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Mechanical properties of Si_3N_4/BN fibrous monolithic ceramics at elevated-temperature

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The mechanical properties at high temperature of Si_3N_4/BN fibrous monolithic ceramics were tested. The flexural strength of SiC whisker reinforced Si_3N_4/BN fibrous monolithic ceramics from 25°C to 1200°C were investigated. The strength degraded slowly from 1000°C to 1200°C which was different to Si_3N_4 monolithic ceramics. The creep behaviors of the material at different temperatures were characterized. Si_3N_4/BN fibrous monolithic ceramics possess high creep resistance. The chemical composition and microstructure of the composites were analyzed by XRD and SEM.

1. Introduction
Silicon nitride-based ceramics possess excellent high temperature strength, oxidation resistance, good thermal shock resistance, low density and low coefficient of thermal expansion [1, 2]. These properties make them ideal candidate materials for high temperature applications, such as aerospace structures and turbine engines. However, the nature of brittleness and thereby the lack of damage tolerance is one of the most crucial problems in their applications.

In recent years, fibrous monolithic ceramics is developed to improve the toughness of ceramic by changing the structure of composites [3–7]. The mechanical properties were investigated at elevated temperature in this paper.

2. Experimental procedure
The fabrication methods for producing fibrous monoliths have been described in detail elsewhere [8]. The cell material was prepared Si_3N_4 (Founder High-Tech ceramic Corp., China) powders with 8 wt% Y_2O_3 (purity $> 99.9\%$), 2.5 wt% Al_2O_3 ($>99.9\%$) and 1.5 wt% MgO ($>99.9\%$) added as sintering aids and 20 wt% SiC whisker. Hexagonal boron nitride and Aluminum oxide was used to fabricate the cell boundaries.

The test specimens were cut into 4 mm × 3 mm × 36 mm or 4 mm × 6 mm × 36 mm rectangular bars, then polished with diamond pastes down to 7 μm. Edges were chamfered to 45° to remove inadvertent edge damage from cutting.

The flexural strength of testing material was measured by three-point bending method with the specimen of 4 mm × 3 mm × 36 mm, and the fracture toughness was measured by single edge notched beam (SENB) method with the specimen of 4 mm × 6 mm × 36 mm with a notch 2.5 mm in deep. The creep testing was conducted using a creep tester which consisted of three-point bend test fixture of α-SiC, Loads were applied to the upper ram via a lever arm having a 5 : 1 leverage ratio. Load-point deflections to center-point deflections of creeping specimens were measured directly using LVDT. In experiment, the rate of rising temperature was 500°C/h, and before the load was applied, the time of keeping temperature was 15 minutes. After tested, the tensile zones of the crept specimens were examined using XRD to determine the phases in materials and scanning electron microscopy to characterize the creep deformation mechanisms.

3. Results and discussion
3.1. Mechanical properties at room temperature
The flexural strength of Si_3N_4/BN monolithic ceramic at room temperature was 705.4 ± 61 MPa, and the fracture toughness was 20.17 ± 1.17 MPa·m$^{1/2}$.

The result indicated that the fibrous monolithic structure could improve the toughness of ceramic greatly, so changing the structure of the material was an effective method to improve the mechanical properties.

3.2. The flexural strength at high temperature
The strengths of testing material at different temperatures were given in Fig. 1. It could be seen from the figure that the flexural strengths of Si_3N_4/BN fibrous monolithic ceramic were almost unchangeable from 25°C to 1200°C. The flexural strength of Si_3N_4 monolithic ceramic degraded obviously above 1000°C, but the flexural strength of Si_3N_4/BN monolithic ceramic possess not only the high strength and toughness at ambient temperature but also kept high strength at elevated temperature. The excellent properties of fibrous

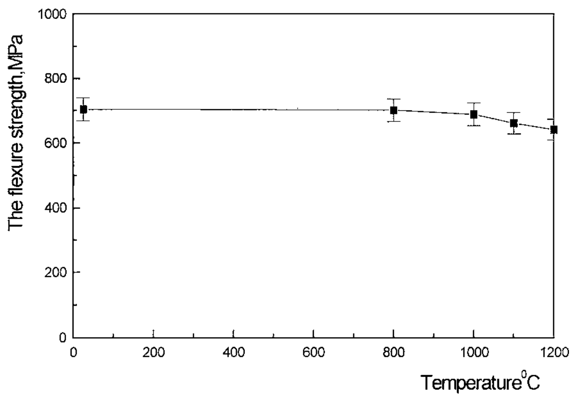

Figure 1 The strengths of testing material at different temperatures.

monolithic ceramic provided a method for design the material structure.

3.3. The creep resistance

The creep deform recorded during the experiment was center deflection. In the ceramic samples deform with the three-point bending, if the integrate and physics nonlinear was not considered, the center deflection W and the maximum strain ε_m existed that:

$$\varepsilon_m = \frac{6WH}{L^2}$$

where L was span, H specimen height. According to this equation, the center deflection W could transform to creep strain. Figs 2–4 showed the correlation between the creep strain and time at different temperatures under different stresses.

The creep curves indicated that creep failure occurred either in the initial stage of creep when the creep rate was high or in the second stage of creep after a long time when the creep rate slowed down considerably. Another obvious feature exhibited by these creep curves is their extensive primary creep and the lack of tertiary creep. There was a substantial primary creep response, which, in fact, accounts for most of the measured strain. From the figures, it could be seen that the materials possessed excellent resistance to creep.

The creep could regard as a heated active process controlled by the stress. The vitreous phases of the crystal boundary increased softening which leaded to the crystal boundary slippery and produced creep. Due to the

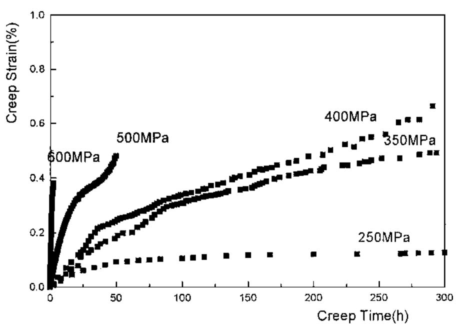

Figure 2 Typical three-point bend creep curves at 1000°C under variety of stresses.

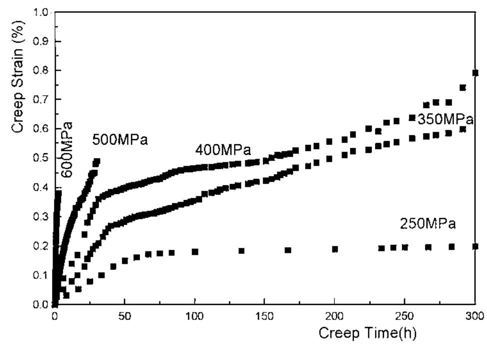

Figure 3 The creep curves at 1100°C under different stresses.

sintered assistance and impurity almost diffuse to the interlayer BN whose structure was loose and had the capacity to absorb glass during the sintered process, the crystal boundary in the matrix was cleaned. Because of the crystal purified [9, 10], the materials possessed high creep resistance. As is known to all, BN was unstable in the air atmosphere at high temperature and was easy to oxide. At 1200°C, Most of BN began to oxide, and formed boride oxide. The boride oxide reacted with aluminum oxide and made the loose structure compact, so the property at elevated temperature was excellent. The viscosity of the glass in the BN interlayer was degraded and occurred the viscosity flow and produced stress concentration that made to increase the neighboring phase plastic deform and resulted in fracture.

3.4. The effect of the structure and composition at the elevated temperature on mechanical property

From Fig. 5, It could be seen that there are mainly Si_3N_4 and SiC and BN peaks and little of the others peaks at 1000°C and 1100°C, but there existed BN diffraction peak, meanwhile the $2Al_2O_3{\cdot}B_2O_3$ diffraction peak can be seen, which indicated that BN began to oxide and form B_2O_3. The B_2O_3 reacted with Al_2O_3 and resulted in $2Al_2O_3{\cdot}B_2O_3$ at 1200°C. Through the Al_2O_3-B_2O_3-SiO_2, we could verify that the reaction existed. Fig. 6 showed the phases diagram of Al_2O_3-B_2O_3-SiO_2

$$4BN(s) + 3O_2 \rightarrow 2B_2O_3(l) + 2N_2(g)$$

$$2Al_2O_3 + B_2O_3 \rightarrow 2Al_2O_3 \cdot B_2O_3$$

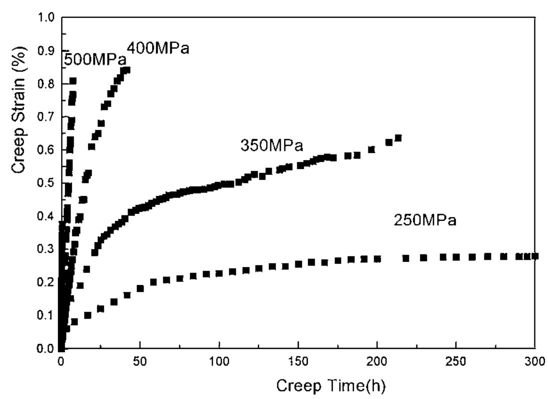

Figure 4 The creep curves at 1200°C under different stresses.

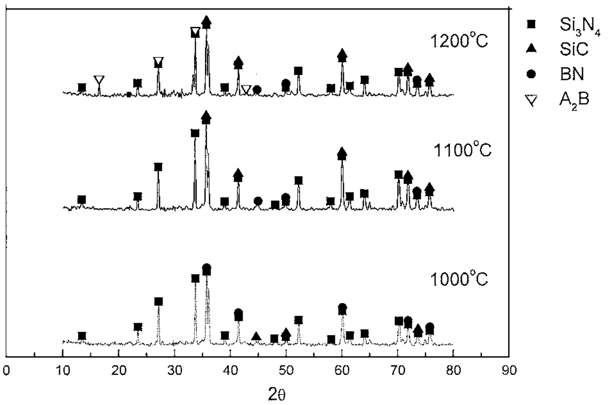

Figure 5 The X-ray diffraction pattern of Si_3N_4/BN fibrous monoliths after creep tests at different temperatures.

The $2Al_2O_3{\cdot}B_2O_3$ formation strengthened the combination between BN and Si_3N_4, which was the main reason that the materials possessed the high strength and excellent resistance creep.

3.5. Microstructure observations and analysis

In order to study the property at high temperature of the Si_3N_4/BN fibrous monolithic ceramic, the microstructure was observed and analyzed. Fig. 7 showed the morphology of the fibrous monolithic ceramic after creep at 1000°C, and Fig. 8 showed the fracture surfaces of the specimens.

The Si_3N_4/BN fibrous monolithic ceramic was made by extrusion process and hot pressing, the whiskers became aligned such that the major axes were preferentially oriented perpendicular to the direction of pressing. Whisker orientation affected the strength and fracture toughness of this material; therefore its effect on creep deformation was investigated [15]. In the case of whisker-oriented alignment, most of whiskers were perpendicular to the crack plane, i.e. parallel to the direction of stress, so that whiskers could effectively transfer stress and develop well. Consequently, debonding and whisker pulling-out in this case would

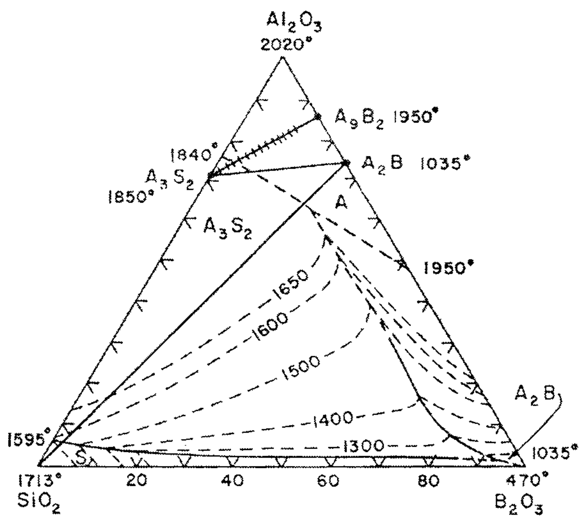

Figure 6 The phases diagram of Al_2O_3-B_2O_3-SiO_2.

Figure 7 SEM microstructure of samples after creep at 1000°C.

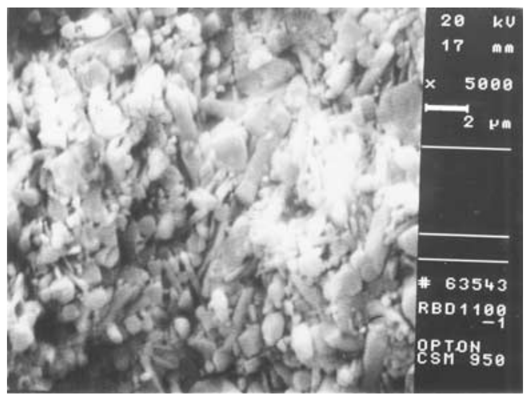

Figure 8 Fracture surfaces of samples after creep at 1000°C.

be observed. The bridging ligaments carried part of the applied load by bridging the crack faces, leading to the reduction of the effective driving stress of crack growth. The whisker improved the creep resistance greatly. From the figures, it could be seen that there was little glass on the Si_3N_4 crystal boundary that agreed the analysis before. From the fracture surface photo, it was found that the crystal particles were smooth and the glass existed. The glass on the BN interlayers softened lead to the interlayer sliding and resulted in creep. The creep micro mechanism could be regarded as the "hard cell" and "soft cell boundary" sliding slowly under continues stress.

4. Conclusions

1. Si_3N_4/BN monolithic ceramic possessed not only the high strength and toughness at ambient temperature but also kept high strength at elevated temperature. The flexural strength of Si_3N_4/BN fibrous monolithic ceramics were almost unchanged from 25°C through 1200°C. The Si_3N_4/BN fibrous monolithic ceramic possess excellent elevated mechanical property.

2. Si_3N_4/BN fibrous monolithic ceramics had high creep resistance at different temperatures.

3. The XRD indicated that BN cell boundary began to oxide at 1200°C, and formed to $2Al_2O_3{\cdot}B_2O_3$.

Due to the reaction, the materials became compact and improved the property of the materials. SiC whisker pulling-out improved the creep resistance greatly.

4. The microstructure by SEM of the fibrous monolithic ceramic indicated that Si_3N_4 pillar crystal and SiC whisker had better orientation and BN cell boundary had capacity to absorb glass and purify the Si_3N_4 grain boundary. These were the main reasons that the materials possessed the high mechanical property at elevated temperature and excellent creep resistance.

Acknowledgements
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