented the sudden appearance of performance degradation and material failure. In short, SiC/Si-B-C-N and SiC/SiC ceramic matrix composites had similar fracture behaviors, and both of them possessed excellent pseudo-elastic behavior which would be favorable to increase the strength and toughness [12].

3.4. High temperature oxidation behavior of SiC/Si-B-C-N ceramic matrix composites

The oxidation tests of SiC/Si-B-C-N and SiC/SiC ceramic matrix composites were carried out in muffle furnace under 1200°C, then mechanical properties and morphology were characterized after the given processing time among 2 to 100 hours. Oxidation tests showed that flexural strength declined obviously from 341MPa to 261MPa with strength retention of 76.54% after 2 hours. Then, flexural strength dropped to 129 MPa with strength retention of 37.83% after 60 hours and fell to 102 MPa with strength retention of 29.91% after 100 hours. On the contrary, SiC/Si-B-C-N ceramic matrix composites showed excellent high temperature oxidation resistance. The flexural strength remained almost unchanged after 2 hours of oxidation at 1200°C and only 14.00% strength loss appeared after 60 hours of oxidation. It is worthwhile to note that the flexural strength of SiC/Si-B-C-N ceramic matrix composites reached as much as 80.57% when oxidized at 1200°C for 100 hours which was superior to SiC/SiC ceramic matrix composites. In conclusion, the high temperature oxidation resistance was improved significantly due to the introduction of boron and nitrogen elements which could favor the application of ceramic matrix composites in aeroengine hot structural components.

As shown in Figure 6, the morphology of SiC/Si-B-C-N and SiC/SiC ceramic matrix composites oxidized at 1200°C for 100 hours were characterized by scanning electron microscopy (SEM). SiC ceramic matrix was oxidized into SiO₂ which possessed loose structure and high fluidity at 1200°C, so the oxidation products could not fill the road of oxygen diffusion and permeation effectively leading to the further oxidation. Moreover, amorphous phase Si₃C₂O₈ existing in SiC fiber and ceramic matrix might decompose at 1200°C which could lead to the degradation of material performance.

On the contrary, oxidation products of SiC/Si-B-C-N ceramic matrix composites at 1200°C showed compact structure, and elemental analysis showed the oxidation products consisted of silicon, boron and oxygen elements which might be the mixture of B2O3 and borosilicate. Liquid B2O3 or borosilicate glass with suitable fluidity could act as a protective layer to reduce oxidation rate due to the low vaporization rate and oxygen diffusivity.

![Figure 5. Flexural strength of the SiC/Si-B-C-N and SiC/SiC composites after oxidation experiment.](image-url)
The morphology analysis of SiC/Si-B-C-N and SiC/SiC ceramic matrix composites was consistent with the trends in mechanical properties after oxidation reaction. That is to say, the formation of liquid B2O3 or borosilicate glass inhibited the oxidation SiC/Si-B-C-N ceramic matrix composites which favored performance stability of under high temperature and oxidation environment [13-15].

![Morphology analysis of SiC/Si-B-C-N and SiC/SiC ceramic matrix composites](image)

**Figure 6.** Morphology of the SiC/SiC(a) and SiC/Si-B-C-N(b) composites after oxidation experiment.

### 4. Conclusion

1. Si-B-C-N multiphase ceramics were prepared through polymer pyrolysis process, and the growth of SiC grain and the formation of crystalline phases transformation effectively restrained due to the introduction of boron and nitrogen element, which could help to keep the amorphous state of Si-B-C-N multiphase ceramics up to 1400°C.

2. SiC/Si-B-C-N ceramic matrix composites possessed excellent high temperature oxidation resistance due to the formation B2O3 or borosilicate glass, and the oxidation products with suitable fluidity could act as a protective layer and lower oxygen diffusivity which effectively inhibited the high temperature oxidation reaction of SiC/Si-B-C-N ceramic matrix composites.

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