

Fracture strength and damage resistance of freeze cast mullite matrix layered composites

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Symmetrical three-layer mullite-matrix composites with the addition of m-ZrO₂ in the outer layer and t-ZrO₂ in the inner layer have been prepared by sequential freeze casting followed by sintering at 1500–1700 °C. The composites have been characterized in terms of their microstructures and mechanical properties. In this type of layered composite, the toughness and flaw tolerance can be maintained with scarcely any reduction in the fracture strength. The layered material densified at 1700 °C exhibited a maximum value of fracture strength (~215 MPa) and toughness (~6.5 MPa·m^{1/2}). The strength of specimens with Vickers diamond indents as a result of applied loads of 9.8–294 N was measured. The contact damage resistance was superior in the layered composites when compared with monolithic ceramics, possibly due to the development of relatively large compensating residual stresses and microcracks in the outer layers and the inner layer.

Key words: Layered composite, Freeze casting, Flaw tolerance, Toughness, Fracture strength, Contact damage resistance.

Introduction

The stable intermediate compound mullite (3Al₂O₃·2SiO₂) which is formed in the Al₂O₃-SiO₂ system [1] is a potential candidate material for advanced structural applications because it has a high melting point, low coefficient of thermal expansion, excellent creep resistance, good chemical stability and high strength at high temperature. However, mullite could readily find many uses in an even wider range of applications if its low fracture toughness (~2 MPa·m^{1/2}) could be improved. A well-known processing route to improve the fracture toughness of mullite is to disperse or precipitate tetragonal zirconia (t-ZrO₂) in a mullite matrix, this results in transformed monoclinic (m-ZrO₂) under an applied stress [2–4]. This stress-induced phase transformation accompanied by volume expansion and shear deformation can cause beneficial toughening mechanisms [5] to become operative.

To achieve both strength and toughness, three-layer composites with a symmetrical structure have attracted attention. These are generally designed to consist of two outer layers which are under a compressive stress and an inner layer under tension [6–8]. The presence of surface compressive stresses can effectively increase the mechanical properties, such as fracture strength and toughness, and also introduce damage resistance [9]. The residual compressive stresses are usually obtained using a thermal expansion mismatch between the central and outer layers, arising on cooling from the sintering temperature. In the present study,

symmetrical three-layer mullite-matrix composites have been fabricated by freeze casting, and their mechanical properties measured. In order to generate residual compressive stresses in the outer layers, tetragonal (t)- and monoclinic (m)-ZrO₂ were selectively added to the inner and outer layer mullite matrix, respectively.

Experimental Procedure

Mullite (Baikalox-SASM, Baikowski Chimie), 3 mol% Y₂O₃-doped ZrO₂ (t-ZrO₂) (TZ3YS-E, Tosho), and m-ZrO₂ (Advanced Materials) powders were used as the starting materials. The specifications of the powders were as follows: mullite with $d_{50} = 0.99 \mu\text{m}$, $S_{BET} = 13.3 \text{ m}^2/\text{g}$; t-ZrO₂ with $d_{50} = 0.28 \mu\text{m}$, $S_{BET} = 7.2 \text{ m}^2/\text{g}$; and m-ZrO₂ with $d_{50} = 0.49 \mu\text{m}$, $S_{BET} = 38.2 \text{ m}^2/\text{g}$. Two types of slurries were prepared, aqueous suspensions of mullite/m-ZrO₂ and mullite/t-ZrO₂ (85/15, vol%) with solid loadings of 50 vol% were made using a colloidal processing technique [10].

The symmetrical three-layer stacks were fabricated by sequential slurry casting in the sequence: mullite/m-ZrO₂ (layer 'A'), mullite/t-ZrO₂ (layer 'B'), and mullite/m-ZrO₂ (layer 'A') slurries, into silicon rubber molds (30 mm × 60 mm). The green bodies were then frozen, removed from the mold, and sublimated in a freeze drier (Labcono 77540, Western Medics). After calcining the layered green compacts at 600 °C in air to remove organic processing additives, firing was carried out for 2 h at 1500–1700 °C with a heating and cooling rate of 2 K minute⁻¹.

Sintered bulk density was measured by the water immersion method. The relative sintered density was calculated using the rule of mixtures, based on the theoretical density of mullite (3.15 g/cm³), t-ZrO₂ (6.80 g/cm³), and m-ZrO₂ (5.75 g/cm³). The crystalline phases present were determined

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by X-ray diffraction (XRD, D/max-IIA, Rigaku). The sintered, polished, and fracture surfaces were examined using scanning electron microscopy (SEM, JSM-200CX, Jeol). To evaluate the damage resistance of both monolithic and layered specimens, indentation strength was measured with using five ground and polished test bars under four-point bend conditions. A universal testing machine (model 6025, Instron) with a crosshead speed of $0.5 \text{ mm minute}^{-1}$, a supporting span of 30 mm, and a loading span of 10 mm was used. The specimens were indented at the center of the outer layer side using a Vickers indenter with a load ranging from 9.8 to 294 N, and with the contact time of the indenter $\sim 25 \text{ s}$. The fracture toughness was evaluated by the indentation technique [11] (136° Vickers indenter, 196 N, 10 s).

Results and Discussion

Mullite and m-ZrO₂ characteristic peaks were confirmed in XRD traces of the layer 'A' specimens while t- and m-ZrO₂ phases together with mullite were identified in the layer 'B' specimens. The presence of both t-ZrO₂ and m-ZrO₂ incorporated in the sintered mullite-zirconia composite could be expected to result in improved mechanical properties. With an increase in the firing temperature up to 1700 °C, the diffraction intensity of the m-ZrO₂ phase increased with a corresponding decrease in the peak intensity of the t-ZrO₂ phase (Fig. 1). The transformation of t-ZrO₂ to monoclinic during cooling from the firing temperature depends on its chemical composition, grain size and shape [12], together with the overall stress conditions. The t-ZrO₂ particles larger than a certain critical grain size (D_c) will spontaneously transform to monoclinic during cooling and the value for D_c in a 3 mol% Y₂O₃-ZrO₂ is typically $\sim 1 \mu\text{m}$ [13].

Microstructures of polished and thermally etched surfaces of layered composites obtained by sintering at 1600 and 1700 °C for 2 h were examined. The sintered microstructures in the layer 'A' were basically similar to those in the layer

'B'. At 1500 °C, ZrO₂ inclusions ($< 1.5 \mu\text{m}$) were dispersed at the grain boundaries of the mullite matrix and coarse ($> 3.2 \mu\text{m}$) voids existed locally (Fig. 2(a)). After sintering at 1600 °C, relatively small polygonal and elongated mullite grains (black) formed the matrix phase, and fine intergranular pores ($\sim 0.2 \mu\text{m}$) were spread over wider areas, together with large voids and agglomerated ZrO₂ particles (Fig. 2(b)). With an increase in the sintering temperature up to 1700 °C (Fig. 2(c)), the pore content decreased somewhat but the pore size increased compared with those present after sintering at 1600 °C. Grain growth of the matrix and the dispersed zirconia phases had taken place; for this case, small spherical ZrO₂ ($< 0.5 \mu\text{m}$) particles were located intragranularly in the matrix whereas large particles were situated at the grain boundaries. The sintered bulk densities

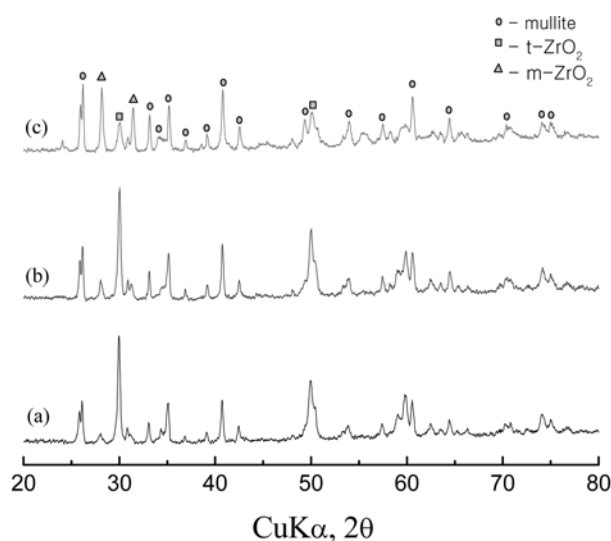


Fig. 1. XRD patterns of monolithic 'B' composite sintered at (a) 1500, (b) 1600, and (c) 1700 °C for 2 h.

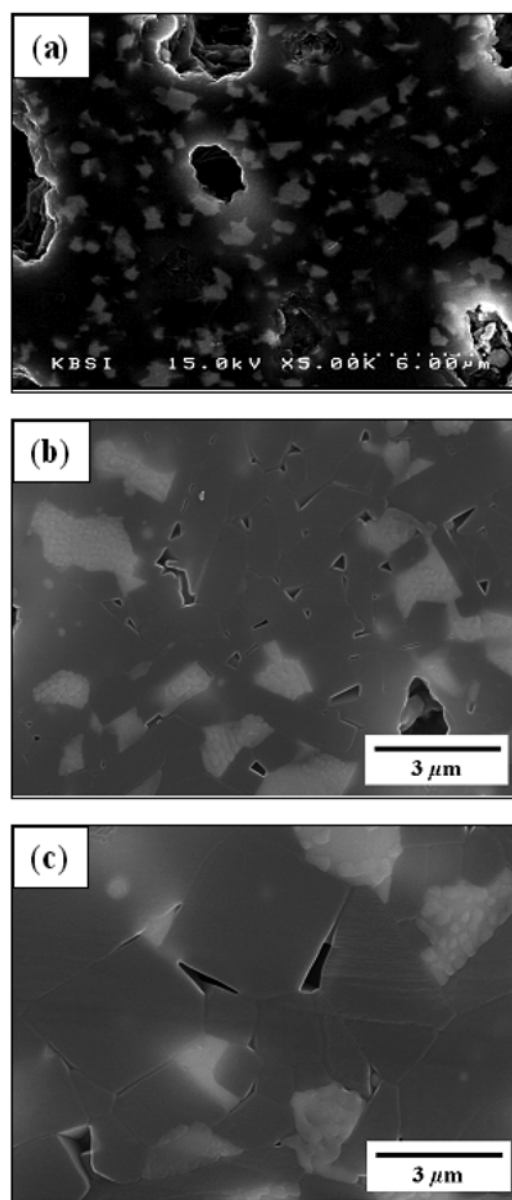


Fig. 2. SEM micrographs of polished and etched surfaces of outer layer 'A' composite sintered at 1500 °C, (b) inner layer 'B' at 1600 °C, and (c) inner layer 'B' at 1700 °C.

of the layered composite were similar to those of monoclinic 'A' and 'B' composites: 93.5% (1500 °C), 94.7% (1600 °C), and 97.2% (1700 °C) of the theoretical density.

The bend strengths and toughness of sintered specimens are shown in Figs. 3 and 4, respectively. With an increase in the sintering temperature, the strength and toughness of the monolithic and layered composites increased, mainly due to enhanced densification. After sintering at 1700 °C, the strength of the layered composite was somewhat higher (10–30 MPa) than that of monolithic 'A' and 'B' composites. The fracture toughness of the monolithic layer 'B' specimen sintered at 1600 °C was relatively low compared with the specimen sintered at 1500 °C. It is suggested that this decrease of toughness is due to the existence of relatively large amounts of t-ZrO₂, possibly transforming to monoclinic during cooling after sintering at 1600 °C; this could scarcely contribute to stress-induced transformation toughening of ZrO₂ particles. Again at 1500 °C the monolithic layer 'B' specimen exhibited a high toughness compared to the layer 'A' but the reverse appeared in the layered composite,

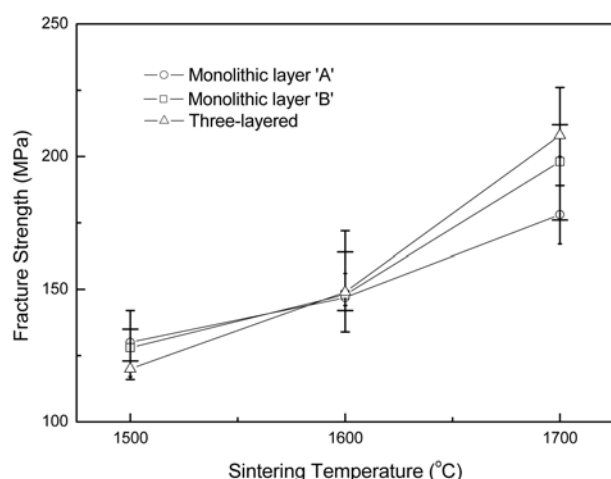


Fig. 3. Fracture strength measured by four-point bend strength for monolithic and layered composites.

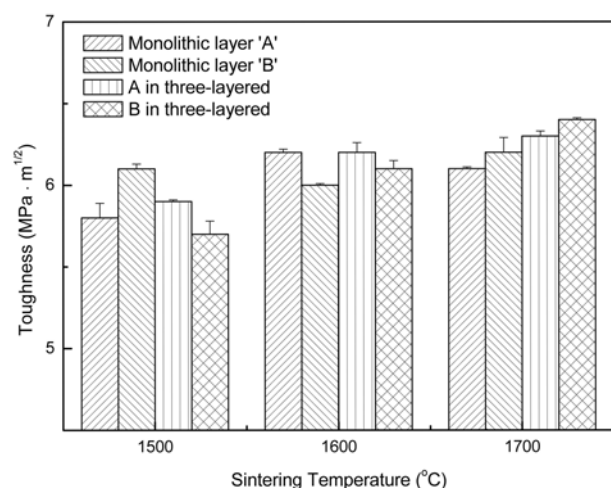


Fig. 4. Toughness for sintered monolithic and outer/inner layer in symmetrical three-layer composites.

i.e., the toughness of outer layer 'A' was higher than that of the inner layer 'B', indicative of the residual compression stress produced in the outer layer 'A'. This effect could decrease with an increase in the sintering temperature because of relatively small amounts of t-ZrO₂ remaining in the 'B' layer.

The coefficient of thermal expansion (CTE) of m-ZrO₂ ($\alpha = \sim 6 \times 10^{-6} \text{ K}^{-1}$) is lower than that of t-ZrO₂ ($\alpha = \sim 9 \times 10^{-6} \text{ K}^{-1}$). After sintering at 1600 and 1700 °C, the monolithic layer material with a high toughness also demonstrated a high toughness in the layered composite. The toughness of the central layer 'B' sintered at 1700 °C had the highest value of toughness ($\sim 6.5 \text{ MPa} \cdot \text{m}^{1/2}$). It is assumed that this higher toughness is partially due to the presence of further microcrack networks produced by the spontaneous t $\rightarrow$ m transformation of ZrO₂ particles on cooling, and partially due to the stress-induced phase transformation of the remaining t-ZrO₂. Fig. 5 shows microcrack propagation profiles in the layered specimen sintered at 1600 °C. Microfracture with bridging grains, crack deflection, and intragranular fracture of secondary particles were observed.

The average indentation bend strength of the monolithic and layered composites, sintered at 1700 °C, is shown in Fig. 6. With an increase in the indent load from 9.8 to

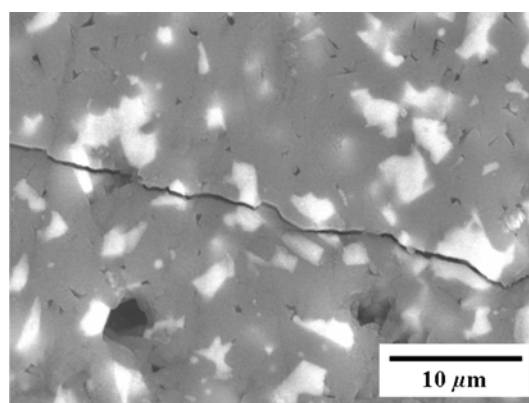


Fig. 5. Profiles of induced Vickers indentation cracks for layer 'B'.

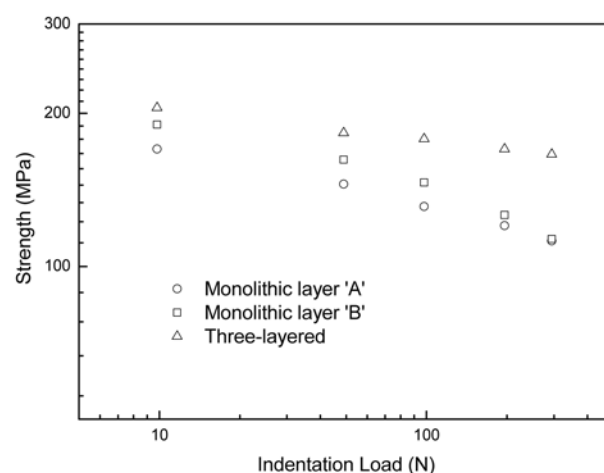


Fig. 6. Bend strength of monolithic and layered composites sintered at 1700 °C after indentation at different loads.

294 N, the degree of strength reduction was considerably reduced in the layered specimens, compared with the monolithic layer 'A' and 'B' specimens. It may be the case that the residual compression stress in the outer layer 'A' is not so large because the majority of the t-ZrO₂ particles in the inner layer 'B' spontaneously transformed to the monoclinic phase during cooling after sintering (Fig. 1), this resulting in the small difference of CTE in the outer layer and the inner layer. Such a tendency will increase in the layered specimen sintered at 1700 °C, due to the increased amount of t-ZrO₂ having grown above D_c .

An increasing reduction of strength in the monolithic specimen with increasing indentation load strongly implies that the crack introduced by the indent is acting as the critical flaw for failure. However, the high damage resistance in the layered specimen suggests the possibility of strength-limiting flaws other than those introduced by the indents as the fracture origin. A possible explanation is that the layered structure and the induced residual stresses act to neutralize the surface indentation flaw, by redirecting it along the layer interface, thus allowing a different population of flaws to act as the critical failure source.

Conclusions

Sintered three-layer mullite/zirconia composites with a high toughness and flaw tolerance properties were processed using a freeze casting technique. Powders of m-ZrO₂ and t-ZrO₂ were added to mullite in the outer and inner layers, respectively. After sintering at 1700 °C, the layered composite exhibited superior damage resistance when compared with monolithic blocks of each individual material. We suggest that this can be attributed to the layered structure and the residual stresses acting to neutralize the surface indentation

flaw. The surface damage of the monolithic layer is more sensitive in a lower toughness material. The mechanical properties of monolithic and layered composites appear to be mainly governed by the grain size of the major phase, the presence of microcracks and residual stress.

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