Mechanical Behaviors of $\text{Si}_3\text{N}_4\text{-SiC/Si}_3\text{N}_4\text{-Si}_3\text{N}_4$ Layered Composites

Ding-Fwu LII, Jow-Lay HUANG* and Feng-Chi CHOU*

*Department of Electrical Engineering, Chinese Naval Academy, Kaohsiung, Taiwan, 813 R.O.C.***Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan, 701 R.O.C.* $\text{Si}_3\text{N}_4\text{-SiC/Si}_3\text{N}_4\text{-Si}_3\text{N}_4$ 層状複合体の機械的挙動

李 丁福・黄 肇瑞*・周 峯吉*

海軍官校電機系，中華民國台灣省高雄市左營區

*國立成功大學材料科學及工程學系，中華民國台灣省台南市大學路一號

The present study involves the fabrication of three-layered ceramics with an interior layer of $\text{SiC/Si}_3\text{N}_4$ which has a greater thermal expansion coefficient than the two outer surface layers formed of monolithic Si_3N_4 . Surface compressive stress develops upon cooling owing to the higher thermal expansion coefficient of the inner layer. The bending strength and toughness of layered Si_3N_4 composites are substantially greater than those of monolithic Si_3N_4 because of the surface compressive stress on the outer layer and crack deflection by the interfaces. The residual stress increases with the addition of SiC in the inner layer and with the inner layer thickness. Crack behavior in layered samples is affected by the residual stresses, interfaces and free sample surfaces. Theoretical stress calculated based on beam theory is compared with the experimentally determined residual stress.

[Received November 27, 1995; Accepted May 15, 1996]

Key-words: Si_3N_4 , SiC , Layer, Composites

1. Introduction

Silicon nitride is one of the best ceramic materials for structural applications, mainly because of its excellent mechanical, thermal, and chemical properties. Many potential applications are, however, still limited by its lack of toughness and reliability. Ceramic-reinforced Si_3N_4 has drawn considerable attention over the past decade because of substantial improvements in its properties. The toughening materials investigated, such as SiC , TiC , WC , TiN , and TiB_2 ¹⁾⁻⁵⁾ have the morphology of particulates, platelets, whiskers and fibers.⁶⁾⁻⁹⁾

Silicon carbide is extensively used for reinforcing alumina^{10),11)} and silicon nitride^{12),13)} on account of its high modulus, excellent mechanical properties and chemical inertness. There have been no reports of obvious chemical reactions between SiC and ceramic matrix due to its chemical inertness.

Ceramic materials with layered microstructure, which exhibited a significant improvement in fracture toughness, strength and tolerance to flaws, have recently been reported.¹⁴⁾⁻¹⁷⁾ Laminar composites containing layers of Ce-ZrO_2 and Al_2O_3 have been fabricated using a colloidal technique that resulted in increased toughness.¹⁸⁾⁻²⁰⁾ Moya et al. used sequential slip casting to develop a new family of dense functionally gradient ceramics with tailored microstructures and properties.²¹⁾ Abe and Yamada used centrifugally pressed multilayer composites to strengthen the layer interface by introducing a compositional gradient. The strengthened layer interface contributed to crack deflection and possibly crack pinning at the layer interface.²²⁾

Watanabe and Kimura²³⁾ prepared two-layered hybrid composites containing different amounts of SiC whiskers in alumina, by hot pressing. Outstanding improvement in the strength and fracture toughness due to the thermal expansion mismatch was reported. Philipps et al.^{24),25)} manufactured specimens by viscous processing of SiC powder into sheets, which were then laminated with thin carbon interlayers and sintered in nitrogen. The most promising approach for the improvement of toughness lies in controlling the critical strain energy release rate and the thickness of individual

laminar.

Substantial enhancement in strength by the introduction of surface compressive stress has been documented in numerous materials.^{17),26),27)} The toughness and sensitivity to surface flaws were also considerably increased due to hindrance of crack propagation by the residual surface compressive stress.^{28),29)}

The present study involves the fabrication of three-layered composite ceramics consisting of outer layers that contain Si_3N_4 , and an inner layer that contains SiC in Si_3N_4 matrix. Surface compressive stress develops upon cooling owing to the higher thermal expansion coefficient (CTE) and Young's modulus of SiC in the inner layer. By controlling the inner layer thickness and the composition of SiC , the depth of the compression zone and the level of compressive stress can also be tailored.³⁰⁾

In this study, the effects of SiC composition and inner layer thickness on the mechanical properties of layered composites were investigated and compared with those of monolithic Si_3N_4 . The crack behaviors in layered composites, especially near the interfaces, were investigated. Microcracking indentation was used for examining the gradient of residual stress. Experimental results were compared with theoretical calculations derived from beam theory.

2. Experimental procedure

2.1 Sample preparation

Silicon nitride powder (H.C. Starck, LC-12N) with particle size of $0.6\ \mu\text{m}$ was mixed with yttria (Molycorp, 5603, 6 mass%) and alumina (Alcoa, 16SG, 2 mass%) in a polyurethane bottle with high-purity alumina balls and ethanol for 23h. The ratio of ball to charge was 8 : 1. Silicon carbide (Cerac, S-1058, 10 and 20% of total volume) with particles size of $7.0\ \mu\text{m}$ was dispersed by means of an ultrasonic probe in ethanol, then added to the Si_3N_4 slurry, and they were milled for another 1h. The slurry was immediately dried in a rotating vacuum condenser. Dried agglomerates were ground with an alumina mortar and pestle to pulverize aggregates and screened through a 100-mesh screen.

Green sample layers were formed using a steel die (≈ 50

mm) by applying a biaxial pressure of 10 MPa. The layer compacts were then stacked in a sequence of Si₃N₄, SiC/Si₃N₄, and Si₃N₄ in a graphite die, and hot pressed at 1850°C for 1h at 24.5 MPa in nitrogen atmosphere (High Multi 5000, Fuji Dempa). The total thickness of hot-pressed layer composites is 3 mm.

2.2 Characterization

Samples for testing bending strength were machined into bars with dimensions of 3 × 4 × 45 mm and polished to 6 μm before conducting a four-point bending test using a universal testing machine (Shimadzu Corp., AGS-500D) at a loading rate of 0.5 mm/min. Sample edges were chamfered before testing for the purpose of minimizing variation due to stress concentration. The inner and outer spans used for testing were 10 and 30 mm, respectively. Each data point was the average of measurements from more than eight samples.

Fracture toughness was measured by the surface indentation technique following Evans and Charles' derivation.³¹⁾ Samples were finely polished to 1 μm before forming a microhardness indentation at 30 kg for 15 s.

Both an optical microscope and scanning electron microscopy (SEM; Hitachi Ltd., S-2500) were used to examine the crack propagation behaviors, especially near the interfaces. X-ray microprobe analyzer (XMA) mapping was used for elemental analysis to identify the location of interfaces.

3. Results and discussion

3.1 Stress distribution in three-layered samples

The elastic modulus (*E*) and thermal expansion coefficient (*α*) of materials used in this study are shown in Table 1. The thermal expansion coefficient of SiC is greater than that of Si₃N₄. The layered samples therefore have an interior layer of SiC/Si₃N₄ with a greater coefficient of ther-

mal expansion than the two outer surface layers formed of monolithic Si₃N₄. After the hot-pressed body was cooled to room temperature, the outer layer was compressed in the direction parallel to the interfaces, and extended perpendicular to the interfaces.^{17),30),32)-34)} A qualitative, two-dimensional representation of residual stress upon cooling is shown in Fig. 1.

3.2 Mechanical properties

3.2.1 Bending strength

The bending strength of layered samples was measured as a function of the inner layer thickness, as shown in Fig. 2. Samples with inner layer thicknesses of 0 and 3 mm indicate monolithic Si₃N₄ and single-layered SiC/Si₃N₄, respectively. The layered samples consistently exhibited higher strength than that of monolithic silicon nitride. Examination of fractured surfaces indicated that part of the crack propagation path deviated along the interface before final failure. A typical optical micrograph revealed uniform distribution of SiC particulates in Si₃N₄ matrix. No evidence of chemical reactions between SiC and Si₃N₄ was observed, and no obvious process or differential microcracks were detected at the layered interfaces (Fig. 3).

3.2.2 Fracture toughness

The fracture toughness of layered samples containing 10 and 20 vol% SiC in the inner layer is shown in Fig. 4. Toughness was enhanced by 44 to 52% in Si₃N₄-SiC/Si₃N₄-Si₃N₄ samples relative to that of monolithic silicon nitride. This improvement was especially pronounced in samples containing 20 vol% SiC.

3.2.3 Effects of residual stress on the crack behavior

In order to understand the distribution of residual stress

Table 1. Physical Properties of Materials Calculated Based on the Simple Rule of Mixture

	Si ₃ N ₄	SiC	SiC/Si ₃ N ₄	
			10 Vol%	20 Vol%
E(Gpa)	304	400	313.6	323.2
α(10 ⁻⁶ /k)	3	4.3	3.13	3.26
Δε _s (10 ⁻⁴)	0	0	2.01	4.02

Fig. 1. Schematic representation of the residual stress distribution in a three-layered composite.

Fig. 2. Bending strength vs. inner layer thickness for Si₃N₄-10% SiC/Si₃N₄-Si₃N₄ and Si₃N₄-20% SiC/Si₃N₄-Si₃N₄ layered composites.

Fig. 3. Optical micrograph clearly showing the interface in Si₃N₄-20% SiC/Si₃N₄-Si₃N₄.

Fig. 4. Fracture toughness vs. inner layer thickness of Si_3N_4 -10%SiC/ Si_3N_4 - Si_3N_4 and Si_3N_4 -20%SiC/ Si_3N_4 - Si_3N_4 layered composites.

across the three-layered samples, Vickers indentation was performed along a line perpendicular to the interfaces. The definitions of positive and negative distance, left and right, and upper and lower crack length used in this report are illustrated in Fig. 5. The length of a crack indicates the amount of tensile or compressive stress remaining at the corresponding indentation location after hot pressing.

The crack lengths in different directions in Si_3N_4 -10%SiC/ Si_3N_4 (0.4 mm)- Si_3N_4 and Si_3N_4 -20%SiC/ Si_3N_4 (0.4 mm)- Si_3N_4 samples were determined as a function of indentation location (Figs. 6 and 7). When the indentation was formed at the center of the inner layer ($-200\text{ }\mu\text{m}$ from the interface), the cracks parallel to the interface (upper and lower cracks) were considerably shorter than the perpendicular (left and right) cracks. This was probably because the upper and lower cracks were under perpendicular residual compressive stress in the inner layer while the left and right cracks were subjected to perpendicular tensile stress (Fig. 1). An optical micrograph showing cracks propagating from an indentation formed at the center of the inner layer is exhibited in Fig. 8(a). Extended left and right cracks running across the interfaces are revealed in this micrograph.

When the indentation was formed from the center of the inner layer toward the right interface, as illustrated in Fig. 5, the parallel cracks (upper and lower cracks) extended rapidly and continued to increase in length (Figs. 6 and 7).

Fig. 6. Crack length in different directions vs. indentation location for Si_3N_4 -10%SiC/ Si_3N_4 (0.4 mm)- Si_3N_4 layered composites.

This might have resulted from the effects of the residual tensile stress perpendicular to the direction of crack propagation in the outer layer (Fig. 1). The influence of free sample surfaces could also play a role in crack propagation in the outer layer since some parallel cracks were curved and propagated toward the free sample surfaces.

In contrast to that of parallel cracks, the length of perpendicular cracks (left and right cracks) decreased as the in-

Fig. 5. Schematic representation of the definition of upper, lower, left and right crack lengths.

Fig. 7. Crack length in different directions vs. indentation location for Si_3N_4 -20%SiC/ Si_3N_4 (0.4 mm)- Si_3N_4 layered composites.

dentation moved toward the outer layer from the inner layer (Figs. 6 and 7). This was probably due to the effects of the residual compressive stress perpendicular to the left and right cracks in the outer layer, as illustrated in Fig. 1. A typical optical micrograph showing crack extension from an indentation introduced in the outer layer is shown in Fig. 8(b). In contrast to those in Fig. 8(a), the left and right cracks were actually shorter than the upper and lower cracks.

There were no obvious differences in length between the upper and lower cracks, as shown in Figs. 6 and 7. This was not the case for the left and right cracks for which a considerable difference in length was observed. Results shown in Figs. 6 and 7 indicate that the left cracks were substantially longer than right cracks when the indentation was formed near the right interface. However, this difference in crack length was not apparent when the indentation was further away from the right interface toward the outer layer surface. This may be explained by the boundary effects. When the indentation was formed near the right interface in the outer layer, the left cracks were in the inner layer and subjected to tensile stress in the perpendicular direction. The right cracks were, however, in the outer layer, and under a perpendicular compressive stress. An opposite tendency was observed in the length of left and right cracks as the indentation was moved from the center of the inner layer toward the left interface (Figs. 5, 6 and 7).

In order to investigate the effects of SiC addition, the lengths of upper and lower cracks shown in Figs. 6 and 7 were plotted together (Fig. 9). The crack length in Si_3N_4 -

Fig. 8. Optical micrographs showing the indentations on the polished surfaces of Si_3N_4 -20%SiC/ Si_3N_4 (0.4 mm)- Si_3N_4 layered composites.

(a) Indentation formed the inner layer, (b) indentation formed in the outer layer.

Fig. 9. Upper and lower crack lengths vs. indentation location in Si_3N_4 -10%SiC/ Si_3N_4 (0.4 mm)- Si_3N_4 and Si_3N_4 -20%SiC/ Si_3N_4 (0.4 mm)- Si_3N_4 layered composites. L : lower crack length, U : upper crack length.

20%SiC/ Si_3N_4 (0.4 mm)- Si_3N_4 samples was consistently longer than that in layered samples containing 10 vol% SiC. This suggested that greater residual stress developed in the layers when SiC was added in the inner layer.

3.3 Stress analysis

3.3.1 Theoretical calculations

Cutler et al.^{17,32} used beam theory to determine the

stress distribution in three beams. The corresponding residual stress in the outer and inner layers can be expressed as

$$\sigma_1 = -E_1 E_2 d_2 \Delta \epsilon_0 / [(1-\nu)(2E_1 d_1 + E_2 d_2)] \quad (1)$$

$$\sigma_2 = 2E_1 E_2 d_1 \Delta \epsilon_0 / [(1-\nu)(2E_1 d_1 + E_2 d_2)] \quad (2)$$

where the moduli of the outer and inner layer materials are E_1 and E_2 , and the thicknesses of the outer and inner layers are d_1 and d_2 , respectively. The amount of free expansion of the outer layer in relation to the inner layer is $\Delta \epsilon_0$. Poisson's ratio (ν) is assumed to be the same (0.25) for the inner and outer layers. By substituting the physical properties of materials (Table 1) and thermal properties of SiC/Si₃N₄ reported by Koester et al.³⁵⁾ into Eqs. (1) and (2), the residual stress in the outer and inner layers can be calculated as a function of inner layer thickness (Fig. 10).

The condition $2d_1 + d_2 = 3$ mm is used to calculate stress in Eqs. (1) and (2). The calculated value is expected to be quite different from the experimental observations¹⁷⁾ when d_2 is equal to 0 or 3 mm since no residual stress resulted from the constrained layers in a monolithic ceramic material. Equations (1) and (2) are still applicable since they give clear pictures of the possible stress distributions in layered composites and are valuable for comparison with the experimental observations.

The dotted and solid lines in Fig. 10 represent the residual stress in 10 and 20 vol% SiC layered samples, respectively. The difference in stress between the inner and outer layers was especially prominent for samples containing 20 vol% SiC. This may explain the greater toughness (Fig. 4) observed for samples containing 20 vol% SiC than those for samples containing 10% SiC. Microcracks could be observed since the differences in thermal expansion between the inner and outer layer were considerable.³⁶⁾

3.3.2 Experimental measurements

Some researchers³⁷⁾⁻⁴¹⁾ developed an equation for evaluating stresses in the surfaces of brittle material (σ_c) from changes in indentation crack dimensions (c):

$$\sigma_c = 1/2(\pi/c)^{1/2}(K_c - K_c^0) \quad (3)$$

where K_c and K_c^0 are the toughnesses of layered and monolithic Si₃N₄ samples, respectively, used in this study.

This equation is important because the evaluation of residual stress is thereby reduced to a measurement of crack dimensions in the stressed and nonstressed states.

By substituting the measured crack length obtained from the results of surface indentation into Lawn and Evans' derivation,³⁸⁾ the residual compressive stress in the outer layer can be plotted as a function of inner layer thickness, as shown by the solid lines in Fig. 11. For comparison, the theoretical residual stress in the outer layer (Fig. 10) was also plotted in Fig. 11 as shown by the dotted lines. The

Fig. 10. Theoretical residual stress vs. inner layer thickness in SiC-containing three-layer composites. I : inner layer, O : outer layer.

Fig. 11. Theoretical and measured residual compressive stresses vs. inner layer thickness in Si₃N₄-SiC/Si₃N₄-Si₃N₄ layered composites. T : theoretical stress, E : experimental stress.

residual compressive stress increased with inner layer thickness, and the theoretical residual stress was lower than measured values. This was probably because the stress gradient and boundary effects were not considered in the theoretical calculations.

4. Summary and conclusions

(1) The layered samples used in this study had an interior layer of SiC/Si₃N₄ with a greater thermal expansion coefficient than the two outer surface layers formed of monolithic Si₃N₄. When the hot-pressed body was cooled to room temperature, the outer layer was then compressed in the direction parallel to the interfaces and extended perpendicular to the interfaces.

The residual stress increased with the addition of SiC in the inner layer and with the inner layer thickness.

(2) The bending strength and toughness of layered Si₃N₄ composites are substantially greater than those of monolithic Si₃N₄. This was attributed to residual surface compressive stress and crack deflection by the interfaces. The effects of residual stress were particularly marked when the SiC composition was increased from 10 to 20 vol%.

(3) Crack behavior in layered samples was affected by the residual stresses, interfaces and free sample surface.

(4) Theoretical stress calculated based on beam theory was lower than the experimentally determined residual stress. This was probably because the stress gradient and boundary effects were not considered in the theoretical calculation.

Acknowledgement The authors thank the National Science Council of the Republic of China for financial support under grant No. NSC 84-2216-E-006-013.

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