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Development of a tape casting process for making thin layers of Si_3N_4 and Si_3N_4 + TiN

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Abstract

A process for the tape casting of silicon nitride ceramics has been developed and is described in detail. A solvent (ethanol) based recipe was developed using polyvinyl butyral and polyethylene glycol as the binder and plasticizer, respectively. The effect, of milling times, dispersant, solvent, plasticizer and binder contents were all investigated as well as that of the binder to plasticizer ratio. In addition the beneficial effect of multi-stage milling of the slip was evaluated. The removal of the ceramic tape from the carrier film is described. In addition the recipe and process used for producing silicon nitride tape was successfully adapted for the production of two different silicon nitride + titanium nitride composite based tapes. From the tapes produced it was possible to hot press dense multi-layer laminate structures with the thinnest layers being 45 μm thick.

Keywords: Tape casting; Si_3N_4; TiN

1. Introduction

Tape casting is an established method for manufacturing thin sheets or layers of ceramic materials. Typically ceramic tapes are produced in the range of 100 μm to 1 mm thickness. Applications include thick and thin film substrates for the ectronics industries, typically from alumina and aluminum nitride ceramics.[1–4] The thin sheets produced by tape casting lend themselves well to multilayer stacking and other applications of these ceramic tapes include multilayer capacitors and actuators made from piezoelectric and other electro-ceramics.[5,6] In addition tape casting has found numerous applications in recent developments for photovoltaic cells and in solid oxide fuel cells.[7–9]

In the current work we are interested in producing thin tape of ∼100 μm in the green state and ∼50 μm in the sintered state for high toughness multi-layer laminate structures for mechanical applications. To produce tough laminate structures we require two materials with similar sintering behaviour but with different coefficients of thermal expansion.[10] In the present work we are interested in developing both silicon nitride (Si_3N_4) and Si_3N_4 + titanium nitride (TiN) based tapes for use as alternating layers in laminated structures. The TiN is added to increase the coefficient of thermal expansion of Si_3N_4 and is also chemically stable in Si_3N_4 up to the sintering temperature.

The equipment used for tape casting is relatively cheap and simple to construct and to operate. However a number of processing variables can effect the ability to produce a suitable slip for tape casting. A tape cast slip usually consists of at least the following components: a ceramic powder, a solvent, a binder, a plasticizer and a dispersant/deflocculant. Often more than one chemical is used for a single purpose.

Although water based tape casting is of increasing interest due to environmental issues, in the current work an organic solvent based system is developed. This is due to processing issues including the ease of drying, stability of a solvent based slip (compared to water) and due to the fact that Si_3N_4 powder is hydrophilic. Although tape casting has been well investigated

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for processing ceramics, there are many different recipes and the in depth process know-how is not always published. A review of aqueous systems was presented by Hotza and Greil and this shows the lack of and variance of published information, e.g. milling times, the sequence of when certain additives are added to the slip, information on de-airing, etc.[11] In addition information in the literature on tape casting of Si_3N_4 materials is limited.[12–15] We present a detailed account of the processing steps to produce Si_3N_4 and Si_3N_4 + TiN ceramic tapes.

2. Experimental

Initially a tape casting recipe and the associated processing was developed to produce tape from Si_3N_4 powder with yttria (Y_2O_3) and alumina (Al_2O_3) sintering additives. The process was then modified for producing tape where TiN powder was also added to the starting powders. The starting ceramic powders used were Si_3N_4 (Grade M11, $d_{50} = 0.6–0.78\ \mu m$, H.C. Starck, Germany), Y_2O_3 (Grade C, $d_{50} = 0.8\ \mu m$, H.C. Starck, Germany), Al_2O_3 (CT3000SG, $d_{50} = 0.76\ \mu m$, Alcoa, Germany) and TiN (Grade C, $d_{50} = 1.7\ \mu m$, H.C. Starck, Germany). The as received powders were sieved through a 125 μm mesh to remove soft agglomerates and dried at 150 °C for 12 h to remove chemically absorbed water from the particle surfaces.

All milling was performed in a Retsch PM400 planetary mill, using Y-TZP lined mills with a capacity of 250 ml and 10 mm diameter Y-TZP milling balls. For all processing experiments a ceramic powder charge totalling 100 g was used. Tape casting procedures for three different "ceramic compositions" were developed and these compositions are presented in Table 1.

Polyvinyl butyral (PVB) and polyethylene glycol (PEG) were used as the binder and plasticizer, respectively. The PVB binder (Mowital B 30 H, Kuraray Specialities Europe, Germany) was supplied as a free flowing fine-grained powder and the PEG plasticizer (PEG 300, Fluka Chemie GmbH, Switzerland) was obtained in a liquid form. After evaluation of a number of different possible dispersants (see Section 3), the ceramic powders were dispersed with the use of a polymeric alkoxylate supplied as a viscous liquid (Solsperse 20000, Noveon Division Lubrizol Ltd., UK), the solvent used was 99.9% pure ethanol.

Although many slips were prepared during the process development, in the current work only the processing of six slips is summarized. These slips were prepared with different organic contents and processing steps in order to establish an effective tape casting process. The following factors were varied in the slips:

1. The amount of dispersant was varied from 2 to 3.9 g. To improve the coating of the ceramic powders by the dispersant, the dispersant was pre-dissolved in the solvent in the planetary mill prior to the ceramic powders being added.
2. The amount of ethanol (solvent) was varied from 52 to 72.5 g.
3. The total amount of binder and plasticizer were varied from 27 to 45 g. In addition the binder to plasticizer ratio was altered from 1:1 to 1:2.
4. The sequence of the preparation steps and addition of ingredients, including single and multi-step milling, premixing of binder and plasticizer. Variation of milling times of all steps, with the aim of reducing the total milling time. For the first slip, all ingredients were loaded in the mill together. For the remaining five slips multi-step milling was used; the first step involved milling the powder, solvent and dispersant, whilst the second step involved adding the remaining organics (binder and plasticizer).
5. De-airing (degassing), removal of the trapped air in the slurries was performed in the planetary mill with different rotation speeds and milling times.
6. Release of the tapes from a 30 μm thick polypropylene carrier film (Trespaphan NND 30, Treofan, Germany) which was corona treated on one side by the manufacturer. The ease of release on both sides of the tape was investigated. In addition the tape was coated with different lubricants (silicon spray, silicon oil and washing detergent) to aid release of the tape.

Table 1
Ceramic composition of the three different materials which were tape cast

	Si_3N_4 (g)	Y_2O_3 (g)	Al_2O_3 (g)	TiN (g)
Si_3N_4	92.59	4.63	2.78	0
Si_3N_4 + 15% TiN	78.70	3.94	2.36	15
Si_3N_4 + 30% TiN	64.81	3.24	1.95	30

Tape casting was performed on a semi-continuous laboratory sized tape casting machine with a moving doctor blade that was designed and constructed in house (Fig. 1), the maximum possible length of the tape castable was 1.8 m. The polypropylene carrier film was placed on to float glass which was first sprayed with ethanol to help the carrier film adhere better to the glass. A doctor blade with a width of 150 mm was purchased from Richard E. Mistler Inc., USA. In order to obtain a dry tape of ~100 μm thickness, it was determined that a blade gap width of 300 μm was optimal (shrinkage of the cast tape during drying was ~65%). A constant tape casting speed of 254 mm/min was used throughout. Casting was performed at ambient temperature and humidity and all tapes were dried at room temperature for approximately 12 h before releasing from the carrier film.

3. Results and discussion

The dispersant agent is added to the slip to keep the powder particles stable in the suspension. Initially a number of dispersing agents were evaluated by measuring the slip rheology. The possible dispersants evaluated included fishoil, diethanolamine, triethanolamine, Hypermer KD-2 and KD-6 (polyoxyalkylene amine derivatives, Uniqema, Belgium) as well as Solsperse 20000 and 41000. Rheology measurements were made on Si_3N_4 slip loaded to 55 wt.% ceramic powder (and with 13 wt.% binder) containing 1 wt.% of the dispersing agents. The results are shown in Fig. 2(a) for shear rate versus shear force and Fig. 2(b) for shear rate versus viscosity. All the slips showed a non-Newtonian flow behaviour, i.e. a decrease in viscosity with increasing shear rate. Among the dispersants evaluated

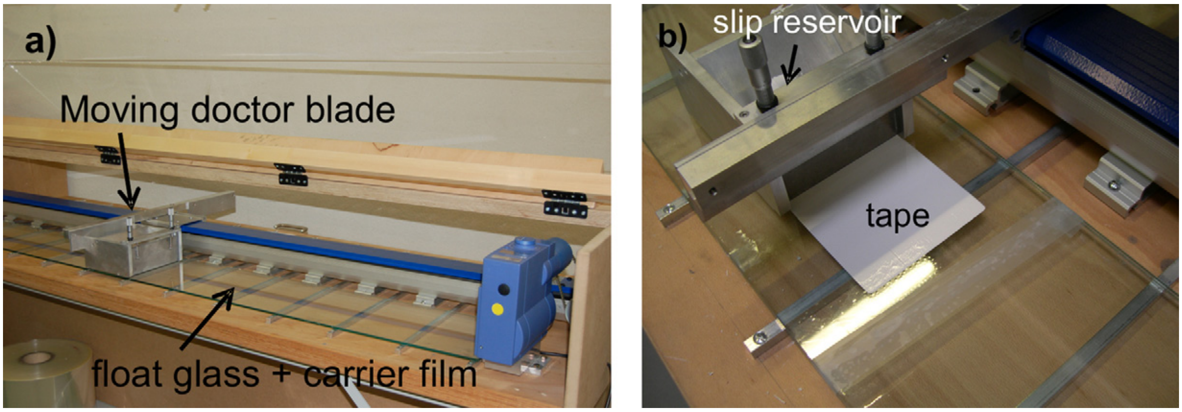

Fig. 1. (a) The tape casting equipment used for the development and production of Si_3N_4 based tapes and (b) close-up showing the beginning of the tape casting of a Si_3N_4 slip.

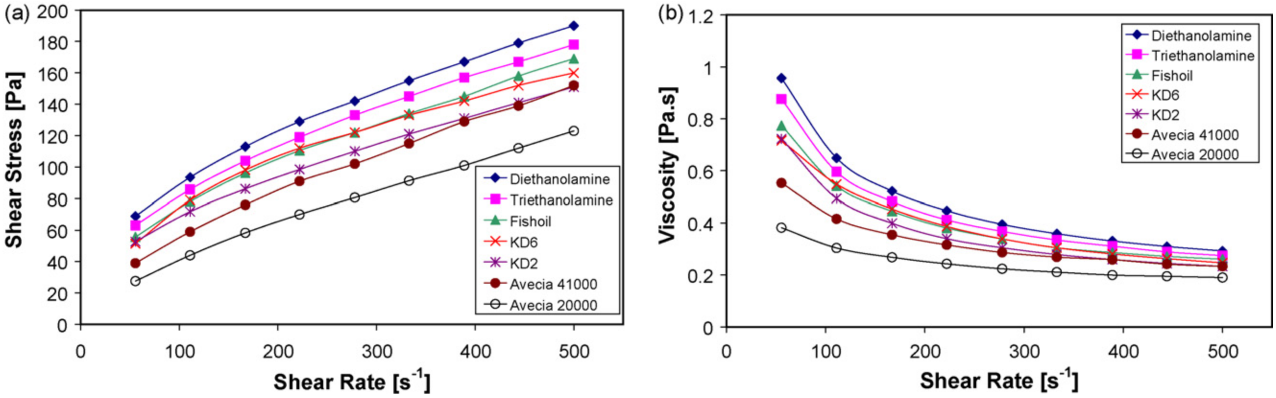

Fig. 2. The effect of 1 wt.% addition of different dispersing agents on the rheological behaviour of Si_3N_4 slip containing binder: (a) shear stress against shear rate and (b) viscosity against shear rate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Solsperse 20000 was selected as the most suitable, rheology measurements showing it to have the lowest shear force at all shear rates. The relatively high viscosity and fast drying times of ethanol based slurries preserves a homogeneous distribution of the ceramic powders by reducing the mobility of the slurry components. Ethanol based slips can also exhibit a certain amount of thixotropic behaviour, which can be useful during casting and drying.

3.1. Slip processing

The differences in the processing procedures used for the different slips with the different milling sequences and addition of ingredients are shown as flow diagrams in Fig. 3 (batches 2–6). Initially a single stage milling process was used where all the ingredients where placed into the mill together (batch 1), however this required 48 h of milling to produce a stable slip. It should be noted for batches 2 and 3 that initially 30 g ethanol was added at the start of the processing and the rest was added in small amounts as required with the Si_3N_4 powder additions up to the total amount as stated in Table 2.

For all batches, the Solsperse 2000 dispersant was dissolved in ethanol in the planetary mill for 5 min at a speed of 75 rpm, at the beginning of the procedure before adding any ceramic powder. Initial trials showed pre-dissolving of the dispersant in the ethanol to be more effective in stabilizing the ceramic slip, rather than adding the ceramic powders, solvent and dispersant simultaneously together in a first step. The effect of the dispersant on the stability of the slurry was verified by checking the visual appearance of the slurry after the first stage of milling (a smooth slip with no agglomerates was desired). (Stage 1 of milling refers to the homogenous mixing of the ceramic powder in the solvent and is also referred to as “dispersion milling”.) When all the agglomerates of the powder were successfully broken apart and all powder particles were covered with the dispersant the suspension appears smooth and shiny. The amount of the dispersant needed for a particular composition is also strongly dependent on the time of dispersing milling. In the

Table 2
The amounts of the different organic additions used for the different slip batches during process development (based on 100 g of ceramic powder)

Batch no.	Solsperse 20000 (g)	Ethanol (g)	PVB (g)	PEG (g)
1	3	52	13	26
2	2	52	10	18
3	3	65	13	26
4	3.15	57.5	15	30
5	3.9	67.4	13.5	13.5
6	3.9	72.5	13.5	13.5

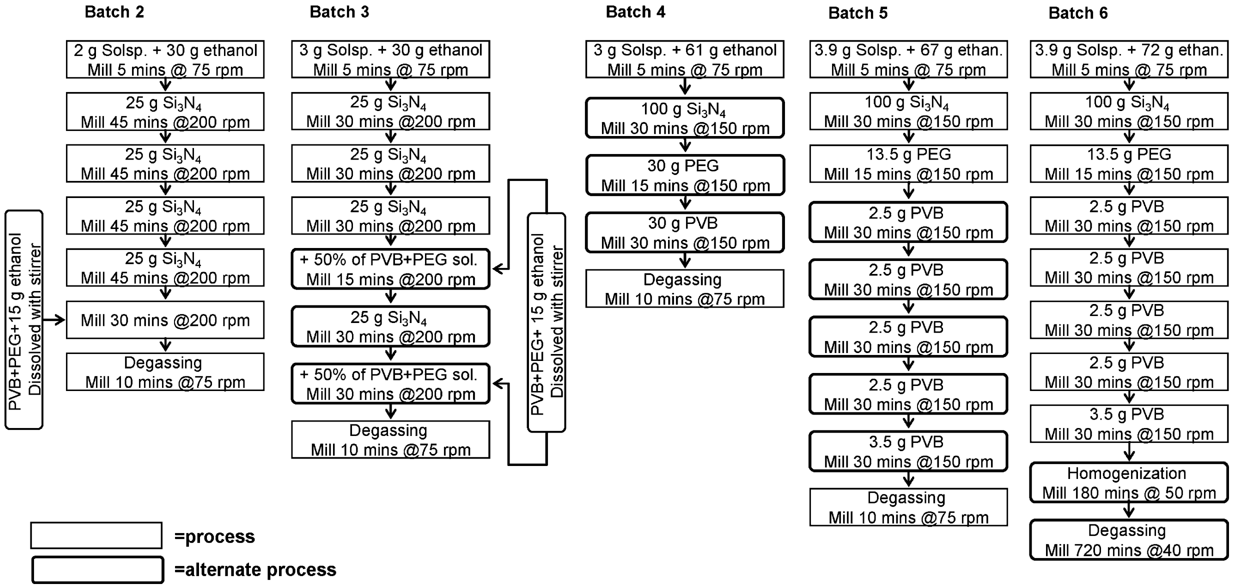

Fig. 3. Flow diagram showing the differing processing steps used for slip batches 2–6.

current work 2 g of Solsperse 20000 was found to be insufficient to produce a smooth and stabilized slurry after 3 h of milling. The amount of dispersion was increased to 3.9 g and this content was found to be optimal with a dispersion milling time of 30 min (batches 5 and 6).

The amount of solvent used is crucial since tape casting is a viscous liquid based forming process. It was observed that if the amount of solvent is lower than 40 wt.% with respect to solid loading, the slurries became very stiff and difficult to cast. A lack of solvent in the suspension resulted in incomplete dispersion of the powder during the first stage of milling, which resulted in a stiff, dry appearance of the slurry as well as making proper mixing of the organics impossible. When the amount of solvent is much greater than 40 wt.%, the slurries were easily flowing into the reservoir, but the obtained tapes were susceptible to exhibit surface cracks due to higher lateral stresses that the tape suffers during drying, as observed in Fig. 4. The ideal solvent content was in the range of 39–42 wt.% of the solid loading content for the Si_3N_4 (+sintering additives) powder. As will be discussed later the addition of TiN powder changes the amount of solvent required.

The binder and plasticizer are referred to as wt.% of the total ceramic powder, dispersant, binder and plasticizer content, i.e. the solvent is excluded. When a high total amount of binder and plasticizer is used the tape cast surface contained small agglomerates of binder (max. agglomerate size ∼5 μm, observed in the optical microscope) and have a surface appearance which is rough both visually and to the touch. The rough surface of such a tape from batch 4 with a binder content of 20.2 wt.% can be seen in Fig. 5. Therefore it was preferable to reduce the amount of binder as much as possible (to 10.3 wt.%) while still being able to produce a tape that could be removed from the carrier film without tearing. Reduction of the binder content is also beneficial for the debinding process. In addition it was found that

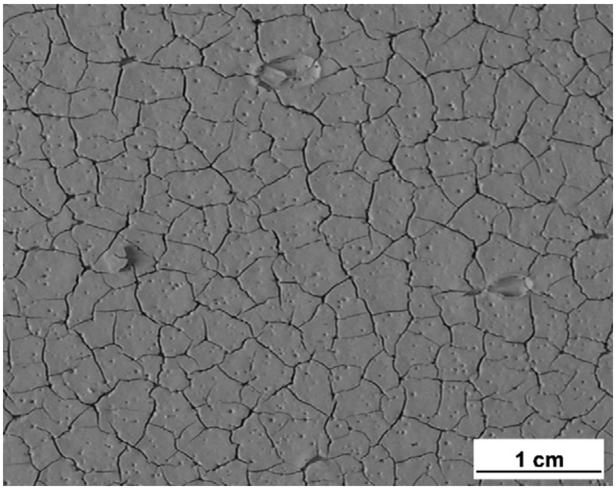

Fig. 4. Surface cracks on cast tape caused when the solvent content exceed ∼42 wt.%, pin-holes are also clearly visible.

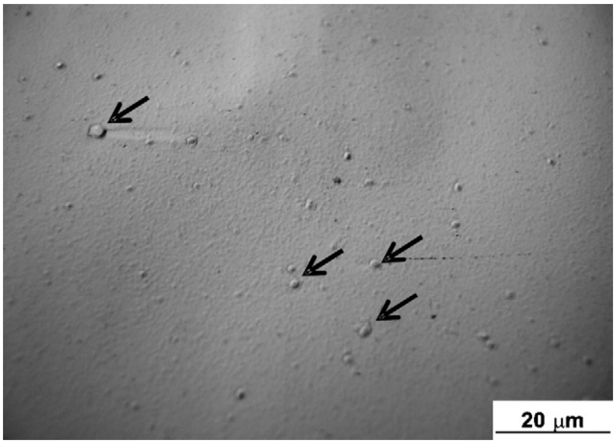

Fig. 5. Optical micrograph of the surface of process batch 4 which contained 20.2 wt.% PVB, shows agglomerates of binder which are not dissolved during the milling, the larger agglomerates are arrowed.

a very smooth slurry could be achieved if the PVB was added in small amounts and the slurry milled between the additions as described for batches 5 and 6. During organic composition optimization, the effect of the binder to plasticizer ratio was also considered. It was found that the tapes with binder to plasticizer ratio of 1:2 (or 1:1.8) strongly adhere to the casting surface following drying, and were difficult to remove from the carrier film. Tapes cast with a final ratio of binder to plasticizer 1:1, had sufficient flexibility and strength as well as ease of removability.

The effect of single and multi-step milling processes plays a significant role on the quality of the final slurry. In addition, the sequence of adding the components to the slurry during milling affects the slurry quality, in terms of homogenization and elimination of agglomerates. The results showed that the different organic components namely the binder and the dispersant compete for absorption on the free surface of the ceramic powder. Initial results showed that the milling process is not effective when the single step milling is used, i.e. when all components are added to the mill together. Incorrect addition of components reduces the effectiveness of the milling process. Two different effects were observed when the organic components were added incorrectly.

First if the slip is not properly deflocculated before adding the PVB a "zipper bag" effect[16] was observed, where agglomerates of ceramic powder are encased by the binder, an example is shown in Fig. 6. As the binder particles in the slip are not well dispersed/dissolved and are thus larger than the ceramic particles the binder molecules can attach to multiple sites of the ceramic powder particle surfaces, resulting in a large agglomerated particle that remains till the end of the milling process.

The second effect observed in initial trials when the dispersant and binder were added together is referred to as the "displacement effect".[16] Here the cast tapes crack into long streaks, which are perpendicular to the casting direction (Fig. 7). During the displacement effect, the binders especially from the vinyl family tend to displace the dispersant back into the solvent and instead the ceramic particles are coated by the binder. This reduces the amount of binder between particles hence reducing tape strength.

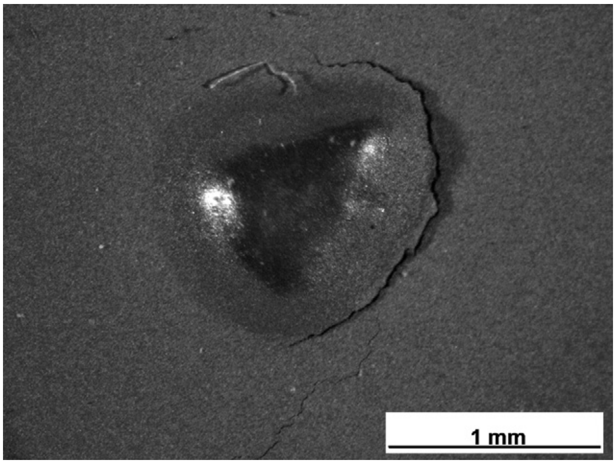

Fig. 6. "Zipper-bag" effect where a ceramic agglomerate is encased in the binder.

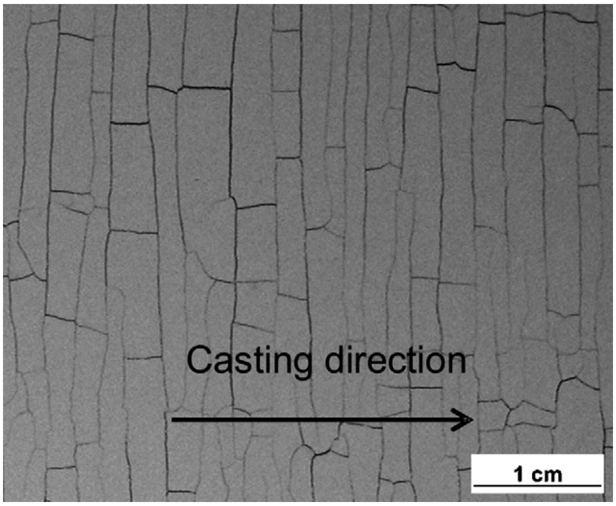

Fig. 7. The surface of cast tape showing elongated cracks perpendicular to the casting direction due to "displacement effect".

Therefore during the process development, the milling process was split into different stages. The first stage was the "dispersion milling" stage where the ceramic powder is deflocculated in the solvent/dispersant mix. The stability of the slip is of most importance to obtain a homogenously mixed slurry. The dispersion milling should allow sufficient time and energy for all ceramic particles to be coated by the dispersant. In the second stage the organics are mixed into the deflocculated slip, in the current work it was determined that adding the liquid plasticizer to the mill prior to the binder allowed improved homogenization of the organics. This is followed by the third stage of the process the "homogenization milling" allowing complete inter-mixing of the organics in the slip and allowing the binder to attach to particles and create inter-particle bridges. This is followed by the last stage of "de-airing" to remove entrapped air from the slip.

De-airing can be performed by a number of methods including by vacuum or centrifugation.[11] In the current work de-airing was performed in situ in the planetary mill by reducing the speed to 75 rpm for 10 min. However this was not sufficient for complete removal of entrapped air. Small pin holes caused by air entrapments lead to crows foot cracking originating from the pinholes (Fig. 8). Complete de-airing of the slip was possible by milling for 12 h at a very low speed of 40 rpm.

3.2. Tape release

After drying overnight the average thickness of the tapes was ~90 μm with a variation of less than 10%. The cast tape was removed from the film by first peeling of a small corner of the tape and then using a plastic ruler to apply a uniform force across the tape width whilst the ceramic tape was pulled slowly away from the carrier film. Tape casting trials were performed on both sides of the carrier film (one side was treated by corona), and no discernable effect was noticeable. In addition the use of the liquid washing detergent had no influence on the removability of the tape from the carrier film. When the carrier film was covered with a thin film of silicon oil, the film of oil was too "thick" and

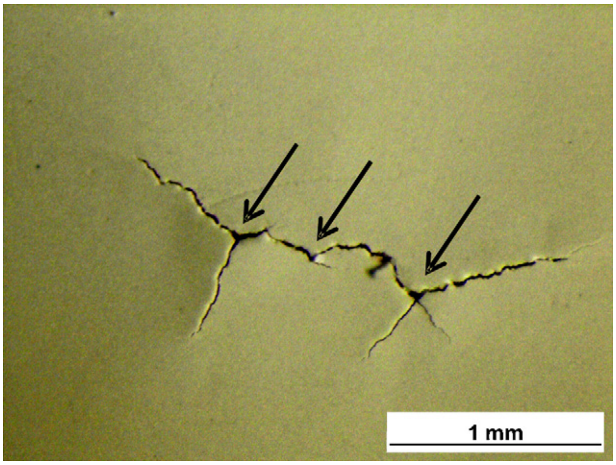

Fig. 8. Two joined “crow’s feet” cracks originating from pin-holes due to insufficient de-airing of the slip prior to tape casting.

it was not possible to cast the tape on the film as the friction between the slurry and the film was too low. However, when using silicon spray casting was possible, the silicon spray had two beneficial effects; the cast tape surface was quite smooth (SEM image of green tape in Fig. 9) and the removal of the cast tape after drying was significantly easier than when casting directly on to the carrier film.

Furthermore, as previously mentioned it was found that the binder to plasticizer ratio has a big influence on tape releasing. Tapes with a binder to plasticizer ratio 1:2 (and with silicon spray applied on the carrier film) were releasable only partially, however tapes with a binder to plasticizer ratio 1:1 were easily removable.

3.3. Si_3N_4 + TiN composite tapes

Based on the final composition and processing of the Si_3N_4 slips, two additional compositions were developed for producing tapes of Si_3N_4 + 15 wt.% TiN and Si_3N_4 + 30 wt.% TiN. The amount of solvent was decreased with increasing TiN content due to the fact that Si_3N_4 is more hydrophilic than TiN. In addition the starting particle size of the TiN ($d_{50} = 1.7\ \mu m$) is larger than that of the Si_3N_4 particles ($d_{50} = 0.6–0.78\ \mu m$). The difference in particle size of the starting powders can also be observed in the hot pressed microstructure of the Si_3N_4–TiN composites.[17] The total organic content (binder and polymer) was also decreased with increasing TiN content due to the difference between specific surface areas of Si_3N_4 and TiN particles and the reduced solvent content. The final compositions used are presented in Table 3, the actual processing procedure used is similar to that of batch 6, in general the TiN addition appears to have no adverse effects on slip stability.

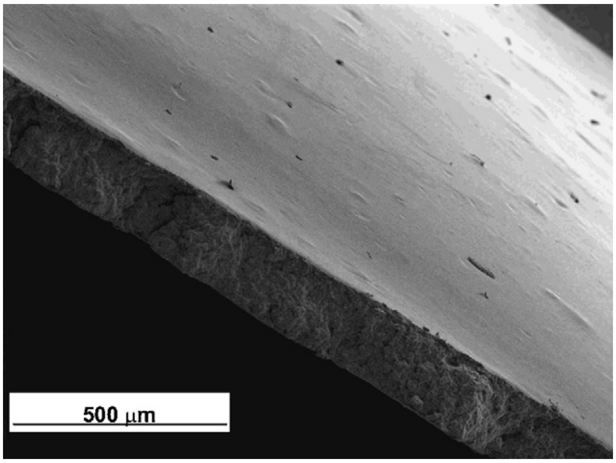

Fig. 9. SEM image of a green Si_3N_4 tape produced using the process described for batch 6.

Table 3
The finalized organic recipes for producing the three different materials that were tape cast

	Ethanol (g)	Solsperse 20000 (g)	PVB (g)	PEG (g)
Si_3N_4	72	3.9	13.5	13.5
Si_3N_4 + 15% TiN	65	3.9	12.4	12.4
Si_3N_4 + 30% TiN	55	3.9	12.0	12.0

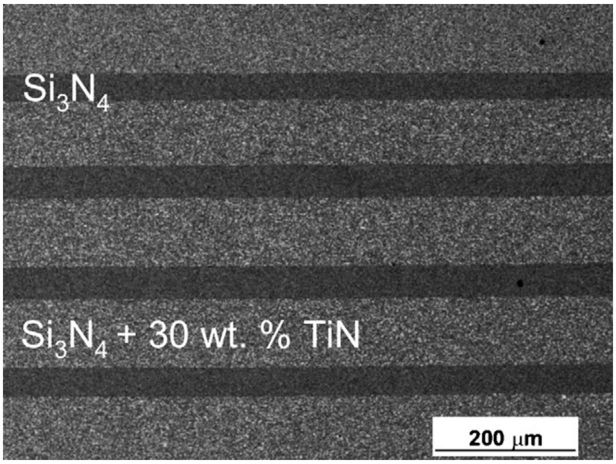

Fig. 10. SEM image of part of a hot pressed multi-layer laminate consisting of Si_3N_4 layers (∼45 mm thick) and Si_3N_4 + 30 wt.% TiN layers (∼90 mm thick).

From the dried tapes circular discs of 49 mm diameter were cut using a hollow punch tool. Alternating discs were stacked in a multi-layer laminate structure to the required designs to produce high toughness laminates.[18] The sintering of the tapes has already been described in more detail elsewhere.[18] For the laminate designs investigated it was necessary to have Si_3N_4 layers of 40–50 µm thickness and Si_3N_4 + TiN layers of 90–100 µm thickness after hot pressing. Hence one layer of tape cast Si_3N_4 and two layers of Si_3N_4 + TiN were used. The microstructure of a sintered laminate is shown in Fig. 10. It can be seen that a high sintered density has been achieved and there are no cracks between the layers.

4. Conclusions

Stable slips of all three ceramic compositions, Si_3N_4, Si_3N_4 + 15 wt.% TiN and Si_3N_4 + 30 wt.% TiN were obtained and these gave defect-free good quality cast tapes. The developed tape casting process and materials allowed the production of high quality, high toughness laminate structures. It was experimentally proved that multi-stage milling is more beneficial than a single stage milling, in terms of total milling time and quality of final tape. In addition the entire milling process and de-airing process was performed in a single type of mill. The main conclusions to improve the casting process and quality of the cast tape are:

- The dispersant should be added to the solvent and dissolved, prior to addition of ceramic powder to increase the effectiveness of the dispersant.
- The PEG plasticizer is added prior to the addition of the PVB binder.
- The PVB should be added in small amounts and milled between each addition to aid dissolution in the slip and to eliminate binder agglomerates.
- Tapes with a binder to plasticizer ratio of 1:1 are easy to remove from the carrier film.
- A thin layer of sprayed silicon (which is compatible when processing Si based ceramics such as Si_3N_4) on the carrier film leads to a smooth tape surface and easier release of the tape from the carrier.

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