

# **Design and processing of a ceramic laminate with high toughness and strong interfaces**

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**Keywords:** A. Layered structures B. Mechanical properties D. Mechanical testing E. Slip casting

## **Abstract**

An alumina-aluminium titanate laminate designed to combine high crack deflection capability with strong interfaces is proposed. It is constituted by relatively stiff and brittle external layers with microcracked internal layers to produce multiple crack deflection at the microstructural scale. The most important difference of the laminated structure proposed here and that of other laminates with high capability for crack deflection is that the crack deflection process occurs at local level, thus, delamination lengths are limited and delamination does not lead to the lost of structural integrity.

A symmetric structure formed by five layers has been design to minimise residual stresses taking into account the strain on cooling and the Young's modulus of monolithic materials of the same compositions as those of the layers and fabricated using the same processing procedure as that of the laminate.

Special care was given to adjust the processing variables that permitted the fabrication of the designed laminated by sequential slip casting and sintering.

Mechanical characterisation has been done in terms of strength (4-points bending), dynamic Young's modulus, work of fracture and apparent toughness. The two latter parameters have been determined by 3-points bending of Single-Edge-V-Notch-Beams (SEVNB) and fractographic analysis has been performed on the tested samples. The apparent toughness value at the point of failure ( $12 \text{ MPam}^{1/2}$ ) was comparable to values reported for the stationary state of transformation-toughened ceramics. Work of fracture ( $62 \pm 3 \text{ Jm}^{-2}$ ) was significantly higher ( $\approx 26 \%$ ) than that obtained by calculation from the values corresponding to monolithic materials of the same composition as that of the layers, revealing the synergic effect of the laminated structure on the mechanical behaviour of the material.

## **1.- Introduction**

Ceramic materials are being proposed and used as substitutes for metals in structural applications that involve high temperature in severe erosive and corrosive environments and/or compressive loads. The major problem for the structural use of ceramics is related with their brittle fracture mode, which implies the variation of strength of different components within the same batch as a function of the distribution of strength limiting flaws. Although particularly weak components can be removed from the batch by proof testing, once a component enters service, subcritical growth of preexisting flaws or the formation of new cracks, for instance by erosion, can lead to unpredicted failure of the components [1].

One of the most promising new approaches to avoid the lack of mechanical reliability of ceramics is that of layered materials. Nature offers a number of simple layered structures, such as shells or teeth, which present improved failure behaviour as compared to that of the individual components. For example, layers of stiff, hard and brittle aragonite platelets held together by a easily to deform and tough proteinaceous matrix make nacre a rigid material in which both toughness and strength are significantly higher than those of aragonite, which constitutes the 95vol.% of nacre. Several mechanisms leading to energy dissipation have been identified to occur during the fracture of nacre [2-3]: sliding of the aragonite layers, stretching of the filaments in the proteinaceous matrix and crack deflection around the aragonite plates.

On the basis of the toughening mechanisms proposed for nacre, two groups of materials have been developed. One of them combines relatively thick rigid external layers with thin internal layers capable of deformation and energy absorption during fracture. A number of ceramic-metal and ceramic-polymer laminates have been developed on this basis [4-8] which main drawback is the lack of stability at high temperature due to the characteristics of the metal and polymeric layers. On the other hand, since the seminal work by Clegg et al. [9] ceramic-ceramic layered composites have been designed and processed on the basis of weak interfaces between layers to originate crack deflection [1,10-11]. An alternative way to produce crack deflection is to incorporate porous layers of the same composition between dense ceramic layers [12-14]; for deflection to be efficient very high values of the porosity are needed [12]. Main drawback of the second approach is that crack deflection limits the wear resistance of the materials.

From all ceramics, alumina ( $\text{Al}_2\text{O}_3$ ) presents the highest thermal stability together with high hardness sustained up to temperatures over  $1200^\circ\text{C}$ , therefore, is the natural ceramic for wear.

In this work, we present an alumina-based layered ceramic-ceramic laminate designed on the basis of a combination of both discussed approaches. It is constituted by relatively stiff and brittle external layers and microcracked internal layers to produce multiple crack deflection at the microstructural scale, thus, limiting delamination lengths in order not to lose structural integrity. Special care was given to adjust the processing variables that permitted the fabrication of the designed laminated by sequential slip casting and sintering.

As internal material an alumina-aluminium titanate ( $\text{Al}_2\text{TiO}_5$ ) composite containing 30 vol.% of aluminium titanate previously studied was chosen [15]. In this material, extensive deflection and branching of the main crack along the pre-existing microcracks occurred during fracture. An alumina-aluminium titanate composite with relatively high strength (10vol.% aluminium titanate,  $\sigma_f = 261 \pm 6$  MPa, 3-points bending, samples  $2 \times 2.5 \times 30 \text{mm}^3$ , span 20mm [16]) was chosen to constitute the external layers. External composite layers instead of pure alumina ones were chosen at the expense of strength (for monophase alumina  $\sigma_f = 456 \pm 29$  MPa, 3-points bending, samples  $2 \times 2.5 \times 30 \text{mm}^3$ , span 20mm [16]) in order to assure compatible sintering between the layers. On the one hand, it is well known that titania accelerates the initial sintering of alumina [17-19] and, on the other, the formation of aluminium titanate is expansive ( $\Delta V \approx 11\%$ , calculated using density values of  $3.99 \text{ g}\cdot\text{cm}^{-3}$  for  $\alpha\text{-Al}_2\text{O}_3$ , ASTM File 42-1468,  $3.70 \text{ g}\cdot\text{cm}^{-3}$  for  $\beta\text{-Al}_2\text{TiO}_5$ , ASTM File 26-0040, and  $3.89 \text{ g}\cdot\text{cm}^{-3}$  for  $\text{TiO}_2\text{-anatasa}$ , ASTM Files 21-1272) thus, an arrest of the

shrinkage rate occurs at the temperature of aluminium titanate formation ( $\approx 1390^\circ\text{C}$ ) [20-21].

The laminate design was done taking into account the total strain of monolithic materials of both compositions when cooling from the sintering temperature and their Young's modulus in order to limit tensile residual stresses in the external layers.

The work of fracture has been chosen as mechanical parameter to establish the relationships between the mechanical behaviour of the laminate and that of the constituent layers. The advantage of this energy parameter is that it does not require any assumptions about the constitutive equation of the body with the crack to discuss its propagation [22]. Thus, it can be used to describe behaviours which separate from linearity and it is an additive parameter that makes it possible to quantify the different contributions to energy dissipation during fracture [23-27].

The apparent toughness as proposed by Clegg et al. [9,28] for laminates with weak interfaces has been used to compare the mechanical performance of the proposed laminate with that of other structural ceramics.

## **2.- Experimental**

The starting materials were commercial Alumina ( $\alpha\text{-Al}_2\text{O}_3$ , Condea, HPA05, USA) and Titania (anatase- $\text{TiO}_2$ , Merck, 808, Germany) powders.  $\text{Al}_2\text{O}_3/\text{TiO}_2$  mixtures with relative  $\text{TiO}_2$  contents of 5 and 15wt.% were prepared to obtain alumina/aluminium titanate composites with second phase contents of 10 and 30vol.% after reaction sintering, named A10 and A30 respectively.

The mixtures were dispersed in deionised water by adding 0.5wt.% (on a dry solids basis) of a carbonic acid based polyelectrolyte (Dolapix CE64, Zschimmer-Schwarz, Germany). Suspensions were prepared to a solids loading of 50 vol.% and ball milled with Al<sub>2</sub>O<sub>3</sub> jar and balls during 4h. These conditions were selected from a previous work [29].

Solid discs with 20mm in diameter were slip cast in plaster of Paris moulds in order to determine the casting rate of each suspension by determination of the dry wall thickness (Mitutoyo, JDU25, Japan) after different casting times (1-16min). For Young's modulus and strength, plates with 70x70x6 mm<sup>3</sup> dimensions were obtained by slip casting of the A10 and A30 slips. The cast bodies were carefully removed from the moulds and dried in air at room temperature for at least 24h.

The reaction sintering behaviour was studied with a differential dilatometer (Adamel Lhomargy, DI24, France) to 1550°C using small (5x5x5mm<sup>3</sup>) green samples of the monoliths with alumina detector and the sintering schedule was selected from the obtained results. To obtain the monolithic composites, the dried plates were sintered in air in an electrical box furnace (Termiber, Spain) at heating and cooling rates of 2°Cmin<sup>-1</sup>, with 4h dwell at 1200°C and 2h dwell at the maximum temperature, 1450°C. Densities of the sintered compacts were determined by the Archimedes method in water (European Standard EN 1389:2003) and relative densities were calculated from these values and those of theoretical densities calculated taking values of 3.99 g·cm<sup>-3</sup> for alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, ASTM 42-1468) and 3.70 g·cm<sup>-3</sup> for aluminium titanate ( $\beta$ -Al<sub>2</sub>TiO<sub>5</sub>, ASTM 26-0040).

Additional sintering experiments (samples 12x5x5mm<sup>3</sup>) were performed in a differential dilatometer (Setaram, Setsys 16/18, France) with alumina detector reproducing

the same thermal treatment schedule as that used to obtain the final materials in order to determine strain during cooling.

The sintered blocks of the monoliths were machined into bars of  $50 \times 3 \times 4 \text{ mm}^3$  for dynamic Young's modulus determinations, from the resonance frequency of the bars in flexure (Grindosonic, J. W. Lemmens, Belgium) and bend strength tests (4-points bending, 40-20 mm span,  $0.5 \text{ mm min}^{-1}$ ; Microtest, Spain). Reported Young's modulus and bend strength values are the average of five measurements and errors are the standard deviations.

A symmetric laminated structure of five layers was fabricated by casting each suspension alternately. Casting times were fixed to reach the desired layer thickness considering the casting kinetics and sintering shrinkage of each composition. The laminate had the central ( $1200 \text{ }\mu\text{m}$ ) and outer layers ( $\cong 2100 \mu\text{m}$ ) made of A10 and the two inner layers ( $\cong 300 \mu\text{m}$ ) of A30.

Microstructure of polished cross sections was characterised in a field emission gun scanning electron microscopy (FEG-SEM, Hitachi, S-4700, Japan). Thermally etched ( $1440^\circ\text{C}$ -1min) specimens were analysed. Additional observations were performed on chemically etched (HF 10vol% - 1min) specimens in order to assure that the thermal etching did not produce further microcracking in the sintered specimens.

Single-Edge-V-Notch-Beams (SEVNB) of  $4 \times 6 \times 50 \text{ mm}^3$ , machined from the laminated sintered blocks, were tested in a 3-points bending device using a span of 40 mm and a cross head speed of  $0.005 \text{ mm} \cdot \text{min}^{-1}$  (Microtest, Spain). The notches were initially cut with a  $150 \text{ }\mu\text{m}$  wide diamond wheel. Using this slot as a guide, the remaining part of the notch was done with a razor blade sprinkled with diamond pastes of successively 6 and  $1 \text{ }\mu\text{m}$ .

Specimens with relative notch depths of about 0.8 of the thickness of the first external layer, corresponding to 0.26 of the specimen thickness ( $W$ ), were tested. The tip radii of all notches were determined from optical observations and they were always found to be below 20  $\mu\text{m}$ . The curves load - displacement of the cross-head of the load frame were recorded and corrected by subtracting the compliance of the testing set up (machine, supports, load cell and fixtures,  $1.5 \cdot 10^{-7}$  m/N) determined by testing a thick ( $25 \times 25 \times 100$  mm<sup>3</sup>) unnotched alumina bar. Three specimens were tested and the curves were found to be practically coincident. The fracture toughness parameters, i.e. critical stress intensity factor,  $K_{IC}$ , and work of fracture,  $\gamma_{WOF}$ , were calculated from the curves obtained during the SEVNB tests. Optical and scanning electron microscopy observations were performed on the fracture surfaces.

Additional laminated plates of  $70 \times 70 \times 0.6$  mm<sup>3</sup> were fabricated to get bars ( $50 \times 3 \times 4$  mm<sup>3</sup>) for strength testing. In these samples, the relationship between the width of the A10 and A30 layers ( $t_{A10}/t_{A30} \approx 5$ ) was slightly higher than that between the internal layers in the thick specimens ( $t_{A10}/t_{A30} \approx 4$ ).

### **3.- Results and discussion**

#### **3.1.- Laminate design and processing**

During slip casting of suspensions of both compositions, the well-known proportionality between the square of wall growth and the slip time was found. Casting kinetics of 0.9 and 1.2 mm<sup>2</sup>/min for the A10 and A30 slips were determined. As described elsewhere [29], for a fixed wall thickness casting time shortens with titania content.



In Figure 1, dynamic sintering curves for alumina and both studied composites are plotted. Shrinkage was initially retarded for the composites with respect to that of pure alumina due to the presence of a second phase and then it was accelerated between 1200 to 1400°C. For the composites, the shrinkage levels during heating were coincident at 1240°C (Fig. 1.a) and the sintering rates were coincident at 1150°C (Fig. 1.b). A significant slope change occurred at about 1380°C in agreement with the reported temperature for the expansive reaction between  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  to form aluminium titanate [20].

From these curves (Fig. 1), a two-step sintering treatment, with a rather low heating rate  $2^\circ\text{Cmin}^{-1}$ , was designed to favour co-sintering of A10 and A30 layers in the laminated structure. An initial dwell of 4h at 1200°C was chosen for homogeneous shrinkage before reaction, this temperature being a compromise between those for coincident levels of shrinkage, 1240°C, and of shrinkage rate, 1150°C. A 2 h dwell at 1450 °C was selected for final sintering, as this was the temperature at which shrinkage was almost arrested in both composites. This relatively low temperature for final sintering assured the control of grain growth.

The properties of the monolithic materials of compositions A10 and A30 are summarised in Table 1. For the laminated structure, the composition with the highest strength was chosen for the external layers whereas that of the highest work of fracture was chosen for the internal ones.

To design the symmetric structure with five layers the level and sign of the expected residual stresses was analysed and the thicknesses of the layers were chosen in order to

minimise tensile residual stresses. The residual stresses at the centre of the layers of a symmetrical laminate can be evaluated using the simplified model of a symmetric plate constituted by alternate layers of the same thickness having a uniform biaxial distribution of stresses across each layer [30]. Using this approach, the residual stresses at the centre of the composite A10 and A30 layers, are given by:

$$\sigma_{A10} = -\frac{\Delta\varepsilon E_{A10}}{1 + \frac{E'_{A10} n_{A10} t_{A10}}{E'_{A30} n_{A30} t_{A30}}} \quad (1)$$

$$\sigma_{A30} = -\sigma_{A10} \frac{n_{A10} t_{A10}}{n_{A30} t_{A30}} \quad (2)$$

where  $\Delta\varepsilon$  is the thermal expansion mismatch between the layers, E is the Young's modulus and  $n_{A10, A30}$ ,  $t_{A10, A30}$  are the number of layers and their thickness.

The actual difference between the dimensional variations of the layers during cooling ( $\Delta\varepsilon$ , Eq. 1-2) was determined from the corresponding part of the sintering curves of the monoliths shown in Figure 2, as described previously for alumina-aluminium titanate composites [31]. In alumina based materials, deformation mismatch at temperatures higher than 1200°C can be accommodated by diffusion [32], whereas, from 1200°C to room temperature, this mismatch originates stresses. Therefore, in order to evaluate the stress level and sign in the laminate, the differences between the dimensional variations of specimens during cooling from the "stress free" temperature, 1200°C, were analysed. In figure 2b, these variations are plotted together for both monoliths, after correction for coincident dimensions at 1200°C. In the considered interval of temperatures (1200-50°C) the shrinkage for the A10 composite ( $\cong 19.7 \cdot 10^{-4}$ ) was slightly larger than that of A30

( $\cong 16.3 \cdot 10^{-4}$ ), which would imply tensile residual stresses in the central and external high strength A10 layers and compressive residual stresses in the internal A30 layers, respectively.

Taking into account that, according to Eq. 1-2, the minimisation of the tensile residual stresses of the external A10 layers would require relatively thin A30 internal layers and wider A10 layers, the laminated structure shown in Fig. 3 was selected a relationship between the width of the central A10 layer and A30 layers  $t_{A10}/t_{A30} \cong 4$ . In order to simplify, a conservative model with the three A10 layers having the same width as the central one in the laminate ( $\cong 1200 \mu\text{m}$ , Fig. 3) can be considered to calculate the residual stresses using Eq. 1-2 and the properties of the monoliths. Dynamic Young's modulus values from Table 1 were used for calculations which, being always higher than the static ones, would also lead to conservative values of the residual stresses. Tensile stresses of about 15 MPa and compressive stresses of about 90 MPa were expected in the A10 and A30 layers, respectively. In the case of the small bend strength specimens ( $50 \times 3 \times 4 \text{ mm}^3$ ), with a relationship between the width of the central A10 layer and A30 layers  $t_{A10}/t_{A30} \cong 5$ , the expected residual stresses would be similar; tensile stresses of about 12 MPa and compressive stresses of about 90 MPa were calculated.

### **3.2.- Microstructure**

In Table 2 the desired thicknesses according to Figure 3 and the casting times required for the processing of the laminate plates by sequential slip casting are summarised. The obtained thicknesses, determined directly in the SEM, were systematically larger than the

desired ones which could be explained by the relatively higher efficiency for filtration of the large plaster moulds used to cast the plates as compared to that of the small ones used to fabricate the disc specimens.

Figure 4 shows characteristic microstructures of the specimens. At low magnification (Fig. 4a), long microcracks ( $\approx 200\mu\text{m}$ ) with large crack opening displacement (Fig. 4 b) were observed. These microcracks were not randomly oriented as occurred in the monolithic A30 material taken as a reference [15] but preferentially oriented parallel to the interfaces between the layers. This orientation can be explained taking into account that the internal layers in the laminate will be subjected to compression during cooling from sintering. The Poisson effect will lead to the development of tensile stresses perpendicular to the interfaces inside the internal layers which, added to the local stresses developed at the grain boundaries due to thermal expansion mismatch, will produce the formation of the observed microcracks. The fact that edge cracks [33-34] were not observed in this laminate in which internal compressive residual stresses develop during cooling indicates that there was a significant release of residual stresses due to microcrack formation.

### **3.3.- Fracture behaviour**

Figure 5 shows a characteristic corrected load-displacement curve; the load increased linearly with the displacement of the testing frame up to a maximum value ( $\approx 150\text{N}$ ) after which a sudden load drop occurred. The initial linearity indicates that the initial deformation behaviour was controlled by the linear and stiff external and central layers until the initiation of crack propagation at  $K_{0\text{app}}$  of  $\cong 4.1 \text{ MPa}\cdot\text{m}^{1/2}$ . The most interesting

feature of the curves was that the load drop was arrested at about 55 N and then, the specimens admitted further deformation without increasing the load up to their complete failure.

In Figure 6 the fracture modes of the different layers are shown. All layers of composition A30 presented different fracture planes forming steps that followed the orientation of the pre-existing microcracks, which indicates that the main crack was deflected and/or branched along them; fracture of the A10 layers was flat relatively to that of the A30 ones. In Figure 7 the crack paths in the lateral surfaces are shown. The propagation of the main cracks was never completely straight due to the above mentioned crack deflection and/or branching processes, nevertheless, significant differences were found depending on the particular layer of the laminate. The deflection distances through the first A10 layers and part of the first A30 ones were very small and multiple cracking was not observed whereas significant deflection distances and multiple cracking were observed in the other layers. Fig. 7 a shows how a main crack reaches a pre-existing microcrack, and seems to be arrested by it emerging at a certain distance ( $\approx 80-100\mu\text{m}$ ) of the point of impingement to traverse the remaining part of the first A30 and the second A10 layers. When the crack reaches the second A30 layer (Fig. 7 b) it impinges also a pre-existing microcrack but in this case multiple cracks emerge at different distances of the point of impingement. Moreover, the same process occurs with the emerging cracks.

The aspect of the load-displacement curves can be inferred from the fracture features just discussed (Figs. 6-7). The initial load drop observed, corresponding to the kinetic propagation of the main crack, will be associated to its propagation to reach the second A30

layer. The observed crack deflection in the first A30 layer (Fig. 7 a) would not be enough as to produce significant strain in the specimens. Conversely, the multiple deflection and formation of secondary cracks perpendicular to the layers in the second A30 layer (Fig. 7 b) will allow the specimens to deform without increasing the load, as observed in the load-displacement curves before the complete failure.

Strength values are summarised in Table 1. The fact that the strength values for A10 specimens obtained here were lower than those previously reported [16] for small specimens (2.5x2x30mm<sup>3</sup>) of this material tested in 3-points bending (20mm span) can be explained by the Weibull effect. The strength values for the layered material were lower than those of the A10 monolith which can not be explained at this point, as the expected residual stresses were very low and, moreover, they should have been partially released as discussed above. Special care should be taken in order to improve the quality of the microstructure of the external layers in this kind of structures. Nevertheless, strength values of the laminate were higher than those of the monolith of the same composition as that of the internal A30 layers while presenting a significantly higher toughness.

#### **4. Concluding remarks**

From the load-displacement curves obtained and the observed fracture paths it is possible to calculate the apparent toughness at the point of failure of the studied laminate [9,28]. As previously discussed for the load-displacement curve in Fig. 5, the load drop was arrested at about 55 N, and then, the specimens admitted further deformation due to multiple deflection and formation of secondary cracks perpendicular to the layers in the second A30 layer (Fig. 7 b). From such load value (55 N, Fig. 5), the failure stress for the

discerned formation of secondary cracks was calculated from the stress distribution under 3-points bending on a prismatic bar formed by layers with different elastic properties [40] by assuming a propagating crack with a length equal to the location of the center of the second A30 layer ( $a/W=0.76$ ; Fig. 7 b). From the failure stress, and taking into account a general stress intensity formulation [41], an apparent toughness of  $\cong 12 \text{ MPa m}^{1/2}$  was calculated.

This value is slightly lower than that reported for the most performing crack-deflecting laminates ( $15\text{-}18 \text{ MPa m}^{1/2}$  [9,28,35-39]) constituted by SiC and graphite. Nevertheless, it is comparable to values reported for the stationary state of transformation-toughened ceramics ( $\approx 6 \text{ MPam}^{1/2}$  [42],  $9\text{-}12 \text{ MPam}^{1/2}$  [43]), which are the toughest oxides.

The work of fracture value calculated from the area under the semistable fracture curves (Fig. 5,  $62\pm 3 \text{ Jm}^{-2}$ ) was significantly higher ( $\approx 26 \%$ ) than that obtained by calculation, taking into account the additive character of the work of fracture, from the work of fracture values of monolithic materials of composition A10 ( $35\pm 3 \text{ Jm}^{-2}$  [16]) and A30 ( $53\pm 4 \text{ Jm}^{-2}$  [15]) processed in the same way, and the surface fraction of the crack corresponding to each layer ( $s_{10}\approx 0.83$  and  $s_{30}\approx 0.17$ , and  $s_{10}\approx 0.86$ ,  $s_{30}\approx 0.14$  for specimens with notch lengths of 0.4 and 0.8, respectively). This fact reveals a synergic effect of the laminated structure on the mechanical behaviour of the material.

The most important difference of the laminated structure proposed here and that of other laminates with high capability for crack deflection is that the crack deflection and branching processes occur at local level, as demonstrated by the micrographs of fractured

samples in Figures 5 and 6. As a consequence, the new design for ceramic laminates proposed allows reaching high apparent toughness and work of fracture while maintaining the structural integrity of the piece after the initiation of crack propagation under shear stresses as those that develop in wear applications. Further improvements of the proposed structure will be reached by laminated designs with larger numbers of thinner layers to originate graceful fracture.

### **Acknowledgments**

The authors would like to acknowledge the support of the Project MEC MAT2006-13480 C02, Spain.

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