Mechanical Properties of Three-Layered Monolithic Silicon Nitride–Fibrous Silicon Nitride/Boron Nitride Monolith

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A three-layered composite, composed of a strong outer layer (monolithic Si$_3$N$_4$) and a tough inner layer (fibrous Si$_3$N$_4$/BN monolith), was fabricated by hot-pressing. For the inner layer, a Si$_3$N$_4$–polymer fiber made by extrusion was coated by dipping it into a 20 wt% BN-containing slurry. The three-layered composite exhibited excellent mechanical properties, including high strength, work of fracture, and crack resistance, because of the combination of a strong outer layer and a tough inner layer. In other words, the strong outer layer withheld the applied stress, while the tough inner layer promoted crack interactions through the weak BN cell boundaries. Also, the residual thermal stress on the surface due to the anisotropy in the coefficient of thermal expansion of BN affected a median/radial crack generation after indentation.

I. Introduction

Silicon nitride (Si$_3$N$_4$) is regarded as one of the most promising materials for high-temperature structural applications because of its excellent thermomechanical properties, including high strength, hardness, and resistance to creep and oxidation at elevated temperatures. However, its applications have not been fully utilized because of its catastrophic failure behavior. Many efforts have been made to prevent the catastrophic failure of ceramics, including the use of fiber-reinforced composites, laminated ceramics, and fibrous monoliths.1–5 Among these composites, fibrous Si$_3$N$_4$/BN monoliths have shown noncatastrophic failure at room temperature and high temperature as a result of extensive crack interactions through weak BN cell boundaries.6–10 However, in most ceramic composites, strength and toughness exhibit a trade-off relationship; that is, when the strength increases by making composites, toughness inevitably decreases.

Much research has been made to increase the strength and toughness at the same time.1,4,11–14 One of the promising methods is to fabricate a three-layered composite composed of a strong outer layer and a tough inner layer.12–14 Therefore, in this research, a three-layered composite has been fabricated, composed of monolithic Si$_3$N$_4$ and fibrous Si$_3$N$_4$/BN monolith for outer and inner regions, respectively, to improve the strength and toughness at the same time. Mechanical properties of the three-layered composite, including strength, work of fracture (WOF), and $R$-curve behavior, have been obtained and compared with monolithic Si$_3$N$_4$.

II. Experimental Procedure

Si$_3$N$_4$ powder (E-10, Ube Industries, Tokyo, Japan), with 5 wt% Y$_2$O$_3$ (Grade F, H. C. Starck GmbH and Co., Berlin, Germany) and 2 wt% Al$_2$O$_3$ (HP-DBM, Reynolds, Bauxite, AK) as sintering additives, was ball-milled for 24 h in ethanol using Si$_3$N$_4$ balls. The mixed powder was dried and mixed again with polymer binder (methyl cellulose), plasticizer (glycerol), and solvent (distilled water). BN-containing slurry was prepared by ball-milling BN powder (Grade MBN, Boride Ceramics and Composites, Ltd, U.K.) with 20 wt% Al$_2$O$_3$ as a sintering aid and with polymer binder (PVB), dispersant (menhaden fish oil), and solvent (trichloroethylene/ethanol).

The Si$_3$N$_4$–polymer was extruded using a syringe with a piston through a 300 μm orifice and then dip-coated by passing it through the BN-containing slurry at 20 and 0 wt% concentrations. The coated fiber was uniaxially arrayed and then dried in an oven at 80°C for 12 h to improve the shape and the strength of the fiber by hardening. The green billet was inserted into a 40 mm × 40 mm mold and pressed at 0.5 MPa. After binder burnout, the billet was hot-pressed at 1800°C for 1 h under an applied load of 30 MPa in a flowing nitrogen atmosphere.

For mechanical testing, a hot-pressed billet was machined bar shape with dimensions 3 mm × 4 mm × 25 mm and then ground using an 800 grit diamond wheel. The tensile surface of the specimen was polished to 1 μm using diamond slurries and, subsequently, chamfered to minimize machining flaws. The flexural strength was measured using a four-point flexural configuration with a crosshead speed of 0.05 mm/min, and inner and outer spans of 10 and 20 mm, respectively. By analyzing the load versus the crosshead deflection response, the WOF was calculated. The crack resistance ($R$-curve behavior) of the specimens was determined by observing the relation between indentation load (9.8–490 N) and fracture strength. Also, the specimens were analyzed using X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

III. Results and Discussion

The cross-section view of the three-layered composite is shown in Fig. 1. Dark and bright contrasts represent the Si$_3$N$_4$ cell and BN cell boundary, respectively. The outer layer (monolithic Si$_3$N$_4$) with the thickness of 0.3 mm exhibited no cell boundaries, whereas the inner layer exhibited the traditional microstructure of fibrous monolith consisting of cells (Si$_3$N$_4$) surrounded by cell boundaries (BN). No cracking was observed at the interface of Si$_3$N$_4$ and BN.

The representative flexural responses of the monolithic Si$_3$N$_4$ and the three-layered composite are shown in Fig. 2. As expected, the monolithic Si$_3$N$_4$ exhibited catastrophic failure (Fig. 2(A)), whereas the three-layered composite exhibited noncatastrophic failure (Fig. 2(B)) because of the extensive crack interactions within the inner layer (fibrous Si$_3$N$_4$/BN monolith). Furthermore, the retained strength after first drop caused by the fracture of the surface layer (monolithic Si$_3$N$_4$) was >30% and was maintained for a significant displacement, which showed its excellent load-bearing

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Manuscript No. 187165. Received February 5, 2002; approved July 29, 2002.

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capacity. In other words, after surface fracture, the energy for crack propagation was dissipated by crack interactions through weak BN cell boundaries in the inner layer.

The mechanical properties of the monolithic Si$_3$N$_4$ and the three-layered composites are summarized in Table I. The flexural strength of the three-layered composite was lower compared with the monolithic Si$_3$N$_4$; however, this value was much higher than that (227 MPa) of fibrous Si$_3$N$_4$/BN monolith. This high strength was attributed to the strong outer layer (monolithic Si$_3$N$_4$) that could retain the higher applied load. Moreover, the WOF of the three-layered composite was increased remarkably (1414 J/m$^2$) because of extensive crack interactions, such as crack delaminations and crack deflections, through weak BN cell boundaries within the tough inner region, as shown in Fig. 3.

Crack resistances with crack lengths (R-curve behavior) of the monolithic Si$_3$N$_4$ and three-layered composite were estimated from a relationship between the indentation load and indentation strength (fracture strength of the indented specimen), as shown in Fig. 4. When the material possessed flat R-curve behavior, the slope of the log–log plot of the indentation load versus indentation strength was $-1/3$. The slope of the monolithic Si$_3$N$_4$ was $-0.291$ (Fig. 4(A)), which implied a rising R-curve behavior of the material, presumably because of the crack interactions with elongated $\beta$-Si$_3$N$_4$ grains. The slope of the three-layered composite was markedly less steep ($-0.201$), which implied a stronger R-curve behavior (Fig. 4 (B)). This remarkable increase in crack resistance was attributed to the composite’s flaw-tolerant nature and extensive crack interactions with BN cell boundaries and with elongated $\beta$-Si$_3$N$_4$ grains. The flexural response of the three-layered composite showed noncatastrophic failure regardless of indentation loads. When the three-layered composite was indented with a load of 196 N, the retained stress was $>40\%$, and the specimen withstood a significant displacement, similar to the specimen before indentation.

With a relatively low indentation load ($\leq198$ N), the crack lengths were slightly shorter than that of the monolithic Si$_3$N$_4$, which implied that the compressive stress was developed on the surface because of the lower coefficient of thermal expansion of
crack generation; however, as indentation load increased, a crack penetrated into the inner layer and propagated through a preferential crack propagation path (i.e., fiber alignment direction). However, when the specimen was indented 45° off the axis of the fiber alignment, the anisotropy of crack lengths was not observed (Fig. 5(B)), which implied that the biaxial stress state was developed on the surface layer.

IV. Summary and Conclusions

The hot-pressed three-layered composite, composed of monolithic Si₃N₄ (outer layer) and fibrous Si₃N₄/BN monolith (inner layer), showed excellent mechanical properties. These improved mechanical properties were attributed to the combination of a strong outer layer and a tough inner layer. In other words, the strong outer layer retained applied stress, which resulted in high strength, whereas the tough inner layer generated extensive crack interaction through weak BN cell boundaries (crack delaminations and crack deflections), which resulted in the high WOF and crack resistance. Also, anisotropic crack generation after high indentation load was observed because of the biaxial residual thermal stress.

Fig. 5. SEM micrographs of the specimen after indentation with a load of 490 N (A) in parallel direction and (B) in 45° orientation to the fiber alignment.

the outer layer than the inner layer. This residual compressive strength was generally beneficial to the strength of the material. However, with an increase in indentation load (to 490 N), anisotropic crack propagations were observed, as shown in Fig. 5(A). After hot-pressing, biaxial thermal stress was developed on inner layer (fibrous Si₃N₄/BN monolith) because of the different coefficient of thermal expansion values of BN depending on the basal plane of BN, which was parallel to the fiber alignment. Therefore, when the indentation load was relatively low, a median/radial crack was arrested in the outer layer, which showed isotopic

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