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Influence of the aging time of yttria stabilized zirconia slips on the cracking behavior during drying and green properties of cast tapes

María P. Albano *, Liliana B. Garrido

Centro de Tecnología de Recursos Minerales y Cerámica (CETMIC), C.C. 49 (1897) M.B. Gonnet, Provincia de Buenos Aires, Argentina

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Abstract

Tape-casting process was used to produce yttria stabilized zirconia (YSZ) substrates in an aqueous system using a low amount of an acrylic latex binder. Concentrated suspensions with different aging times were cast, and the influence of the slip aging time on the drying kinetics and cracking behavior of the tapes were studied. In addition, the effect of the slip aging time on the properties of the resultant green tapes was investigated. The latex particles consolidated by coalescence during the aging time of the slips and resulted in an increase in the smaller pore size of the cast tapes. The pore radius increased with increasing the slip aging time up to 14 days thereby decreasing the capillary pressure in the liquid. Aging times over 14 days did not change the pore radius and consequently the capillary pressure. The capillary tension drove the consolidation; the tapes produced from slips with lower aging times which had higher capillary pressure shrank more, had lower pore volume and consequently higher green density. Cracking was found in tapes prepared from slips with aging times shorter than 14 days; the crack area decreased with increasing the slip aging time. For slip aging time $\geq$14 days cracking was not observed. Aging before casting up to 14 days reduced cracking in tapes prepared with low amounts of latex; however, the lower capillary pressure resulted in low green density of the cast tapes.

Keywords: A. Tape-casting; D. ZrO_2; Cracking behavior; Green properties

1. Introduction

Tape-cast layers serve as basic building blocks in many electroceramics components, including multilayer ceramic packages and capacitors. Yttria stabilized zirconia ceramics find applications as solid electrolytes for sensors and solid oxide fuel cells [1].

Tape-casting produces a thin layer on a carrier surface via the doctor blade technique [2,3]. Ceramic substrates were traditionally fabricated using non-aqueous formulations [4,5]. Recently, more efforts have been put on the development of aqueous formulations using water soluble binders [6,7]. Unfortunately, water soluble binders such as poly(vinyl alcohol) and cellulose must be added in large quantities to ensure mechanical integrity of green sheet [8]. This increase the slip viscosity and severely limit the total solids loading achievable in suspension [9].

Smay and Lewis [10] have developed aqueous lead zirconate titanate system that use an insoluble acrylic latex binder. By tailoring interparticle forces in these binary colloidal system, a high solids loading could be achieved [10]. Building on this approach, we have developed an aqueous-based YSZ/latex system for tape-casting of functional electroceramics.

The tape dries to form a flexible film that consists of a particle-filled, polymeric matrix with appreciable porosity. Drying of the films often causes the formation of cracks unless relatively large amounts of organic binders are added. The presence of large amounts of binder strengthen the green body. However, from our experience, large amounts of latex binder reduces the YSZ packing density resulting in an incomplete densification of the sintered tape. The purpose of this work was to produce a crack-free YSZ tape using a low amount of latex.

It has been demonstrated [11,12] that gels subjected to various periods of aging in their own pore liquid reduce the risk of fracture within the body. We have found that the aging of the slips strongly influences the drying behaviour of the granular tapes. Based on this observation, the slip aging time was considered to minimize cracking in YSZ tapes which contain a

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* Corresponding author. Tel.: +54 2148 40247; fax: +54 2171 0075.
E-mail address: palbano@cetmic.unlp.edu.ar (M.P. Albano).

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low amount of latex; studies on this subject have not been previously reported. In this work, the influence of the slip aging time on the drying kinetics and cracking behavior of the cast tapes were studied. In addition, the effect of the slip aging time on the properties of the resultant green tapes was investigated.

2. Experimental procedure

2.1. Materials

A commercial yttria doped zirconia powder (Y8Z01, Saint-Gobain, France) was used in this study. The mean particle diameter and the specific surface area were 0.5 μm and 8.3 m^2/g, respectively.

A commercial ammonium polyacrylate solution (Dolapix CE 64, Zschimmer & Schwarz, Germany) was used as a dispersant. The binder was an acrylic latex emulsion (Duramax B1000, Rohm and Haas Co., Philadelphia PA) with solids loading of 55 wt.%, an average particle size of 0.37 μm, and a glass transition temperature of −26 °C.

2.2. Slip preparation

YSZ slips were prepared by deagglomeration of 20 g YSZ in 5 ml de-ionized water with 0.3 wt.% NH_4PA (dry weight basis of powder), by ultrasonic treatment, with subsequent addition of 11 wt.% latex. The pH of the suspensions was adjusted at 9.0 with ammonia (25 wt.%). The slips were aged different times up to 24 days before casting.

2.3. Tape-casting

Slips were cast on a fixed Mylar carrier film using the doctor blade method. The casting speed was constant at 1 cm/s and the gap between the blade and the carrier film was adjusted at 0.4 mm. The cast tapes were dried in air at room temperature up to constant weight; afterwards, they were stripped from the film.

2.4. Weight loss measurements during drying

Slips with different aging times were cast on Mylar to produce tapes of surface area and initial tape thickness values of 32.5 cm^2 and 0.4 mm, respectively. These samples were immediately placed on a balance (Denver Instrument Model XL-3100) and their mass was recorded as a function of time. From these curves the drying rate and the water weight loss (relative to the initial total water content in the suspensions) were calculated.

The time of water flow from the supersaturated region to the saturated one was measured.

2.5. Characterization of green tapes

The pore size distribution of green tapes prepared from slips with different aging times was performed using mercury porosimetry (Porosimeter 2000 Carlo Erba, Italy).

The thickness of the tapes was measured using a Mitutoyo absolute ID-S 1012 Digimatic Indicator; then, the drying shrinkage expressed as percentage of the blade opening was calculated. The tapes were weighted and measured to determine the green density.

The microstructures were observed by scanning electron microscopy (SEM) (JEOL, JSM-6360). The crack length and width were measured by SEM.

3. Results and discussion

3.1. Drying kinetics and characterization of green tapes

Fig. 1 shows the sample weight as a function of drying time for tapes prepared from slips with different aging times. The curves showed a linear initial stage followed by a falling rate stage. Therefore, the drying process of the tapes was divided into the constant rate and falling rate periods.

The first stage of drying is called constant rate period, because the rate of evaporation per unit area of the drying surface is independent on time [13]. The evaporation rate is close to that from an open dish of liquid in which the overall rate of the drying process is controlled by the interfacial evaporation at the surface [14]. Therefore, the drying process of the tapes was controlled by the evaporation process from the interfacial phase until the drying curve deviated from the straight line. Almost the same drying rate in the initial stage of about 5×10^{-3} g/min was found for all the tapes. Since the linear region was an interfacial evaporation controlled process it was dependent on the ambient temperature and humidity, and the slip aging time had no influence upon the drying process.

In the falling rate period (second stage of drying), the drying kinetics are controlled by the transportation of water to the solid surface, thus a diffusion controlled process [14].

The water weight loss during the first stage varied with the slip aging time. This behavior will be explained in a posterior paragraph.

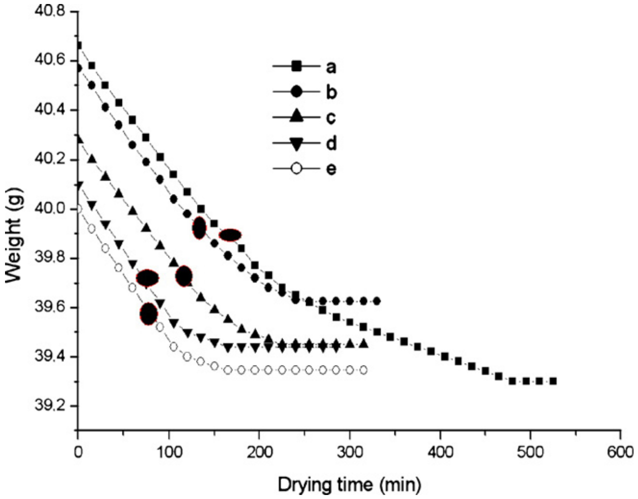

Fig. 1. Sample weight as a function of drying time for tapes prepared from slips with different aging times: (a) 0 days, (b) 5 days, (c) 10 days, (d) 14 days, (e) 24 days. The oval indicates the time when the supersaturated region disappears.

Three regions – supersaturated, saturated, and dry – could be identified by optical microscopy in the drying tapes. These regions are described in a previous study [15]. The drying forces responsible for the redistribution of liquid during drying is a result of capillary pressure gradients associated with different pore sizes in the packed porous structure [15]. Therefore, different pore sizes in the tapes would be expected.

Fig. 2 is a representation of the micropore size distribution as dV/dlog r (differential pore volume) versus pore radius of tapes produced from slips with different aging times. Two pore sizes were observed in the tapes: a more frequent pore radius of about 0.13 μm which was the pore between the packed YSZ particles, and a smaller and less frequent pore radius which increased from 0.015 to 0.08 μm with increasing the aging time of the slips from 0 to 14 days; and remained constant with further increasing of the slip aging time. The smaller pore was probably the one between the latex particles.

The observation of the slips during aging permitted to explain the different pore sizes. There is a larger density difference between the YSZ powder and the latex solution, the densities are 5.90 and 1.05 g/cm^3, respectively. Aging allowed time for the YSZ particles in the suspension to settle, leaving the latex aqueous solution of lower density above the YSZ particles. With increasing the aging time the volume of YSZ particles sediment also increased retaining greater amounts of liquid. This produced an increase in the concentration of the supernatant solution of latex. Thus, as the aging time increased the concentration of the latex aqueous solution above the sediment also increased.

The onset of latex coalescence is expected to occur when the volume fraction of latex particles in the solution approaches 0.6, its maximum solids loading [10]. Latex coalescence involves a complex sequence of particle consolidation caused by evaporation, deformation of the lattices and rupture of the emulsifying layer by capillary pressure, and, finally, permanent deformation driven by capillary pressure and polymer interfacial tension [10]. As the concentration of the latex solution approaching 0.6 the latex coalescence increased the particle size. This suggested that, during aging, the concentration of the latex solution above the sediment would also increase the latex particle size. For aging times of the slips from 0 to 14 days an increase in the latex particle size and consequently in the smaller pore size of the resultant cast tape was expected. Further increasing of the aging time over 14 days did not produce an increase in the smaller pore size of the cast tapes.

There was a capillary migration of liquid from the larger pores to the smaller ones; thus, a capillary suction of the smaller pores occurred. Capillary suction withdraws liquid from the supersaturated region such as a wick pulls liquid from a reservoir to the saturated region composed of the smaller pores. The greater tension in the liquid in the smaller pores can be calculated by the equation:

$$P = 2\phi\frac{\gamma}{d} \tag{1}$$

where ϕ is a particle packing factor, γ the surface tension of the liquid phase and d is the particle diameter. Since the particle size and pore size are directly proportional, the capillary tension is inversely proportional to the pore radius and directly proportional to γ, therefore $P\alpha\gamma/r$. The surface tension of deionized water is 72 mN/m. Thus, $P\alpha 72/r$ (mN/m^2) decreased with increasing the pore radius. Fig. 3 shows the pore radius and the capillary pressure in the smaller pores as a function of the slip aging time. An important decrease in the capillary pressure (increase in the pore radius) up to 5 days was found followed by a lesser decrease with further increasing of the aging time. Aging times over 14 days did not change the pore radius and consequently the capillary pressure.

The oval on the kinetics curves (Fig. 1) indicated the time when the supersaturated region disappeared. The constant drying rate was independent of the presence of the supersaturated region. Indeed, the rate remained constant even though the supersaturated region disappeared, as shown in Fig. 1(d) and (e).

The volumetric flow rate of liquid (Q) is given by:

$$Q = uA \tag{2}$$

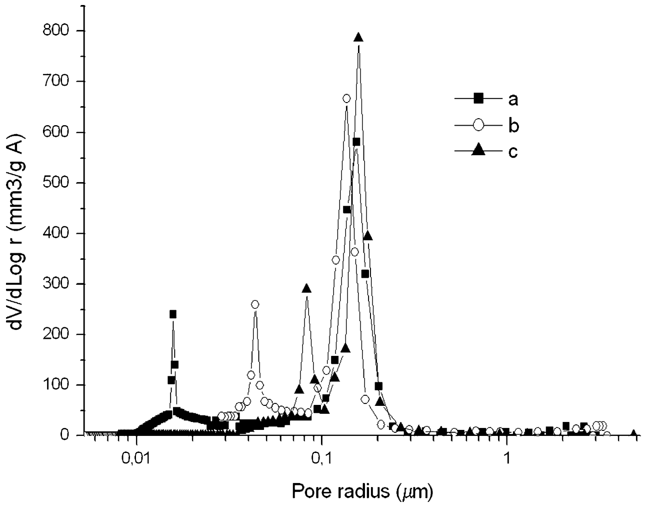

Fig. 2. dV/dlog r (differential pore volume) vs. pore radius of tapes produced from slips with different aging times: (a) 0 days, (b) 5 days, (c) 14 days.

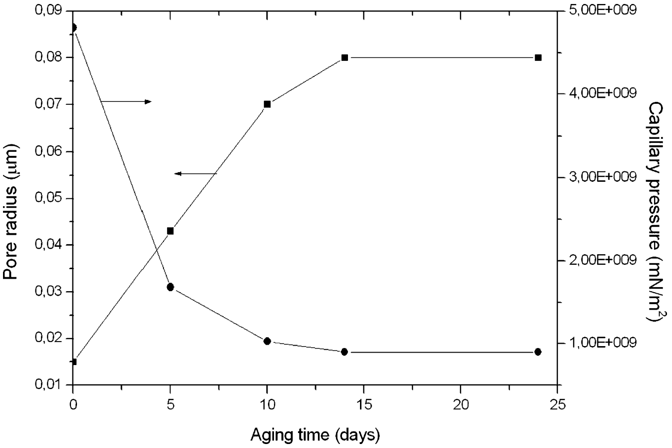

Fig. 3. Pore radius and capillary pressure as a function of the slip aging time.

where u is the fluid velocity and A is the transversal area of the tape. The fluid velocity through a porous medium is given by the Kozeny equation [16], which is:

$$u = -\frac{d^2\varepsilon^3}{150\mu(1-\varepsilon)^2}\frac{\delta P}{\delta x} \tag{3}$$

where μ is the liquid viscosity, ε the void fraction, d the granular particle size and $\delta P/\delta x$ is the pressure gradient. Substitution of the fluid velocity in Eq. (2), gives an expression for the volumetric flow rate:

$$Q = -\frac{d^2\varepsilon^3 A}{150\mu(1-\varepsilon)^2}\frac{\delta P}{\delta x} \tag{4}$$

which shows that the volumetric flow rate of liquid is proportional to the porosity of the tapes.

The pore volume by mass unit of the tapes increased from 200 to 245 mm^3/g when the aging time increased from 0 to 14 days. As the pore volume of the tapes increased the volumetric flow rate of liquid also increased whereas the time of liquid flow through the plane of the tape until the supersaturated region disappeared, decreased. The tape would be uniformly saturated when the supersaturated region disappeared.

Fig. 4 shows the time of liquid flow until the supersaturated region disappeared as a function of the pore volume of the tapes. The time of liquid flow decreased from 162 min for a pore volume of 200 mm^3/g to 82.5 min for a pore volume of 245 mm^3/g, in accordance with Eq. (4). For tapes with higher porosity (slips aging time ≥14 days) the liquid flow from the supersaturated region finished before the constant rate period end while for the tapes with lower porosity (slips aging time 0 and 5 days) the liquid flow end after finishing the constant rate period (Fig. 1).

The capillary pressure in the liquid during drying is the force that produces the shrinkage of the solid network [13]. As drying proceeds, the liquid/vapor meniscus deepens and the tension in the liquid rises correspondingly [13]. Once the radius of the meniscus becomes equal to the radius of the pores, the liquid exerts the maximum capillary tension [13]. That marks the end of the constant rate period; beyond that point the tension in the liquid cannot overcome further stiffening of the network, so the meniscus recedes into the pores [13]. Fig. 5 is a representation of the capillary pressure and the water weight loss during the first stage versus the drying shrinkage of the tapes in the thickness direction. The maximum capillary pressure (the tension in the smaller pores) increased with decreasing the slip aging time (Fig. 3). The tapes produced from slips with lower aging times which had higher capillary pressure shrank more (Fig. 5).

The end of the constant rate period is called the critical point, and it is at this point that shrinkage virtually stops [13]. Thus, the water weight loss during the initial stage was expected to be proportional to the thickness shrinkage of the tapes. A linear correlation between the water weight loss and the drying shrinkage was found (Fig. 5). Thus, tapes fabricated from slips with lower aging times (higher capillary pressure) shrank more and lose greater amounts of water during the initial stage.

Fig. 6 shows the pore volume and the green density of the tapes versus the capillary pressure. The increase in

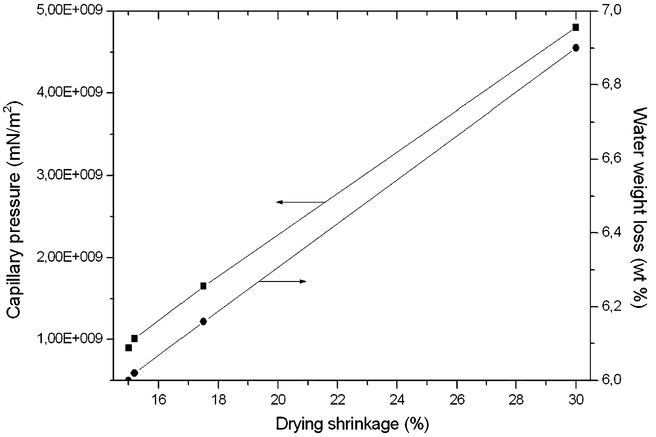

Fig. 5. Capillary pressure and water weight loss during the first stage vs. the drying shrinkage of the tapes in the thickness direction.

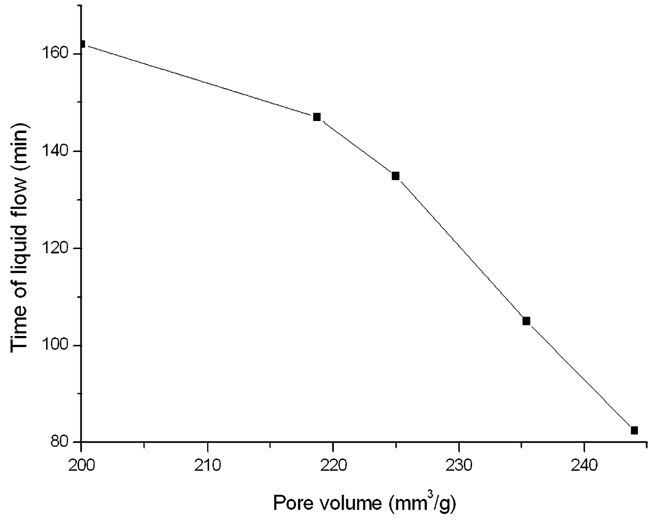

Fig. 4. Time of liquid flow until the supersaturated region disappeared as a function of the pore volume of the tapes.

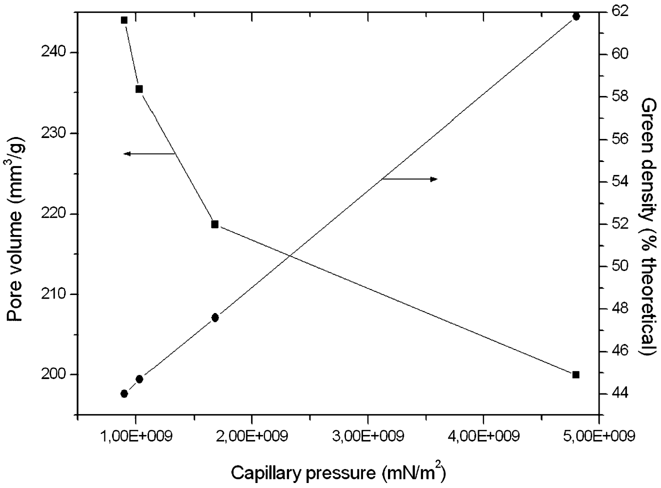

Fig. 6. Pore volume and green density of the tapes vs. the capillary pressure.

the thickness shrinkage with increasing the capillary pressure produced a decrease in the pore volume of the tapes. As the capillary pressure increased the pore volume decreased thereby increasing the green density of the tapes; thus, the capillary pressure drove the consolidation. The highest green density (61.8% of theoretical density) was found in tapes produced from slips without aging time which had the maximum capillary pressure (Figs. 3 and 6).

3.2. Cracking behavior

Micrographs of the tapes prepared from slips with aging times of 0 and 14 days are shown in Fig. 7. An increase in the pore volume of the tapes with increasing the slip aging time from 0 to 14 days could be observed. This qualitative observation was previously verified by measuring the pore volume of the tapes for different slip aging time. The crack, which appeared in tapes produced from slips without aging time, decreased with increasing the slip aging time and disappeared for slip aging time ≥14 days.

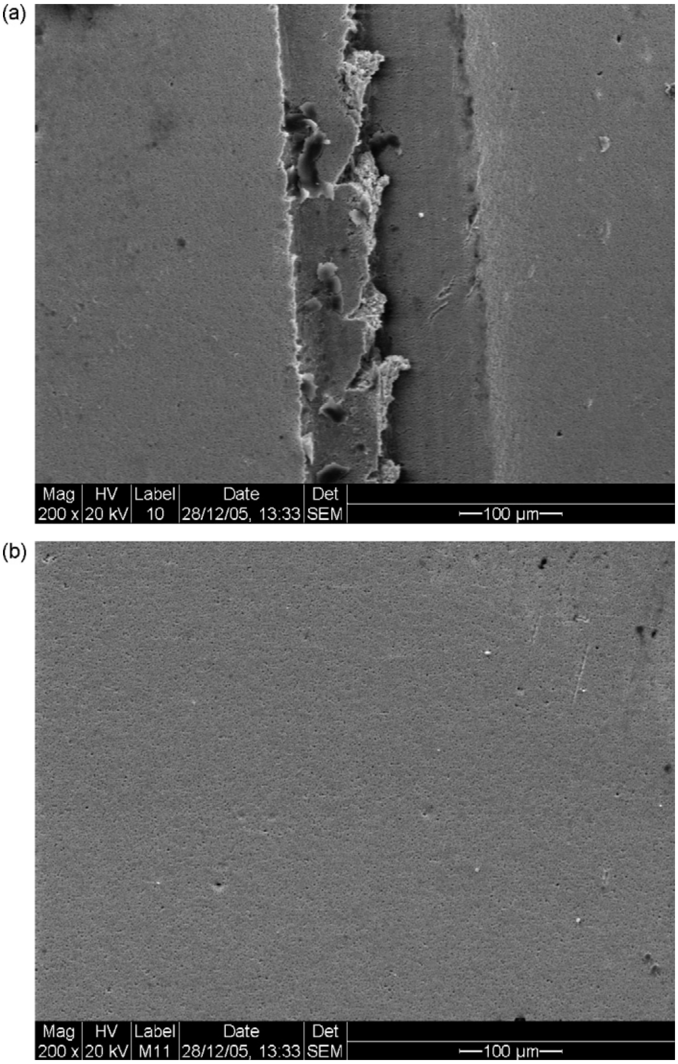

Fig. 7. Micrographs of tapes prepared from slips with different aging times: (a) 0 days, (b) 14 days.

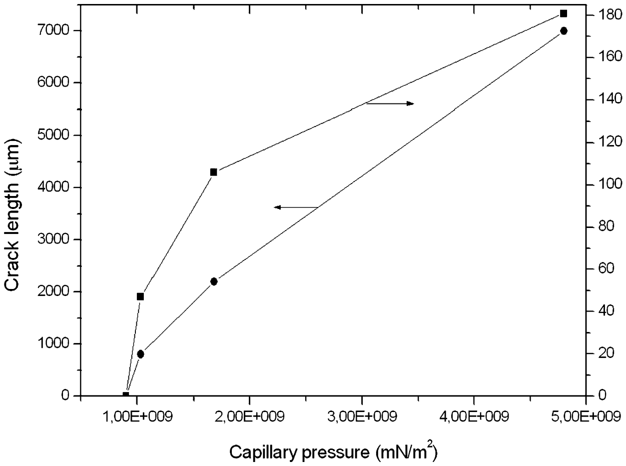

Fig. 8. Crack length and crack average width as a function of the capillary pressure.

Fig. 8 shows the crack length and the crack average width as a function of the capillary pressure. Cracking was not found for capillary pressure $<9 \times 10^8$ mN/m^2; an increase in the crack length and width up to about 12×10^8 mN/m^2 was found followed by a lesser increase with further increasing of the capillary pressure. The crack length and width, thus the crack area, increased with an increase in the capillary pressure which was consistent with a capillary nature of the drying stress. The drying stress which caused cracking is proportional to the capillary tension in the pore liquid [16]. Therefore, the drying stress and consequently the crack area were inversely proportional to the pore size. Tapes fabricated from slips with longer slip aging time which had larger pores were less susceptible to cracking. Cracking was not observed in tapes produced from slips with aging times ≥14 days which had the largest pores. Thus, the observed reduction in the crack area with increasing the slip aging time was attributed to the corresponding reduction in the capillary pressure because of the presence of larger pores.

Tapes produced from slips with shorter aging times (<5 days) had lower pore volume and consequently higher green density. However, they were more susceptible to cracking. The results showed that cracking could be reduced by increasing the pore size of the tapes. This was achieved by increasing the aging time of the slips before casting up to 14 days. Since larger pores and higher pore volume will demand higher sintering temperature or longer times at a given temperature, there is a tradeoff between easy drying and easy sintering.

4. Conclusions

Eighty weight percent YSZ slips with 11 wt.% latex were prepared. The slips were aging different times and cast to produce YSZ substrates.

The latex particles consolidated by coalescence during the aging time of the slips and resulted in an increase in the smaller pore size of the resultant cast tape. The pore radius increased with increasing the slip aging time up to 14 days thereby decreasing the capillary pressure in the liquid. Aging times over 14 days did not change the pore radius and consequently the capillary pressure.

The drying of YSZ tapes involved a two-stage process: the initial stage was a constant rate period and the second one was a falling rate period. A water flow from the supersaturated region to the saturated one was observed as a consequence of the different pore sizes in the packed porous structure. The time of liquid flow decreased with increasing the slip aging time due to the increase in the pore volume of the tapes.

The tapes produced from slips with lower aging times which had higher capillary pressure shrank more and lost greater amounts of water during the initial stage. The increase in the thickness shrinkage with increasing the capillary pressure produced a decrease in the pore volume of the tapes thereby increasing the green density; thus, the capillary pressure drove the consolidation.

Cracking was found in tapes prepared from slips with aging times shorter than 14 days. The crack area decreased with increasing the slip aging time; this was attributed to the corresponding reduction in the capillary pressure because of the presence of larger pores.

Aging before casting up to 14 days reduced cracking in tapes prepared with low amounts of latex. However, the lower capillary pressure resulted in low green density of cast tapes. Although the proposed processing route avoid cracking in tapes produced with low amounts of latex, it led to low green densities. Therefore, this route involved a tradeoff between the elimination of cracks during drying and the sinterability of the tapes.

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