Joining green ceramic tapes made from water-based slurries by applying low pressures at ambient temperature

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Abstract
The production of multilayer ceramics by laminating stacked green ceramic tapes is one of the most attractive methods to fabricate layered materials. In general, organic additives are employed which implies high pressures (up to 130 MPa) and temperatures (up to 110 °C) to originate mass flow between stacked green ceramic tapes which is time and energy consuming. The complete elimination of the residues before sintering of the bodies involves environmental unfriendly emissions, while expensive raw materials are just burned out and, in general, the sintered materials present rather high porosity levels.

In this work, a lamination technique for joining ceramic green tapes fabricated from aqueous ceramic slurries is investigated. As a first approach to the problem, the feasibility of obtaining monolith samples made of six tapes of the same composition (95 vol.% Al₂O₃–5 vol.% YTZP) was investigated to establish the optimum conditions to obtain defect-free sintered materials. The cross-section of sintered pieces was investigated for large defects and for delaminations using dye-penetrating techniques; polished cross-sections of the samples that did not show any cracking at this observation level were further analysed by optical and scanning electron microscopy. Results were correlated with the engineering stress–apparent strain curves recorded during pressing and with the green density values. The control of the stress–strain curves during the pressing process was demonstrated as an adequate means to optimise the lamination parameters.

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1. Introduction
The production of multilayer ceramics by laminating stacked green ceramic tapes is one of the most attractive methods to fabricate layered materials due to its suitability for mass production and its ability to control material “architecture” by varying the individual layer composition and thickness as well as the stacking order.1–4

In general, tapes are cast-formed using suspensions on the base of organic solvents with polymer binders; lamination is performed by compression at temperatures above the glass transition point of the binder.1,3

For ideal lamination, the boundary between two adjacent tapes should be undetectable after compression. According to Hellebrant,7 during the thermo-compression process this can only be achieved if individual particles at the surfaces of the tapes in contact move and interpenetrate within a thin, surface-near region, thus smoothing the micro-roughness of the tapes and forming a homogeneous structure. To initiate this movement of particles, not only the right temperatures and pressures need to be selected, but also, the compositions of tapes employed have to have optimized volumetric ratios between the ceramic particles, the organic additives and the pores.

The literature gives variable values for the temperatures and pressures employed to reach mass transport between adjacent layers.1,6–8 Schwartz and Wilcox1 and Mistler,6 report broad ranges for temperature (25–110 °C) and pressures...
of expensive raw materials. Therefore, large efforts have been devoted to development of aqueous ceramic slurries to attain low porosity materials.

Such a process involving the application of both temperature and pressure to obtain the laminated green piece is time and energy consuming. Therefore, new lamination techniques have started to emerge, in order to simplify this processing step during the production of laminate ceramic materials.

As reported by Roosen and coworkers, a way to minimize the pressures and temperatures employed for the lamination process is to use an adhesive film placed between adjacent layers during the lamination process. The formation of a low-viscosity melt from this adhesive film during the low temperature stages of sintering is the main prerequisite in this joining method. The movement of the melt through the pores causes the ceramic tapes to approach one another and to form a homogeneous structure. For the joining process, a low range of pressures 2.5–5 MPa applied at room temperature was reported to be sufficient. A disadvantage of this joining method is the requirement to have sufficient pore volume for the flow of the polymer melts and the limitations related to grain size of the powder particles.

The processing of ceramic materials using high levels of organic additives implies slow and careful heat treatments at relatively high temperatures to allow the complete elimination of the residues before sintering of the bodies and, in general, the sintered materials present rather high porosity levels. Moreover, elimination of the organic solvents involves environmentally unfriendly emissions during sintering and the associated loss of high amounts (20–40 vol.%) of expensive raw materials. Therefore, large efforts have been devoted to development of aqueous ceramic slurries for tape casting, to attainment of low porosity materials and to work safety, environmental and cost considerations.

In this work, the possibility to laminate green tapes processed by tape casting from aqueous ceramic slurries by using low additions of a polymeric emulsion as a binder is investigated. In order to facilitate the formation of the junction between two adjacent layers, a water dispersion of the same polymeric emulsion was used in the boundary as a gluing agent. The control of the engineering stress–apparent stress curves during the pressing process is proposed as a way to optimise the lamination parameters. By these means, results would be applicable to pieces with different sizes and shapes. As a first approach to the problem, the feasibility of obtaining monolith samples made of six tapes of the same composition was investigated and the optimum conditions to obtain defect-free sintered materials were established and correlated with the characteristics of the stress–strain curves. Further work will extend the method to tapes with other compositions and to the fabrication of layered materials.

2. Experimental

2.1. Slurry formulation and tape casting

The slurry formulation and tape casting experiments were carried out for production of the tapes using high purity α-Al2O3 and t-ZrO2 powders and deionised water as dispersing media. The starting powders were α-Al2O3 (Condea HPA 0.5, USA), with mean particle size of 0.35 μm and specific surface area of 9.5 m2/g, and a t-ZrO2 stabilised with 3 mol% Y2O3 (TZYS, TOSOH, Japan), with a mean particle size of 0.4 μm and a specific surface area of 6.7 m2/g. A polyelectrolyte (Dolapix CE 64, Zschimmer & Schwarz, Germany) was used for powder dispersion. A water-based polymeric emulsion Mowilith DM 765 E (Celanese, Spain), with a Tg of −6°C and solid content 50 vol.%, particle size 0.05-0.15 μm was used as binder.

Optimum conditions to fabricate tapes containing 95 vol.% of α-Al2O3 and 5 vol.% of t-ZrO2 (named A-SYTZP) were fixed for starting slurries with a solid content of 50 vol%. First, slurry stabilisation was performed with 0.8 wt.% (referred to solid contents) polyelectrolyte and ball milling with alumina balls for 4 h. Then 5 wt.% of binder (referred to solid content) was added to the deflocculated suspension and further mixing with a blade mixer for 30 min was done. The tape casting was performed on stationary polypropylene film using a moving tape casting device with two doctor blades (laboratory developed device, Fig. 1). The final casting parameters were 10 mm/s casting velocity and 500 μm gap height between the blades and the carrier film. After drying in ambient air for 24 h, the green ceramic tapes were subjected to further drying at 60°C for 48 h and after this final shaping by punching out square and round shape pieces of tape was performed. As a result, two kinds of shapes were obtained: square (25 mm × 25 mm) and discs (diameter Φ = 26 mm), that will be named square and round tapes correspondingly. Green densities of the tapes were measured after the drying cycle described above, by geometrical method using six discs of each composition of the green tape. The final...
thickness of the dry tapes obtained varied between 460 and 480 μm.

2.2. Lamination by gluing and pressing

Each monolithic piece was made using six tapes of the same shape and size. Before pressing, pieces were formed by sequentially stacking the tapes. A thin layer of the gluing agent was applied using a painting brush on the top surface of the piece before stacking the subsequent tape. Aqueous dilutions of the binder Mowilith DM 765 E (Celanese, Spain), used for the tape formulation, were investigated as the gluing agent. The dilutions were of 5, 25 and 50 wt.% binder using distilled water.

Before applying the gluing agent, the tapes were subjected to two different treatments. One, which is referred to as “dry” treatment, consists of applying the gluing agent directly on the ceramic tape. The second, which is referred to as “wet” treatment, consists of dipping the ceramic tape in distilled water, at room temperature during 1 min, before applying the glue.

The pressing experiments were carried out using a universal testing machine (Microtest SA, Spain) with steel compression plates. In order to avoid friction with the plates, the stacked pieces were placed between two sheets of polypropylene film. No pressing die was used to eliminate additional lateral friction. The pressure was applied using a load frame with a load cell precision of 100 N and a load displacement rate of 0.05 mm/min. The load (load cell precision 100 N) and the displacement (precision 1 μm) of the load frame were recorded during the pressing process, and engineering stress–apparent strain curves were calculated assuming uniaxial compression and using the initial dimensions of the pieces formed by the stacked tapes. In order to assess the variability of the response of different pieces to the pressing procedure, the stress–strain curves of two individual pieces of each composition pressed up to the maximum stress values (∼90 MPa) and curves of five individual pieces of each composition pressed at low stress values (3–20 MPa) were characterised.

The apparent densities of green pieces obtained using different pressure levels, were measured by Archimedes method in mercury by applying the same drying cycle as for single tapes, and were then compared to those of the dry green tapes. Relative green densities were calculated as % of the calculated theoretical density of the studied composition, using 3.99 g/cm³ for α-Al₂O₃ (ASTM 42-1468) and 6.10 g/cm³ for t-ZrO₂ (ASTM 83-113).

The obtained green pieces are termed dry square, dry round and wet round in the following sections, corresponding to the characteristics of the constituent tapes.

2.3. Thermal treatment and sample analysis

Binder burn out and sintering was performed in a single thermal treatment cycle. The binder burn out was carried out with heating at the rate of 1 °C/min up to 600 °C, with a dwell time of 30 min. With this treatment delamination during the initial heating was avoided. Right after this the sintering was carried out by increasing the temperature with a heating rate of 5 °C/min up to 1550 °C with a dwell time of 2 h. Density values of sintered pieces were determined by the Archimedes method in distilled water and relative densities were calculated as described for green densities.

The cross-section of all sintered pieces was investigated for large defects by submerging into a dye penetrating liquid and later examining with a binocular magnifying glass employing ultraviolet light. Polished cross-sections of the pieces that did not show any cracking at this observation level were further analysed by optical microscopy (Carl-Zeiss H-P1, Germany) and by scanning electron microscopy (Zeiss DSM-950, Germany).

3. Results and discussion

3.1. Shape and treatment influence on the tape behaviour under stress

Fig. 2 shows the effect of shape on the engineering stress–apparent strain curves. Results for dry square pieces showed very high variability at all deformation levels, and maximum stress values that could be reached without macroscopic failure of the pieces (Fig. 3a) were about 15 MPa.
Failure was easily distinguished in the stress–strain curves as a decrease in slope (Fig. 2a). Conversely, the curves corresponding to dry round pieces were coincident up to stress levels of about 25 MPa and macroscopic failure of the pieces occurred for stress values higher than 30 MPa (Fig. 3b), from this point, the slope of the stress–strain curves also decreased significantly (Fig. 2b). Moreover, from this stress level, differences between the curves corresponding to different samples arose. Such large differences between the behaviour of round and square pieces have to be attributed to the heterogeneous stress distribution at the corners of the square ones, and, therefore, round shaped pieces should be recommended for pressing and were used in the following sections.

The engineering stress–apparent strain curves for different wet round pieces were fairly coincident (Fig. 4). In all cases, stresses up to 90 MPa were reached for increasing imposed deformations and no macroscopic failure was observed (Fig. 3c).

From Figs. 2 and 3, it is clear that macroscopic failure of the dry pieces (Fig. 3a and b) is detected in the stress–strain curves by a significant decrease in the slope (Fig. 2a), meaning that increasing deformation led to very little stress increase. This slope change of the stress–strain curve reveals the weakening of the structure due to crack formation. Conversely, in the curves corresponding to wet pieces the slope increases monotonously across the whole pressing interval (Fig. 4) as would correspond to increasing contact between particles without macroscopic cracking (Fig. 3c).

Not only the macroscopic behaviours of the wet and dry round pieces pressed up to 90 MPa were totally different, as discussed above, but also the macrostructures of sintered pieces after pressing at low pressures were extremely different, as shown in Fig. 5. In both cases, elongated porosity located at the interphase between tapes indicating a lack of interphase formation during pressing was observed. An additional system of cracks perpendicular to the interfaces was detected in the dry round pieces (Fig. 5a). These cracks originated during pressing due to a lack of strain accommodation once the rigid dry tapes came in contact, whereas the lubricant effect of water in the wet pieces improved mass flow.

In order to investigate whether the failure of the dry pieces at low stress levels could be derived from the stress–strain curves, as occurred for macroscopic failure, the engineering stress–apparent strain curves of five pieces fabricated using low stress levels was analysed. The curves for dry pieces (Fig. 6a) were fairly coincident up to 10 MPa, from this point different stress levels for similar strains were reached for different pieces. Conversely, the curves corresponding to wet pieces (Fig. 6b) were coincident in the whole stress interval. Good fits were found for third degree polynomials for both sets of curves. Therefore, to represent the behaviour of the pieces, the average of the polynomial curves of samples fabricated under the same conditions was represented, taking as the variability the standard deviation of the five values. In Fig. 7, the average curves are plotted together with the derivatives. An inflexion point, highlighted by the derivative plot, is observed in the stress–strain curve of dry pieces at strains 0.04–0.06 (Fig. 7a), which corresponds to the stress levels for which perpendicular cracks, developed in the sintered pieces (about 10 MPa, Fig. 5a). After the inflexion point, the rate of stress increase with deformation starts to decrease, indicating the weakening of the structure due to the formation of the observed perpendicular cracks (Fig. 5a). Conversely, both curves, the engineering stress–apparent strain and its derivative, grow monotonously for the wet pieces in the strain range considered (Fig. 7b). Therefore, detailed observation of the
stress–strain curves also serves in to predict the perpendicular cracking (Fig. 5) in the pieces. From these observations, it can be concluded that shape and pre-treatment (wet/dry) of the tapes before forming the piece are determinant parameters for the behaviour of the pieces during pressing. The only valid combination from the ones studied is that of wet round pieces, as pressing of the dry round ones leads to structural damage of the tapes before the interlayer porosity disappears by particle rearrangement.

3.2. Selection of the gluing agent concentration

Once macroscopic failure (Fig. 2a and b) and perpendicular cracking (Fig. 5a) are avoided, the processing parameters

![Fig. 5. Optical micrographs of polished cross-sections of round (Ø = 26 mm) pieces pressed up to 10 MPa using the gluing agent of 25 wt.% dilution. (a) Piece fabricated from dry tapes. Elongated porosity located in the interfaces as well as cracks perpendicular to the interfaces is observed. (b) Piece fabricated from wet tapes. Elongated porosity located in the interfaces is observed.](image1)

![Fig. 6. Behaviour during pressing at low pressures of round (Ø = 26 mm) pieces fabricated using the gluing agent of 25 wt.% dilution. (a) Two representative engineering stress–apparent strain curves corresponding to dry round pieces. (b) Two representative engineering stress–apparent strain curves corresponding to wet round pieces.](image2)

![Fig. 7. Behaviour during pressing at low pressures of round (Ø = 26 mm) pieces fabricated using the gluing agent of 25 wt.% dilution. Third degree polynomial fit of the average engineering stress–apparent strain curves of five samples fabricated under identical conditions and its derivative. The size of symbols represents the standard deviation. (a) Dry pieces. (b) wet pieces.](image3)
The aspect, at low magnification, of sintered pieces fabricated using different stress and dilution of the gluing agent levels is shown in Fig. 9. Separation between layers, clearly revealed by the dye penetrating ink, is observed in the cases of gluing agents with higher binder contents and/or low pressures whereas interfaces were not detected for the highest pressure and lowest binder content (5 wt.% dilution) investigated. Fig. 10 shows the aspect of the interfaces at SEM level. Defects revealed by the dye penetrating ink (Fig. 9) are constituted by linear low density zones and pores, whose width and occurrence was larger for lower pressures and lower dilution levels of the gluing agent (Fig. 10a and b). Moreover, some smaller defects were also observed at SEM level in the pieces fabricated using the lowest binder concentration in the gluing agent and 10 MPa (Fig. 8). These last were smaller, not only in length but also in width, and much less frequent.

The above discussion demonstrates that the dilution level of the gluing agent is a processing parameter with a strong effect on the final microstructure of sintered pieces. Nevertheless, this fact cannot be inferred from the green density values, generally used to determine the adequacy of the green processing. As shown in Table 1, green densities are coincident for one stress level notwithstanding the differences between the microstructure of the interphases found for different dilution levels of the gluing agent used to fabricate the pieces.
3.3. Effect of pressure

In order to check whether the remaining defects in the pieces could be avoided by increasing the pressure levels, additional pieces were fabricated using pressures up to 18 MPa and the gluing agent with the lowest binder concentration (5 wt.%). In all cases, the engineering stress–apparent strain curves were obtained in order to verify that fracture had not occurred during pressing, as discussed previously. Density values for these pieces are included in Table 1. The pressures

(Fig. 10). This occurs because density values will be determined, not only from the density of the individual layers and the possible voids between them but also by the density of the gluing agent. Sintered densities are lower when lower pressures and higher binder concentrations are used, in agreement with the microstructure trends showed in Figs. 9 and 10.

From these results, the gluing agent with the lowest binder concentration was selected as the most suited to fabricate pieces by pressing together the water-based cast tapes.

Table 1

<table>
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<tr>
<th>Dilution level</th>
<th>Stress (MPa)</th>
<th>( \rho_{\text{green}} ) (g/cm(^3))</th>
<th>( \rho_{\text{piece/} \rho_{\text{single tape}}} ) (g/cm(^3))</th>
<th>( \rho_{\text{pressed}} ) (g/cm(^3))</th>
<th>( \text{wt} % )</th>
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<tr>
<td>5</td>
<td>3</td>
<td>2.39 ± 0.01</td>
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<td>3.99 ± 0.01</td>
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<td>98.4 ± 0.4</td>
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<td>2.39 ± 0.01</td>
<td>98.4 ± 0.4</td>
<td>3.96 ± 0.01</td>
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<tr>
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<td>98.4 ± 0.4</td>
<td>3.98 ± 0.02</td>
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<td>97.5 ± 0.2</td>
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Errors are the standard deviation of five pieces processed identically.
applied over 15 MPa did not have any significant effect on the values of the green and sintered densities. The observation by SEM of samples produced using pressures of 15 and 18 MPa, confirmed the formation of good interface union (Fig. 11a). The typical linear low density defects observed in pieces made using 10 MPa pressure (Fig. 10c) were observed for pieces produced using 15 MPa, but at a much smaller scale (Fig. 11b). The frequency of these defects was observed to be highest at the middle zone of the produced piece.

The increased values of the pressure up to 18 MPa, served to minimize the frequency and size of the interface defects. As shown in Fig. 11c, the piece produced using 18 MPa pressure had interface defects within the scale of material microstructural defects.

4. Conclusions

The possibility to fabricate defect-free laminate ceramic materials by laminating green tapes, processed with tape casting procedure from aqueous ceramic slurries, at room temperature and using a dissolved adhesive of the same type as the binder of the green tapes has been proved.

The responses of pieces formed by six stacked tapes during pressing in the form of engineering stress-apparent strain curves make it possible to establish the right pressure ranges and pre-treatment of the tapes to avoid macroscopic failure and microscopic cracking of the samples. Higher effectiveness of pressure and gluing agent dilution in the sense of elimination of interface porosity between layers is shown in these curves as higher-pressure levels for similar strains; it cannot be derived from green density values.

Optimum conditions include the stacking of wet round tapes using a gluing agent with low binder concentration between the tapes. The minimum pressure value, for fabrication of monolithic A-5YTZP laminated ceramics without interface defects was determined to be 18 MPa with the gluing agent with 5 wt.% of binder.

Further work will extend the method to tapes with other compositions and the fabrication of layered materials.

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