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Alumina/Zirconia Multilayer Composites Obtained by Centrifugal Consolidation

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Abstract

An attractive method for the fabrication of Al_2O_3–ZrO_2 laminar composites is described in this paper. The process consists in the centrifugation of colloidal suspensions containing alumina and zirconia particles. With this procedure, it is possible to grow thin layers with different composition and smooth interfaces. The effects of the slurry compositions, as well as aging times and centrifuging conditions on the morphology of the laminae are discussed.

Introduction

Laminar ceramic composites are attractive materials because superior mechanical performances can be achieved by tailoring the properties, geometry and interfaces of the different layers.[1–3]

In particular, brittle ceramics can be toughened by introducing weak interfaces transverse to the growing crack or by developing internal stresses.[4–6] These tensile and compressive stresses are a consequence of the different thermal contractions and determine a deviation of the propagating cracks.

From this point of view the Al_2O_3–ZrO_2 system is interesting because the thermal expansion coefficients of the oxides are quite different, therefore, it is possible, by changing the ratios between alumina and zirconia in the layers, to obtain laminar composites with high internal stresses. Furthermore Al_2O_3–ZrO_2 based ceramics are known to be high toughness materials due to the stress-induced transformation of the metastable tetragonal zirconia inclusions.

So far, ceramic laminates have been prepared through chemical methods, the doctor blade technique and the slip casting route.[6–10] In this paper an alternative methodology is presented. It consists of the centrifugation of a relatively dilute aqueous suspension, in the removal of the supernatant liquid and in the addition, on the consolidated layer, of a new suspension with a different Al_2O_3–ZrO_2 ratio. Further, centrifugation induces the consolidation of a new layer and the process is repeated until the composite has the desired number of laminae.

The advantage of this method consists of obtaining thin layers of powders free of aggregates. In fact, during suspension preparation, repulsive interactions are generated between the particles, consequently the aggregates, which are deleterious for the sinterability of the powders and for the microstructure homogeneity, are broken down. Finally, this procedure results in smooth interfaces between the laminae and therefore a sharp variation of the sign of the internal stresses. This variation causes the deviation of the propagating cracks when they cross the interfaces. Furthermore, if the outer layers are in compression, the materials are damage resistant and therefore both mechanisms give rise to better mechanical properties.

Experimental

The starting materials were commercial submicron powders of Al_2O_3 (Sumitomo AKP-20) with an average particle size of 0·5 μm and t-ZrO_2 with 3 mol.% of Y_2O_3 (ICI Advanced Ceramics) with an average particle size of 0·3 μm.

Mixtures of Al_2O_3 and ZrO_2 powders were dispersed with a blender for 20 min in distilled water (6000 r.p.m). The pH values of the suspensions were adjusted to 4·0 using HNO_3 (1 M). This pH was chosen on the basis of previous work[11] and corresponds to the minimum viscosities for both alumina and zirconia slurries.[6]

Under these conditions, the submicron oxides' particles were positively charged, electrostatic repulsive interactions were generated, the aggregates

broken down and the solid phase sedimentation inhibited.[12]

After different aging times, the solutions were ultrasonically homogenized for 15 min at 300 W in order to break down the hard aggregates.[13] The duration of this treatment was decided on the basis of a previous study.[14]

After ultrasonication the pH of several slurries were changed to 8 using NH_4OH.

Under these conditions the zeta potential of Al_2O_3 and ZrO_2 particles was close to zero and the solid phase flocculates[15,16]. In other slurries, before the ultrasonication, NH_4NO_3 was introduced to induce strong short range repulsive forces between the particles. The reasons, as well as the effects of these additions will be discussed in the next section.

Quantities of slurry sufficient to yield the desired layer thickness were placed in a teflon cylindrical container (diameter = 50 mm). The vessel was put in a centrifuge and spun at various speeds for various periods.

After centrifuging, the supernatant aqueous solution was removed and another volume of suspension, containing a solid phase with different composition, was placed in the container in order to deposit the next layer. This procedure was repeated until multilaminar symmetric composites were obtained. The sequence of the operations is shown in Fig. 1.

After water removal, the samples were kept in the container at room temperature for several hours. During this stage, a certain quantity of water evaporated and the material contracted and consolidated. The laminates were removed from the container, dried at 60°C for 24 h, cold pressed at 1000 MPa and fired at 1580°C for 3 h.

Density was measured by immersion in distilled water and the microstructure was examined on polished samples with a scanning electron microscope.

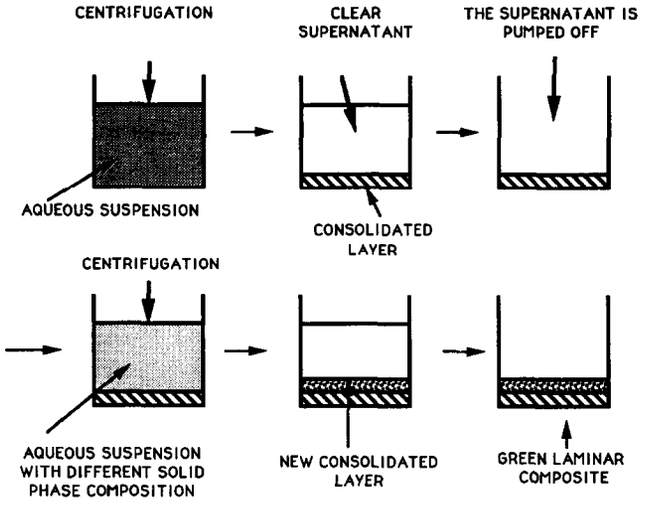

Fig. 1. Flow sheet of the procedure used for the preparation of compacts.

The suspension viscosities were measured at 25°C with a Rotowisko RV 100 viscometer. The zeta potential (ζ) was determined with a Rank Brothers Mark II equipment. For this purpose the slurries were prepared in 10^{-1} M KNO_3 solution in order to maintain a constant electrical double layer thickness.

The sedimentation rate was measured in a 100 ml graduated cylinder by observing the height of the interface between the settling suspension and its supernatant over an 8 h period.

Results and Discussion

For the the preparation of suspensions we used four powder mixtures with the following compositions:

Al_2O_3 85 vol.% – ZrO_2 15 vol%,
ZrO_2 85 vol% – Al_2O_3 15 vol.%,
Al_2O_3 65 vol.% – ZrO_2 35 vol.%,
ZrO_2 65 vol.% – Al_2O_3 35 vol.%.

The above compositions were chosen on the basis of previous experiments which showed that higher composition differences lead to the obtainment of composites containing laminae with very different thermal expansion coefficients. During the cooling, this thermal mismatch causes thermal stresses exceeding the tensile resistance of zirconia reach layers.

The influence of the chemical composition and thickness of the laminae on the composite mechanical properties is discussed elsewhere.[17]

The solid phase content of the suspensions was set to 15 vol%. This value was chosen on the basis of previous experience and on the basis of practical considerations, in fact, slurries with a high solid loading (>20 vol.%) are not able to break down the aggregates[8] and therefore homogeneous microstructures cannot be obtained.

On the other hand, high volumes of dilute suspensions are needed in order to develop layers of sufficient thickness. Therefore the considerable distance between the suspension surface and the container bottom can induce, during spinning, a concentration gradient of the oxides in the lamina.

Centrifugation conditions

The first attempts were made by centrifuging at 3000 r.p.m. for 30 min immediately after dispersion and ultrasonication pH = 4 suspensions. The results were not satisfactory because the supernatant liquid was cloudy. Longer spinning times did not cause the complete sedimentation of the solid phase. The layer thickness varied across the

diameter and reached a maximum near the walls of the container, therefore after drying and sintering the samples warped (Fig. 2) and exhibited delamination phenomena.

Furthermore, the ZrO_2 reach suspensions (85 vol.% of zirconia and 15 vol.% of alumina) exhibited on the surface a high quantity of 'bubbles'. These inhomogeneities remained also on the surfaces of the consolidated layers and were not destroyed by the deposition of other laminas (Fig. 3). Therefore, after sintering the composites exhibited irregular and porous interfaces.

Measures were taken in order to overcome the above mentioned shortcomings. An appropriate sequence in the spinning operations was studied in order to decrease the thickness differences across the samples. The best results were obtained by centrifuging the suspensions at 800 r.p.m. for 2 h and increasing the speed to 3000 r.p.m. during the last 5 min of the operation. With this procedure, the warping phenomenon was avoided.

During the centrifugation, in order to provoke complete separation of the solid phase the suspension pH was adjusted to 8 after ultrasonication. Under these conditions the zeta potential of the particles approaches zero value and the solid phase flocculates.[11]

By adopting this procedure, the supernatant liquid was clear after centrifugation, but the SEM examination of sintered samples showed the presence of large aggregates at the interfaces between the laminas, therefore no smooth interfaces were obtained using flocculated suspensions (Fig. 4). The examination of micrographs also showed a higher concentration of ZrO_2 aggregates in the bottom of layers.

These results are not in agreement with those found in another study.[18] In fact, in the paper mentioned above, homogeneous microstructures were observed in the compacts obtained with flocculated and centrifuged slurries. At present, no explanation can be given for this discrepancy.

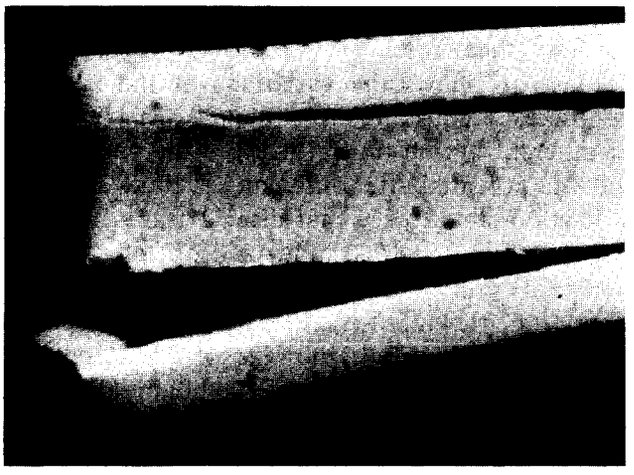

Fig. 2. Warping and delamination at the end of a sintered laminate, ZrO_2 content in the central layer 65 vol.%, in the external layers 35 vol.%. Warping and delamination are due to the different thicknesses throughout the length.

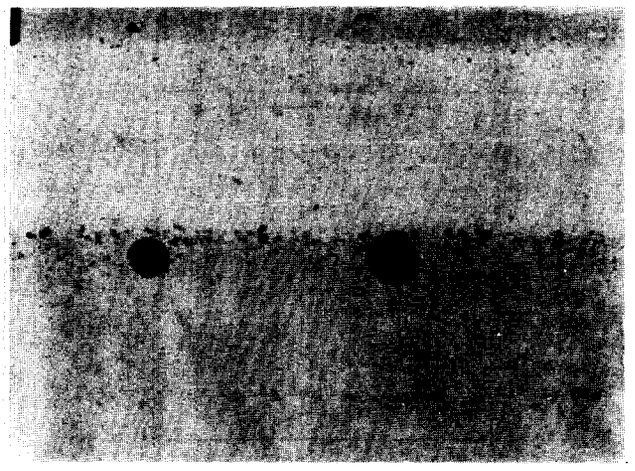

Fig. 3. Optical photomicrograph of the interface between a layer containing 15 vol.% of ZrO_2 (gray stratum) and another one containing 85 vol.% of ZrO_2. The presence of 'bubbles' is evident.

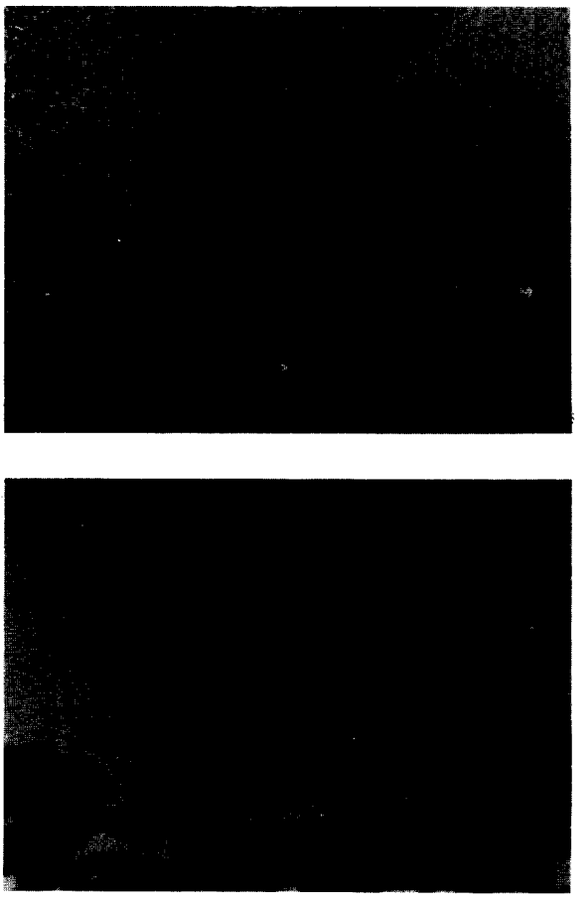

Fig. 4. SEM back-scattered micrograph of the interface between a layer containing 15 vol.% of ZrO_2 (gray stratum) and a layer containing 85 vol.% of ZrO_2 (brighter stratum). The powders were flocculated at pH = 8 before centrifugation. The presence of a large alumina aggregate is evident (darker particle).

Ageing of the suspensions

In order to eliminate the bubbles present on the surface of the zirconia reach suspensions, anti-foaming agents were used, but the best results were obtained by submitting the slurries to gentle mixing with an electric stirrer for 4 h. This treatment enabled the bubbles to deflate. After ultrasonication, the suspensions were centrifuged: smooth surfaces and an almost clear supernatant liquid were obtained. The good separation of the solid phase was surprising; therefore a short investigation was undertaken in order to explain this behavior.

For this purpose we examined the rheological behavior as a function of different ageing times of a zirconia reach suspension (ZrO_2 85 vol.%).

The results are summarized in Fig. 5 where the shear stresses measured after different rest times and at different shear rates are reported. The measurements were taken every 30 min over a period of 4 h, but in the graph, for sake of clarity, only the curves relative to 0, 90, 120, 150, 210 and 240 min of ageing times are reported. The slurry was prepared and aged using the procedures mentioned above and ultrasonicated immediately before the measurements.

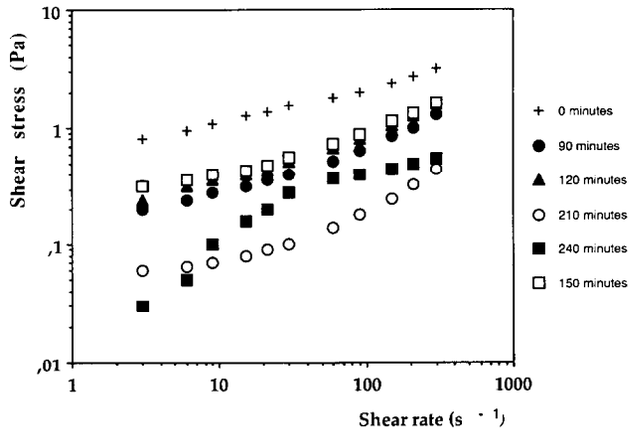

Fig. 5. Rheological behavior of aqueous suspensions aged for different times. Solid phase content = 15 vol.%, solid phase composition: ZrO_2 = 85 vol.%, Al_2O_3 = 15 vol.%, pH = 4).

The hysteresis loop method was used in order to ascertain the presence in the suspensions of a time-dependent behavior, but no thyxotropic phenomena were observed. According to the results reported by other authors for slurries of similar composition, the Herschel–Bulkley model is suitable to describe the rheological behavior of this system.[19]

$$\tau = \tau_0 + K\,\gamma^n \qquad (1)$$

Where τ is the shear stress, τ_0 is the yield value, γ the shear rate and n a constant.

However the Herschel–Bulkley equation cannot describe the behavior of suspensions aged for 4 h (see the curve in Fig. 3 indicated with full squares). Other models were used, (Casson, Bingham), in order to characterize this slurry, but the experimental and calculated data were at variance. In addition, fluctuation of the shear stress values (τ) were observed during the measurements at constant shear rate.

Figure 6 shows the variations of the apparent viscosities at constant shear rate (30 s^{-1}) as function of different ageing times. In Fig 7 the variation of the zeta potential after different rest times is shown.

It is possible to see that after 210 min, the suspensions exhibited a sudden drop of the zeta potential and a consequent viscosity increase. Therefore, the repulsive interactions between the particles are lowered, the size of the aggregates increases and the stability of the colloidal suspensions decreases. This fact can explain the obtainment of clear supernatant liquid when suspensions aged for 4 h are centrifuged. In this manner, it is also possible to explain the difficulties in characterizing the slurries aged for 4 h from the rheological point of view and the fluctuation of the τ values. Both inconveniences can be imputed to the friction of the aggregates on the walls of the measurement device.

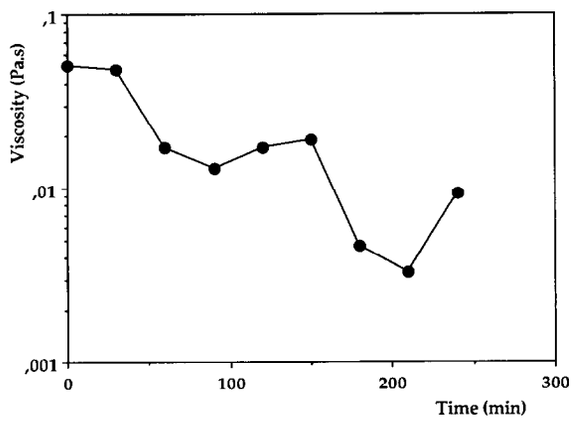

Fig. 6. Influence of the ageing times on the suspension viscosity (constant shear rate = 30 s^{-1}). The slurry composition is the same as that reported in the caption of Fig. 5.

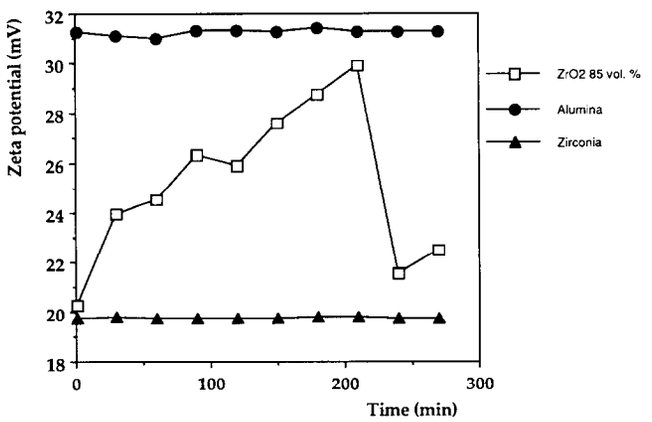

Fig. 7. Variation with the time of the zeta potential of alumina, zirconia and a mixture of 85 vol.% of ZrO_2 and 15 vol.% of Al_2O_3. Solid phase content 15 vol.%, pH = 4.

Figure 7 also shows the variations of the zeta potential of suspensions containing only zirconia and alumina powders. The preparation method and the solid phase content are the same as those used for the Al_2O_3–ZrO_2 systems. Because the zeta potentials of oxide particles remain constant during ageing, one can suppose that the variations of ζ in the suspension containing the Al_2O_3–ZrO_2 mixtures are essentially due to the interactions between the Y^{3+} ions and the surfaces or the double layers of the alumina particles. The yttrium ions in fact are released from the tetragonal stabilized zirconia in acidic conditions[20] and can decrease the stability of the slurries.

The kinetics of the interaction of Y^{3+} with the alumina are probably complicated and the observation of Figs 6 and 7 revealed the presence of several steps.

Improvement of the solid phase separation

The results obtained with flocculated and ultrasonicated suspensions aged for 4 h were encouraging and the laminae appeared homogeneous to SEM observations. These results are not in agreement with the paper of Velamakanni *et al.* [20] which showed that the centrifugation of Al_2O_3–ZrO_2 deflocculated slurries leads to a non-uniform distribution of the components; we would point out however that we did not undertake a systematic study on the distribution of the two oxides across the consolidated layers.

In Fig. 8, the microstructure of a laminar composite prepared using the procedure mentioned above is shown. The compositions of the alternating layers were 15 vol.% of ZrO_2–85 vol.% of Al_2O_3 and 15 vol.% of Al_2O_3–85 vol.% of ZrO_2 respectively.

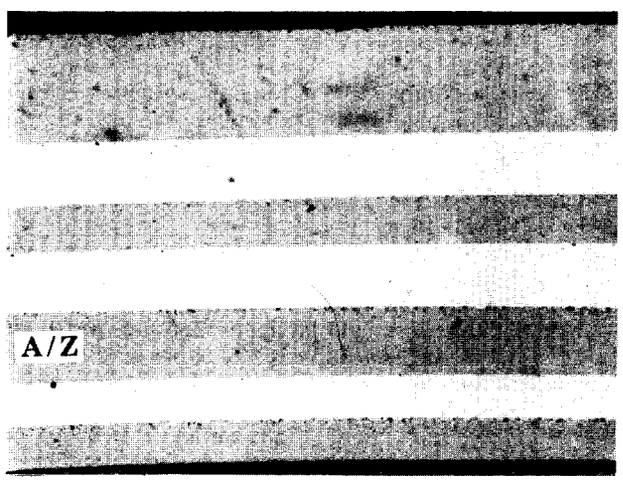

Fig. 8. Optical photomicrograph of a composite obtained by centrifugation of an aqueous suspension at pH = 4 after a gently mixing for 4 h. The slurry was ultrasonicated immediately before centrifugation. For the composition's layers, see the text.

In order to obtain a complete separation of the solid phase we added NH_4NO_3 to the suspensions. In fact the presence in the slurry of a high quantity of electrolite strongly decreases the long range electrostatic repulsive interactions and develops strong short range hydration repulsions.[20]

The salt addition provokes a viscosity increase and a destabilization of the suspension, but the permanence of a repulsive lubricating hydration layer allows the obtainment of high density bodies with well packed particles (coagulated suspensions).

The slurries were prepared using the previously discussed methods and the ammonium nitrate was added, after a certain rest time, immediately before ultrasonication. The salt concentration in the liquid phase was 1 M.

The sedimentation rate of a coagulated suspension was compared to that of a deflocculated one with the same solid phase composition (ZrO_2 85 vol.%), (Fig. 9).

Also in this case, the suspensions were aged in order to eliminate the bubbles, therefore, the evolution of the rheological behavior of the zirconia reach slurries was studied.

In order to avoid the problems related to the solid phase sedimentation, the viscosity measurements were performed immediately after the salt addition.

Again the Herschel–Bulkley model is suitable in order to describe the rheological behavior of the slurries, the only difference being that in the case of the coagulated suspensions the yield value (τ_o) is near to zero.

Good results were obtained by centrifuging the salt added slurries aged for times ranging from 1 to 4 h. Figure 10 shows the microstructures of a multilayer composite with the same composition as that of Fig. 8. Using this procedure laminae with less than 30 μm were easily obtained.

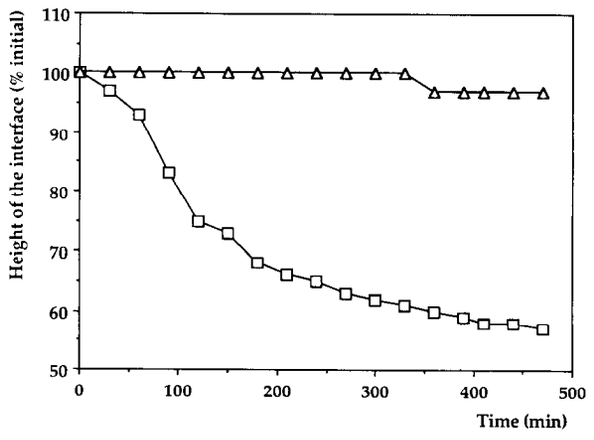

Fig. 9. Sedimentation rate of an aqueous suspension containing NH_4NO_3 1 M (squares) and without salt addition (triangles). For the slurry composition, see the text.

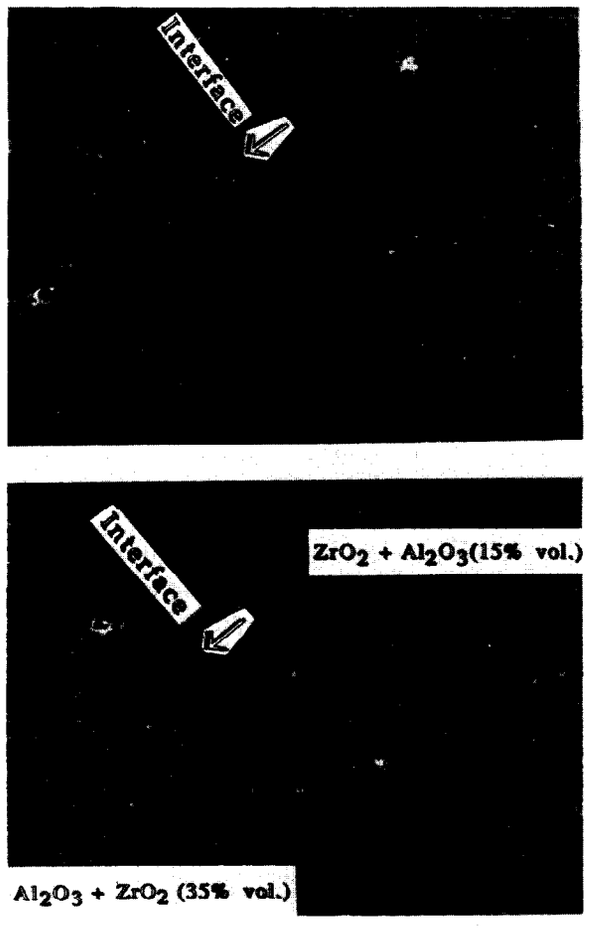

Fig. 10. SEM back-scattered micrograph of a laminar composite obtained by centrifugation of $NHNO_3$ added suspensions. The smoothness of the interface and the homogeneity of the layers are evident.

Sintering of multilayer composites

Densities of about 98–99% were reached by sintering the composites obtained from deflocculated slurries at 1580°C for 3 h (heating rate 5°C/min).

In the case of NH_4NO_3 added materials, a more complicated sintering process was needed in order to gently decompose the salt. The powder compacts were heated at 2°C/min up to 200°C and kept at this temperature for 45 min. Successively, the heating rate was increased by 5°C/min and the composites were fired for 3 h at 1580°C. With this thermal cycle, densities close to the theoretical value were obtained.

Conclusions

Zirconia and alumina based laminar composites can be fabricated by centrifuging aqueous suspensions containing the two oxide powders.

Good results were obtained using relatively dilute slurries (solid phase = 15 vol%). Strong repulsive interactions were generated by adjusting the pH at 4 with HNO_3 additions.

Centrifugation was performed in two different steps. The first one at low g and the other one, shorter, at high g. In this manner, samples with homogeneous thickness were obtained. Before centrifugation, the zirconia reach suspensions required long ageing times in order to eliminate the bubbles present in the suspensions. After 4 h, a decrease of the zeta potential of these suspensions was observed, together with a viscosity increase. The centrifugation of these aged suspensions led to an almost complete solid phase separation. This behavior at present cannot be explained. The best results were obtained with coagulated suspensions (containing NH_4NO_3 1 M) aged for several hours. With these slurries thin laminae with smooth interfaces were obtained.

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