Preparation and properties of fibrous monolithic ceramics by *in-situ* synthesizing

GUO HAI, HUANG YONG, WANG CHANG-AN
State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, People's Republic of China
E-mail: hy-dms@mail.tsinghua.edu.cn

Preparation processes of fibrous monolithic ceramics *in-situ* synthesized is a simple and cheap way to make ceramics with high performance. In this paper, the process of *in-situ* synthesizing Si_3N_4 fibrous monolithic ceramics and the main factors which affect properties of the material were investigated in detail. It is found that the reinforcing effect comes from the synergism of the toughening in two different scale. One is the oriented growth of grains or oriented distribution of whiskers in the fibrous cells. The other is the effect of the special fibrous monolithic structure formed by the weak interfaces between fibrous cells. The results showed that the fractural toughness of the fibrous monolithic ceramics can reach 23.95 MPa $\cdot$ $m^{1/2}$ at room temperature.

1. Introduction

Ceramic fiber reinforced ceramic matrix composite (CMC) have been certified to be an effective method of making ceramics with high performance. But many disadvantages exist, for example, it is very expensive and complex in the processes of making ceramic fibers and composites.

At 1988, Coblenz [1] invented a novel and powerful method to fabricate ceramic fibers. Ceramic powders were mixed with some organic binder into a plastic mixture, then green fibers can be conveniently made by spinning (or extruding) the mixtures. Binder gives the green fibers sufficient strength of resistance to breaking. The green fibers will change to polycrystalline ceramic fibers through sintering. This method can lower the cost of making fibers and at the same time it is very convenient to control the diameter and structure of fibers.

To design ceramic macro- and micro-structure, green fibers were used to instead of ceramic fibers in making fiber reinforced CMCs. Green fibers were placed in graphite die by means of a specially designated arrangement way, but without any matrix, only with some thin interface to separate them. And then arranged green fibers were HP sintered into bulk materials. This material was made up of *in-situ* synthesized fibers which acted as its basic structure units. Each unit was separated by a thin interface. We call this materials as *in-situ* synthesized fibrous monolithic ceramics which is first introduced by Basharan [2–6]. This materials has a special micro structure which has strong fibrous cell units and weak interfaces that can induce crack propagation and improve toughness [7]. At the same time, because fibers were *in-situ* synthesized after sintering, the structure of materials can be easily designed by controlling the fiber's diameter and its arrangement.

Preparation of green fibers is an important step for making *in-situ* synthesized fibrous monolithic ceramics. It is easy to design the inner-structure of fibers due to its obviously anisotropy. Kiyoshi [8] have developed a novel process to control the microstructure of self-reinforced silicon nitride. The key point of this process is that size and distribution of elongated large grains are controlled by seeds of rodlike β-Si_3N_4 single crystals which are preferred orientation through tape-casting. For silicon nitride ceramics fabricated by this method, fracture toughness was improved up to 11.1 MPa $\cdot$ $m^{1/2}$. In our experiments, the fabrication of green fibers was attempted by extruding of raw powders with rodlike β-Si_3N_4 seeds or SiC whiskers. It is expected to have more orientation than tape-casting and a further improvement of fracture toughness should be attained.

2. Experimental

The preparation process of *in-situ* synthesized fibrous monolithic ceramics is illustrated in Fig. 1.

Firstly, powders of α-Si_3N_4 (the properties were listed in Table I; Founder High Tech. Ceramic Corp., China) with 7 wt % Y_2O_3 (purity > 99.9%, Hokke chemicals, Japan), 3 wt % Al_2O_3 (purity > 99.9%) and 20 wt % SiC whisker (TWS-400, Hokke chemicals, Japan) or 3 wt % β-Si_3N_4 seeds were milled for 24 hours in alcohol medium. The β-Si_3N_4 seed particles were prepared by heating powder mixture of α-Si_3N_4, Y_2O_3 and Al_2O_3 at 1850 °C for 1.5 hours under nitrogen pressure of 0.5 MPa [9]. Synthesized seed particles consist of high pure rodlike β-Si_3N_4 single-crystal particles with an average diameter of 0.5 μm and an average length of 4.0 μm.

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TABLE I Properties of raw Si_3N_4

Powder	Average particle size (μm)	Specific surface area (m^2/g)	Main impurity content in the powder (wt %)					
			Si	N	O	Fe	Al	Ca
TH-1	0.69	9.9	60	33.4	5.52	0.53	0.26	0.10

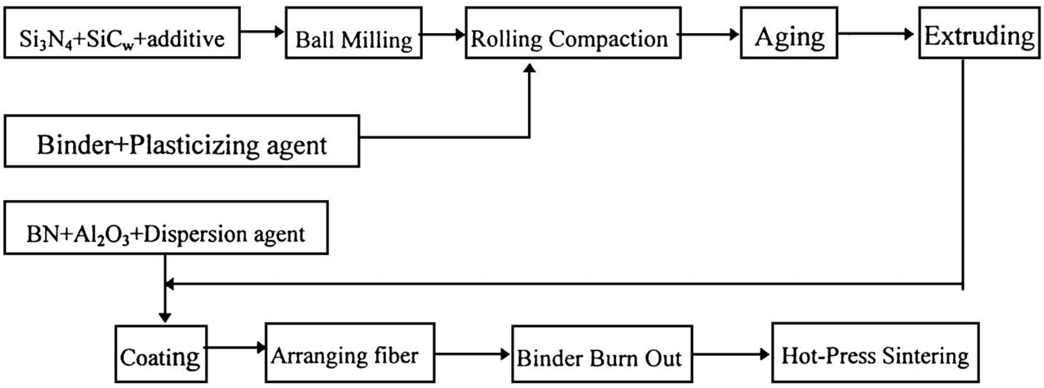

Figure 1 Flow chart describing fabrication procedure of *in-situ* fibrous monolithic ceramics.

Subsequently, the ceramic powders milled were mixed with 10 wt % organic polymer binders (PVA) and 3 wt % plasticizing agent (glycerine), and then repeatedly rolled turning into a well-distributed plastic mixtures. Next, the mixtures were put into a cylinder with a piston, and forced through orifices with different diameter (1.0 mm, 0.7 mm, 0.5 mm, 0.3 mm) to form green fibers respectively.

The green fibers were coated by dipping in a slurry containing 75 wt % BN and 25 wt % Al_2O_3. The coated fibers were dried in the air and arranged in certain order into a graphite die. (The thickness of the coating depends on the concentration of the slurry and dipping time. Fig. 2 shows a 40 μm thick coating on Si_3N_4 green fiber). Uniaxial alignment of coated green fibers were used in this report.

The body with green fibrous undergoes a conventional binder burnout through heating at 260 °C for 2 hours, and then to 400 °C for 4 hours. The body removed binder was hot pressed at 1800 °C for 1.5 hours under N_2 atmosphere.

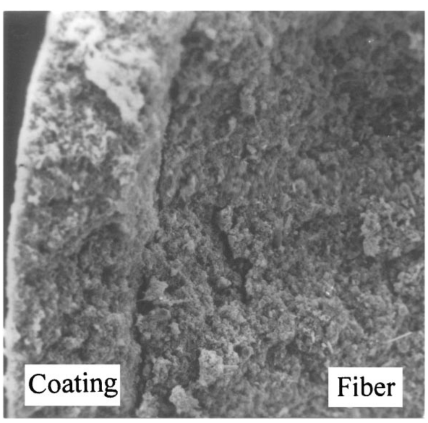

Figure 2 Micrograph of the cross-section of a Si_3N_4 green fiber after coated BN.

The microstructure of the composite was examined by SEM (CSM900). The specimens were sliced into test bars (3 mm × 4 mm × 32 mm for bending strength and 4 mm × 6 mm × 32 mm for fracture toughness) which are parallel to the layout direction of fibers. Three-point bending testing carried out at room temperature with a span of 30 mm, crosshead rate of 0.5 mm/min. Fracture toughness was determined by the single-edge-notch-beam method at room temperature with a crosshead rate of 0.05 mm/min.

3. Results and discussions

3.1. Micro-structure of fibrous monolithic ceramics

The microstructure of *in-situ* synthesized Si_3N_4/BN -Al_2O_3 fibrous monolithic ceramic is illustrated in Fig. 3. On the two side planes of the specimen, which is paralleling to the pressed direction, fibers which are arranged in uniaxially direction regularly could be obviously observed (Fig. 3a). At two end planes of the specimen, it could be seen that the cross section of the cells seems more like a hexagon rather then like a round as shown in Fig. 3b. Note that the cells are not single crystallic fibers, but rather domains of polycrystalline Si_3N_4. The cell boundary phases BN acts as a weak interface, while the cells and the interfaces are separated clearly. Fig. 4 shows SEM photographs of Si_3N_4 fibrous cells. An obviously one-dimensional orientation of elongated grains and whiskers can be seen.

3.2. Mechanical properties of fibrous monolithic ceramics

The mechanical properties of *in-situ* synthesized fibrous monolithic silicon nitride with seeds or whiskers are summarized in Table II. It is found that the diameter of green fiber has an obviously effect on the properties of bulk material (Fig. 5). The strengths decrease

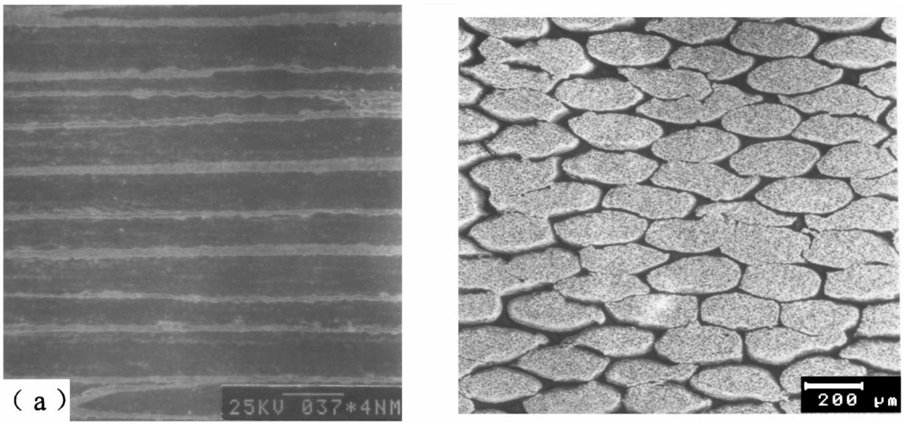

Figure 3 Micrograph of the *in-situ* Si_3N_4/BN fibrous monolithic ceramics (a) side planes paralleling to the pressed direction, (b) end planes of ceramics.

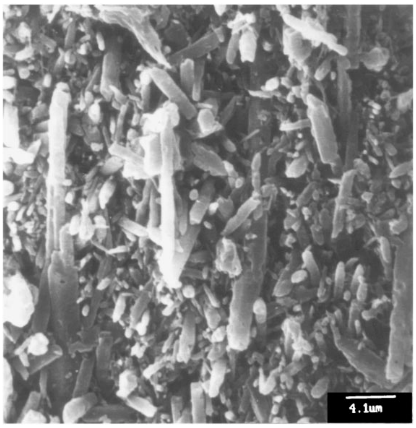

Figure 4 SEM observation of Si_3N_4 fibrous cells with whiskers.

TABLE II Mechanical properties of *in-situ* Si_3N_4 fibrous monolithic ceramics

	Add seeds		Add whisker	
Diameter of green fiber (mm)	σ (MPa)	K_{IC} ($MPa \cdot m^{1/2}$)	σ (MPa)	K_{IC} ($MPa \cdot m^{1/2}$)
1.0	689.3	8.98	705.4	20.01
0.7	602.1	11.52	678.1	22.56
0.5	562.4	14.11	639.7	22.96
0.3	530.6	17.16	619.8	23.95

with increasing the diameters of green fibers, and the toughness increase with increasing diameters of green fibers. Along with the decreasing of the diameter of green fibers, the cell scale also decreased. At the same time, as the thickness of the interface keeps almost unchanged, the fraction of the weak interface will be increased with the decreasing of the diameter of green fiber, which leads that more energy can be absorbed by the propagation of cracks, and K_{IC} is obviously improved. However, the strength of materials will decreased with the increasing of the weak interface.

In order to improve mechanical properties of *in-situ* synthesized fibers, whiskers are added to the fibrous cells of the monolithic structure. The results show that the bending strength can be improved obviously and the fracture toughness can be raised up to more than 20 $MPa \cdot m^{1/2}$. The cells are not single crystal fibers but rather polycrystalline ceramic domains. The whisker acts as reinforcements in fibrous cells just as it does in a bulk ceramics, Therefore the adding of whisker strengthens the basic structure unit and plays an obstructing role for the propagation of cracks, which can lead an improvement of properties of materials.

A typical load-deformation curve for this system is shown in Fig. 6. It can be seen that the *in-situ* synthesized fibrous monolithic ceramics revealed unusual and potentially useful fracture behavior. Failure in flexure occurred in a non-catastrophic manner. The load which leads to crack development and breaking of composites will increase with the decreasing of diameter of green fibers. The material becomes more reliable and its apparent work-of-fracture evaluated from the load-deformation curve reaches a potential level of more than 4000 J/m^2.

3.3. Crack propagating behavior

Fig. 7 showed a typical crack propagation manner of the *in-situ* fibrous monoliths. As shown in Fig. 7a, a major crack propagates through the specimen under tensile. Sometimes the major crack progresses through fibrous cells to the next interface, sometimes it extends along the interface between fibrous cells. A branch-like crack can remarkably be observed in Fig. 7b.

In addition, pull-out and debonding of whiskers inside the cells can be seen from this Fig. 7c. Therefore, the propagation and extension of the crack inside the cell can also take place so as to enhance toughness and strength of the materials. This phenomenon is almost same as in a bulk material.

4. Conclusions

1. Through fibrous monolithic structure design, the toughness of materials can be improved greatly.

2. The oriented growth of grains and oriented distribution of whiskers can be gotten by a extrusion technique, which lead to further improvement of fracture toughness up to 23.95 $MPa \cdot m^{1/2}$ due to their reinforcing effect in fibrous cells. The apparent work-of-fracture can reach to 4000 J/m^2.

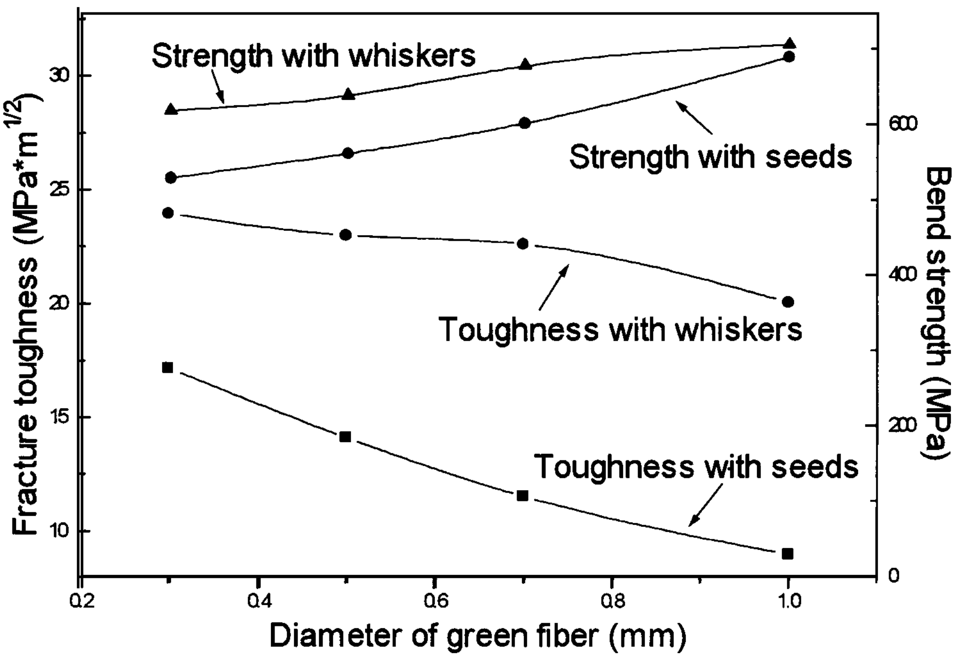

Figure 5 Mechanical properties of *in-situ* Si_3N_4 fibrous monolithic ceramics.

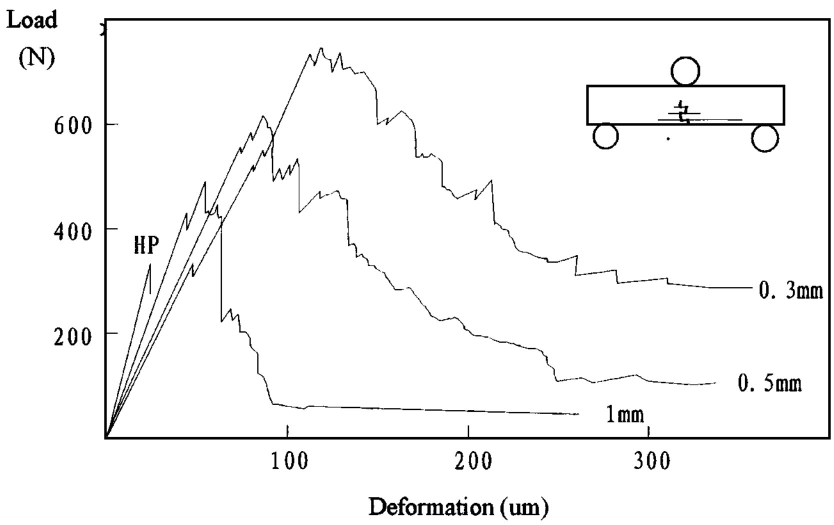

Figure 6 Typical load-deformation curve of *in-situ* fibrous monolithic ceramics.

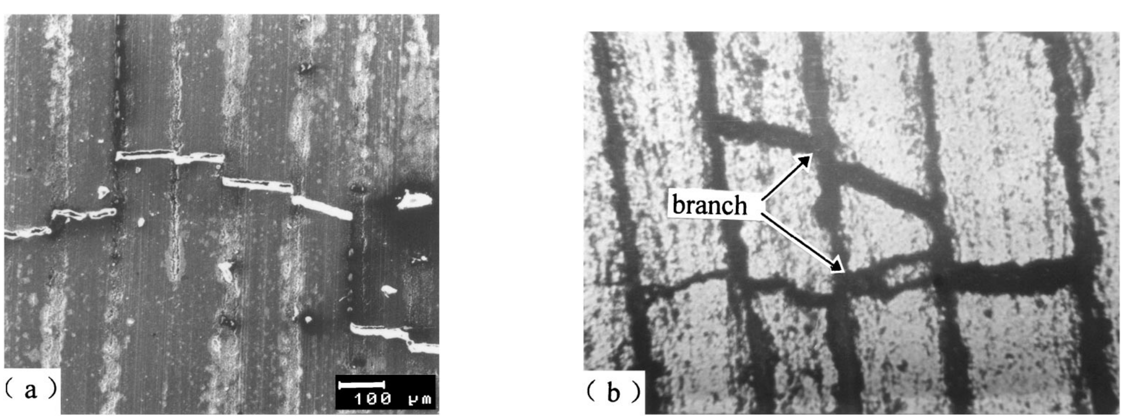

Figure 7 SEM micrograph of crack propagation in *in-situ* fibrous monolithic ceramic (a) major crack (b) branch-like crack (c) pull-out and debonding of whiskers inside the cells.

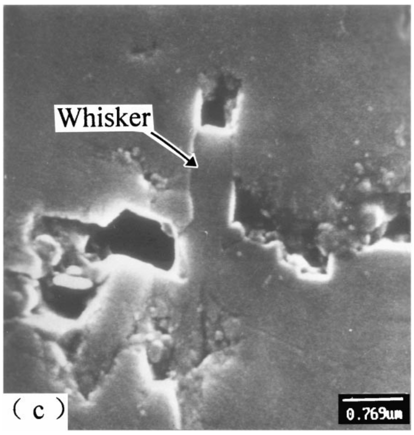

Figure 7 (*Continued*).

3. The reinforcing effect comes from the synergism of the toughening in two different scale, one is the oriented growth of grains or oriented distribution of whiskers in the fibrous cells, the other is the effect of the special fibrous monolithic structure formed by the weak interfaces between fibrous cells.

Acknowledgements

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