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Fabrication and properties of laminated Al_2O_3/TiC composites

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Abstract

High solid content Al_2O_3–TiC slurries for tape casting were obtained by selecting the appropriate solvent, dispersant, binder, and other organic additives. Some factors which affected the viscosity of the slurries, such as the TiC:Al_2O_3 ratio, pH value and the dispersant concentration, were discussed. Al_2O_3–TiC laminated composites with weak interfaces can be obtained after laminating and stacking the tapes, binder removal and hot-pressing the green body. Compared with the monolithic composite, the crack propagation in the Al_2O_3–TiC laminated composites showed a large scale deflection and multi-fracture, which increased the work of fracture of the laminates significantly. The results showed that the laminated structure was an effective way to improve the fracture toughness and the work of fracture of the composites.

Keywords: A. Tape casting; Laminated composite; Slurry; Viscosity

1. Introduction

Tape casting is a low cost and useful process for preparing thin ceramic sheets. It has been widely used to produce ceramic substrates, multilayer capacitors, solid oxide fuel cells etc. [1–5]. In addition to the advantages which all other slurry processes have, tape casting has several other potential benefits, which are not easily achieved by conventional powder processing. Tape casting allows us to meet specific requirements for structural design by using tapes of different compositions and thicknesses. Tape casting is a very convenient and useful method for preparing a laminated composite. It has been recently used to design laminated structural composites with improved mechanical properties, because the laminated composites, such as Si_3N_4–BN, SiC–C, and mullite–Al_2O_3, offers many advantages for improving the fracture resistance (high fracture toughness and work of fracture, etc.) and total fracture toughness [6–8]. Laminated composites with weak interfaces are most suitable for this purpose. Catastrophic failure is avoided in these composites because crack propagation is arrested at the weak interface, and the work of fracture significantly increases. Matsui et al. [9] used tape casting to fabricate SiC-whisker-reinforced 20 wt.% Si_3N_4-matrix composites with a high degree of orientation and K_{IC} values as high as 9.5 MPa $m^{1/2}$. The high-temperature bending strength of these composites was 1180 MPa at 1250°C, twice that of Si_3N_4 alone, and the fracture toughness was also higher than that of Si_3N_4. Chartier and Rouxel [10] used tape casting to fabricate an Al_2O_3/ZrO_2 laminated composite with residual surface compressive stresses to increase the bending strength from 380 to 560 MPa and the fracture toughness from 3.7 to 8.0 MPa $m^{1/2}$. Huang et al. [11] designed a Si_3N_4–TiN/Si_3N_4–Si_3N_4 trilayered composite with residual surface compressive stress which resulted in improved mechanical properties. During tape casting, some particles with an anisotropic morphology (e.g. whiskers and platelets) would be aligned as they passed the doctor blade and a preferential alignment in SiC whiskers [12] or platelet reinforced Al_2O_3 [13] matrix composites have been obtained. The objective of this study was to prepare laminated structural Al_2O_3–TiC composites to improve the mechanical properties, and some factors which effected the slurry properties, such as dispersant concentration, pH value, etc., are discussed.

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2. Experimental procedure

High-purity Al_2O_3 powder with an average particle size of 0.48 μm and a specific area of 5.7 m^2/g (Shanghai Wushen Chemical plant, Shanghai China) and TiC powder with an average particle size of 0.1 μm and a specific surface area of 10 m^2/g (Chendu Institute of Organic Chemistry, Chinese Academy of Science, Sichuan Chen Du, China) were used in the experiment. A triglyceride was used as the dispersant and polyvinylbutyral (PVB) as a binder; dioctylphthalate and glycerol were used as plasticizers, and a mixture of ethanol and trichloroethylene was used as the solvent.

The Al_2O_3 and TiC powders were mixed with the triglyceride dispersant and the ethanol/trichloroethylene mixture (volume ratio of 3:1) in a polyethylene jar and then ball-milled for ~20 h using Al_2O_3 balls as the grinding media. The binder and plasticizers were then added to the slurry, and the mixture was ball-milled for another 16 h. The ball-milled slurry was degassed under vacuum, to remove any gas bubbles, cast onto a glass substrate, and naturally dried. The tapes were cut into 40×50 mm squares. In order to control the resulting stresses between the interfaces, a SiC/C slurry was used to paint the tape surfaces, the solid content of the slurry was 30 wt.%, [50 wt.% SiC (particle size 2.1 μm) + 50 wt.% C (particle size 3.5 μm) without any other organic addition], the solvent was ethanol. After stacking, laminating and binder removal, the laminated green body was hot-pressed at 1700°C and 30 MPa. The samples were machined to 2.5×5×26 mm bars for measuring the three-point bending strength with a 20 mm span; 5×2.5×26 mm bars were prepared for measuring the fracture toughness using the single-edge-notch-beam method (20 mm span, notch beam width 0.25 mm) and 3×4×26 mm bars for measuring the work of fracture with a V-type notch. The mechanical properties were measured using an Instron-1195 testing machine. The microstructure and the crack propagation of the composites were analyzed using a SEM and an optical microscope. The viscosity of the slurries was measured with a NDJ-7 type viscometer.

3. Results and discussion

3.1. Dispersant and solvent

The criterion for the solvent selection depends mainly upon the solubility of the binders, plasticizers, and other organic additives. In order to get a well-dispersed and stable slurry, the relation between the powder, solvent, dispersant and other additives has to be considered. The ceramic powders must be chemically stable and should not react with the organic additives. Although water is a common solvent, some ceramic powders, such as nitrides, and carbides can react with water and form oxidized thin films on the surface of the particles during long time ball-milling. Therefore, water is rather difficult to use as a solvent to prepare a non-oxide slurry for tape casting. An organic solvent, which has a low boiling point and high vapor pressure, is preferred for the preparation of a slurry for tape casting. On the other hand, most organic solvents have a low dielectric constant, and are flammable and toxic. The low dielectric constant makes the ion concentration decrease and the electrostatic energy is not large enough to make a stable slurry. In order to overcome some deficiencies of a single solvent, a mixture of solvents or binary azeotropic solvent mixtures are often used to obtain good dielectric properties, a low boiling point as well as a good solublility for the organic additives. TCE(trichloroethylene)/EtOH(ethanol) [14], MEK(methyl ethyl ketone)/EtOH [20] mixtures are often selected as solvents in tape casting. Normally, the dispersants can be classified into four groups based on their charges on the surface active part of the molecule, (1) non-ionic (2) anionic (3) cationic and (4) zwitterionic. Triglycerides, zwitteric molecules, are often used in Al_2O_3 [15] and ZrO_2 [16] tape casting processing. In this experiment, a mixture of TCE/EtOH and triglycerides were chosen as the solvent and dispersant respectively.

3.2. Properties of the slurry

According to the DLVO theory [17], van der Waals forces and repulsive forces originate in the double electrical layers surrounding the particles. Because the counterions have a strong influence on the diffuse double electrical layer, moreover, the surface charge of the particles are dependent on the pH value, the concentration of the other specifically adsorbed ions and the ionic strength of the slurry; therefore, the adjustments in the pH value and the ionic strength are helpful to obtain a high surface charge density which results in a strong double-layer repulsion; the electrostatic repulsion is responsible for particles far from the point of zero charge of the powder and result in well-dispersed ceramic slurries. Although the electrostatic repulsion energy in non-aqueous media is less than that in water due to the low ionic concentration and the low dielectric constant, the electrostatic repulsion energy in a nonaqueous slurry is important, even if the nonaqueous ceramic slurry is stabilized by a steric mechanism. In this experiment, the pH value of the mixture solvent, trichlocthylene and ethanol (volume rate is 1:3), was about 8.67. After adding Al_2O_3 and TiC, the pH value of the mixture solvent has changed. Table 1 shows the effect of the dispersant and the powder on the pH value of the solvent. It is obvious that the dispersant and powders have an effect on the pH value of the slurries in the TCE/EtOH mixture. The electrophoretic results showed that the Al_2O_3

particles and the TiC particles exhibited a positive surface charge and a negative surface charge, respectively. However, after the dispersant is added, the Al_2O_3 particle surface charge changed to negative. The organic molecules absorbed on the surface of the powder changed the property of the surface charge, therefore, the electrostatic energy which affected the stabilization of the nonaqueous slurries cannot be ignored. The effect of the dispersant concentration on the viscosity of the slurries is shown in Fig. 1. With increasing concentration of the dispersant, the viscosity of the Al_2O_3–TiC slurry goes through a minimum. For the different ratios of TiC and Al_2O_3, the minimum viscosity value for the slurries was different. The effect of the pH value on the viscosity of the Al_2O_3–TiC slurries are shown in Fig. 2. The viscosity of the slurries decreased and then increased with increasing pH, but the value of the viscosity had a close relation to the weight ratio of TiC and Al_2O_3. The pH value for the minimum viscosity of a 30 vol.% solid content slurry (weight ratio of TiC and Al_2O_3 45:55, and 35:65) was about 5, 6. Because the particle size of the TiC was much smaller than that of Al_2O_3, and the rheological properties of TiC and Al_2O_3 are different for the same solids content, the viscosity of all slurries increased as the ratio of TiC and Al_2O_3 increased and was sensitive to the pH value variation. Since the composition of the slurry is very complex, it is difficult to explain precisely what are the main factors affecting the viscosity. From the results of the influence of the pH value and the dispersant concentration on the viscosity of the slurries, it was clear that the slurry was stabilized by an "electrosteric" mechanism.

Table 1
Effects of dispersant and powder on the pH value of the solvent

Powder	pH (without dispersant)	pH (with dispersant)
Al_2O_3	7.76	7.31–7.44
TiC	5.08	4.54–5.02
Al_2O_3/TiC	5.78	5.43–5.26

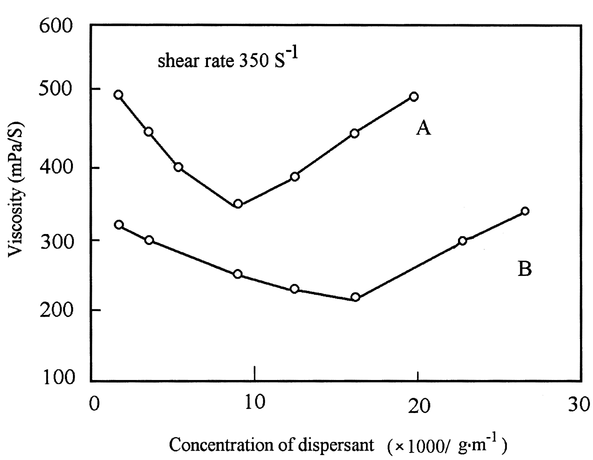

Fig. 1. Effect of the dispersant concentration on the viscosity of slurries A: TiC: Al_2O_3 (35:65) 35 vol.%, B: TiC: Al_2O_3 (25:75) 25 vol.%.

3.3. Tape preparation

There are many factors which affect the properties of green tapes, such as solid content, the amount of organic, the ratio of the binder and plasticizers, temperature as well as vapor pressure of the solvent etc. Table 2 shows the formulation of the Al_2O_3–25 wt.% TiC slurry used in the experiment. A green tape with good flexibility, and without bubbles and cracks could be obtained. Theoretically, the less the organic addition, the better the densification and the mechanical properties of the composites; if the amount of binder and plasticizers was too low, it was difficult to acquire a perfect green tape or the green tape was very brittle. However, a large amount of organic cannot produce a well-dispersed slurry. The air is trapped in slurry and forms bubbles which cannot be removed by ultrasonifiction and vacuum degassing. During slurry drying, the bubbles will form defects and cracks, so the preparation of a uniform slurry is very important for controlling the microstructure of the green tape. Slurry drying is another important process to

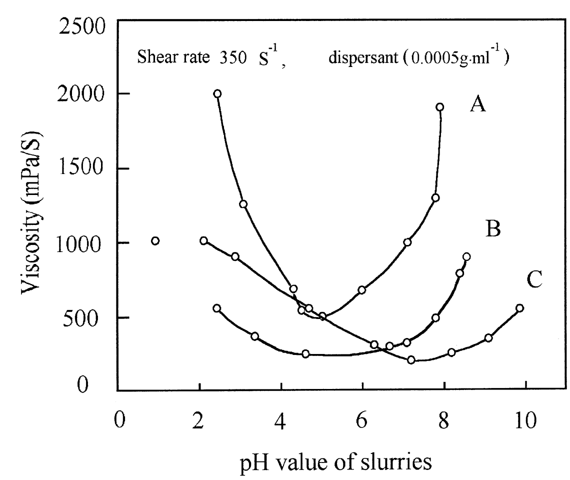

Fig. 2. Effect of the pH value of slurries upon viscosity of Al_2O_3–TiC A: TiC: Al_2O_3 (45:55) 30 vol.%, B: TiC: Al_2O_3 (25:75) 25 vol.%, C: TiC: Al_2O_3 (35:65) 30 vol.%.

Table 2
Formulation of Al_2O_3–25 wt.% TiC slurry

Materials	Composition (wt.%)	Function
Al_2O_3/TiC	52.5	Powder
$Mg(NO_3)_2$ $6H_2O$	1.5	Grain growth inhibitor
PVB	2.9	Binder
Triglyceride	2.1	Dispersant
Trichloroethylene/ethanol	37.9	Solvent
Glycerol/dioctylphthalate	3.1	Plasticizer

control the microstructure of the green body. If the solvents evaporate too quickly, drying shrinkage can cause the disappearance of the evaporating channels and leads to a polymeric skin on the surface of the tape, while the underlying slurry is still in the liquid state; when the solvent vapor evaporates then from the bottom of the tape, cracks can form easily. If the solvents evaporate too slowly, a density gradient can form in the tape. In this experiment, the slurries were dried in a closed chamber at room temperature without any flowing air. The proper solvent vapor pressure can prevent tapes from forming cracks by fast drying and a density gradient due to slow drying.

3.4. Binder removal

The binder removal process has an effect on the microstructure of the green body. If the organic additives decompose too fast, the green tape may be warped, surface craters and bubbles form. In order to find the optimum heating rate, the binder removal process was determined by TGA. TGA curves of the Al_2O_3–TiC tape are shown in Fig. 3. TGA data were obtained in an argon atmosphere using rates of 1°C/min and 5°C/min. The evaporation of solvent from the tapes occurs from room temperature to about 100°C; the organic additives decomposition start about 100°C and was completed at about 600°C. The shapes of the two curves with different heating rates are similar. However, the decomposition of the organic additives occurred at a lower temperature when the heating rate was reduced. This behavior is similar to that mentioned by Scheiffele [18] in the Al_2O_3/PVB system. The shapes of the curves were similar to those in a previous report of the author [19]. The binder removal procedure was very complex. Shih et al. [19] reported that during the decomposition of PVB various products can be detected at different temperature ranges. From 300 to 400°C, the main products were water and butyraldehyde. When the temperature was above 500°C, a variety of aromatic compounds were detected, including benzaldehyde, phenol, acetophenone etc. In this experiment, there were several kinds of organic additives in the green tape; therefore it can be deduced that the decomposition products are even more complex. Based on the TGA measurements, the binder removal process for the laminated composite green bodies at a heating rate of 1°C/min was used and the temperature then kept at 800°C for 3 h to insure that all the organic additives decomposed completely.

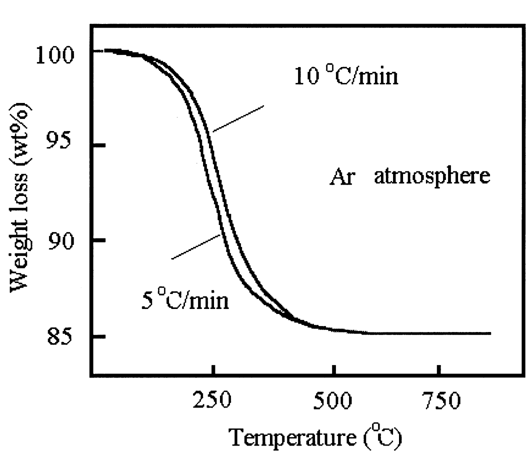

Fig. 3. TGA curves of Al_2O_3–25 wt.% TiC tape binder removal.

3.5. Effect of pressure, pH value and the TiC content on the green body density

The density of the green body (after binder removal), as a function of the pressure is shown in Fig. 4. The green body density increased with the pressure increase, and the experimental results were consistent with the previous observations of Kevin [20]. The green body density, after binder removal, as a function of the TiC content is shown in Fig. 5. The green density decreased as the TiC content increased, because TiC has a small particle size and a large specific surface, which absorbed more organic additives and decrease the density of the green body. The relation between the pH value and the green density is shown in Fig. 6. In general, the green density decreased as the pH value of the slurry increased.

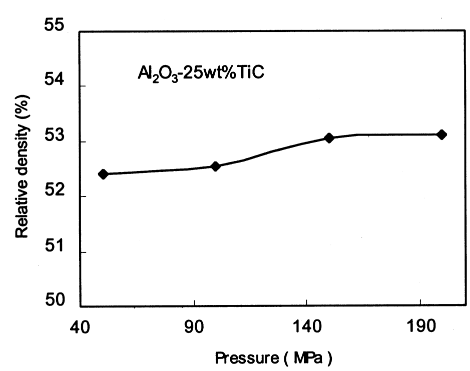

Fig. 4. Green density, after binder removal, as a function of pressure.

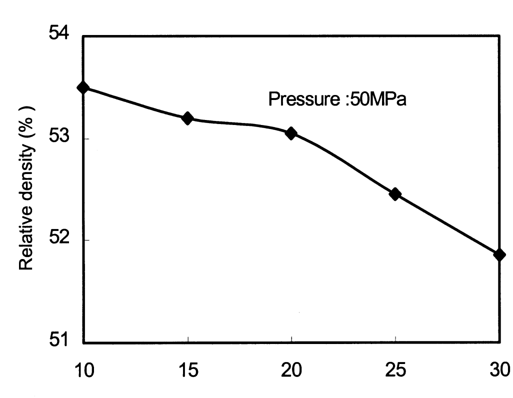

Fig. 5. Green density, after binder removal, as a function of TiC content.

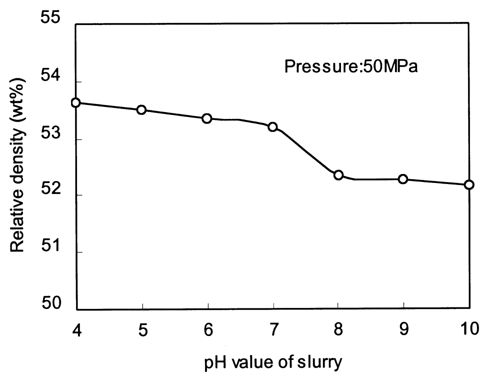

Fig. 6. Relationship between the pH value and the green density.

Table 3
Mechanical properties of Al_2O_3–25 wt.% TiC composites

Method	Fracture toughness (MPa $m^{1/2}$)	Bending strength (MPa)
Monolithic	5.65	762
Laminated structure	5.78	605

When the pH value of the slurry was above 7, the green body density had a rapid decrease, which was in accordance with the change in viscosity of the slurry ; the higher the viscosity of slurry, the lower the green body density.

3.6. Mechanical properties and the work of fracture

In order to compare the differences between the monolithic composite and the laminated composite, the monolithic Al_2O_3–25 wt.% TiC composite was also prepared with Al_2O_3/TiC mixed powder and hot pressing at 30 MPa and 1700°C. The mechanical properties of the Al_2O_3–25 wt.% TiC laminated composite with the SiC/C weak interface and the monolithic Al_2O_3–25 wt.% TiC composites are listed in Table 3. The bending strength and fracture toughness of the laminated composite Al_2O_3–25 wt.% TiC with weak interfaces were 605 MPa and 5.78 MPa $m^{-1/2}$ respectively. The bending strength and fracture toughness of the monolithic composite were 762 MPa and 5.65 MPa $m^{-1/2}$ respectively. From these results, the laminated structure was effective for improving fracture toughness, but the degree was not very large as other paper mentioned [9,10]. Fig. 7 shows an optical micrograph and a SEM micrograph of the Al_2O_3–25 wt.% TiC laminated composite. The thickness of the SiC/C interface was about 2 μm, it was difficult to obtain a high density in the SiC/C at sintering temperature, resulting in weak interfaces in the laminated composite; when cracks propagated and met the weak interfaces, the main crack was deflected and the crack branched under the stresses. Because the main crack deflection and branching can absorb a large amount of energy, it was useful to improve the fracture toughness.

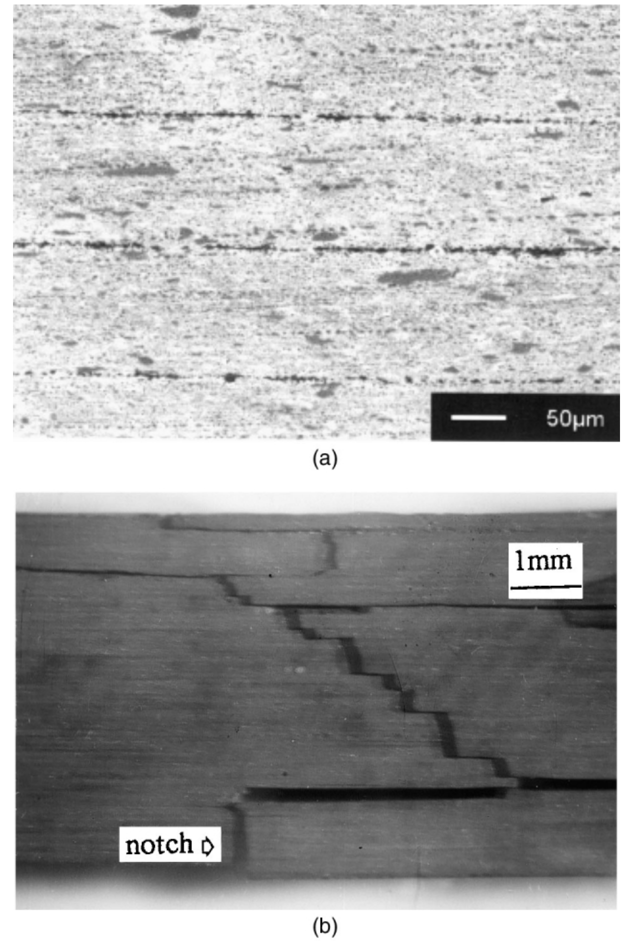

Fig. 7. SEM and optical micrographs of the Al_2O_3–25 wt.% TiC laminated composite: (a) SEM micrograph, (b) optical micrograph.

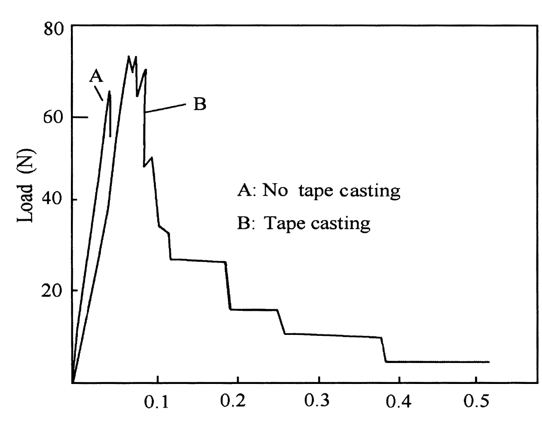

Fig. 8. Load-deflection curves for Al_2O_3–25 wt.% TiC composite tested as notch specimens in three-point bending.

However, many weak interfaces existed in the laminated material which will lead to a bending strength decrease.

Fig. 8 is the load-deflection curves for the Al_2O_3–25 wt.% TiC monolithic composite and Al_2O_3–25 wt.% TiC laminated composite tested as notch specimens in three-point bending. In laminated structure non-catastrophic crack growth occurred as long as the crack reached an interface and the crack was deflected along the interface. The work of fracture of the laminated composite and the monolithic composite determined from the area under the load-deflection curves were 52.4 and 584 J/m^2 respectively. The results showed that the work of fracture of the laminated structure was almost 11 times higher than that of the monolithic composite.

4. Conclusion

Al_2O_3–TiC laminated composites with a weak interface can be obtained by tape casting and hot-pressing. Although dispersed in an organic solvent, Al_2O_3 and TiC powders can effect significantly the pH value of the solvent . For the same solid content, the viscosity of the slurries increased with an increasing TiC:Al_2O_3 ratio and was more sensitive to the change of pH value of the slurry. The green density decreased with an increase in the pH value and the TiC:Al_2O_3 ratio. The TGA analyses indicated that all the organic additives in tapes can be removed above 600°C. Due to the weak interfaces in the laminated composite cracks propagated along these interfaces and allowed stress relaxation; the fracture toughness can be improved; the work of fracture of the laminated composite was about eleven times higher than that of the monolith composite. These results indicated that the laminated structure design might be effective for advanced ceramics to improve fracture resistance.

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