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Tape casting of non-aqueous silicon nitride slips

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Abstract

Tape casting is a powerful method for the manufacturing of flat, large area ceramic components. Silicon nitride is a reference material for high temperature structural applications. Between them, thick film/coating technologies and ceramic–ceramic joining are receiving an increased attention. In this work, the rheological behavior on non-aqueous silicon nitride slips for tape casting was investigated considering different solvent and binding systems, by controlling the total binder and plasticizer content and the binder to plasticizer ratio. A phosphate ester was used as dispersant. The characteristics of the green tapes obtained in different conditions were studied in terms of density, thickness and microstructure and related with the rheological properties of the slips. Once the slip properties were adjusted, manufacturing parameters, such as the casting speed and the gap between the blades and the carrier substrate, were also analyzed in order to improve the green tape properties and the process reliability. In order to obtain sinterable compacts, Al_2O_3 and Y_2O_3 were used as sintering aids. The effect of the sintering aids in both the rheological behavior and the green characteristics was also studied. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Rheology; Tape casting; Microstructure-prefiring; Si_3N_4

1. Introduction

Silicon nitride is considered a key engineering material due to its good performance, especially for high temperature applications.[1–4]. However, its poor sinterability has limited the establishment of a manufacturing technology as a consequence of the many problems involved in the scaling-up of an industrial procedure based on pressure sintering techniques.[5,6] The high costs and the limited shapes attainable by hot press are important problems to be solved. For some applications a big effort is being done to allow joining of previously manufactured ceramic parts. For such cases, the preparation of a thin sheet of a material could allow the joining of two shaped parts of that material.

In order to avoid pressure sintering, colloidal processing studies of silicon nitride have grown up in the last decades.[7–10] In addition to the colloidal behavior, the preparation of pressureless sintered parts of silicon nitride by colloidal shaping techniques has been also described either in water or in organic media. However, an important limitation always present when using silicon nitride is the strong influence of the powder characteristics (specific surface area, oxygen and impurity contents, etc.), and their variation along the subsequent processing steps, such as, mixing and milling, the presence of sintering aids, the liquid vehicle, the possible contamination by plaster moulds, etc.

In a previous set of works, this research group has reported the parameters involved in the manufacturing of pressureless sintered parts of Si_3N_4 by slip casting and pressure casting in water.[11,12] Furthermore, the oxidation at the particle surface at different processing conditions (forming methods, mixing procedure, etc.) as well as the effect of oxidic sintering aids, have also been described.[13,14]

A further step in the slip processing of Si_3N_4, is the possibility to obtain thin sheets by tape casting, which could be used for structural applications (as coating) or for joining ceramic parts.

Tape casting is a readily established method for manufacturing flat surfaces of ceramic materials, where the key role of the additives has been stated elsewhere.[15–19] Most applications of tape casting technology refer to the electronic industry, although some authors have also used this technique for obtaining structural ceramics with enhanced properties.[20,21] However, very few works

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have appeared in the literature dealing with the preparation of tapes of non-oxidic powders,[21,22] and they do not report the control of the process variables.

This work aims to establish a methodology for the manufacturing of silicon nitride green sheets by tape casting. The influence on rheology of slip additives, such as the solvent and the binding systems, is studied. The optimization of the slips is made by proper adjustment of the binder + plasticizer content and the binder/plasticizer ratio. In addition to slip properties, the control of casting variables (such as the casting speed and the gap between the blades and the substrate) is also focused. Further work will be needed to establish the optimal conditions for pressureless sintering.

2. Experimental procedure

The rheological and casting parameters involved in the fabrication of silicon nitride tapes were studied using a commercial silicon nitride powder (Hermann C. Starck, LC12N, Germany). Once the optimal processing conditions were established for pure Si_3N_4, the effect of sintering aids was also studied. Commercially available powders of Al_2O_3 (Condea HPA05, Germany) and Y_2O_3 (Mandoval, UK) were used for such purposes. Compositions containing 3 wt% Al_2O_3 + 3 wt% Y_2O_3 and 3 wt% Al_2O_3 + 8 wt% Y_2O_3 were considered. The main characteristics of the starting powders were reported in Ref. [11]. The coarse starting yttria powder was used for selecting the optimal rheological and casting behavior, but the final optimized tapes were prepared using a previously attrition milled Y_2O_3 up to a mean particle size of 0.7 μm, as described in Ref. [11]. The surface properties and the colloidal properties of these powders were reported also in other works.[13,14]

The preparation of the slips was performed taking into account the important effect of the order of addition of the slip additives, as proposed by Cannon and co-workers.[16] In order to avoid competitive adsorption, the slips were prepared following a two-steps mixing procedure. In a first step the powder, the suspending liquid, and the deflocculant, were mixed together. In a second mixing step the polymers (binders and plasticizers) were added. In all cases a rotary ball mill with nylon-coated jar and nylon balls were used.

In the first stage, the deflocculation of non-aqueous slips of Si_3N_4 was studied for a variety of solvent systems by preparing the slips to a solid loading of 29 vol% using the same deflocculant at different concentrations. The following solvent systems were tested: cyclohexanone (CHN), methyehtylketone/ethanol (MEK/EtOH), trichloroethylene/ethanol (TCE/EtOH) and methylisobutylketone/methyehtylketone/cyclohexanone (MIBK/MEK/CHN). The last three consisted on azeotropic mixtures in order to avoid differential evaporation.

A phosphate ester (Emphos PS21A, Whitco Chem., USA, labelled as EPH) was selected after testing with different deflocculants. For this deflocculant, the best results were obtained for the azeotropic mixture of MIBK/MEK/CHN at relative concentrations of 36.7/29.8/33.5. For the selected deflocculant content and solvent composition, homogenization time was then optimized.

In the second stage, different concentrations of binding system were tested changing the total content of binder + plasticizer (B + P) in relation to the powder weight for a relative binder/plasticizer ratio (B/P) of 1/1. Once the total content of binding system was optimized, the relative B/P ratio was then changed.

The binding system (BS) consisted of a mixture of a binder (polyvinyl butyral, PVB Aldrich-Chemie, Steinheim, Germany) and two plasticizers: polyethyleneglycol (PEG400, Panreac, Barcelona, Spain) and benzilbutylphtalate (BBP, Merck, Hohenbrunn, Germany). According to most experimental compositions reported in the literature [16–19] for tape casting technology, PEG and BBP are widely used plasticizers offering a good slip performance when they are added in a ratio 1:1. The main characteristics of the organic additives used in this work are shown in Table 1. Different concentrations of BS were introduced directly on the 29 vol% slips, then the concentration of powder

Table 1
Main characteristics of the organic additives used in this work

Solvents	CHN	MEK	MIBK
Molecular weight	98.40	72.11	100.16
Melting point (°C)	−16.4	−87	−84.7
Boiling point (°C)	155.6	79.6	116.8
Density (g/cm^3)	0.998	0.805	0.801
Vapor pressure (mm Hg, 25°C)	7	100	8
Binder and plasticizers	**PVB**	**PEG**	**BBP**
Molecular weight	36 000	380–420	312.3
Density (g/cm^3)	1.08	1.13	1.10
Purity (%)	99.99	99.99	98.00
Deflocculant		**EPH**	
Density (g/cm^3)		1.04	
Surface tension (dynes/cm^2)		28.8	

Table 2
Main properties of organic solvents considered in this work

Solvent	Evaporation rate (g/cm^2/s× 10^8, 25°C)	Dielectric constant	Viscosity (mPa s)	Hydrogen bonding strength	Surface tension (dynes/cm^2)
EtOH	1950	24.0	1.2	High	22.39
MEK	3620	15.45	0.4	Moderate	24.6
MIBK	1094	13.11		Moderate	25.4
CHN	290	18.3		Moderate	35.18
TCE		3.0	5.5		

decreased in the final tape casting slip including the binding system.

The rheological behavior of all studied slips was determined using a rheometer (Haake RS50, Karlsruhe, Germany) capable to operate at both controlled shear rate (CR) and controlled shear stress (CS) conditions. The first mode was used to measure the flow curves, and the second for determining the yield values, calculated from the double logarithmic plot of deformation versus shear stress. The measurements were performed using a concentric cylinders system, with a rotor diameter of 40 mm at a constant temperature of 25°C.

Tape casting experiments were performed in a self-made machine with a stationary carrier and a container that moves at controlled speed. The slip passes through a double blade system assuring an uniform thickness of the tape, whose height can be adjusted by means of micrometer screws. Slips were cast onto tempered glass substrates. For the selection of suitable tape casting formulations, the blade gap was maintained constant at 300 μm. A casting speed of 3.8 mm/s was applied. In order to simulate the rheological conditions operating in the slip when it flows through the moving doctor-blades, and considering the imposed gap and the casting speed, the shear rate during casting was estimated to be 13 s^{-1}. This value was taken for viscosity plots to build up the deflocculation curves. Further experiments were made changing the gap for a selected slip formulation at the same casting speed and changing the casting speed for a fixed gap.

The cast tapes had always a length higher than 80 cm and a width of 10 cm and were characterized in terms of density and thickness. To attain a more accurate determination the green tapes were punched to obtain disks with 30 mm in diameter. The disks were weighted and their thickness measured with a graduated ocular using a reflected light optical microscope. The green tape properties were correlated with the slip formulation characteristics.

After adjusting all rheological and casting parameters for the silicon nitride slips, Al_2O_3 and Y_2O_3 were then introduced in order to obtain sinterable sheets. Tape casting was performed with slips prepared at a solid loading of 60 wt% prior to the addition of binding system, BS, and 52 wt% after that. Yttria was used as received (mean particle size of 3.5 μm) and milled to a similar particle size to that of silicon nitride for a complete optimization of the process. Microstructural observations were performed on green tapes using scanning electron microscopy on as cast upper and bottom surfaces.

3. Results and discussion

3.1. Dispersing tests

The selection of a solvent system was a first step for the preparation of the slips. Table 2 shows the main characteristics of the solvents used in this work. The evaporation rate is an important characteristic to be considered. According to Mistler et al.,[17] the extremely volatile solvents, such as ketones, are most suitable to obtain thin tapes, and the lower volatility solvents seem best to obtain thicker films. However, Descamps et al.[23]

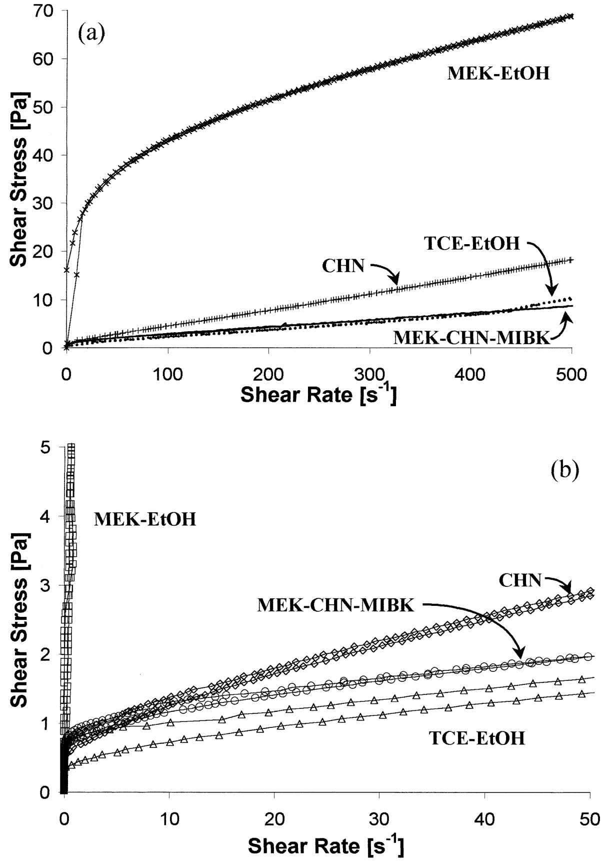

Fig. 1. Slips prepared to a solid loading of 29 vol% with 2 wt% dispersant in different solvent systems, after 4 h milling. (a) CR flow curves, (b) CS yield curves.

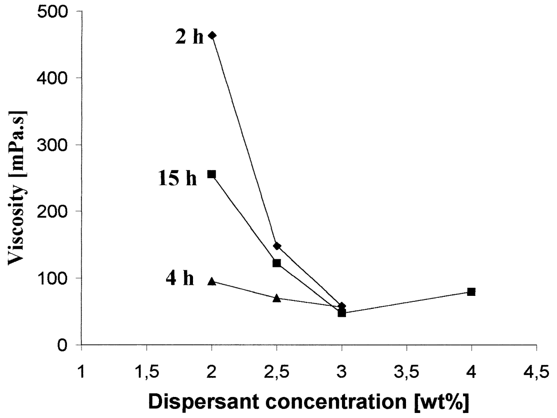

Fig. 2. Deflocculation curves of 29 vol% silicon nitride slips (at a shear rate of 13 s^{-1}), prepared in MEK–CHN–MIBK after homogenization times of 2, 4 and 15 h.

have pointed out that between the two mechanisms involved in crack formation — evaporation rate and capillary pressure due to open porosity — the latter is the major cause of tape cracking. In water systems, differential drying occurs as water is not volatile, so that differential shrinkage takes place, this being the reason why water gives very high crack sensivity. In our case, to obtain thin tapes (100–200 μm), a volatile solvent was useful to reduce drying time. On the other hand, surface tension is also critical, because the adhesion process between particles and polymers must be higher than the adhesion between the tape and the carrier film or substrate to allow an easy pull out of the dry tape. This can be improved by action of the surfactant. In this work, dispersion was achieved by means of an anionic surfactant, as EPH. This deflocculant has been demonstrated to be very effective for non-aqueous slips due to a charging mechanism associated to the phosphate group.[24] Consequently, the dielectric constant of the liquid is also a factor to be considered in the efficiency of the dispersant. A high dielectric constant may help to reduce the surface charge required to provide a sufficiently high repulsive pair potential. This is because the repulsive potential between similar particles is proportional to the dielectric constant and to the square of the surface charge. Then, stability increases either with the dielectric constant or with the surface charge.[18] Having in mind these considerations, mixtures of the solvents reported in Table 2 were used. The use of an alcohol or mixtures of alcohols was avoided to reduce the tendency to hydrogen bonding, which could be formed by means of siloxane groups present at the surface of Si_3N_4 particles under the acidic conditions provided by the EPH.

In order to evaluate a proper solvent for tape casting, the flow curves of slips prepared by 4 h milling were measured for the following solvents: CHN, MEK/EtOH, TCE/EtOH and MIBK/MEK/CHN. The slips were dispersed with 2 wt% deflocculant and a solid loading of 29 vol%. The corresponding solid loadings in weight were 56.2, 62.1, 50.0 and 60.0, respectively. Although the dispersing conditions of each system were not yet optimised, it is expected that for any other dispersant concentrations the viscosity values can change, but always maintaining the same relative order and tendency. The strong influence of the solvent properties on the slip stability is evident in Fig. 1. Fig. 1a shows the flow curves of the slips measured in control rate mode. The maximum viscosity corresponds to MEK/EtOH, probably due to the strong tendency to hydrogen bonding of the alcohol. Slips prepared in TCE/EtOH and MIBK/MEK/CHN have very low viscosities. However, the first tends to behave as dilatant for high shear rates, while the slip prepared in MIBK/MEK/CHN has a pseudoplastic behaviour, which is one of our objectives for the slip prior to the addition of binders and plasticizers. A more accurate rheological analysis is necessary

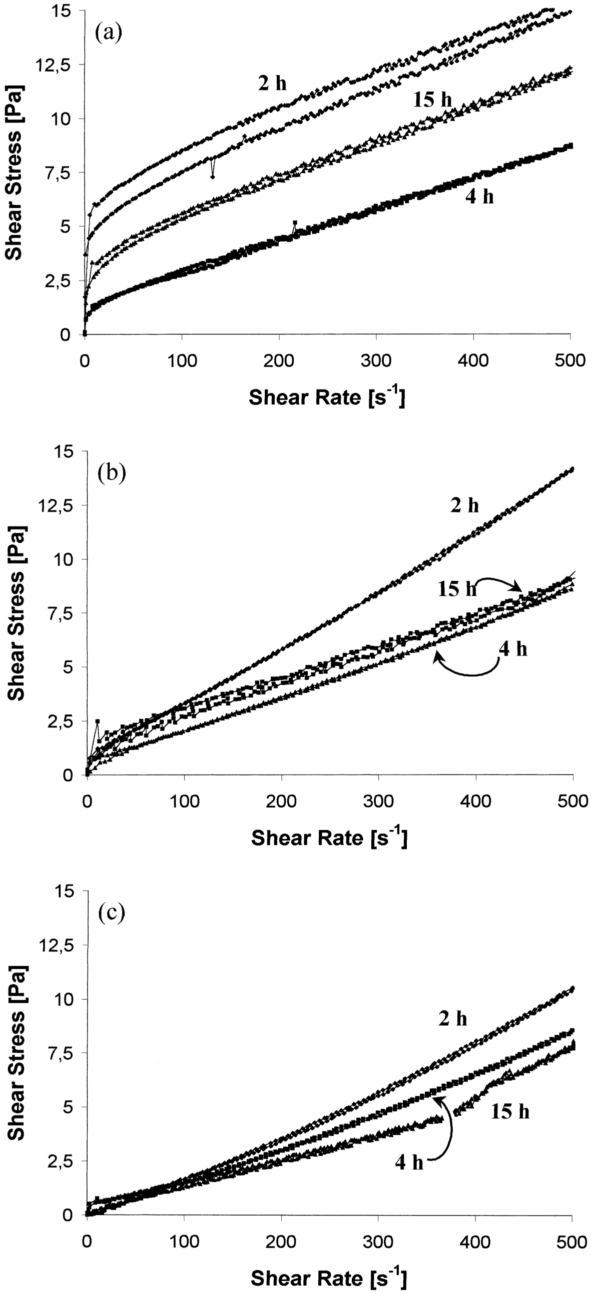

Fig. 3. Effect of homogenization time on the flow curves of silicon nitride slips prepared in MEK–CHN–MIBK for dispersant concentrations of (a) 2 wt%; (b) 2.5 wt%; (c) 3 wt%.

Table 3
Rheological properties of silicon nitride slips prepared in MEK–MIBK–CHN at different milling times

Milling time	Bingham parameters		Yield stress	Viscosity	Thixotropy
(h)	Yield point (Pa)	Limit viscosity (Pa s)	(log–log curves) (Pa)	(at 13 s^{-1}) (Pa s)	(Pa/s)
2	6.24	0.019	1.5	0.44	405
4	1.24	0.015	0.6	0.09	−50
15	3.65	0.018	1.3	0.26	109

to dilucidate which solvent provides a better behaviour. To do this, the flow curves were also determined in control stress mode. Fig. 1b shows the control stress curves for all the solvents. At low shear rates the TCE/EtOH shows some thixotropy. That is, this solvent gives slightly lower viscosities but the slip is thixotropic, which is not recommended during casting and, on the other hand, at high shear rates (as those required for a good mixing) it behaves as dilatant. According to these results, the MIBK/MEK/CHN was chosen as the best solvent for the silicon nitride slips.

However, further improvement can be achieved by changing either the deflocculant content or the homogenization time up to complete stabilization. Fig. 2 shows the viscosity at 13 s^{-1} of slips containing different deflocculant contents prepared at different milling times. The lowest viscosities are found for 3 wt% deflocculant for any milling time. The slips with lower contents have also low viscosities when milled for 4 h. The optimum concentration to be added depends not only on one value of viscosity but on the whole flow curve behaviour. The flow curves of slips prepared at milling times of 2, 4 and 15 h with deflocculant contents of 2.0, 2.5 and 3.0 wt% are plotted in Figs. 3a, b and c, respectively. The slips with 3 wt% present a dilatant behaviour, although the viscosities are lower. The dilatancy makes processing more difficult, as high shear occurs during milling, and on the other hand, during casting it is desired that viscosity increases immediately after the shearing effect of the blades. Some dilatancy is also found for slips dispersed with 2.5 wt%. For a concentration of 2 wt% dispersant a milling time of 2 h is not sufficient to stabilize the slip and the flow curve reveals a higher viscosity and thixotropy. For 4 h milling, the viscosity maintains low and neither dilatancy nor thixotropy is observed. After 15 h milling the viscosity increases again, and some thixotropy appears also. According to these results, a concentration of 2 wt% was selected as the optimum dispersant content for the preparation of stable slips, by 4 h ball milling.

Table 3 summarizes the yield point of the 2 wt% deflocculant slips, evaluated after fitting the flow curves, and calculated according to the double logarithmic method, where two regions with different slopes can be detected, marking the range of elastic deformation (lower slope) and that of viscous flow (higher slope). This method is sensitive and provides useful information for small or large yield points. The viscosity at a shear rate of 13 s^{-1} (estimated shear rate during casting) and the viscosity resulting from the best fit (Bingham model) are also reported. In addition, the thixotropy, calculated as the area enclosed between the up and the down curves, is also shown in Table 3. From all these data it is clear that a milling time of 4 h provides the best rheological conditions for casting. The yield point is very low (0.6 Pa), very near to a pseudoplastic behavior, desirable in many colloidal processing methods including tape casting, contrary to the apparent Bingham flow corresponding to the best fit observed in the CR flow curves.

3.2. *Effect of binder and plasticizer*

Considering the dispersing conditions described above, the effect of the binding system on the rheological behavior was studied before the sintering aids were introduced. Total concentrations of B + P from 10 to 30 wt% (referred to solids) were considered, maintaining the relative binder/plasticizer ratio as 1:1. Fig. 4a plots the measured flow curves, showing an increase of viscosity with increasing (B + P) additions as well as a plastic Bingham flow with an increasing yield point. Large additive concentrations strongly increase the viscosity, thus making more difficult an optimum homogenization of the mixture. It has been observed that additions of binder system above 25 wt% are difficult to prepare because the amount of solvent present in the slip is not sufficient to completely dissolve all the added PM As a result, large binder agglomerates are formed, which strongly adhere to the substrate, introducing pores and

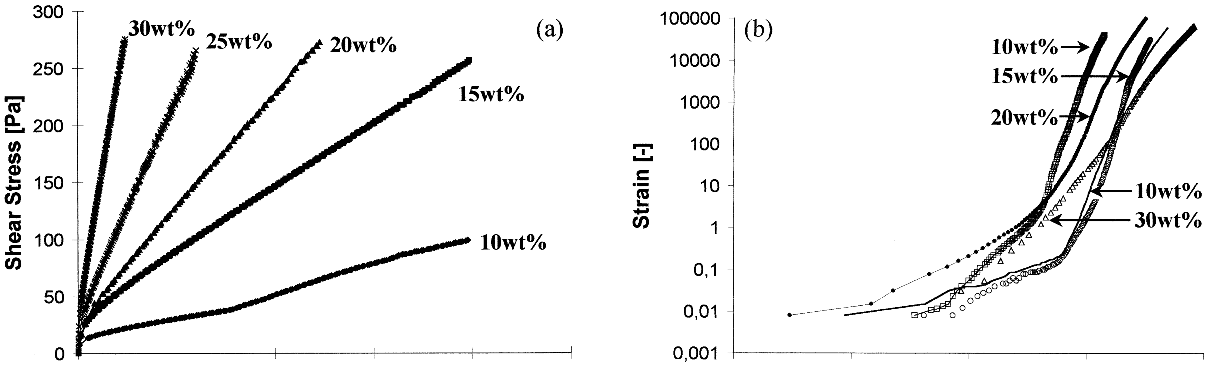

Fig. 4. Effect of binding system (BS) content on the rheological behavior of optimized silicon nitride slips: (a) CR flow curves; (b) CS (log–log) curves.

unhomogeneities in the green tape. The double logarithmic plot of shear stress vs. strain can be seen in Fig. 4b.

Microstructural observations on the green tapes clearly reveal the differences in the packing behavior and the presence of binder agglomerates depending on the slip formulation. Fig. 5 shows the SEM microstructure of green tapes obtained with B/P = 1 and total (B + P) concentrations of 20% (a), 25% (b) and 30% (c). The tape with 25% has a more uniform microstructure, with smaller grain size and without agglomerates. The presence of such agglomerates is evident in the tapes prepared with higher (B + P) contents, as a consequence of the higher viscosity which makes the homogenization of the slip more difficult.

The selection of the total (B + P) concentration needed a further characterization of the green tape properties. Tapes were cast at 3.8 mm/s with a blade height of 300 μm. The thickness was determined by direct observation at the optical microscope. Density was evaluated by weighting disks with 3.0 cm in diameter obtained by punching the green tapes. Table 4 reports the characteristics of the tapes and summarizes the rheological properties of the corresponding slips. The thickness decreases when BS content increases from 20 to 25 wt% and increases again for 30 wt%. The green density shows the opposite tendency. The green tape properties are not the only function of the slip viscosity, but the binding efficiency of the polymers is a determining factor, so an insufficient quantity of polymer results in lower compaction where not all the particles are duly covered by the polymers. Since an addition of 25 wt% of BS provides the minimum thickness and the maximum density this was selected as the optimum content. For this composition, a green density > 57%th and a thickness of 135 ± 5 μm are obtained.

At this point, the thickness differences can be explained in terms of drying behavior. Drying process consists of two stages.[25–27] The first is controlled by capillary migration of the solvent, and the second is controlled by solvent diffusion through the solidified part of the film with a decreasing drying rate. In the case of organic media, several authors[25–28] showed that this first drying stage is very short. At the beginning of the first drying stage, particles approach each other, the viscosity of fluid phase is low enough to allow particles rearrangement, avoiding internal stresses and the shrinkage occurs perpendicularly to the casting plane and hence balancing the solvent loss. However, as the evaporation proceeds, the liquid phase becomes enriched in polymeric binder, increasing viscosity and changing fluid motion within particle–particle pores, modifying evaporation rate. Therefore, the liquid/vapor meniscus penetrates into the tape, because the upper green tape surface is in solid state and the drying process shifts to diffusion solvent stage, which is lower than first drying stage rate and increasing total drying time. During second

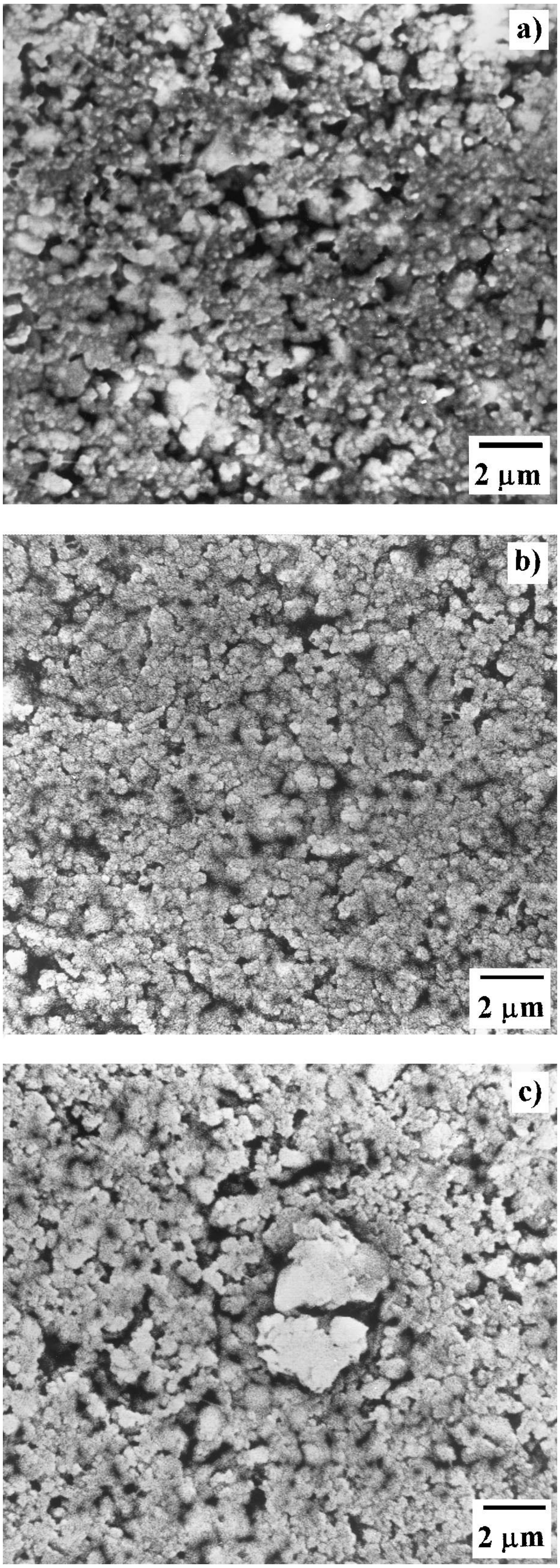

Fig. 5. SEM micrographs of green tapes with different binding system content: (a) 20 wt%; (b) 25 wt%; (c) 30 wt%.

stage of drying, internal stresses occur which could lead to crack formation in green tapes. The generated stresses are owed to two opposite phenomena: one tending to increase the stress level due to constrained volume shrinkage and the other one tending to decrease the stress level due to the relaxation of the polymeric phase. The presence of these stresses is owed to adhesion force of green tape to the substrate and shrinkage could only occur perpendicularly, along the tape thickness.

In the case of slips prepared with less than 25 wt% of binder system, we can assume that the polymer content is not high enough to balance the stresses, which are larger than those generated by volume shrinkage, producing the crack formation and poor handling properties. On the other hand, slips with polymer content of 25% compensate the stress balance and no crack formation appears, but for larger polymer concentration solvent is insufficient to completely dissolve the PVB added.

A second aspect to be considered when the binding system is added is the relative concentration of B/P. This has significant effects on the green tape characteristics, since plasticizers confer flexibility to the green tapes, decreasing the binder Tg by reducing Van der Waals forces between large binder molecules bonds. So, for an optimized (B + P) content of 25 wt%, different relative binder to plasticizer ratios were studied. Fig. 6a plots the flow curves of slips containing B/P ratios between 0.66 and 2.0 measured in CR mode. The viscosity increases with increasing B/P ratio, as could be expected, raising a maximum for 1.5, which maintains for a ratio of 2. The viscosity is very high for high B/P ratios, promoting binder agglomeration which makes difficult castability. The flow behavior is always linear with a significant yield value, and can be fit to a Bingham plastic model. However, the yield points need to be more accurately determined. Accordingly, the CS mode was used for a first evaluation of those yield values. The resulting flow curves are shown in Fig. 6b as a double logarithmic plot. The rheological properties of these slips as well as the characteristics of the corresponding green tapes are also shown in Table 4. Green tape thickness increases when B/P ratio increases from 0.66 to 1, and then decreases again for increasing ratios, where viscosity also increases. With regard to density, it follows the same tendency as the thickness, that is, for a B/P ratio of 1 the tape is thicker, but also denser. The lower densities obtained for ratios of 1.5 and 2 could be related to the lack of homogeneity of the tape, where the presence of agglomerates is detected. This is in good agreement with the rheological measurements. These slips present higher viscosity and much higher thixotropy,

Table 4
Main characteristics of slips and green tapes with different binding system content and different binder/plasticizers ratio (casting speed 3.8 mm; gap 300 μm)

Constant binder/plasticizers ratio = 1

	Bingham parameters						
BS content (% wt)	Yield point[a] τ_0 (Pa)	Limit viscosity[a] η_∞ (Pa/s)	Yield stress (log–log curves) (Pa)	Thixotropy (Pa/s)	Viscosity (at 13 s^{-1}) (Pa/s)	Green tape density (g/cm^3)	Green tape thickness (μm)
10[b]	8.44	0.226	3.93	−3074	1.08	–	–
15[b]	30.44	0.572	6.11	−263.8	2.38	–	–
20	26.54	1.006	4.54	0	2.81	1.54	205
25	26.84	1.976	6.52	−1903	4.04	1.82	135
30[c]	29.60	5.247	10.39	1720	7.74	1.73	159

Constant binding system content = 25wt% (referred to solids)

	Bingham parameters						
BS ratio	Yield point τ_0 (Pa)	Limit viscosity[a] η_∞ (Pa/s)	Yield stress (log–log curves) (Pa)	Thixotropy (Pa/s)	Viscosity (at 13 s^{-1}) (Pa/s)	Green tape density (g/cm^3)	Green tape thickness (μm)
0.66	23.92	1.062	8.54	3754	2.73	1.69	114
1	26.84	1.976	6.47	−1903	4.04	1.82	135
1.5	31.56	5.829	6.08	106.5	8.60	1.71	124
2	37.34	5.856	9.3	6996.5	9.03	1.67	120

[a] Bingham parameters ($\tau = \tau_0 + \eta_\infty \dot{\gamma}$).

[b] Strong adhesion to the substrate.

[c] Green tapes show binder agglomerates.

resulting in a worse dispersing level, hence giving place to a thinner tape. The tapes obtained from a B/P ratio of 0.66 strongly adhere to the substrate, being very difficult to pull out. A B/P ratio of 2 produces a quite poor tape, and binder agglomerates can be directly observed. According to these results, the final B/P ratio was maintained at 1.0 to reach good dispersing conditions, as well as good green tape characteristics.

3.3. Effect of casting variables

Once the optimized binder system and the relative B/P content were established, tape casting speed was introduced as a process parameter affecting both the green tape density and the thickness. Casting speed was varied from 3.8 to 24 mm/s, keeping constant the gap between blades and carrier substrate at 0.3 mm. Fig. 7 shows the effect of switching casting rate on the density and thickness of the resulting green tapes. As is known, the slip flow changes according to casting conditions when it is passing under the blades. Therefore, we expected that thickness and green density should change because the slip moves at a different shear rate, modifying the slip flow behavior and hence modifying particle packing.

As can be seen, tape casting speed has a strong effect on green tape thickness and density. The thickness tends to increase up to a casting speed of 5 mm/s and then tends to decrease again. Below that critical casting rate the shearing is very low and the fluidity of the slip when passing through the blades is also low. Higher casting speeds produce a lowered thickness, this being probably related to the lower viscosity of the slips passing through the blades at those strong shear conditions. On the other hand, the variation of the green density with casting speed shows a maximum at 5 mm/s, and maintains constant at increasing speeds. As density does not change, the tape thickness is affected by the casting speed in terms of quantity of slip passing through the blades, but packing is not affected.

In the light of these results, the next step was to study the influence of a new process parameter, such as the gap opening, keeping constant the casting speed that provides the best density results (5 mm/s). The gap was

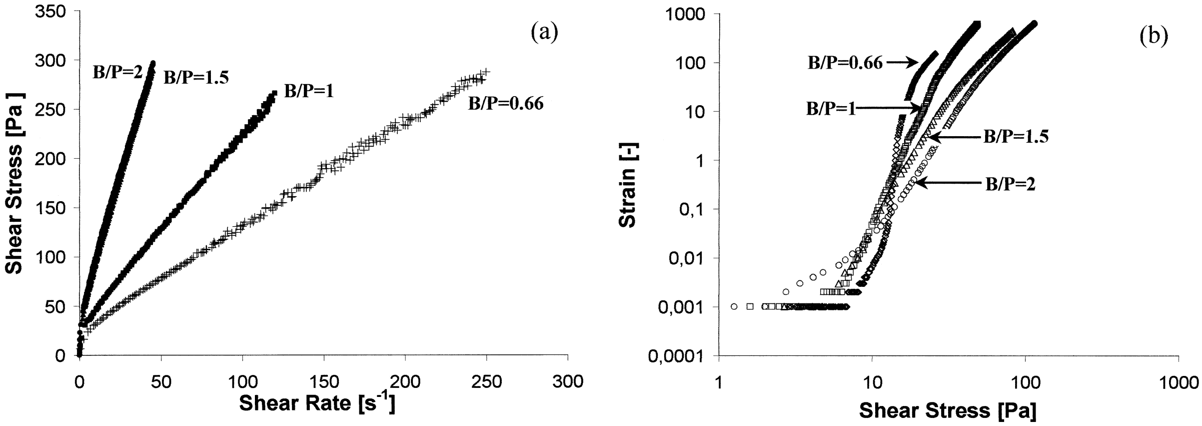

Fig. 6. Effect of binding to plasticizer (B/P) ratio on the rheological behavior of optimized silicon nitride slips: (a) CR flow curves; (b) CS (log–log) curves.

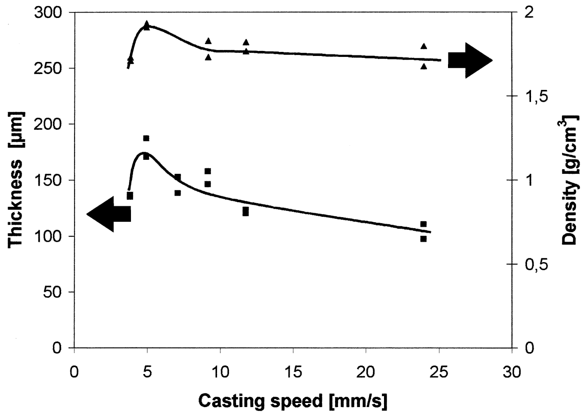

Fig. 7. Variation of green tape density and thickness with casting speed.

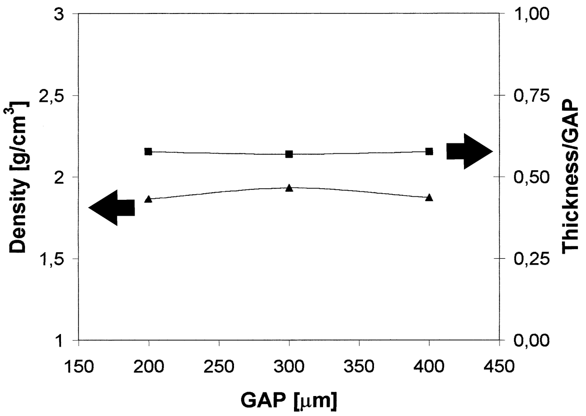

Fig. 8. Effect of gap opening on green tape density and thickness/gap ratio.

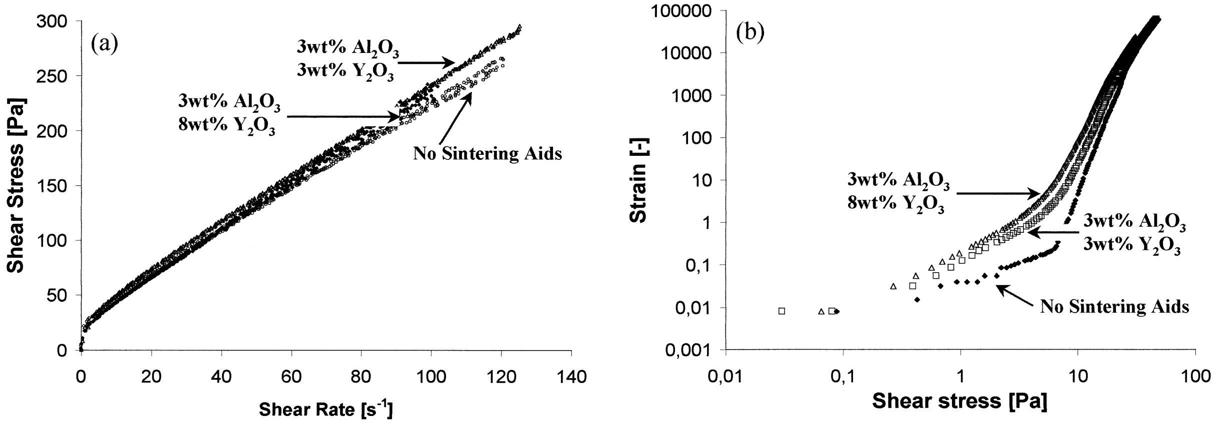

Fig. 9. Influence of sintering aids on the rheological behavior of silicon nitride slips: (a) CR flow curves; (b) CS (log–log) curves.

Table 5
Characteristics of optimized green tapes with sintering aids (casting speed 5 mm/s; gap 300 μm)

Sintering aids content	Green tape density (g/cm^3)	Green tape thickness (mm)
No sintering aids	1.93	170
3% Al_2O_3, 3% Y_2O_3[a]	2.02	172
3% Al_2O_3, 3% Y_2O_3[b]	2.01	172
3% Al_2O_3, 8% Al_2O_3[b]	2.15	178

[a] Coarse yttria.
[b] Milled yttria.

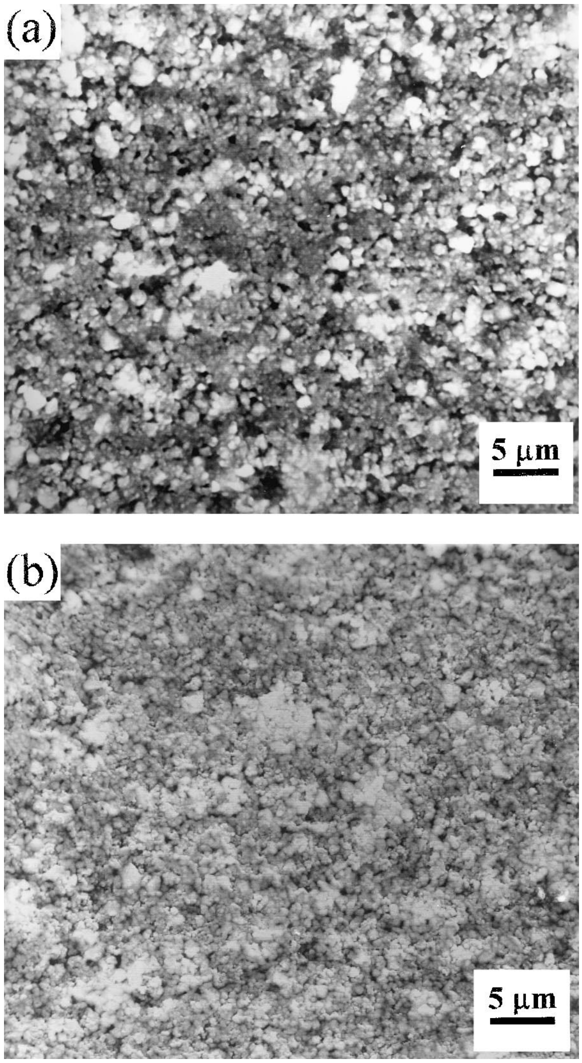

Fig. 10. SEM microstructure of upper green tapes surface prepared with 3% Al_2O_3 and 3% Y_2O_3: (a) as-received coarse yttria; (b) milled yttria.

varied from 200 to 400 μm. Fig. 8 plots the variation of green tape density and thickness as a function of the blade height. A nearly constant density is obtained for the three considered heights. The thickness obviously increases with the gap, being 115, 170 and 230 μm for blade heights of 200, 300 and 400 μm. When considering the ratio between the resulting thickness and the imposed gap, it is found that a similar value of 0.57–0.58 is obtained in all three cases. This means that both thickness ratio and density keep constant independently of the imposed gap. However, for lower heights the tape shows higher tendency to adhere to the substrate. Higher gaps tend to promote crack formation as the slip formulation was made considering high volatility of the solvent in order to produce thin tapes. From these data a height of blades of 300 μm was selected as the optimum.

3.4. Effect of sintering aids

Once the rheological properties, the casting behavior, and the green characteristics of pure silicon nitride were optimized, the next step was to include sintering aids and to evaluate their effect on the rheological properties. The flow curves of slips prepared with a total content of (B + P) of 25 wt% and a ratio B/P = 1, for the pure silicon nitride and for two compositions including Al_2O_3 and Y_2O_3 as sintering aids, in proportions of 3 wt% each and 3 and 8 wt%, respectively, were determined. There are not significant differences in the flow curves when sintering aids are introduced. This was expected from previous works,[11,12] which demonstrated that the

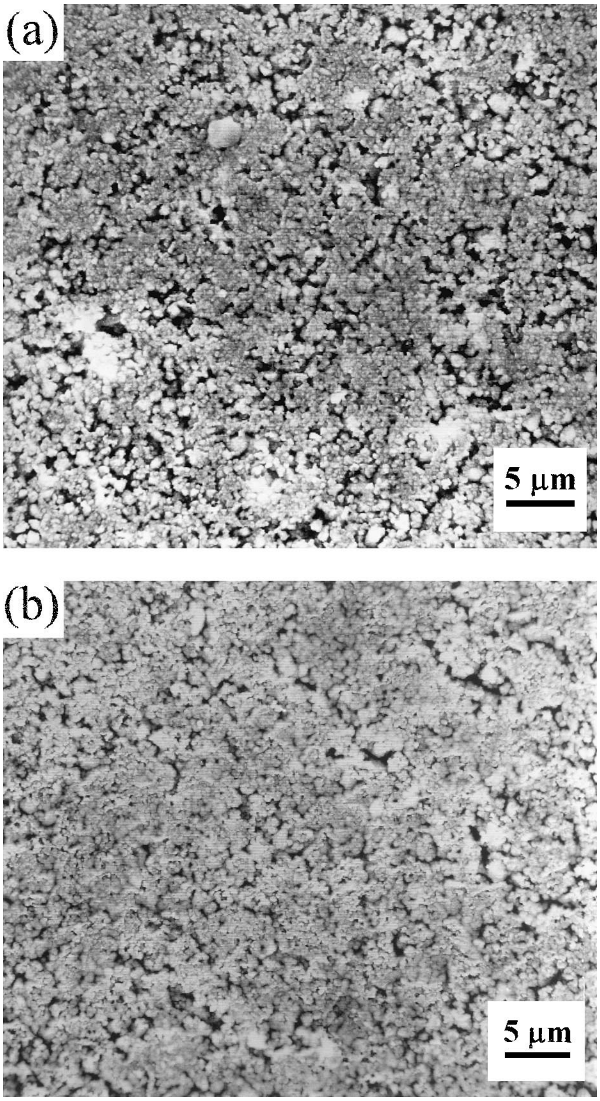

Fig. 11. SEM microstructure of bottom green tapes surface with sintering aids content of 3% Al_2O_3 and 3% Y_2O_3: (a) as-received coarse yttria; (b) milled yttria.

rheological parameters involved in the preparation of aqueous slips of the same powder and sintering aids for colloidal filtration were not altered by the presence of such additives, so that the optimization of the slip could be done using the slip without sintering aids. Figs. 9a and b show the flow curves and the double logarithmic stress/strain curves for slips of only Si_3N_4 and those of Si_3N_4 with 3 wt% Al_2O_3 and 3 wt% of Y_2O_3 and with 3 wt% Al_2O_3 and 8 wt% of Y_2O_3. It can be seen that the yield point is quite similar for the three compositions (5–6 Pa), and the flow curves are nearly the same too.

The effect of sintering aids on the green tape characteristics, such as thickness and density, is summarized in Table 5. The total density increases as the content of additives increases, due to their higher density, but the relative density is maintained constant. The tape thickness is also the same for the different compositions. All this demonstrated that low concentrations of secondary phases, as those used as sintering aids, do not affect the processing parameters studied before.

These data were obtained for tapes prepared using the milled yttria. For comparison purposes, a tape with 3 wt% Al_2O_3 and 3 wt% of the starting coarse yttria was also cast. Although the macrostructural properties are the same, as observed from the data shown in Table 5, the SEM observation reveals strong differences, which should affect the properties of the sintered tape. The Y_2O_3 particles distribution is not uniform along the tape thickness, but tends to concentrate in the upper tape surface, especially for the as-received yttria. The milled one gives a more homogeneous microstructure. Fig. 10 compares the SEM microstructures of green tapes obtained with the as-received (Fig. 10a) and the milled Y_2O_3 (Fig. 10b) performed on the upper tape surfaces. The corresponding SEM pictures of the bottom surfaces are shown in Fig. 11.

Some preliminary sintering experiment has been also performed. However, the optimization of sintering conditions is not the objective in this phase of the work. Further work is now in progress to determine the optimum conditions for the obtention of dense tapes, where burning out of the slip additives constitutes a key parameter to be controlled in order to avoid the oxidation of the particles surface, which could limit sinterability as well as the properties of the final tapes.

4. Conclusions

In this work the obtention of silicon nitride sheets by tape casting has been reported step by step. The optimization of the process for an improved performance requires the control of both the slip properties and the casting variables.

Regarding the slips, the best dispersion was achieved using an azeotropic mixture of MEK/MIBK/CHN as solvent, prepared with 2 wt% of EPH and 4 h of homogenization time. The optimum content of binding system (binder + plasticizer) was 25 wt% (referred to solids), with a relative binder/plasticizer ratio of 1, where neither adhesion of the tape nor cracking or inhomogeneities are observed.

On the other hand, better green properties can be obtained for a selected slip by a proper selection of casting conditions. In this work, green densities higher than 1.9 g/cm^3 (>60%th) were obtained maintaining a casting speed of 5 mm/s and a gap between blades and substrate of 300 μm. The resulting thickness is 170 ± 5 μm after drying. The shrinkage occurs in the perpendicular direction to the casting plane, but no variations in length or width were detected. The introduction of sintering aids does not modify either the rheology of the slip or the green tape properties, although the particle size distribution clearly affects the microstructure and hence, the final properties.

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