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Biomimetic structure design — a possible approach to change the brittleness of ceramics in nature ☆

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Abstract

Based on the analysis on structure of natural biomaterials, two kinds of ceramic composites with high toughness have been designed and prepared: one is fibrous monolithic Si_3N_4/BN composite imitating bamboos or trees in structure, the other is laminated Si_3N_4/BN composite imitating nacre in structure. Plastic forming methods, including extrusion and roll compaction, respectively, followed by hot-pressed sintering are used to prepare these two materials with particular structures. Both of the two composites have high values of fracture toughness and work of fracture: fracture toughness are 24 MPa $m^{1/2}$ and 28 MPa $m^{1/2}$, respectively, for fibrous monolithic and laminated Si_3N_4/BN composites, and works of fracture are both more than 4000 J/m^2. The load-displacement curves reveal that these two materials with biomimetic structure exhibit non-brittle feature when applied load to fracture. Through analysis on fractographs of the materials, it is revealed that high toughness comes from the synergistic toughening among multi-level toughening mechanisms in different scales: weak interfaces, whiskers and elongated grains toughening in ceramic matrix cells.

Keywords: Biomimetic structure; Fibrous monolithic; Laminated; Si_3N_4/BN composites

1. Introduction

A major problem in the service of ceramics as structural materials is their brittleness. Even though many attempts have been used to increase their toughness, including incorporation of fibers, whiskers or particles reinforcements, and ZrO_2 phase transformation reinforcing, etc., up to date the brittleness of ceramics has not been overcome in nature. It seems that it is impossible for conventional ways to solve this problem.

On the other hand, in the research on the structure of natural biomaterials, such as bamboos, trees and nacres, it has been found that these natural biomaterials have very reasonable structures which gives them many excellent properties, such as good carrying capacity, good toughness, self-healing, and so on. Furthermore, these biomaterials have very fine and special structures rather than complicated compositions, which are distinctly different from what we seek for ceramic materials with high toughness through composition control. For example, trees and bamboos are typical long, fiber-reinforced composites. Their fibers have different sizes and arranged modes in structure so that they can display the optimal behaviors under tensile, bending, compressing stress and other applied load. Another typical biomaterial is nacre, the structure of which is laminated with brick wall structure. It consists of more than 99 vol.% inorganic phase, aragonite wafers, and less than 1 vol.% organic phase, mortar of proteins. This particular configuration imparts over one order of magnitude higher bending strength and toughness than those of aragonite single crystals. The work of fracture of nacre is 3000 times higher than that of pure aragonite [1]. So, the complicated and reasonable structure of natural biomaterials can give us an important insight into making better structure materials through biomimetic design.

Coblenz [2] in 1988 put forward a fibrous monolithic structure imitating the structure of trees or bamboos. In the structure, fibrous polycrystalline cells are arranged parallel, and separated and combined by very thin interfacial phase. Baskaran et al. [3] in 1993 firstly prepared SiC/C fibrous monolithic structure ceramics according to the

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above design mode. Clegg et al. [4] in 1990 reported a pioneer work of preparing a laminated SiC composite separated by graphite layers, so that very high toughness and flaw tolerance were obtained: 15 MPa $m^{1/2}$ of fracture toughness and 4625 J/m^2 of work of fracture. In recent years, much attention has been paid to biomimetic structure ceramics and many good results and opinions have been obtained [5–7].

In the present paper, according to the structures of trees or bamboos and nacres, we designed and prepared two kinds of ceramic composites with high toughness, fibrous monolithic and laminated composites, and a lot of active results were achieved.

2. Experimental procedure

Ceramic raw powders (Si_3N_4, β-SiC whiskers and sintering aids) were mixed with organic binder (PVA), plasticizing agents (glycerine) and lubricant (liquid paraffin) and then repeatedly rolled, turning into a well-distributed plastic mud pie. Fibrous green bodies (green fibers) were obtained through extrusion. The mud pie was extruded through orifices with different diameters (1.0, 0.7, 0.5 and 0.3 mm) to form green fibers. Laminated green bodies (green sheets) were obtained through roll compaction. The green bodies (fibers or sheets) were then coated by dipping in slurry containing mainly BN. The coated green bodies were dried in air and arranged in a certain order into a graphite die and hot-pressed at 1800°C/1.5 h/22 MPa pressure under flow N_2 atmosphere. In addition, rod-like β-Si_3N_4 seeds (3 wt.%) or β-SiC whiskers (20 wt.%) were added into Si_3N_4 matrix cells for further toughening. Al_2O_3 or Si_3N_4 was added into the BN interfacial phase for the purpose of adjusting the interfacial bonding state between Si_3N_4 matrix cells.

Bending strength was determined by three point bend testing (test bars $4 \times 3 \times 36$ mm^3). The tensile surface of the samples was polished with diamond paste down to 1 μm and the long edges of the tensile surface were rounded. Fracture toughness was measured by SENB method (test bars $4 \times 6 \times 30$ mm^3), and the width of the notch was less than 0.25 mm. The curve of load-displacement and work of fracture of the specimen were determined using an A-2000 Shimadzu universal materials testing machine with a crosshead speed of 0.05 mm/min. The microstructure of specimens was observed with SEM.

Table 1
Mechanical properties of in-situ fibrous monolithic Si_3N_4/BN composites

Average diameter of green fiber (mm)	Add seeds		Add whiskers	
	σ_f (MPa)	K_{IC} (MPa $m^{1/2}$)	σ_f (MPa)	K_{IC} (MPa $m^{1/2}$)
1.0	689.3 ± 68	8.98 ± 1.04	705.4 ± 71	20.01 ± 1.17
0.7	602.1 ± 62	11.52 ± 0.98	678.1 ± 62	22.56 ± 1.01
0.5	562.4 ± 51	14.11 ± 1.00	639.7 ± 60	22.96 ± 0.88
0.3	530.6 ± 42	17.16 ± 1.02	619.8 ± 47	23.95 ± 0.92

Table 2
Mechanical properties of laminated Si_3N_4/BN composites

Average thickness of green layers (mm)	Average thickness of matrix layer after sintering (mm)	σ_f (MPa)	K_{IC} (MPa $m^{1/2}$)
0.2	0.087	709.51 ± 89.61	28.90 ± 4.14
0.4	0.13	740.64 ± 78.94	28.40 ± 4.49
0.8	0.36	518.93 ± 112.94	18.75 ± 4.41
1.6	0.61	704.09 ± 127.19	9.55 ± 1.49
3.2	1.31	572.50 ± 73.02	11.67 ± 3.53

3. Results and discussion

3.1. Mechanical properties

Table 1 summarizes the mechanical properties of fibrous monolithic Si_3N_4/BN ceramics. It can be found that the fibrous monolithic Si_3N_4/BN ceramics have very high toughness compared with conventional monolithic Si_3N_4 ceramics. Table 2 shows the mechanical properties of laminated Si_3N_4/BN ceramics with different thickness of matrix layer in which 20 wt.% SiC whiskers were added. It can be seen that the laminated Si_3N_4/BN ceramics can reach more than 28 MPa $m^{1/2}$ of fracture toughness.

In Tables 1 and 2, it can be seen that the size of the matrix cells (fiber or layer) obviously has an effect on the properties of the composites. With the decrease in the size of matrix cell, the fracture toughness of the composites is markedly improved while the bending strength has no obvious change. Moreover, in literature [4,7] the bending strength of this kind of ceramic with weak interfacial phase at room temperature was considerably reduced due

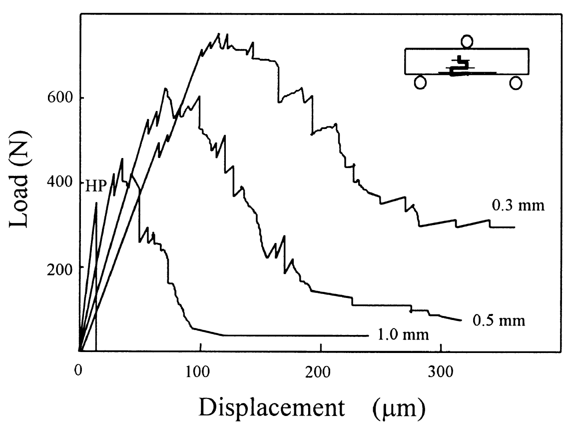

Fig. 1. Typical load-displacement curve of fibrous monolithic Si_3N_4/BN composites.

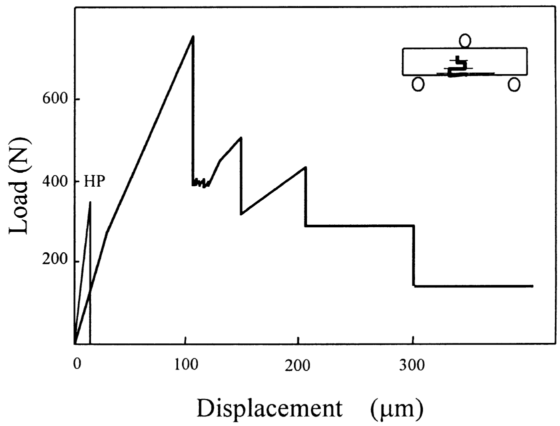

Fig. 2. Typical load-displacement curve of laminated Si_3N_4/BN composites.

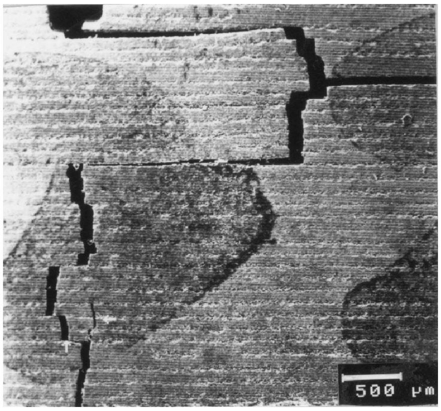

Fig. 4. Microstructure of laminated Si_3N_4/BN composites.

to the presence of weak separating interfacial phases. However, in the present paper, the mechanical properties can be improved obviously by adding whiskers or seeds into the matrix phase.

3.2. Curve of load-displacement and work of fracture

Fig. 1 and Fig. 2 are curves of load-displacement for fibrous monolithic Si_3N_4/BN ceramics and laminated Si_3N_4/BN ceramics, respectively. Compared with monolithic Si_3N_4 ceramics, fibrous monolithic Si_3N_4/BN ceramics and laminated Si_3N_4/BN ceramics exhibit a non-brittle failure manner while the conventional monolithic Si_3N_4 fractures catastrophically. Furthermore, the size of the matrix cell has an obvious influence on the mechanical performance as shown in Fig. 1. According to the area covered by the curves of load-displacement, work of fracture for two biomimetic materials can be calculated as more than 4000 J/m^2 in general, while that of monolithic Si_3N_4 ceramics is only 100 J/m^2 or so. Hence, it may be inferred that the mechanical performance of ceramic materials can be substantially improved by special biomimetic structural design.

3.3. Microstructure and multilevel toughening mechanisms

Fig. 3 displays the microstructure of Si_3N_4/BN fibrous monolithic ceramics. On the two sides planes of the specimen fibers, which are arranged in uniaxial direction regularly, can be observed (Fig. 3a). At two end planes of the specimen, it can be seen that the cross-section of the cells are more like an hexagon, just like Coblenz's design mode [2]. Fig. 4 shows a photograph of crack propagation of laminated Si_3N_4/BN ceramics, which exhibits a laminated structure and crack deflection. Note that the cells (fibers or layers) are not single crystals but domains of polycrystalline Si_3N_4. The BN interfacial phase acts as cell boundary phase to separate the cells.

The common characteristic of the two biomimetic composites is that the strong matrix cells and the relative weak interfacial phases are arranged alternately with each other. There are multilevel toughening mechanisms in different

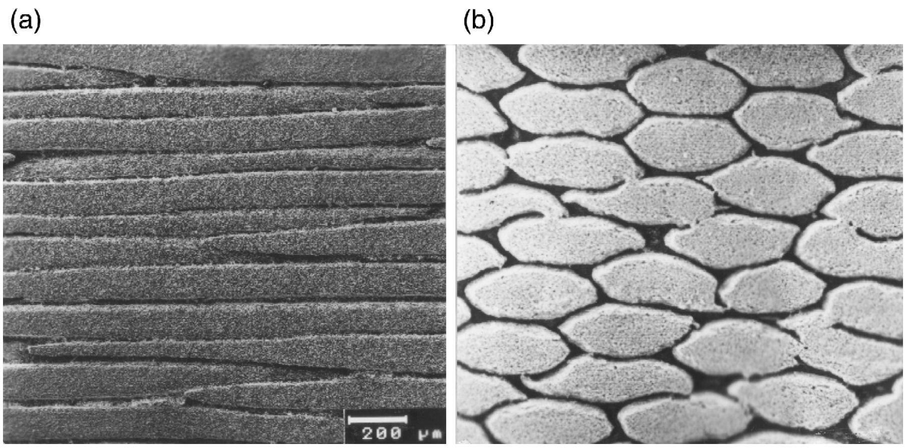

Fig. 3. Microstructure of fibrous monolithic Si_3N_4/BN composites.

scales in these kinds of composites: the 1st-grade toughening mechanism is weak interfacial layer toughening, which is considered as the main reason for the very high toughness of the composites; the 2nd-grade toughening mechanism is whisker toughening in the matrix cells; and the 3rd-grade toughening mechanism is elongated Si_3N_4 grain toughening in the matrix cells. The synergy of multilevel toughening mechanisms leads to fairly high toughness and work of fracture of the composites [8].

4. Conclusion

According to the structures of trees and nacres, two kinds of biomimetic structure ceramic composites, fibrous monolithic and laminated structure Si_3N_4/BN composites, have been successfully prepared with more than 20 MPa $m^{1/2}$ of high toughness and 4000 J/m^2 of work of fracture. The load-displacement curves show that both of the composites exhibit non-brittle fracture properties. The size of the structure cell (fiber or layer) is an important structure parameter influencing the mechanical behavior of the composites. The synergy of multilevel toughening mechanisms, weak interfacial phase toughening, whisker toughening and elongated matrix grain toughening leads to fairly high toughness and work of fracture of the composites.

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