

Mullite/zirconia laminate composites for high temperature application

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Abstract

Mullite/zirconia laminate composites were studied for a better understanding of crack formation and crack propagation behavior at the interface of laminates. The laminate composites were fabricated by tape casting method and hot-pressing. It was demonstrated that the thermal mismatch stress was closely related to the crack formation and crack deflection behavior in the mullite/zirconia laminate composites. Two kinds of cracks were observed in zirconia layers; one is channel cracks in layers subjected to tensile stress, the other is the edge cracks in layers subjected to compressive stress. Among three forms of zirconia (monoclinic, tetragonal, cubic) tetragonal zirconia was effective to deflect the crack at the interface due to the stress induced tetra-mono phase transformation. © 2000 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Oxide/oxide composites have been receiving growing attention, mainly due to their oxidation stability at high temperature applications.¹ The key factor in providing damage tolerant behavior at high temperatures as well as at room temperature is the control of interface properties in order to achieve weak bonding between laminate layers.^{2,3} This depends upon avoiding chemical reactions and upon providing a crack deflection mechanism between individual layers.

Oxide laminate composites have been fabricated by various routes including tape casting,⁴ slip casting,⁵ die pressing,⁶ electrophoretic deposition.⁷ However, various kinds of processing defects are commonly observed in the laminate composites during processing. Typical cracks observed in the laminate composites are channel crack (or tunnel crack) perpendicular to the interface, edge crack (or transverse crack) parallel to the interface, and debonding.⁸ These cracks can be generated during the processing due to the mismatch stresses between layers. Origins of mismatch stresses are related to differential drying, differential densification, and different

thermal expansion coefficients during cooling. Typical cracks observed in laminated composites are related to one or a combination of the origins of mismatch stress.

Recently, many researches have been made on oxide/oxide laminate composites, mainly on alumina/zirconia and several other systems.⁹ However, there are only limited reports on mullite/zirconia laminate composites,¹⁰ even though a large number of studies have been made on mullite/zirconia composites.¹¹ Due to the high diffusion coefficient of atoms in oxides and the reactivity of mullite with other oxides at high temperatures, there exists a limited number of candidate materials compatible with mullite. Zirconia is one of the most promising candidates due to its chemical stability vs. mullite at high temperature. The purpose of this study is to describe the crack formations during the processing of mullite/zirconia laminate composites with different types of zirconia, and to demonstrate crack deflection behaviors at the interface of the laminate.

2. Experimental procedure

Starting powders were mullite precursors composed of γ -Al₂O₃ and SiO₂ (Siral, Condea, FRG); and monoclinic zirconia (TZ-0, Tosho, Japan), tetragonal zirconia

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with 3 mol% Y_2O_3 (TZ-3Y, Tosho, Japan), cubic zirconia with 8 mol% Y_2O_3 (TZ-8Y, Tosho, Japan). The mullite precursor was calcined at $1100^\circ C$ for 5 h in air. Each slip was prepared by planetary ball milling with 70 wt.% solid loading. For the preparation of stable aqueous slip, total amount of 2.5 wt.% polyglycerin, cellulose, and silicon emulsion were added in order to enhance the powder dispersion. Green tapes with dimensions of 60×60 mm were obtained by tape casting. After tape casting, tapes were dried for 24 h at ambient condition. For the binder burn-out, dried tapes were placed in air at $700^\circ C$ for 2 h with a slow heating rate of $2^\circ C/min$.

Three combinations of laminate composites (mM: monoclinic ZrO_2 /mullite, tM: tetragonal ZrO_2 /mullite, cM: cubic ZrO_2 /mullite) were formed by alternating layers (7 layers of ZrO_2 and 8 layers of mullite). Alternating layers of mullite precursor/zirconia were hot-pressed at $1300^\circ C$, 15 MPa, for 15 min in air. After hot-pressing, specimens were cooled down with $8^\circ C/min$ to room temperature without pressure. Hot-pressed specimens were polished with a diamond paste of $3 \mu m$, and then Vickers indentation was carried out. Indentation load with 10 kg was enough to produce an observable crack. X-ray diffractometer (Siemens D-5000, Germany) was used for the phase identification of specimen. Microstructure characterization of layered composites has performed by SEM (Philips, 525M, Netherlands) on the polished and the fracture surfaces of the specimens. Dilatometer measurements have been carried out to study the densification behavior of each layer including mullite precursor, mono-zirconia, tetra-zirconia, and cubic zirconia. These measurements were carried out up

to $1300^\circ C$ and 15 min holding time with controlled heating and cooling rate. Thermal expansion coefficients of each layer were measured on a dilatometer (Bahr-thermoanalyse, Germany) for temperatures up to $1300^\circ C$.

3. Results and discussion

Phase composition and microstructure of as-processed laminate reveal that the tapes produced from the calcined mullite precursor are fully crystallized into mullite after hot-pressing at $1300^\circ C$ for 15 min under 15 MPa in air, as shown in Fig. 1. The ZrO_2 tapes produced from unstabilized ZrO_2 powder yield purely monoclinic phase, whereas partially stabilized ZrO_2 with 3 mol% Y_2O_3 tapes retained mainly tetragonal phase and partial content of monoclinic phase. Fully stabilized ZrO_2 with 8 mol% Y_2O_3 tapes retained only cubic phase under the given condition.

Fig. 2 shows SEM micrographs of the laminate composites, fabricated with an alternating layer of mullite and monoclinic ZrO_2 (a), tetragonal ZrO_2 (b), cubic ZrO_2 (c). After hot-pressing, all samples display channel cracks parallel to the hot pressing direction. In the samples tM and cM, the channel cracks are in the ZrO_2 layer, while in the sample mM the channel cracks are in the mullite layer. Additionally, in the sample mM, edge cracks perpendicular to hot-pressing direction are observed in the ZrO_2 layers.

Typical cracks originated from mismatch stress are dependent on the several factors, such as differential drying, differential densification, and different thermal expansion coefficients during cooling. During the drying

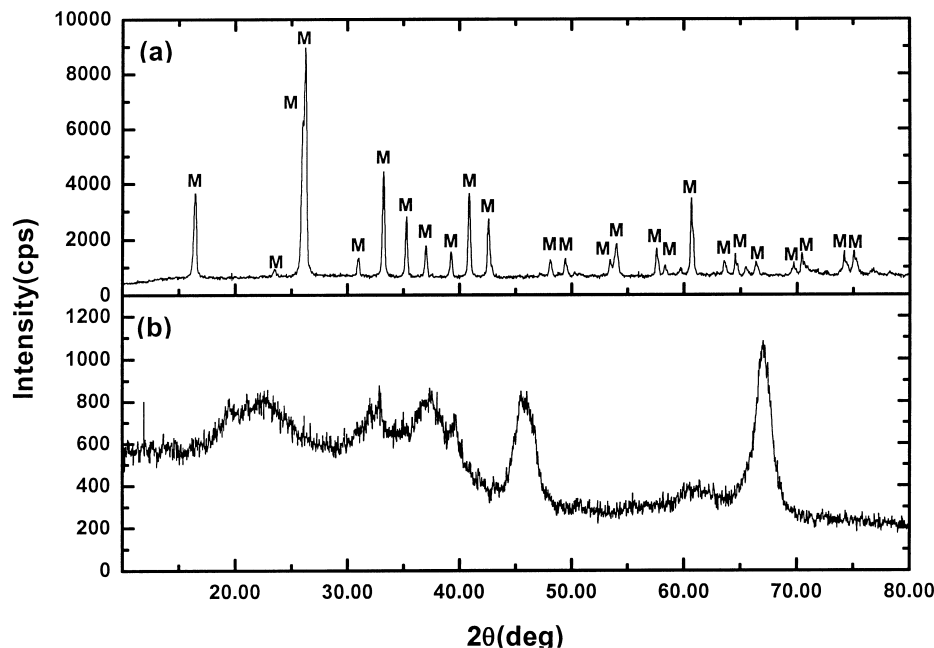


Fig. 1. X-ray diffraction patterns for (a) the sample hot-pressed at $1300^\circ C$, 15 MPa for 15 min in air and (b) mullite precursor powder.

period, rapid drying rate or high content of binder can be contributed to residual stress in the laminate. In this study, however, such a differential stress due to drying can be eliminated by the careful control of the drying rate. When the layers have different densification rates and thermal expansion coefficients, thermal mismatch stresses are generated during the densification process or cooling process. Hillman et al.¹² reported that two classes of cracks were observed in $\text{Al}_2\text{O}_3/\text{ZrO}_2$ laminate composites. Cracks with a large opening displacement are originated from drying and subsequent densification period, whereas cracks with a small opening displacement originated from thermal expansion mismatch during the cooling period. However, it is somewhat difficult to conclude which factor is more attributable to the crack formation either in the densification period or the cooling period.

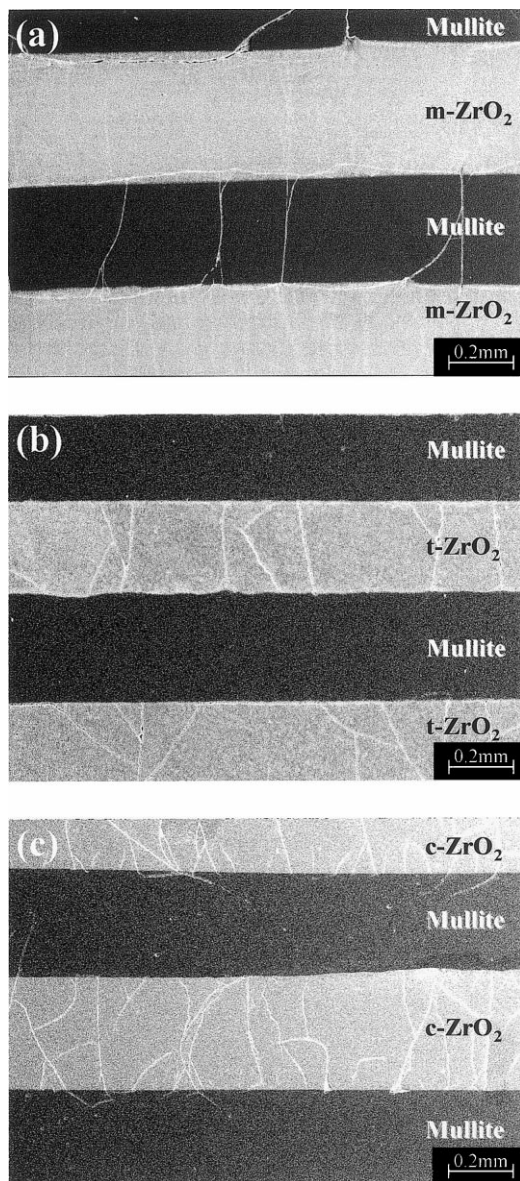


Fig. 2. SEM micrographs of laminates composites: (a) mono- ZrO_2 , (b) tetra- ZrO_2 , and (c) cubic- ZrO_2 .

In order to investigate crack formations in the laminates, dilatometer measurements of each layer were carried out up to 1300°C for 15 min with a constant heating rate ($10^\circ\text{C}/\text{min}$). Dilatometer measurements showed that mullite exhibited a high volume shrinkage (66%) compared to monoclinic and cubic ZrO_2 (50 and 56%, respectively). Thus, the crack formation in the mullite layer is expected rather than in the ZrO_2 layer during the densification of laminates. However, the crack formation in the mullite layer was observed only in the mM specimen, as shown in Fig. 2. Therefore, it is believed that the different densification rate is not the main reason for the crack formations in the laminates during densification.

Therefore, we explored other possibilities resulting in crack formations, such as thermal expansion mismatch during cooling. Thermal expansion coefficients (α) were measured individually on the samples that were pre-sintered at 1300°C . These experiments demonstrate that mullite shows the lowest α ($5 \times 10^{-6}/^\circ\text{C}$) at 1300°C , while the α values of the tetragonal and cubic ZrO_2 are $9 \times 10^{-6}/^\circ\text{C}$, $10.5 \times 10^{-6}/^\circ\text{C}$, respectively, as shown in Fig. 3. However, the thermal expansion behavior of monoclinic ZrO_2 showing a rapid shrinkage at 1150°C was quite different compared to other zirconia. This different thermal behavior in monoclinic ZrO_2 is closely related to the phase transformation of ZrO_2 , i.e. mono-tetra transformation (volume contraction) at 1150°C during heating, and tetra-mono transformation (volume expansion) at 930°C during cooling, as shown in Fig. 4.

Because the thermal expansion coefficient of ZrO_2 is higher than that of mullite, it is believed that ZrO_2 layers contain tensile stress and form channel cracks during cooling from the hot pressing temperature, as schematically shown in Fig. 5. The higher density of channel

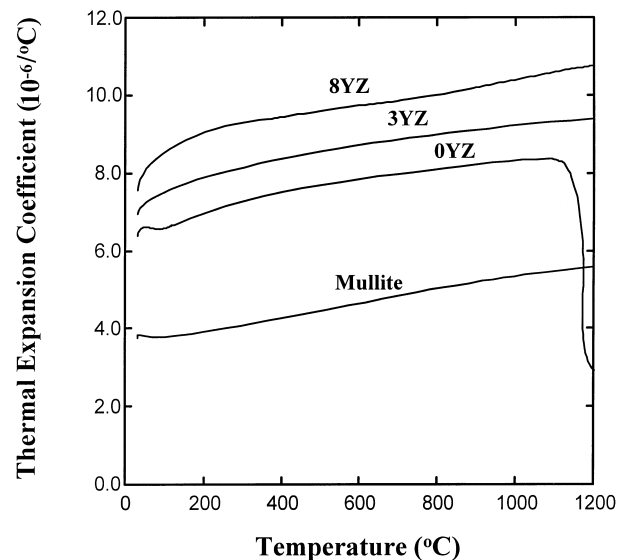


Fig. 3. Thermal expansion coefficient of specimens: mullite, mono- ZrO_2 , tetra- ZrO_2 , and cubic- ZrO_2 .

cracks in the cM specimen, in comparison to those in the tM specimen, is due to the larger thermal mismatch stress. Obviously, residual mismatch stresses in the mM specimen are closely related to mono-tetra phase transformation of ZrO_2 . Due to the volume increase during tetragonal to monoclinic phase transformation of unstabilized ZrO_2 during cooling, the monoclinic ZrO_2

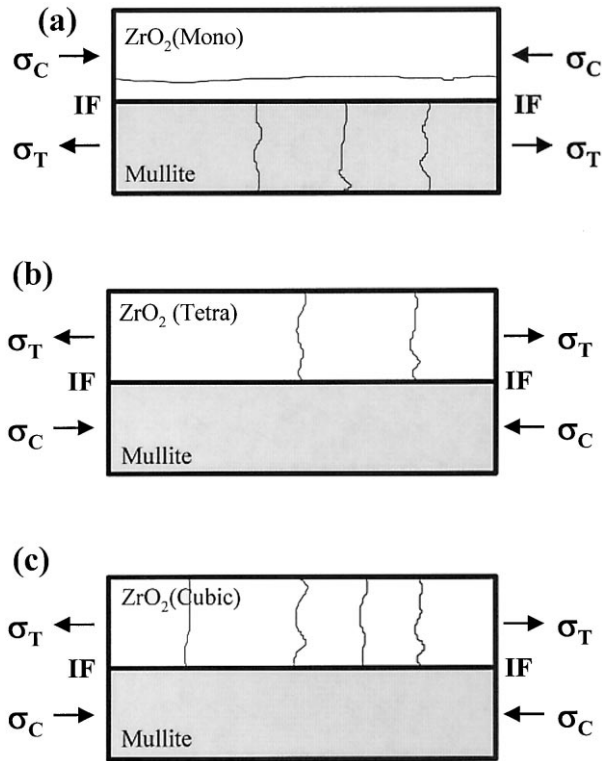


Fig. 4. Schematic demonstration of cracks in mullite/ ZrO_2 laminate composites: (a) mullite/mono- ZrO_2 , (b) mullite/tetra- ZrO_2 , and (c) mullite/cubic- ZrO_2 . (σ_T , Tensile stress; σ_C , compressive stress; IF, interface.)

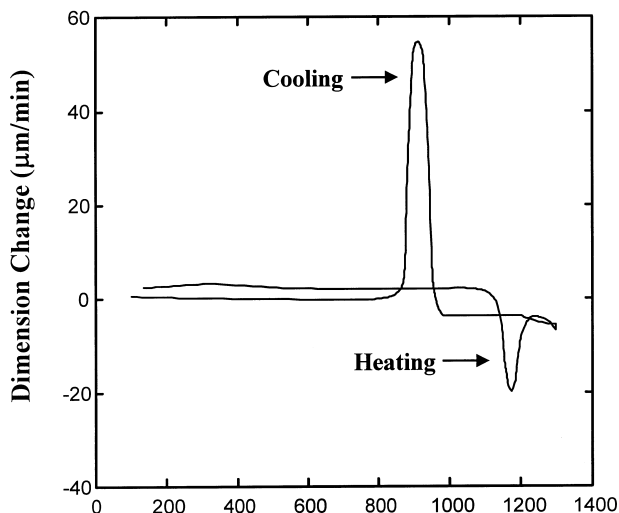


Fig. 5. Dimension change in mono- ZrO_2 during thermal cycle.

layers in the mM specimen are constrained from expansion at $933^\circ C$, producing residual compressive stress in ZrO_2 layers and tensile stress in mullite layers. The polished and the fractured surfaces of the laminate composites were investigated by SEM and as expected no reaction zone was observed at the interface between ZrO_2 and mullite. Only a sharp interface between ZrO_2 and mullite layers was observed in the whole samples.

Indentation was performed into the mullite layer only. This appears straightforward since in our model system, mullite layers to the matrix of ceramic matrix

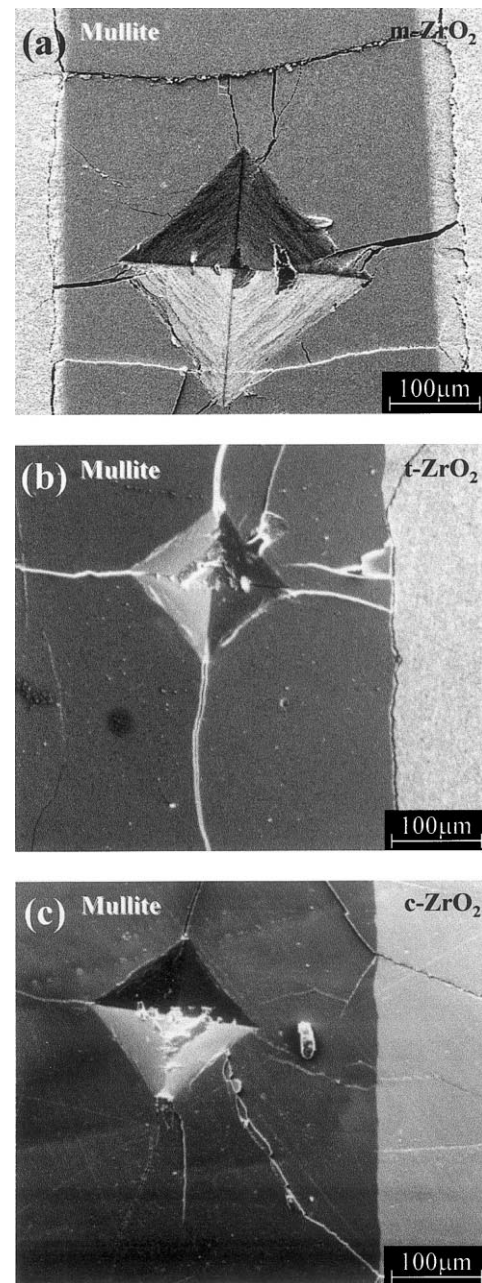


Fig. 6. SEM micrographs of crack propagation at the interface of mullite/ ZrO_2 laminate composites: (a) mullite/mono- ZrO_2 , (b) mullite/tetra- ZrO_2 , and (c) mullite/cubic- ZrO_2 .

composites whereas ZrO_2 refers to the coating layer in the mullite fiber/mullite matrix system. Cracks, coming from the mullite layer, in the mM system are related to crack bifurcation in ZrO_2 layers [Fig. 6(a)]. In this case, the cracks are deflected along the edge crack path in ZrO_2 layer. Considering the stress distribution in the laminates, it can be expected that the indentation cracks at the mullite layer will propagate straight through the mullite layer, since the mullite layer locates in biaxial tensile stress. However, the cracks which enter to the ZrO_2 layer from the mullite layer propagate differently. Recently Lange et al.¹³ observed the crack bifurcation in Al_2O_3/ZrO_2 laminate composites when cracks entered into thin Al_2O_3 layers sandwiched between $Zr(12Ce)O_2$ layers. Because the Al_2O_3 layer is subjected to a compressive stress due to thermal contraction upon cooling, cracks entering the Al_2O_3 layers showed a deflection behavior along the interface without passing through the matrix. This kind of crack propagation observed in ZrO_2 layers of the mM laminate composites, due to the compressive stress, developed from tetra-mono transformation during cooling.

Interestingly, crack propagation was different in the tM laminate composites. The cracks were deflected and arrested at the interface between mullite and ZrO_2 layers,

as shown in Fig. 6(b). XRD analysis of the ZrO_2 layer in the tM laminate composite shows mainly tetragonal and a small content of monoclinic phase at the hot-pressing condition. It might be expected that the tetragonal ZrO_2 located on the crack processing zone would be transformed into monoclinic ZrO_2 during the crack propagation. In the case of the cM sample, however, cracks propagate through the mullite layer into the ZrO_2 layer without any deflection behavior, as shown in Fig. 6 (c). It means that the interface of mullite/cubic ZrO_2 was not effective for crack deflection.

Thermal shock resistance of mM, tM, and cM specimens were investigated by cyclic heating and cooling between room temperature and 1300°C. During the cyclic test, 10 cycles were applied and specimens annealed 1 h at 1300°C. After cyclic test, tM, cM specimens were remained without any changes, while mM specimen was catastrophically degraded due to the repeated tetra-mono phase transformation including a large volume expansion of mono- ZrO_2 layer, as shown in Fig. 7.

4. Conclusions

This study has demonstrated that thermal mismatch stresses are closely related to the formation of cracks and the crack deflection behavior in the mullite/zirconia laminate composites. Two kinds of cracks were observed in zirconia layers; one is the channel cracks in layers subjected to tensile stress, another is the edge cracks in layers subjected to compressive stress. Channel cracks were formed during cooling due to high thermal expansion coefficients of zirconia, and edge crack was formed due to the tetra-mono transformation of zirconia during cooling. Among three forms of zirconia, partially stabilized type (tetragonal phase) was effective in deflecting the cracks at the interface due to the stress induced tetra-mono phase transformation. According to the Al_2O_3 - SiO_2 - ZrO_2 equilibrium phase diagram mullite- ZrO_2 are compatibles in solid state, therefore from a thermodynamic point of view no reaction is possible at the interface. The results obtained in this study suggest that partially stabilized zirconia coating on mullite fiber may provide damage tolerant for mullite/mullite composites.

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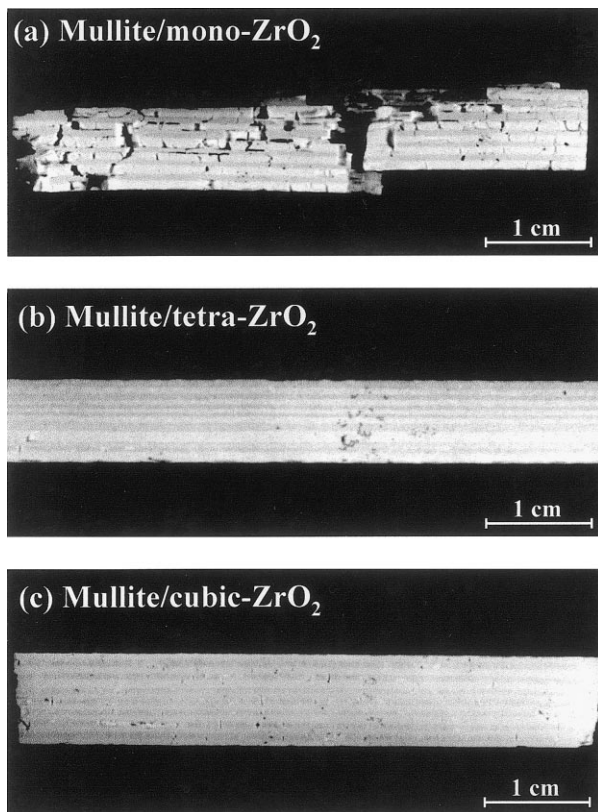


Fig. 7. Mullite/ ZrO_2 laminate composites after thermal cycles: (a) mullite/mono- ZrO_2 , (b) mullite/tetra- ZrO_2 , and (c) mullite/cubic- ZrO_2 .

References

1. Morgan, P. E. D. and Marshall, D. B., Functional interfaces for oxide/oxide composites. *Mater. Sci. Eng. A*, 1993, **162**, 15–25.
2. Kuo, D. H. and Kriven, W. M., Chemical stability, microstructure and mechanical behavior of LaPO₄-containing ceramics. *Mater. Sci. Eng.*, 1996, **A120**, 123–134.
3. Morgan, P. E. D., Marshall, D. B. and Hously, R. M., High temperature stability of monazite-alumina composites. *Mater. Sci. Eng.*, 1995, **A195**, 215–222.
4. Plucknett, K. P., Cacères, C. H., Huhges, C. and Wilkinson, D. S., Processing of tape-cast laminates prepared from fine alumina/zirconia powder. *J. Am. Ceram. Soc.*, 1993, **7**(8), 2145–2153.
5. Requena, J., Moreno, R. and Moya, J. S., Alumina and alumina/zirconia multilayer composites obtained by slip casting. *J. Am. Ceram. Soc.*, 1997, **78**(7), 1511–1513.
6. Wang, H. and Hu, X., Surface properties of ceramic laminates fabricated by die pressing. *J. Am. Ceram. Soc.*, 1996, **79**(2), 553–556.
7. Sarkar, P., Huang, X. and Nicholson, P. S., Structural ceramic microlaminates by electrophoretic deposition. *J. Am. Ceram. Soc.*, 1992, **75**(10), 2907–2909.
8. Cai, P. Z., Green, D. J. and Messing, G. M., Constrained densification of alumina/zirconia hybrid laminates, I: experimental observations of processing defects. *J. Am. Ceram. Soc.*, 1997, **80**(8), 1929–1939.
9. Russo, C. J., Harmer, M. P., Chan, H. M. and Miller, G. A., Design of a laminated ceramic composite for improve strength and toughness. *J. Am. Ceram. Soc.*, 1992, **75**(12), 3396–3400.
10. Melendo, M. J., Clauss, C., Rodriguea, A. D., Herencia, A. J. and Moya, J. S., Microstructure and high-temperature mechanical behavior of alumina/alumina-ytria-stabilized tetragonal zirconia multilayer composites. *J. Am. Ceram. Soc.*, 1997, **80**(8), 2126–2130.
11. Moya, M. S. and Osendi, M. I., Microstructure and mechanical properties of mullite-zirconia composites. *J. Mater. Sci.*, 1984, **19**(8), 2909–2914.
12. Hillman, C., Suo, Z. and Lange, F. F., Cracking of laminates subjected to biaxial tensile stresses. *J. Am. Ceram. Soc.*, 1996, **79**(8), 2127–2133.
13. Oechsner, M., Suo, Z. and Lange, F. F., Crack bifurcation in laminar ceramic composites. *J. Am. Ceram. Soc.*, 1834, **79**(7), 1838.