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The preparation and properties of Al_2O_3–ZrO_2 composites with corrugated microstructures

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Abstract

Zirconia-toughened alumina (ZTA) composites with a corrugated microstructure were prepared from viscous non-polar suspensions of alumina and zirconia powders. Two alumina and one zirconia layers of 1 mm thickness was stacked and rolled together to form 1 mm thick laminates, which were then repeatedly folded and rolled, each time with a 50% reduction in thickness. The transition from laminar to corrugated microstructure was controlled by the rheological properties of the suspensions and the number of plastic deformations. The shrinkage of composites during sintering was between that of the shrinkage of single layers of alumina and zirconia and no sintering cracks were observed after three foldings. The mechanical properties of sintered composites improved with structural refinement. The flexural strength and K_{Ic} for the final composite were 710 MPa and 7.1 MPa$\sqrt{}$m, respectively.

Keywords: Al_2O_3; Composites; Lamination; Mechanical properties; Suspensions; ZrO_2

1. Introduction

Recently, a new type of layered ceramic-matrix composites has been presented, which differ from conventional laminates in that their interface has a tendency to be wavy, with a globular or elongated second phase within a continuous matrix phase.[1,2] The processing technique builds on the destabilisation of an interface that separates two layers with different plasticities under large strain deformation. This phenomenon has been extensively studied for the rolling of metals,[3] and for the extrusion of polymers.[4] Since the interface instability depends primarily on the difference between the yield stresses of the layers a variety of microstructures from flat to wavy laminates to cellular composites can be obtained by manipulating the rheological properties of the starting pastes.[5]

For the experimental verification of this new concept, weakly flocculated aqueous alumina and Ce-TZP pastes were produced according to the principles of "colloidal powder processing".[6,7] They were rolled into tapes and stacked to form the starting laminate, which was then repeatedly rolled and folded until cellular structures were successfully produced. Using a slightly different method, layered alumina/Y-TZP composites were also fabricated by the repeated warm-pressing and folding of bi-material tapes using the standard liquid medium/binder formulation commonly employed in the tape casting of multi-layered functional ceramics.[2] In both cases, these composites show an improved sinterability because the interface instability induced during rolling creates corrugated interfaces with a large layer waviness that reduces the long-range sintering stresses.[6] The better sinterability is also reflected in the mechanical properties of the composites. The strength and toughness increase with progressive layer refinement, and the disruption of the planar connectivity of phases —laminate/corrugated transition— is beneficial to the mechanical performance, and very high strengths and very high fracture toughnesses have been reported.[7]

One of the problems with these two variants of the original process is that the starting pastes cannot be prepared and deformed under constant conditions, nor can they be deformed and solidified at the same temperature. To overcome this problem, a paraffin-oil-based process was suggested, which allows deformation processing and shape retention at room temperature.[8]

In this study paraffin-oil-based process was used for the fabrication of alumina/Y-TZP composites with corrugated microstructures, which were tested in terms of their sintering behaviour and mechanical properties.

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2. Experimental work

Non-polar suspensions of alumina and zirconia powders were prepared using alumina powder (A16, Alcoa, Pittsburgh, USA), with an average particle size of 0.7 μm and a specific surface area of 6.3 m^2/g and yttria partially-stabilized-zirconia powder (TZ-3YS, Tosoh, Japan), with an average particle size of 0.58 μm and a specific surface area of 7 m^2/g. To prevent the harmful influence of environmental humidity on the rheological properties of the suspensions, the alumina and zirconia powders were first hydrophobized with the addition of 0.6 and 1.0 wt.% (with respect to the powder) of stearic acid, respectively. The stearic acid was dissolved in acetone, to which a dried powder was added, and homogenized in a planetary ball mill for 1 h. After homogenization the suspension was dried at 120 °C for 4 h to chemically bond the stearic acid to the surface of the particles.

For the preparation of the suspensions, paraffin oil (Kemika, Zagreb, Croatia) was used as the main component of the liquid phase. Paraffin oil is a low-melting-point polymer liquid that can enable the plastic deformation of the suspensions at room temperature. For modifying the rheological properties of the suspensions, solid paraffin INA 58/62 (INA, Zagreb, Croatia) with a melting point of 58 °C was used. In addition, 0.4 wt.% (with respect to the powder) of polyethylene glycol 400 (Merck, Germany) was added to the suspensions to act as a plasticizer.

The suspensions were prepared on a three-roller mill. This mill can be heated, and the operating temperature during the preparation of the suspensions was 80 °C, which is above the melting point of the solid paraffin. The three-roller mill works in such a way that two of the rollers rotate in opposite directions and at different speeds, which provides shear forces in the gap between the rollers. The gap was set to 20 μm, after four passes a constant-viscosity flow curve from the suspensions was obtained.

The viscosity of the suspensions was measured with a rotational viscometer (HAAKE VT 500, Germany) at 60 °C, the sensor system used was the PK2-1. The viscosity measurements at room temperature were made using an oscillatory viscometer (MSC 200, Paar Physica, Germany), the sensor system used was the MP 50.

After the compounding at 80 °C the alumina and zirconia suspensions were cooled to room temperature and then separately rolled on a twin-roller mill into layers with a uniform thickness of 1 mm. The alumina and zirconia layers were then stacked together in an alumina–zirconia–alumina sequence, so that one zirconia layer was put between two alumina layers. This laminate was then rolled down to a thickness of 1 mm (a reduction of 66%). This composite was then repeatedly folded and rolled up to eight times, with a 50% reduction in thickness, so that the final composite contained 512 layers (calculated). The preparation procedure of stacking and rolling of the laminates is schematically presented in Fig. 1. To prevent sticking during rolling, layers were put in between a type of plastic foil that is used for the tape casting of non-aqueous suspensions (PET 75, Richard E. Mistier Inc., USA).

The prepared composite layers were then cut into specimens with dimensions of 25×4×1 mm^3 and immersed in water at room temperature for 4 h to retain final shape. After this treatment samples had a sufficient strength to prevent deformation during subsequent handling. They were then embedded in high-surface-area alumina powder (GX Grade, Martinswerk, Germany) and slowly thermally debinded with a heating rate of 0.5 °C/min up to 200 °C, where the specimens were kept for an additional 2 h. After debinding, the residual content of the organic phase was 2%, which enabled the easy manipulation of the specimens before sintering. Specimens were then sintered at 1520 °C for 4 h.

Structural studies were performed using an optical microscope (Leitz, Germany). For the microstructural studies a scanning electron microscope (SEM, Jeol 5800, Japan) was used for the polished and thermally etched samples, which were heated to 1420 °C for 1 h. A heating microscope was used to measure shrinkage in the directions parallel (x) and perpendicular (y) to the rolling direction. Debinded samples of 5×5×1 mm^3 were used for the shrinkage measurements. The samples were heated to 1500 °C at a rate of 5 °C/mm. The shrinkage behavior of the rolled alumina and zirconia layers was also characterized for a comparison with the composites.

The polished surfaces of the sintered composites were indented with a Vickers indenter using a load of 98 N. The lengths of the cracks emanating from the indentations

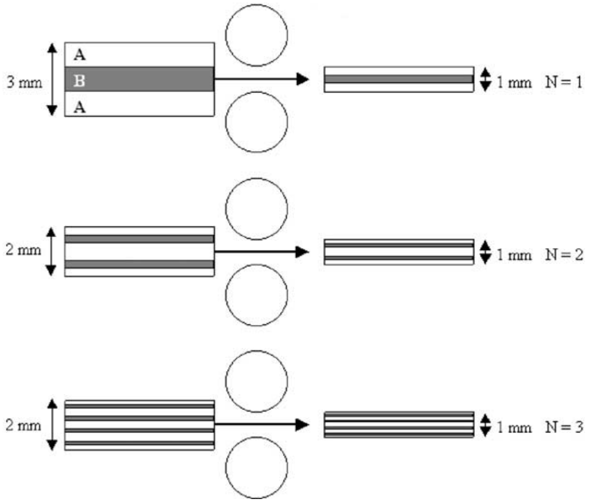


Fig. 1. Schematic presentation of stacking and rolling preparation procedure of laminates.

were used to obtain the indentation toughness, K_{Ic}, of the sintered composites.[9] The interaction of the indentation crack with the microstructure was observed by optical microscope and SEM. The flexural strength was measured using a four-point flexure configuration on a servo-hydraulic testing machine (Instron 1362, USA). The reported flexural strengths are an average of five measurements.

3. Results and discussion

The viscosity flow curves for the alumina and zirconia suspensions at 60 °C are shown in Fig. 2. For shear rates lower than 550 s^{-1} the zirconia suspension exhibit a higher viscosity than the alumina suspension, whereas at higher shear rates the viscosity of the alumina suspension is higher. The difference in the pseudo-plasticity of the suspensions is a result of the different powder characteristics (grain size, BET) and the different composition of the liquid phase used for the preparation of the alumina and zirconia suspensions. In the former case, 20 wt.% of paraffin oil was replaced by solid paraffin, whereas in the latter case the content of the solid paraffin was four times lower (5 wt.%). The solid paraffin caused an increase in the viscosity because it contains longer molecules and has a higher melting point. This modification of the liquid medium was made to increase the difference in the rheological properties of the suspensions, which is a necessary condition for the preparation of laminated composites with corrugated microstructures.

The oscillatory measurements on alumina (59.8 vol.% of powder) and zirconia (57.1 vol.% of powder) suspensions at room temperature are presented in Fig. 3 as the loss (G′) and the storage (G″) modulus, as a function of deformation. Both G′ and G″ are higher for the zirconia suspension, indicating that also at room temperature the zirconia suspension is the "harder" of the two phases, at least at low shear rates. From these measurements the yield stress for the alumina and zirconia suspensions was estimated, which was 0.006 and 0.0525 MPa, respectively.

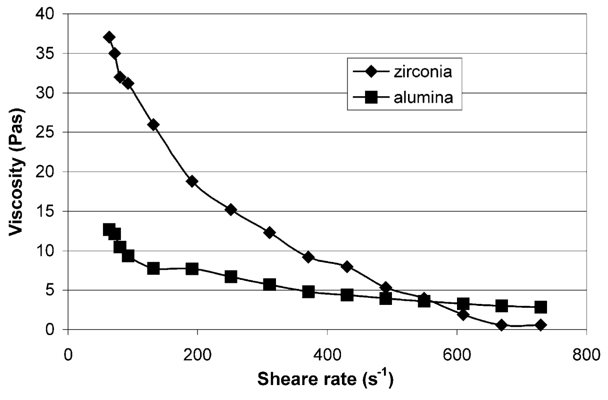


Fig. 2. Viscosity vs. shear rate for the alumina and zirconia suspensions at 60 °C.

An optical micrograph of the sintered starting laminate is presented in Fig. 4, showing flat interfaces between the layers with a slight waviness and porosity due to trapped air introduced during the slurry preparation, which could not be removed by rolling. Further refinement of the composite microstructure with an increased number of foldings is shown in Fig. 5a–h. The microstructure of the once- and twice-folded starting laminate exhibits continuous layers with more wavy interfaces (Fig. 5a and b). In these composites cracks due to constrained sintering were observed. However, the three-, four- and five-times folded composites exhibit no cracks, and the layers were continuous with wavy and corrugated interfaces (Fig. 5c–d). The wavy interface between the layers increases the surface area, which results in a reduced tensile stress per area of interface and an absence of cracks between the layers due to constrained sintering. The calculated thickness of a single layer after four foldings was 40 μm. The composite

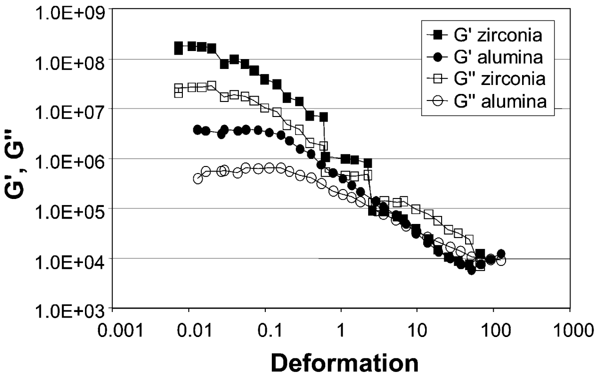


Fig. 3. Dependence of storage (G′) and loss (G″) modulus with deformation for the alumina and zirconia suspensions measured at room temperature.

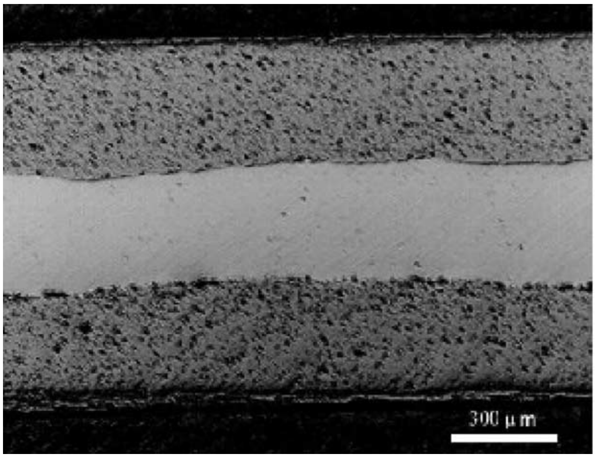
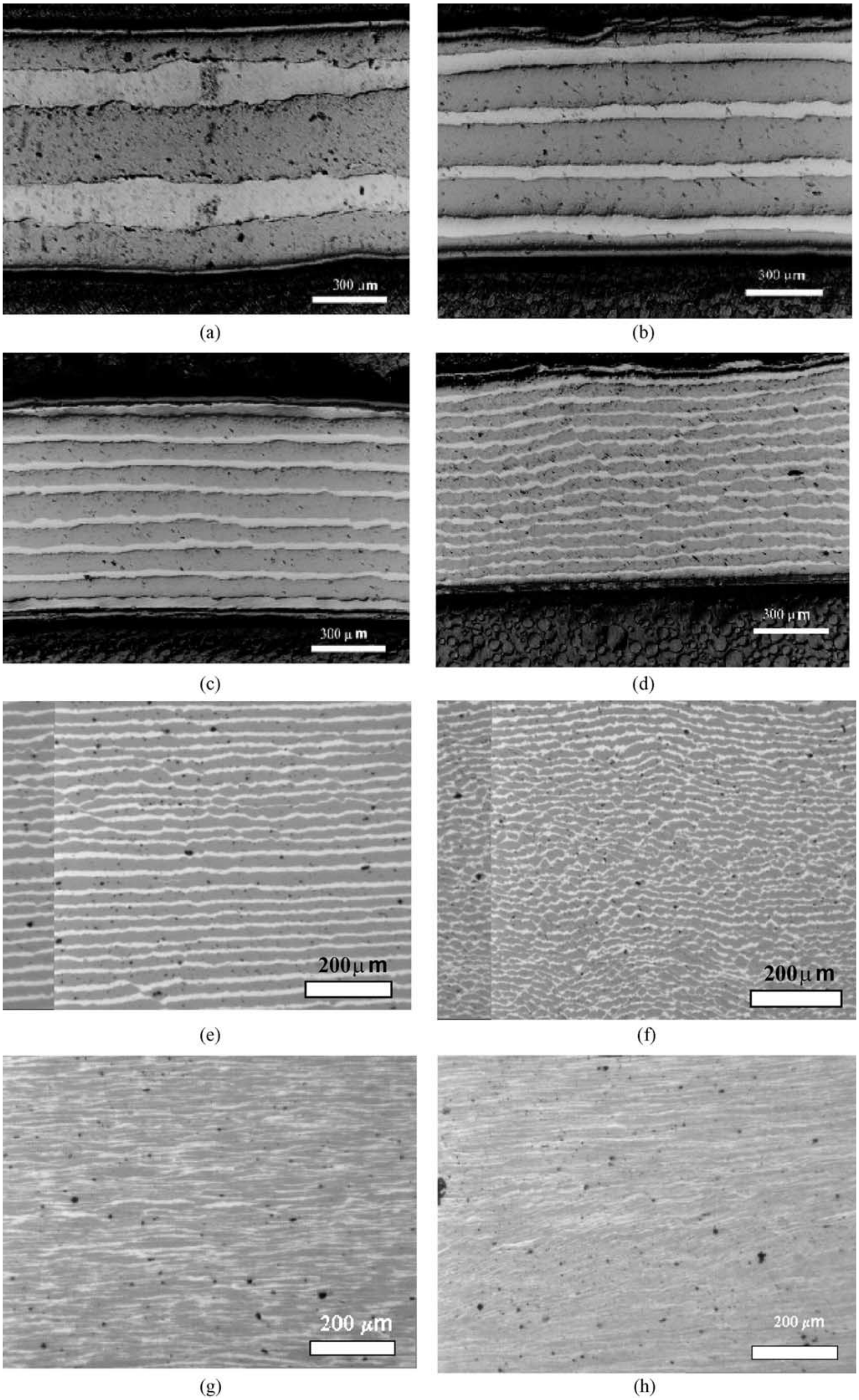


Fig. 4. Optical micrograph of sintered starting laminate in the rolling direction.



(a) (b) (c) (d) (e) (f) (g) (h)

Fig. 5. Optical micrographs of sintered composites, in the rolling direction: (a) once folded, (b) twice folded, (c) three times-folded, (d) four-times folded, (e) five-times folded, (f) six-times folded, (g) seven-times folded and (h) eight-times folded.

microstructure after six foldings can be defined as an intermediate stage between a laminar and a corrugated microstructure, as the layers are wavy and the interface between layers is highly corrugated, but the layers are still continuous. The transition from a laminar to a corrugated microstructure occurred after seven foldings, where the zirconia phase became discontinuous, as shown in Fig. 5g. It is also worth mentioning, that with progressive microstructure refinement, the microstructure of the composites became more isotropic. This can be seen from Fig. 6, which presents a transverse section of a seven-times-folded composite with a highly corrugated layer interface.

A general observation from the sintering curves in Fig. 7a is that the shrinkage of the composites during sintering is between that of the shrinkage of single layers of alumina and zirconia, but much closer to the sintering curve of the major (alumina) phase, which also shows lower sintering shrinkage than the minor (zirconia) phase. As shown in Fig. 7b, the final shrinkage of the five-times-folded composite is nearly the same in the *x* (rolling) direction and the *y* (normal to tape) direction, and even less anisotropy in the shrinkage curves was observed with the eight-times-folded composite. This is in agreement with the observations of Menon and Chen.[6]

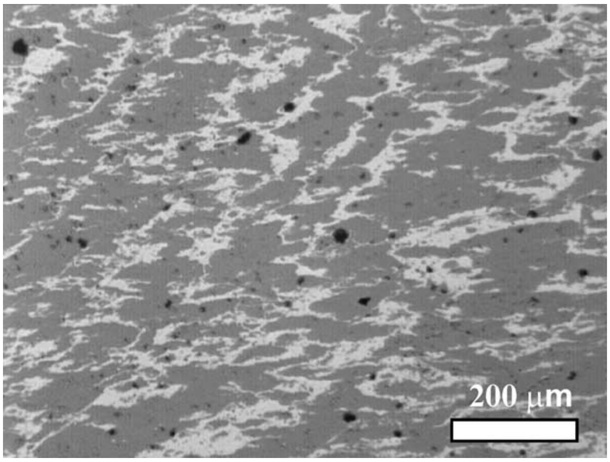


Fig. 6. Optical micrograph of a transverse section of a sintered, seven-times-folded composite with a highly corrugated layer.

In order to observe the sintered composites anisotropy, indentation tests were performed on samples that differ in terms of the number of foldings. After three foldings (Fig. 8a), cracks extending along the layers are much longer than cracks extending in the direction perpendicular to the layers, especially if the indentation was made in the alumina phase, which exhibits a lower toughness than the zirconia phase. With an increased number of foldings the indentation cracks become more and more isotropic. In the case of the five-times-folded sample, shown in Fig. 8b, the anisotropy of the crack length is considerably decreased and, after eight foldings the crack length is almost isotropic (Fig. 8c).

The reason for the decreasing crack anisotropy is the structural refinement with an increasing number of foldings, producing a finer and more isotropic distribution of the tougher zirconia phase in the alumina matrix. As shown in Fig. 8b and c, the path of the crack leads through several zirconia layers in both (parallel and perpendicular to rolling) directions, and in most cases stops in the alumina phase (Fig. 8a and d), which exhibits compressive residual stresses.

With increasing structural refinement the crack has to cross more zirconia layers in both directions, especially after the change from a laminar to a corrugated microstructure. As a result, the 3-D microstructure of such composites increases the crack resistance, which results in shorter cracks i.e. a higher indentation toughness of the composite. The calculated values of the indentation toughness K_{1c} for an eight-times-folded composite in the directions parallel and perpendicular to the layers were 6.6 and 7.1 MPa$\sqrt{}$m, respectively.

The dependence of flexural strength on the number of foldings is shown in Fig. 9. The flexural strength is very low for the starting, as well as for once- and twice-folded composites. In these composites, cracks formed due to sintering constraint are observed, which lower the flexural strength. In three-, four- and five-times-folded

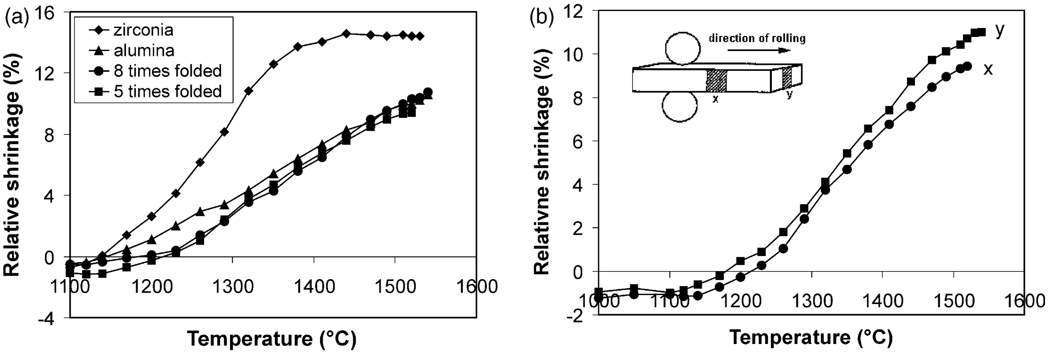
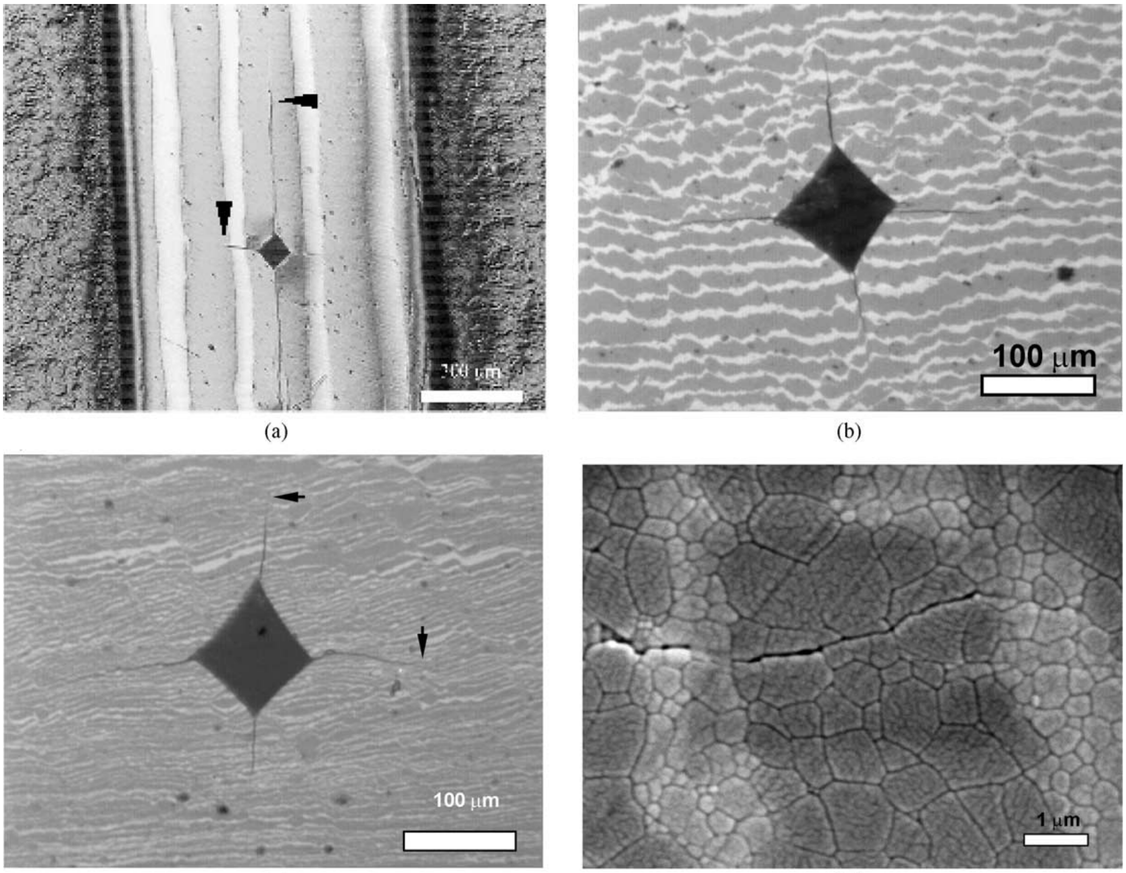


Fig. 7. Sintering curves: (a) for five- and eight-times-folded composites and for single layers of alumina and zirconia; (b) for a five-times-folded composite in the *x* (rolling) direction and the *y* (normal to tape) direction.



(a) (b) (c) (d)

Fig. 8. Indentation of sintered, polished samples: optical micrographs of (a) twice, (b) six- and (c) eight-times-folded composites; (d) SEM micrograph of indentation crack perpendicular to the layers direction for eight-times-folded composites.

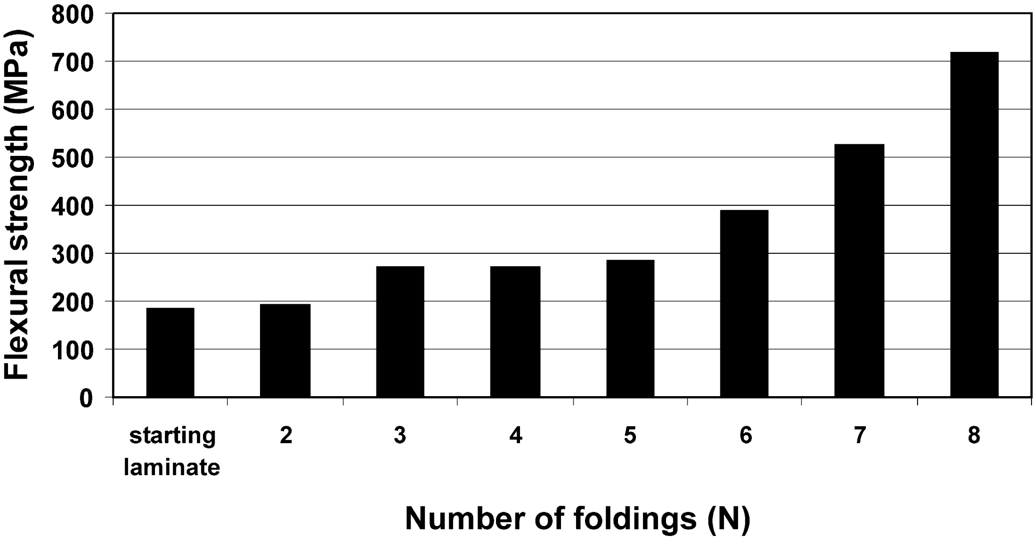


Fig. 9. Dependence of the flexural strength of sintered specimens on the number of foldings.

laminates the flexural strength is higher and constant for all three types of laminates. The microstructure of these composites is still laminar and no effect of the zirconia toughening is observed. The six-times-folded laminate exhibited an appreciable increase in flexural strength, which is the result of the microstructure refinement (intermediate stage, see Fig. 9), and the effect of the zirconia toughening already could be detected. This trend is even more pronounced for seven- and eight-times-folded composites with a corrugated microstructure. In these latter two composites, of the distribution of zirconia phase strengthens the composite significantly, with measured flexural strengths of 520 and 710 MPa, respectively. This strengthening effect is much larger than what has been typically observed in conventional zirconia-toughened alumina composites containing a comparable amount of dispersed zirconia particles.[10]

4. Conclusions

Non-aqueous and non-polar alumina and zirconia suspensions with high solid loadings were prepared with paraffin oil as the main component of the liquid phase. This enables the preparation of thick tapes by rolling at room temperature. These tapes were stacked together to form alumina/zirconia/alumina laminates, which were subsequently subjected to repeated rolling and folding. The interface separating two layers with different flow properties becomes unstable under large strain deformations and the transition from a laminar to a corrugated microstructure was achieved after seven foldings.

In spite of a large difference in the sintering behaviour between alumina and zirconia, no sintering cracks were observed in the composites that were folded and rolled more than three times, i.e. (calculated) layer thickness of less than 40 μm.

Indentation crack stability becomes more isotropic with progressive layer-microstructure refinement because of an increasingly homogeneous distribution of the tougher zirconia phase in the alumina matrix. Flexural strength also increases with layer-microstructure refinement and a considerable increase in the flexural strength occurs when the microstructure of the composites becomes corrugated, due to the strengthening effect of the zirconia phase. This strengthening effect is much larger than what has been typically observed in conventional zirconia-toughened alumina composites containing a comparable amount of dispersed zirconia particles.

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