The microstructure and mechanical properties of silicon carbide fibers with boron nitride interphase

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Abstract: The 2nd generation SiC tows is a type of essentially polycrystalline fibers (SiC₁.₄₆O₀.₀₃). Smooth and uniform boron nitride interphase was deposited on SiC fibers by low pressure chemical vapor infiltration (CVI). The scanning electron microscopy(SEM) was used to characterize the microstructure of the BN interphase and fibers while X-ray diffraction(XRD) and TEM were used to characterize the phase constitute of the fibers. The XRD and TEM results showed that the BN interphase prepared by CVI is turbostratic. The effects of thickness on the mechanical properties of SiC fibers were investigated by using two-parameter Weibull distribution. The fibers with thin BN interphase showed higher strength than the as-received fibers, for healing the surface flaws. However, the soft nature of increasing BN thickness had a more dominant effect and resulted in the decrease of fiber strength.

1. Introduction
Continuous fiber reinforced ceramic matrix composites (CMCs), whose reinforcements are carbon, silicon carbide or oxide fibers, are non-brittle and refractory materials used in severe environments (high temperature, high pressure and corrosive atmosphere). CMCs not only have properties of monolithic ceramics, e.g. high temperature resistance, high strength, corrosion resistance, creep resistance, but also has reinforcements that can effectively prevent the diffusion of cracks in ceramic thus improving the toughness of the CMCs. Silicon carbide fiber reinforced silicon carbide matrix composites (SiC/SiC) have been considered as a potential material for high-temperature structural parts in aero-engines, gas turbine as well as in nuclear reactors due to its superior mechanical performance at high temperatures, thermo-stability, oxidation resistance and corrosion resistance[1-3].

SiC/SiC composites are mainly consisted of SiC fibers, SiC matrix and interphase. The interphase protects SiC fibers against chemical erosion that occurs during processing and service of SiC/SiC composites. It is well-known that the appropriate interphase materials for SiC/SiC should be those with layered structures. Therefore, pyrocarbon (PyC) was...
thought to be the most suitable interphase for improving the mechanical behavior of SiCₐ/SiC composites[4]. However, PyC interphase can easily be consumed in oxidizing atmospheres even at relatively low temperature (~400°C). Hexagonal Boron nitride (h-BN) interphase displays a graphite-like structure and is recognized to be a better interphase than PyC while used in oxidizing atmospheres at higher temperature [5,6].

Low pressure chemical vapor infiltration (CVI) is a technique generally used for depositing interphases on the SiC bundles comprising 0.5-1Kmonofilaments. At present, reports on BN interphase mainly focus on two aspects[7-11]: (1)the processing conditions and (2) the effects of BN interphases on mechanical properties of SiCₐ/SiC composites. However, the effect of BN interphases on SiC fibers themselves was rarely discussed.

Actually, as the reinforcement, the mechanical properties of the SiC fiber determine the ultimate strength of composites. The amount of fibers pullout, which contributes to the toughness of CMCs, is greatly affected by the mean strength of the fibers. Thus, it is important to evaluate effect of BN interphase on the strength and microstructure of the SiC fibers, and the results will provide guidance for application of CVI-BN interphase in SiCₐ/ SiC composites. In this work, BN interphase was deposited on SiC fibers by CVI technique using the gas system of NH₃–BCl₃-N₂at low pressure. The thickness of BN interphase depends on deposition time. The effects of different BN interphase thicknesses on the tensile strength and microstructure of the fibers were investigated.

2. Experiment Procedure

2.1. Materials and deposition of BN interphase.

The 2nd generation SiC tows is a polycrystalline SiC fiber as substrates for deposition. The SiC yarns are consisted of 1000 monofilaments around 13 μm in diameter and 5 nm in grain size. Boron nitride interphase was deposited in a hot wall low pressure CVI equipment. High purity boron trichloride (BCl₃, 99.99%) and ammonia(NH₃,99.99%) were used as the precursor gas and nitrogen was used as the diluent gas. BN coatings were prepared by CVI at a total pressure of 1000 Pa and a temperature of 900 °C, respectively. The ratios of inlet gases were selected as follows:[NH₃]n/[BCl₃]n=1, [N₂]n/[NH₃]n+[BCl₃]n=3. The fibers with different BN interphase thickness were deposited. The thickness of the interphase ranges from 80 to 1500 nm.

![Figure 1. Diagram of a Monofilament Bound to Sample Frame.](image)

2.2. Specimen characterization.

The morphology of BN-coated SiC fibers were examined by scanning electron microscopes (SEM, S4800 Hitachi). The phase compositions were identified by X-ray Diffraction (XRD, Rigaku Dmax-rb) using CuKα line, and the transmission electron microscopy (TEM, TecnaiG20) equipped with X-ray energy dispersive spectrometer (EDS), respectively. Furthermore, the tensile strength of monofilament was measured at room temperature using a universal strength machine equipped with a 5 N load cell.
The gauge length and the crosshead speed were 25 mm and 5 mm min\(^{-1}\) respectively, as shown in Figure 1. The two parameter Weibull model was applied to evaluate the strength distribution of SiC fibers. The mean strength and Weibull parameter were calculated from 30 specimens for each fiber.

3. Results and discussion

3.1. Microstructure of BN interphase
The BN interphase was successfully deposited on SiC fibers by CVI. Figure 2 shows the fracture morphologies of the fibers with different BN interphase thickness. The BN interphase on SiC fibers was rather smooth, and no obvious defects were observed. The SiC fibers were surrounded by uniform BN interphase. The fracture surface of coated SiC fibers also showed different BN interphase thickness. According to the measurements, the thicknesses are 86nm, 330nm, 625nm and 1450nm, respectively. The structure of BN becomes uniform gradually with the increase of deposition time. Since SiC yarns are consisted of 1000 monofilaments, the increase in thickness inevitably causes some fibers to stick together.

![Figure 2. The SEM morphologies of the surface and cross-sectional of the fibers. (a) 5 min, (b) 15 min, (c) 30 min, (d) 75 min.](image)

![Figure 3. The thicknesses and deposition rates of BN interphases.](image)
Figure 3 shows the thicknesses and deposition rates of BN interphases that were deposited on SiC fibers. The thickness of BN interphases was measured by the SEM in the middle of the fibers. The deposition rate could be obtained by dividing the thickness by deposition time. The results show that the deposition rate of BN interphase under this condition is about 18–22 nm/min. As can be seen from Figure 2, the deposition rate increases first and then decreases with time. The reason may be that CVI is a complex process in which precursor gases react on the surface of fibers and produces solid products. Preparing BN interphase by CVI process, the first step is the adsorption of precursor gas on the fibers. The adsorption rate is related to the concentration of active sites. The concentration of active sites on the SiC fibers is lower than that of BN formed during deposition. Therefore, the deposition rate initially increases with time. However, the concentration of active sites tends to stabilize with the prolongation of deposition time. So the deposition rate decrease due to the increasing diameter. The thickness can be calculated by deposition time.

XRD was used to determine information of phase microstructure of the as-received and BN-coated fibers, and the results were shown in Fig. 4. The peak position and intensity of XRD are mainly depended on the grain sizes. The XRD patterns of the as-received SiC fibers show three main peaks at 35.79°, 60.13° and 71.9°, which are assigned to the (111), (220) and (311) planes of the β-SiC, respectively. The XRD peaks at 26.1° and 41.89° of BN-coated fibers are indexed as the planes of the h-BN. Such a peak shape means that the grain size of BN is very small.

![Figure 4. XRD patterns of the as-received and BN-coated fibers (deposition time 30 min).](image)

![Figure 5. The TEM of BN-coated fibers (deposition time 30 min).](image)
Figure 5 shows the TEM morphology of BN interphase on SiC fibers and the detailed structure of the BN interphase could be observed. The result showed that the BN interphase is mainly turbostratic and there are present nanometer-sized randomly oriented areas. Combined with XRD results, it can be concluded that the grain size of h-BN is very small and its main structure is long-range disordered structure.

3.2. Tensile strength and Weibull distribution

The monofilament tensile strength of the as-received and BN-coated SiC fibers was tested to evaluate effect of BN interphase on mechanical property of SiC fibers. The two-parameter Weibull distribution, which is widely used to describe tensile strength of brittle materials, was adopted for evaluation of the strength distribution[12]. The results of the Weibull distribution of as-received and BN-coated fibers are shown in Fig.6. The results of the Weibull analysis are given in Table 1. The results show that the fibers with 86 nm BN have the higher tensile strength than as-received fibers. However, when the interphase's thickness is higher than 330 nm, the tensile strength of fibers begins decrease. The fibers with 86 nm BN interphase had the highest tensile strength of 2.63 GPa. It is difficult to get the sufficient tensile date for the fibers with 1450nm BN thickness due to that the fibers were bound together by the thick interphase. The number of this fibers for test was not sufficient for the Weibull analysis.

The tensile strength of fibers depends on the strength of their weakest points. Weibull modulus (m) not only reflects the distribution of strength, but also essentially reflects the number of defects in SiC fibers. The larger the Weibull modulus means that the fewer defects in SiC fibers and the lower the dispersion of strength. The m value of 86 nm BN-coated fibres was higher than that of uncoated fibers, indicating lower defects in SiC fibers. This showed that BN interphase can heal the cracks on the surface of fibers[13-15]. The tensile strength of the solid material depends on the crack size of the material according to the formula (1):

$$\sigma = \frac{2E\gamma}{\pi C}^{1/2}$$

In which, $\sigma$, $E$, $\gamma$, $C$ are the tensile strength of fibers, elastic modulus, surface energy and crack size on the surface of fibers respectively. It can be seen from the formula that the tensile strength is inversely proportional to the crack size. The SiC fibers were obtained from the pyrolysis of polycarbosilane (PCS), so small cracks occurred on the surface of fibers. These cracks inevitably affect the tensile strength of fibers. The thin layer of BN can reduce the crack size and alleviate the stress, thus improving the tensile strength of SiC fibers (as shown in Figure 7).

| BN thickness | Diameter/μm | m  | $\sigma_0$ | $\sigma$/GPa | E/GPa | CV/% |
|--------------|-------------|----|-----------|-------------|-------|------|
| 0            | 12.93       | 6.10| 2.70      | 2.51        | 226.65| 18.54|
| 86           | 13.12       | 6.48| 2.82      | 2.63        | 227.53| 16.72|
| 330          | 13.51       | 5.96| 2.58      | 2.40        | 225.21| 19.36|
| 620          | 14.03       | 6.72| 2.24      | 2.09        | 215.72| 15.56|
| 1450         | -           | -  | -         | -           | -     | -    |

The strength decreased with increasing BN interphase thickness and the over 330 nm BN-coated fibers showed lower strength than the as-received fibers. The BN interphases increase strength by healing the surface flaw, conversely, the soft nature of the BN interphase results in the decrease of strength with thickness increasing. The relationship between tensile strength and diameter of fibers can be calculated according to the formula (2):

$$\sigma = 4P_{\text{max}}/\pi D^2$$

In which, $\sigma$, $P_{\text{max}}$, $D$ are the tensile strength of fibers, maximum load and diameter of the fibers respectively. It can be seen that the tensile strength is inversely proportional to the square of diameter.
Therefore, for the tensile strength of the BN-coated fibers, it is a competition between the healing effect and the diameter growth effect. For the 86 nm BN-coated fibers, the healing effect was dominant, as indicated by the higher strength than in the as-received. In the case of the 330 nm BN-coated fibers, for which the diameter of the fibers was 13.51 μm, the strength loss by the diameter effect started to overcome the healing effect; thus, the strength of BN-coated fibers was lower than the as-received fibers. For the 625 nm BN-coated fibers, strength was more affected by the diameter effect. Therefore, the tensile strength of coated fibers illustrated that the BN coating with appropriate thickness increased the mechanical properties of SiC fibers. It can be seen from table 1 that the elastic modulus of the coated fibers with different BN thickness did not change significantly. Elastic modulus is an intrinsic characteristic of materials. Its physical essence indicates the size of the binding force between atoms. The greater the binding force between atoms, the higher the elastic modulus. The elastic modulus reflects the average interatomic bond strength. There are many factors that affect the elastic modulus of fibers, such as the diameter, grain size, particle inclusion, flaws, maximum crack length and so on. The composition of fibers and grain size did not change significantly during the deposition process due to the low deposition temperature (~900 °C).

Figure 6. The Weibull curves of tensile strength of the fibers with different BN thickness.

Figure 7. Weibull probability density distribution of the fibers with different BN thickness.
The cumulative failure probability density curves of as-received and BN-coated fibers are obtained, as shown in figure 7. It can be seen that the tensile strength of the BN-coated fibers conforms to the two parameters Weibull distribution. At the same time, it was found that the strength distributions of the as-received and 330 nm BN-coated fibers were mainly concentrated in the range of 1.5~3.5 GPa. The strength distribution of 86nm BN-coated fibers was a little higher, concentrated in the range of 2~3.5 GPa. While the strength dispersion of 625nm BN-coated fibers was significantly lower than that of other fibers, concentrated in the range of 1.5~2.5 GPa.

4. Conclusions
The uniform and dense BN interphase was successfully deposited on the SiC fibers by CVI and the different thicknesses were prepared by deposition time. The BN interphase is mainly turbostratic with nanometer-sized randomly oriented areas. The 86 nm BN-coated fibers showed a little higher tensile strength than as-received fibers due to the healing of the surface flaw. While the 330nm or higher BN-coated fibers showed a lower strength than the as-received, the increasing thickness decreases the strength.

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