Water Based Colloidal Processing of Ceramic Laminates

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Abstract. Multilayered materials and coating are complex structures proposed among others to face the structural requirements of ceramics. The development of reinforcement mechanism by laminated structures can be due to deflection criteria or to the presence of residual stresses and requires of tailored laminates. These designs are characterized by the phases, thickness and distribution of the layers as well as the joining strength between them. In this sense water based colloidal processing techniques are used to fabricate layered structures by consolidating the layers from fluid dispersions of the powders in water. In these processing methods the phases presented in the final laminate are mainly given by the composition of the starting slurries while the changes in thickness and sharpness of the layers are controlled by acting on the processing parameters. The achievement of stable slurries is a shared step for all the colloidal processing techniques. In the water based slurries the stability will be dominated by the polar media, the surface behavior of the particles and the presence of dispersant additives to increase the repulsion between particles. The stable slurry ensures an effective milling and dispersion of the phases as well as high solid loadings, if required. Further processes associated to shaping and consolidation of the layers requires the incorporation of additives and-or water removal. The shaping methods based on aqueous slurries can be classified taking into account the process of solid-water separation. For each of those shaping methods, the nature and amount of the additives is different in order to get the optimum rheological behavior and green strength after drying. Depending on the thickness of layers and coatings as well as the shape and dimensions of the samples, the shapping method can be selected alone and combined with others.

Introduction

Laminar ceramic composites have received a great deal of attention due to their potential for use in emerging structural applications in which higher mechanical performance is demanded. The development of laminated ceramic composites allow the fabrication of new materials with properties superior to those of monolithic ceramics [1]. In general, the enhanced mechanical behavior exhibited by these composites can not be attributed to a simple rule of mixtures of the properties of the constituent materials but also the laminar structure itself [2-4]. Notable examples of some of these reinforcement methods include the broadening of transformation zones ahead of a crack [5], the crack deflection by weak interfaces or porous layers [2,6,7] or the reinforcement mechanism associated to residual stresses. If residual stresses are present, they can be controlled by designing the proper thickness and distribution of the layers in order to optimize the mechanical properties. They can be generated at the surface [8,9] in order to increase the fracture strength as a result of the stresses superposition acting on the intrinsic critical flaw. On the other hand, if the compressive residual stresses are induced at the internal layers [10-12], damage tolerance, and consequently reliability is the property primarily favoured. In ceramic laminates with strong interfaces, the differential strain that develops the residual stresses came from the differences in the thermal expansion coefficients (α) [12,13] or from the phase transformation of one of the components [8,14,15].

Compressive stresses usually are beneficial for the mechanical response as they oppose to the crack growth [16,17] and/or may develop a threshold strength [12]. On the other hand, tensile stresses should be subtracted to the strength of the material, and if they overpass a critical value
tunnelling cracks will appear and consequently the mechanical response will degrade [14,18]. For these reasons thin compressive layers are desirable, as they will create an additional reinforcement as well as diminish the tension associated. Moreover, the thickness of the layers are referred to other observations related to the residual stresses such as edge crack and crack bifurcation for what a critical thickness “t_c” has to be achieved [11,13,19].

All this considerations clearly show that for a laminate composite the composition, thickness, number and position of the layers are very important design parameters that must be controlled in order to get the desired properties. The fabrication of multilayered ceramics by colloidal processing techniques has been widely used due its versatility and reliability. These methods have the advantages that allow to precise control in the composition and, depending on the technique, the thickness of the layers. The colloidal processing techniques described for the fabrication of laminated ceramic include tape-casting [6,15,20,21], centrifugal casting [5,22], sequential slip-casting [12,23-25], electrophoretic deposition (EPD) [26,27], and others [28-30]. All of them are based on the preparation of stable slurries with specific compositions that are piled up by sequentially adding a layer to a previously formed one. Stable slurries that ensure a homogenous and well dispersed composition are obtained by controlling the interparticle potentials developed within the liquid media [31-33]. The thickness is controlled by controlling the processing parameter associated to the technique (casting time [25,27], blades gap [6], amount of slurry [5], etc…).

Preparation of slurries in water.

Environmental, health and economic requirements made to look for aqueous based suspension systems that provide processing capabilities as effective as the organic based systems. As an alternative to the established processes, the use of water as the dispersion media to fabricate the laminates has both advantages and disadvantages. Advantageous is the know-how derived from the traditional water-based processing techniques such as slip casting, enamel dip coating and others that require highly stable slurries [32,34,35]. On the other hand, the slow drying rate of the layers and tapes, the higher crack sensitivity and the reactivity of the powders with water are causes of concern [36-38]. To overcome these problems, a high solid loading is required to increase the drying rate and simultaneously minimize drying stresses in the tape.

The main problem in a colloidal suspension, which is drastic at high solid loadings, is to maintain the particles dispersed throughout the medium since an attractive force exists as particles approach each other [39]. The DLVO theory (Derjaguin, Verwey, Landau and Overbeek) proposed that the stability of a particle in a liquid is dependent upon its total potential energy function V_T. The general equation that define the overall energy of interaction between particles is

\[ V_T = \sum V_A + \sum V_B + \sum V_S \] (1)

The term \( V_S \) is the potential energy due to the solvent, and usually only makes a marginal contribution to the total potential energy over the last few nanometers of separation. Much more important is the balance between \( V_A \) and \( V_R \), these are attractive and repulsive contributions respectively. Attraction between particles is due to the London-Van der Waals dispersion forces. Those are the result of the interaction between permanent, induced or no permanent dipoles and its effect extends to distances of several nanometers from the particle surface. Repulsive interactions has to be developed with a value high enough to make the particle pair potentials to be dominated by the repulsive terms and make the particles to stay one apart from the others.

This repulsion can be achieved by using two different ways denominated electrostatic and steric mechanisms. The electrostatic mechanism consists in provide the surface of the particles, suspended in a polar media (e.g. water), with a high enough electric charge to develop repulsive electrical
potential. The steric mechanism involves polymers added to the system that adsorb on the surface and prevent the particles coming onto close contact. When polar media are used, electrostatic and steric mechanism can act, but if a non-polar media is employed, only steric mechanism are employed to disperse the ceramic powders [31].

![Diagram of repulsion mechanisms](image)

_Figure 1. Scheme of the different repulsion mechanism between particles dispersed in a polar media_

A third mechanism that involves the sum of those two described previously is the electrosteric mechanism. This one is the most extensively used for water based slurries and consists on the absorption on the particle surface of polymeric chains with functional groups that provide an electric charge to the surface. In this case the repulsive term is due to the sum of both the electrostatic and the steric effect. Fig. 1 show a scheme of those three mechanisms

The achievement of high and stable repulsion forces between the suspended particles in the slurry has several effects.

**Effectiveness of milling.** As the particles break in two parts, the new particles became on the conditions of repulsion avoiding the agglomeration, very common when new surfaces are generated. This effectiveness is also achieved for deagglomeration processes without milling (High shear or ultrasounds).

**Dispersion of different components.** The particles in the fluid media have a high mobility. If particles of different composition develop a high repulsive charge between them, a high dispersion will be achieved. Even more, by changing the conditions of the media different microstructures can be achieved and designed [40]

**Low viscosity of the slurries.** High repulsion between particles makes the slurries to show a lower viscosity than in the case of lower repulsions. For the shaping ceramics that requires a mold, it is desirable a low viscosity that facilitate the mold filling and pouring processes.

**High solid content in the slurries.** Usually for shaping methods, a high solid content in the slurry is required in order to achieve a high green density, decrease the shrinkage and the drying rate.

**High packing density.** For a given processing technique and solid content, the slurry with a high repulsion between particles, allows higher green densities. This is because of the mobility of the particles can arrange a packing distribution with the lower energy, that is, the closer packing.

**Shaping from slurries.**

Fabrication of a ceramic green samples from stable slurries requires the consolidation of the dispersed powders with the desired shape (and microstructure). All the shaping methods are based on the increment of the viscosity of the slurry that ends the viscous behaviour and become a solid. The mechanism employed to increase the viscosity can be used to classify the processing method as it is indicated in Table 1. After shaping a compact, a final drying process until complete water removal is required.
The study of the processing methods and its associated variables permits to fabricate multilayered materials by using one or combining several of them. Some methods has been reported to fabricate continuous changes in composition [41,42], but the most common strategy used for laminates has been to use sequential processing of slurries. That is, the layer composition changes are created by changing the composition of the starting slurries and stacking them together after or before drying.

Consolidation of the powders from the slurry requires the addition of additives binders and plasticizers that keep the desired shape, strengthen the layers and help the further handling processes. For the fabrication of multilayered ceramics, those additives are the also responsible of keeping the layers together in the green state. Traditionally organic solvents have been used as vehicle for dispersion of ceramic particles to fabricate layered materials, due to their compatibility with the most common binders and plasticizers [31,43]. The use of water as the dispersion media requires of compatible binders capable to provide consistency and joining capability to the green layer. There are four main types of binders used for shaping from based slurries [44,45]: cellulose ethers, polyvinyl alcohols, latexes and gelling binders. Latexes are polymeric substances with a molecular weight around 10000 Daltons that had been stabilized in water based emulsions. They have sizes ranging from 20 to 300 nm and are prepared in suspensions with a solid content up to 65 vol.%. As they are polymeric particles in suspension, these binders do not have an important influence on the rheology other than the increment in the solid loading. In contrast, cellulose ethers and polyvinyl alcohols do have an effect on the liquid viscosity as they are polymeric chains dissolved in the media and their molecular weight has a strong influence on the rheology. The great thickening of the viscosity caused in the slurries by these binders results in low density green tapes. The fourth types of binders are the chemically induced gelling binders like alginites or synthetic gels. These have inert components in the liquid media that increase the viscosity after a reaction or physical transformation takes place [45-47].

**Processing methods to fabricate ceramic thick layers from slurries**

**Filtration** methods have been extensively used and studied to fabricate both traditional and advanced ceramics. In these methods the particles are consolidated by passing the slurry through a filter (plaster of Paris, porous polymers or metals). The solid-liquid separation process conducts to the formation of the consolidated wall with the shape of the membrane. The shape is maintained because of the separation process has an increment in the solid loading and consequently in the viscosity. Requirements for the slip casting process are a high solid loading in the suspension, in order to get a good packing density, as well as low viscosity, to avoid problems with the mould filling and pouring. The wall formation kinetic is governed by the Darcy law and is summarized in Eq. 2

\[ e = K t^{1/2} \]  
(2)
Where “e” is the thickness of the consolidated layer, “t” is the time and K is the kinetic constant. The kinetic constant can be calculated experimentally and depends of the mould and the slurry conditions. Sequential slip casting has been successfully used to fabricate layered ceramics [12,23-25] where the layer composition is the determined by the composition of the slurries and the thickness is controlled by the casting time according to the kinetic equation. The process is represented in fig. 2. It starts by filling the mould with the slurry of the first layer composition. After a time \( t_1 \) this slurry is poured out and the second slurry is cast in the mould. The new layer consolidates on the previous one and after a time \( t_2 \), the slurry is poured out. This process can be repeated all the times necessary to achieve the designed layered structure. The limits of this method are related to the layer thickness (difficult to get lower than 50µm) and the total thickness of the sample (difficult to get larger than 1,5 cm).

Plot in Fig. 3.a shows an example of casting kinetics measured for slurry with compositions of \( \text{Al}_2\text{O}_3\)-YTZP. This has been used to calculate the casting times employed to fabricate a multilayer with thick and thin layers presented in Fig. 3.b. It has thick layers of alumina with 5vol% of Y-TZP and alumina with 30 vol% of m-ZrO\(_2\) [24]. From this curve two considerations can be extracted. First of all is that the thickness of the sample is limited. Although the equation has not an asymptotic point, thicknesses higher than 1 cm are very difficult to fabricate because of the large time required. The other important consequence is that as the casting time increases the thickness control is more precise.

![Fig 2. Scheme of the sequential slip casting process](image)

![Figure 3. Plot of the casting kinetic for a suspension (a) with the casting time indicated to get the multilayer material shown in (b)](image)
From the Evaporation/Deposition methods, the most employed method to develop layered structures has been the tape casting. It consists in the deposition of the slurry on a flat surface by moving a carrier that has one or two blades to determine the height limit (Dr. Blade method). To achieve high green densities in the tapes, slurries with high solid content are required as in this method there are not a driving force for consolidation different that evaporation of water. Both the binders addition and the high solid content of the slurry, confers the plastic behaviour that will make it fluid while passing though the blades-substrate gap and keeps the tape dimensions after the tape is shaped.

Thermopressure of tapes cast from organic based slurries has been the widest method used to fabricate multilayer. To fabricate ceramic green tapes from water based slurries, latexes are the mostly binders employed nowadays. From the latexes employed for water based tape casting, the acrylic/styrene binders has been the more commonly used as an adhesive to pile up tapes in order to fabricate monoliths [48-50], and multilayers [6,24,51,52]. The formulation of the tapes employed to create those complex structures requires of a relative elevated amount of acrylic/styrene binders (25-30 vol.%) if compared with other casting processes. This high amount of organic leads to low sintered densities and, consequently, to reach a high flaws population as a consequence of the high porosity. To fabricate dense materials for structural applications, it is required to increase the solids content of the slurries and minimize the organics content. Suspensions with high solid loading can be obtained by ensuring the proper stability between ceramic-ceramic, latex-latex and ceramic-latex particles[53].

The use of latexes as an alternative for tape casting has driven new studies in the piling up mechanism. It has been reported that pre-wetting of the tapes and the use of glue products based on the tapes binder conducts to the joining of tapes with different composition at relatively low pressure at room temperature [54]. Excessive amount of glue or small pressures can generate lack of union between layers [50,55]. In this fabrication method for multilayers, the layer thickness is controlled by the substrate-blade gap. The limits in the thickness of the layers are given by the viscosity of the samples and the drying rate. Usually layer thickness range from 200 to 800 µm. Thinner layers present problems of low strength and sticking to the substrate while thick layers usually has associated problems of drying, segregation and rigidity. Figs. 4 a. and b show two different laminates obtained by piling tapes with different composition. To fabricate these laminated the cast tapes were immersed in water to make them plastic, later they were coated with a 5wt% dilution of the binder utilized and pressed at 18 MPa. Fig. 4.c shows a close up to one of the interfaces.

![Figure 4. Examples of layered ceramic of in the alumina zirconia system fabricated by piling up the water based tapes.](image)

Tape casting and slip casting are two of the most important methods employed to fabricate laminated materials from slurries with relatively high layer thicknesses. Other techniques have been
used to develop multilayers materials from slurries or pastes such as co-extrusion or centrifugal casting [5,56], but they have not achieved the interface definition and layer thickness control as in those above mentioned.

**Processing methods to fabricate ceramic thin layers from slurries**

The processing of thin ceramic layers usually requires of a substrate (dense or porous) that support the consolidated layer. From the methods described in table 2 screen printing and dip coating has been used from older times to fabricate the glazing of traditional ceramics. Latter the slurry spray coating and the electrophoretic deposition has been used to fabricate thin coatings and multilayers from water based slurries, usually using low solid contents.

In the **screen printing**, the ceramic slurry with binders is deposited onto the substrate surface through a screen using a squeegee. The screen mesh, geometry and quality determines the thickness of the resulting layer [57]. Also the mesh may have mask areas so that a pattern can be deposited on the surface. The thicknesses of the layers usually range from 20µm to 100µm.

The **dip coating** process allows the achievement of layers that range from a couple of microns to a hundred of them. The process can be divided in three parts as it is schemed in Fig. 5.

![Figure 5. Scheme of the dip coating process.](image-url)

First the substrate is dipped and soaked in the slurry. Second the withdrawal rate of the substrate at a given speed where the layers is created and finally the solvent evaporation. The layer is generated during the wet layer formation. The thickness depends on the substrate parameters (wettability, roughness and porosity), suspension parameter (viscosity, solid content, binders content and surface tension) and process parameters (withdrawal rate, soaking time, temperature and humidity). If the withdrawal rate is in the Newtonian regime of the slurry, the thickness of the layer (h) can be calculated by the Landau-Levich equation (Eq.3)[58].

$$h = K \frac{(\eta \gamma)^{2/3}}{\gamma_{LV}^{1/6} (\rho) / 2}$$  \hspace{1cm} (3)

Where k is a constant, η is the viscosity of the slurry, v is the withdrawal rate, γ_{LV} is the liquid-vapor surface tension ρ is the density of the slurry and g is the gravity.
As an example of the thickness variation, Fig. 6 shows two coating with different thicknesses obtained by dipping a pre-wet green alumina tape (fabricated by tape casting) in zirconia slurries with different solid contents. Coatings obtained from slurry with the 15 wt % (Fig. 6.a) show a higher thickness than the coating obtained with the 7.5 wt% (Fig. 6.b). The thickness vs. solid content curve can be experimentally determined in order to control the thickness. Due to the different porosity between sizes, the thickness is different depending of the tape side. If the coated tapes described above are pressed together (as explained in the tape casting section) and sintered, a multilayered system with different layers thicknesses can be fabricated showing a very high thickness ratio. Fig. 8 shows the cross section one of these multilayers designed with very thin zirconia layers (bright phase) between thick alumina layers.

Electrophoretic deposition (EPD) has proved to be also useful to fabricate laminates as coating or as multilayered structures. The method is based on the movement of the charged particles suspended in water when an electric field is applied. It allows the fabrication of layers with different thicknesses over a conductive substrate. Continuous methods have been described to fabricate coatings with changes in compositions, but they still do not achieve a precise control in the composition nor in the layer thickness. The sequential methods have allowed to fabricate multilayers and graded materials. They have been also help by the incorporation of binders and
gelling agents to slurry. As in previous methods, a kinetics study is precise. The factors that affect the thickness of the layers fabricated by this processing technique are among others: Electrical conditions (voltage and current), solid contents binders and current time [59,60]. Fig. 8 shows a self-supported multilayered material obtained by EPD changing the deposition time.

![Figure 8](image_url)

Figure 8. Self supported multilayer ceramic fabricated by sequential EPD

Also the EPD process can assist the packing of the slurries with binders or gelling agents in the composition that will help to fix the coating on the substrate and help the formation of a multilayer [61].

References
Functional Gradient Ceramics, and Thermal Barriers