Residual Stress on Concentric Laminated Fibrous Al_2O_3 - ZrO_2 Composites on Prolonged High Temperature Exposure

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Abstract This paper investigates the effect of prolonged high temperature exposure on concentric laminated Al_2O_3 - ZrO_2 composites. An ultrafine scale microstructure with a cellular 7 layer concentric lamination with unidirectional alignment was fabricated by a multi-pass extrusion method. Each laminate in the microstructure was 2-3 μm thick. An alternate lamina was composed of 75% Al_2O_3 -(25% m-ZrO_2) and t-ZrO_2 ceramics. The composite was sintered at 1500 °C and subjected to 1450 °C temperature for 24 hours to 72 hours. We investigated the effect of long time high temperature exposure on the generation of residual stress and grain growth and their effect on the overall stability of the composites. The residual stress development and its subsequent effect on the microstructure with the edge cracking behavior mechanism were investigated. The residual stress in the concentric laminated microstructure causes extensive micro cracks in the t-ZrO_2 layer, despite the very thin laminate thickness. The material properties like Vickers hardness and fracture toughness were measured and evaluated along with the microstructure of the composites with prolonged high temperature exposure.

Key words laminated composites, residual stress, multi-pass extrusion, micro-structure, alumina, zirconia.

1. Introduction

Al_2O_3 - ZrO_2 ceramics have been used extensively as an industrial material because of their excellent chemical and thermal stability, hardness and wear resistance properties.^{1,2)} In case of high temperature structural application an important concern is the mechanical stability of the ceramics. However, Al_2O_3 exhibits low fracture toughness, which limits its usability. Many efforts have been made to improve the mechanical properties of ceramics like the exploitation of the reinforcing action of grain anisotropy, the promotion of the crack shielding effects, phase-transformation or micro-cracking to attain higher fracture toughness.³⁾ The advancement on crack-shielding mechanism using microstructure related features with many new microstructure designs has made significant progress in recent time.⁴⁻⁶⁾ Ceramic laminates are considered for structural applications to impart damage tolerance for conditions where cracks extend at constant strains.⁷⁻¹²⁾ Numerous studies have been conducted on the development of different aspects of the contributory effects of the laminated micro-

structure on Al_2O_3 - ZrO_2 composites based on different microstructure and design related features. Crack-shielding phenomena related to the presence of the layers (delamination, crack deflection, etc) were studied and documented.¹³⁻¹⁵⁾ The laminated microstructure is said to induce and modify the residual stress within the alternate laminates depending on their mismatch in co-efficient of thermal expansion (CTE), extent of consolidation, elastic modulus etc during the sintering process. High compressive and tensile residual stresses can be built up in successive thin layers of the laminate.¹⁶⁾ It was reported that the residual stress development was critical for the material performance. Surface compressive residual stress was described to improve the crack resistance behavior. Especially, the laminated phase with a higher CTE can exhibit higher tensile residual stress. Excessive residual tensile stress can potentially fail the material by inducing edge crack channeling. It was established that there is a minimum critical thickness for the planar laminated composites for which cracks cannot appear. High temperature creep behavior has been found to be changed in layered

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microstructure due to the presence of distinct and well developed interface.¹⁷⁾ This kind of microstructure has exhibited enhanced ductility and creep resistance. However, these reports are based on planar laminated composites which is said to have developed anisotropic material characteristics for their microstructural design and partly due to the highly oriented patterned distribution of developed residual stress. Previously we have fabricated a concentric laminated microstructure in $\text{Al}_2\text{O}_3\text{-ZrO}_2$ composites system which reduces the anisotropy of the design with dimensional symmetry in 2 D(normal to the plane of axis of concentric unit cell microstructure).¹⁸⁾ This feature can be thought to use to dwarf the anisotropic residual stress distribution during thermal residual stress development. The design has a unique feature of fabricating very fine laminates in the order of 2 μm . This is far below the critical thickness required for the edge cracking. If the material is required to withstand a prolonged high temperature exposure, these features can be of a great significance. However, apart from the dimension, the geometric configuration of the microstructure too can influence the development and pattern of residual stress. The overall effect of the thermal strain in the residual stress development grossly depends on the entire geometry and distribution of distinct phases of the specimen. At high temperature prolonged exposure the grain growth phenomena alters the microstructural features and the residual stress at grain boundary level is altered. The laminated microstructure under this situation should undergo with associated influences. In the Al_2O_3 system the high temperature grain growth is a concern for the material properties degradation especially for hardness, creep behavior, fracture toughness etc. Grain growth in high temperature environment is due to the thermal diffusion of the atoms or ions at grain boundary layer. Incorporation of a second phase can restrict this successfully by separating phases and creating a barrier. In view of this, a very fine laminated microstructure with the laminate thickness in the order of the grain size and consequently having very fine geometric isolation between phases can successfully restrict the grain growth. We have shown in this paper that exposure at 1450 °C for 72 hours did minimal grain growth in the concentric laminated composites.

This paper investigates this novel microstructure with distributed concentric laminated micro groups regarding to its stability in prolonged high temperature exposure in relation to residual stress development and its effect on the microstructure. The finite dimension of the concentric laminated micro-group had a profound effect by creating extensive edge crack channeling, which seriously hampers the stability of the composites.

2. Experimental Procedure

The starting powders used in this experiment were Al_2O_3 (AKP-50, average diameter 300 nm, Sumimoto, Japan), monoclinic Zirconia(m-ZrO₂) (TZ-0Y, average diameter 80 nm, Tosoh, Japan) and tetragonal Zirconia(t-ZrO₂) (TZ-3Y, average diameter 80 nm, Tosoh, Japan). Polymer laden ceramics powders were prepared by shear mixing as described before.¹⁸⁾ The polymer-laden t-ZrO₂ and $\text{Al}_2\text{O}_3\text{-mZrO}_2$ plastic materials were then extruded in a heated die separately to obtain green filaments 2 mm in diameter and 8 mm in length. These two kinds of filaments were then arranged in a cylindrical steel die of 30 mm in diameter. The t-ZrO₂ filaments were arranged against the die wall making the outer layer. The next inner layer was made with the $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}$ filaments. Successive inner layers were made with alternate t-ZrO₂ and $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}$ filaments filling the entire die. Three layers of $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}$ filaments were arranged sandwiched within four t-ZrO₂ filament layers. A total of 7 alternate layers of t-ZrO₂ and $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}$ filaments made up the entire arrangement. This arrangement of the alternate layers of t-ZrO₂ and $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}$ constitutes the primary microstructure of concentric multilayer. The final green composite filament was fabricated by repeated extrusion as stated earlier¹⁸⁾ to have 3rd passed filament of 3.5 mm diameter. Polymer was burnt out and sintering was done at 1450 °C for 2 hours in air. For checking the effect of high temperature exposure for extended time, samples were kept in the furnace at 1450 °C for different time periods like 24 hours, 48 hours and 72 hours.

The Vickers hardness was measured using Vickers hardness testing machine(HV-112, Akashi, Japan). The fracture toughness was measured by a less reliable but easy to do method named the Vickers indentation method using the Evan's Equation.

The microstructure of the composites was examined using FE-SEM(JSM 6335F, JEOL, Tokyo, Japan).

3. Results and Discussion

Fig. 1 shows the (a) cross sectional and (b) longitudinal SEM images of the 3rd passed multilayered $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}/\text{t-ZrO}_2$ sintered body. The black and the gray contrasts are the $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)}$ and t-ZrO₂ lamina, respectively. The unit cell of the microstructure is clearly shown in Fig. 1(a) which is only around 40 μm in diameter. The individual lamina were 2~3 μm thick only and from Fig. 1(b) it is evident that concentric lamina extended unidirectionally throughout the composites. The detailed microstructural analysis was presented in our previous report.¹⁸⁾

Fig. 1. Microstructure of the 3rd pass composites (a) cross section image and (b) longitudinal section image.

Fig. 2. Edge cracking on boundary t-ZrO₂ layer viewed from cross section after exposing at 1450 °C for different duration. (a) for 24 hours (b) for 48 hours and (c) for 72 hours. (d, e, f) are the enlarged images of (a, b, c), respectively.

The laminated composite was densified at 1500 °C temperature for 2 hours. The coefficient of thermal expansion (CTE) of t-ZrO₂ is larger than Al₂O₃. In the composites

the separated layers of the t-ZrO₂ would contract more than the Al₂O₃-(m-ZrO₂) layers during cooling. The difference in the strains is given by

$$\varepsilon_r = \int_{T_i}^{T_f} (\alpha_{Zr} - \alpha_{Al/Zr}) dT \quad (1)$$

where T_i and T_f are the initial and final temperatures during cooling, and α_{Zr} and $\alpha_{Al/Zr}$ are the CTE's of the t-ZrO₂ layer and the Al₂O₃-(m-ZrO₂) layers, respectively. If the layers are bonded, the misfit strain (1) induces a residual tensile stress in the t-ZrO₂ layer and a compressive residual stress in the Al₂O₃ layer.¹⁷⁾ Practically, the development of residual stress does not start above temperature of 1000 °C ~ 1200 °C in case of Al₂O₃-ZrO₂ composites due to the high temperature stress relaxation. However, this temperature also is high enough to induce a significant extent of residual stress. The sintered sample does not undergo any kind of stress related failure. In the laminated composites it was reported that the transverse and "edge-effect" cracking are due to the in plane tensile stress and can occur only if the laminate passes a critical thickness given by the equation.¹⁹⁾

$$t_c = 4K_{IC}^2 / \pi \sigma_R^2 \quad (2)$$

Where, K_{IC} is the fracture toughness of the layer and σ_R is the residual stress.

In the sintered 3rd pass composites this cracking was successfully eliminate with its fine layer thickness with almost full densification. However, due to the thinner dimension of the lamina in the 3rd pass sample the developed residual stress is also different and is expected to be lower, which in turn make the t_c higher for this finer microstructure.

After exposing the composites for a long time in high temperature the microstructures showed cracking along the boundary t-ZrO₂ layer. Each ceramic layer in the frame region was in the range of 2~3 μm in thickness, which is thinner than the conventional tape cast laminated ceramic composites. The fine tuning of the microstructure was expected to improve the performance at high temperature. Usually the Al₂O₃ ceramics undergo significant grain growth under prolonged high temperature exposure, which may deteriorate the mechanical properties of the ceramic body. In the present composites the microstructural dimension was less than 3 μm. This prohibits the grain growth of Al₂O₃ within this limit in the radial direction of the unit cell at prolonged elevated temperature exposure. However, the microstructure of the Al₂O₃-(m-ZrO₂) layer was sufficient to suppress any potential grain growth of Al₂O₃.

Fig. 2 shows the SEM image of the cross section of the composites after exposing at 1450 °C temperature for different time duration. The low magnification images of Fig. 2(a-c) showed that the boundary t-ZrO₂ layer has edge cracks regardless of the exposure time at 1450 °C temperature. The cracks were mainly bound along the

center of the outer ZrO₂ layer of the concentric micro groups or the unit cells and were traveling along with its curvature. This is contradictory to the notion that the layer thickness reduction significantly reduces the chances of edge cracking in the planer laminated composites. So the geometry of microstructure has invoked significantly different mechanism which led to this wide spread micro-cracking. It is to be noted that the outer t-ZrO₂ boundary layer thickness was almost double to that of the inner t-ZrO₂ layers. The developed tensile residual stress was maximum in this area and served as the flaw initiation zone for crack initiation and propagation. The residual stress development scenario for the current microstructure was not similar with the conventional planer laminated composites. In general the lamina in the planer laminated composites have a common direction of stacking and the elastic strains of the layers are subjected to the same direction. So the residual stresses developed in stacked layers. The local strains of the laminates and the corresponding stresses developed are confined in the respective laminates and rarely there is any interference other than the adjacent laminates. In case of the concentric laminated microstructure it has a different structural environment. The whole volume of the composites system contracts during the cooling time and induce a global contraction. However, the concentric cellular micro groups experience a localized straining behavior. As the alternate concentric layers are continuous cylindrical shells they have apparently a contraction scenario that seems like they are contracting towards the respective central axis with in the micro-group or unit cell. In the micro-group or unit cell the strain misfit of the Al₂O₃-m-ZrO₂ and t-ZrO₂ layers develops alternate compressive and tensile residual stresses, respectively. The contraction of two adjacent concentric micro-groups is in opposite direction with respect to the t-ZrO₂ common boundary layer. The thicker t-ZrO₂ outer boundary layer is already in a tensile residual stress, higher in magnitude due to its larger dimension. These impart the thicker boundary layer to intensify the tensile residual stress. This duel effect from the layer inherent residual stress and that from geometric contribution makes the residual tensile stress of the outer t-ZrO₂ layer higher than the inherent ultimate tensile strength of the layer and cracks are developed along this layer. The residual tensile stress is highest at the middle of the layer and decreases towards the layer interfaces. This is why most cracks propagate along the middle of the boundary t-ZrO₂ layer. In the triple zone (marked T in Fig. 2(c, e)), were three adjacent cellular micro-groups have joined, the cracks are more prolific and intense because tensile residual stress is developed along three directions (sometimes even in four due to adjacency of four micro groups with common boundary).

The high temperature prolonged dwelling can induce grain growth and densification (negligible though) and thereby can alter the grain boundary level residual stress. From Fig. 2(d, e and f) it is evident that the cracks at the boundary laminate were not significantly altered with the variation of exposure time. This indicates that the grain level modification of the microstructure had a little effect on the crack generation. The strain and as a result the residual stress produced due to the geometric effect as stated earlier was much more prominent. Both from Fig. 1 and Fig. 2 it was confirmed that the layer interfaces were not smooth, rather wavy. This is because, prior to extrusion the assembled cylindrical filaments stacking were compacted by warm pressing which made a wavy interface between the filament layers. This remained throughout the repeated extrusion steps. The disruption of the planner connectivity of the layers and the relative higher extent of interface wave make the thickness to change with repeated interval within a narrow range. This translates into the residual stress variation along a single layer. This feature is supposed to pacify the cracking tendency of the tensile layer.

The longitudinal section of the $\text{Al}_2\text{O}_3\text{-(m-ZrO}_2\text{)/t-ZrO}_2$ sintered body, subjected to 48 hours at 1450°C temperatures are shown in Fig. 3. Cracks were found along the layers and interfaces of the t- ZrO_2 layer. The cracks were found to be extended significantly along the interface of the layers. The unidirectional alignment of the laminate helps for this. (P) and (Q) shows the EDS profile of the laminates and shows the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ and t- ZrO_2 . Although the composites were exposed at 1450°C for as long as 72 hours, the grain growth was not significant both in

Table 1. mechanical properties of the composites after exposing at 1450°C for different duration.

	As sintered composites	24 hours of exposure	48 hours of exposure	72 hours of exposure
Vickers Hardness	1406 ± 59	1258 ± 25	1181 ± 10	1103 ± 16
Fracture Toughness	6.9 ± 0.69	6.8 ± 0.25	6.75 ± 0.4	6.1 ± 0.55

case of Al_2O_3 and t- ZrO_2 as shown in Fig. 4(a,b). However, the as received t- ZrO_2 and Al_2O_3 powders were nano-metric (80 nm and 300 nm, respectively), which grows to be around $500\text{ nm} \sim 1\text{ }\mu\text{m}$ at the initial sintering cycle.¹⁸⁾ So the extended exposure time at 1450°C could do a little in the grain growth. Nominal growth was observed for grains. The microstructural feature has suppressed the grain growth of the composites considerably.

From Table 1 the mechanical behavior was investigated depending on the exposure time at high temperature. The longer the exposure time was, the lower the Vickers hardness and the fracture toughness were found. This is predictable as longer exposure time means the grain grows bigger along with a degradation of the mechanical properties.

This paper described an unorthodox phenomenon of crack generation in a specific laminated microstructure with long time high temperature exposure. The findings showed that geometric orientation of the laminates have a profound effect on the residual stress generation which can ultimately fail the material. The findings could be used to make modification to such kind of microstructure that can alter the residual stress profile like designing a

Fig. 3. Edge cracking on boundary ZrO_2 layer viewed from longitudinal section after exposing at 1450°C for 48 hours. (a) low magnification SEM image, (d) high magnification SEM image. (P) and (Q) are EDS profile from the P and Q marked area of (b).

Fig. 4. Grain growth behavior of alumina and zirconia layers after exposing at 1450°C for (a) 24 hours, (b) 48 hours and (c) 72 hours.

composite with a compressive boundary layer and a thinner tensile layer. This may help to design composites with improved mechanical characteristics.

4. Conclusion

We previously developed a cellular and fibrous microstructure with unidirectional alignment and the unit cell comprised with a fine concentric laminated group in Al_2O_3 - ZrO_2 ceramic composites system. The fine alternate laminates of dissimilar phases were investigated as a phase barrier and space limiter to hinder the grain growth and to alter the residual stress distribution after prolonged high temperature application. The implication of the development of alternate tensile and compressive residual stress in the concentric laminated microstructure was investigated in this work. The residual stress development was strongly influenced by the geometric configuration of the microstructure and causes extensive cracking in the composites system. Thermal effect on the type of microstructure was analyzed and suggestions were drawn for future development.

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