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# Aqueous tape casting of silicon nitride

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**Abstract**

Slurries consisting of a low cost silicon nitride powder, sintering aids yttria and alumina, dispersants, binders, defoamers and water as a solvent were optimised for tape casting by electroacoustic and viscosity measurements and by casting experiments. The slurries exhibit shear-thinning behaviour due to the highly shear-thinning binder emulsion. Crack free tapes with a maximum thickness of approx. 250 μm and a binder content of 13–15 wt.% could be obtained. The green tapes with a high flexibility and green strength could be laminated easily by compression at room temperature. After sintering a dense microstructure developed. A significant shrinkage anisotropy parallel and perpendicular to the cast direction was observed. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Dispersion; Electrokinetics; Rheology; $Si_3N_4$; Suspensions; Tape casting

## 1. Introduction

Silicon nitride is a candidate material especially for engine applications because of an interesting combination of thermal and mechanical properties. Although the reliability of silicon nitride has been proven by serial application mass production is restricted because components are still too costly compared to metallic components. Cost reduction can be achieved by using a low-cost powder,[1] by continuous sintering[2] and by using the tape casting technology for certain geometries e.g. substrates. Silicon nitride substrates can be fabricated much thinner than e.g. aluminium nitride parts because of the higher mechanical strength.[3]

Tape casting is a widespread and cost effective method to produce flat, large area components with high quality.[4] Thin tapes are used mostly in the electronic industry.[5] Furthermore it is possible to build up multi-layered parts with complex geometries[6] or improved properties such as higher fracture resistance,[7] better thermal shock behaviour[8] or continuous transition between properties. There are many publications dealing with tape casting of oxides but only few reports are available on the preparation of tapes made from nonoxide powders such as SiC or $Si_3N_4$, respectively.[6,9] In most publications organic solvents are used to disperse the powders. Water as a solvent has the advantage of being non toxic, non flammable, easy available and cheap,[10] but the process becomes more sensitive to casting parameters.[11] Silicon nitride reacts with water developing an oxidized surface.[12] However, this increase of the oxygen content due to hydrolysation is negligible because of the addition of oxidic sintering additives.

A well deagglomerated suspension is necessary to get a high green density.[13] Silicon nitride can be well dispersed in water in the basic pH range without organic additives.[14] But in a mixture with the most common sintering aids yttria and alumina coagulation may occur between the different powder particles. Therefore, it was the aim of this work to obtain a stable aqueous dispersion of silicon nitride including the sintering aids with the aid of dispersants. Based on these results tape casting slurries were prepared by adding a binder emulsion and a defoamer. The slurry composition was optimised with regard to casting suitability and tape properties.

## 2. Experimental procedure

### 2.1. Materials

A low cost silicon nitride powder with high β-content (Silzot® HQ, SKW Trostberg Metallchemie, Germany)

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was homogenized in water with 6 wt.% yttria (Meldform metals, UK) and 4 wt.% alumina (CT3000 SG, Alcoa Chemie, Ludwigshafen, Germany) using an attrition mill (LME 1, Netzsch, Germany). The data of the as delivered and milled silicon nitride powder are summarized in Table 1.

To disperse the powders two dispersing agents (A: Dolapix A88 and B: PC 33, Zschimmer & Schwarz Chemische Fabriken, Lahnstein, Germany) were chosen after different screening tests. A is an aminoalcohol and B a synthetic polyelectrolyte (polyacrylate). A mixture of 90 wt.% A and 10 wt.% B was used in a total concentration of 1 wt.% of the powder amount. A fatty alcohol as defoamer (Contraspum conc., Zschimmer & Schwarz) was added to prevent foaming during homogenization and to improve the wetting behaviour of the slurry for tape casting. A commercial polymer emulsion (Mowilith DM 765, Clariant, Frankfurt, Germany, a copolymer of an acrylic polymer and styrene) was used as the binder. It consists of small polymer particles with an average diameter of 0.17 μm which are dispersed in water. The solid content is about 50 wt.%. Due to the sufficiently low glass transformation temperature of −6 °C the binder is flexible at room temperature. Thus, no further addition of a plasticizer is necessary. The binder has a alkaline pH of 8.5 which fits to the alkaline powder suspension. Binder emulsions have been used successfully for aqueous tape casting by other researchers.[15–18]

### 2.2. Slurry preparation and tape casting

The electrokinetic behaviour of suspensions and tape casting slurries was measured using an electroacoustic technique (ESA-8000, Matec Applied Sciences, UK) at a temperature of 25 °C. The measured electrokinetic sonic amplitude (ESA) is directly proportional to the dynamic electrophoretic mobility and therefore to the zeta potential.[19]

Table 1

$Si_3N_4$ powder data (Silzot HQ®, SKW, Germany)

| Grain size (μm) | As delivered (suppliers data) | After milling |
|---|---|---|
| $D_{10}$ | 0.7 | 0.1[a] |
| $D_{50}$ | 1.6 | 0.4[a] |
| $D_{90}$ | 4.1 | 1.9[a] |
| Specific surface area ($m^2$ $g^{-1}$) | 4.5 | 9.2 |
| Amount of nitrogen ($N$/%) | 38.6 (40.2[b]) | 38.2[b] |
| Amount of contaminations: | | |
| O/% | 0.50 (0.84[b]) | 1.50[b] |
| C/ppm | 0.085[c] | 0.11[c] |

[a] Lasergranulometer (Typ LS 230, Coulter).

[b] Leco, TC-436.

[c] Leco, C-400.

The suspensions for ESA-measurements were prepared by adding 15 g of powder to 200 ml distilled water with 0.01 n KCl and ultrasonic treatment for 5 min. The changes of the zetapotential with pH were recorded by titrating the suspensions with 0.1 n HCl. The start pH was set to 11–12 with 0.1 n NaOH.

The tape casting slurries were prepared by filling water, dispersing agents and defoamer in the appropriate fractions in a PE-bottle. To overcome the shear-thickening behaviour of the concentrated powder suspension the binder was added before all of the powder was filled in. The total homogenisation time of the slurry was 72 h. The homogenized slurry was degassed in a rotary evaporator at 200 mbar at room temperature for 1.5 h.

The viscosity of the homogenized tape casting slurries was measured using a rotary viscosimeter (VT550, Haake, Germany) with the following procedure: after a waiting period of 120 s the shear rate was continuously increased up to 200 $s^{-1}$ in 100 s. Then the shear rate was decreased with the same ramp to observe any time dependent behaviour. The shear-thinning ($P$) of a slurry can be characterized by the ratio of the viscosities at small and high shear rates:[20]

$$P = \frac{\eta\ (\dot{\gamma} = 1\ \mathrm{s}^{-1})}{\eta\ (\dot{\gamma} = 10\ \mathrm{s}^{-1})} \tag{1}$$

When $P = 1$, the substance shows Newtonian behaviour at the observed shear rates, i.e. the viscosity is constant. The greater $P (P > 1)$, the greater is the shear-thinning.

Tape casting was carried out on a continuous working tape casting machine (Hutter, Lohmer, Germany) with a dual doctor blade system. A polypropylene polymer film (NNA 40, Hoechst Trespaphan, Neunkirchen, Germany) with a thickness of 40 μm was used as a carrier. The casting speed was adjusted to 0.2 m/min. The shear rate can be estimated by the ratio of velocity and gap height and was approx. 7 $s^{-1}$ (500 μm gap). Drying was performed under air convection at room temperature.

### 2.3. Characterization of the cast tapes, lamination and sintering

The green tapes were assessed qualitatively for homogeneity, surface quality and for cracks or bubbles. The thickness was measured using a micrometer and the geometric green density by additional weight determination. Surface roughness was determined using a profiler (Tencor P-1, Tencor Instr., UK). Lamination has been performed by compression of the green tapes at 14 MPa for 20 s at room temperature. Pyrolysis was carried out under a flowing nitrogen atmosphere up to 750 °C with a heating rate of 5 K/min. The pyrolysed tapes were sintered in a gas pressure furnace (FPW, FCT, Rödental, Germany) at 1800 °C for 60 min under a nitrogen pressure of 5 MPa in a silicon nitride powder bed. The heating rate was 20 K/min up to 1100 °C and 10 K/min up to 1800 °C. Cooling was controlled down to 1500 °C with a rate of 10 K/min. The average linear shrinkage during sintering was calculated from at least 5 samples. To observe any anisotropy it was distinguished between the shrinkage parallel and perpendicular to the cast direction. The density of the sintered tapes was measured by the Archmimedes' principle in water with a wetting agent to avoid air bubbles on the thin light samples. The microstructure was investigated by scanning electron microscopy (SEM, CamScan, Cambridge, UK).

## 3. Results and discussion

### 3.1. Slurry characterisation

The used binder emulsion (pH = 8.5) is only stable at an alkaline pH value. Thus, for the proposed tape casting processing must be done in the basic pH range, as well. Pure silicon nitride can be well dispersed in this pH range without organic additives.[14] However, with the sintering aids yttria and alumina, which have been used in the ratio of 6:4 at a total amount of 10 wt.%, coagulation would occur at a pH of 7–9 due to the different surface charges of the powders (Fig. 1). Although the pH of the powder suspension without organic additives is approx. 9.5 and outside the coagulation range, its stability is poor due to the low value of the zetapotential of yttria and alumina at this pH. Furthermore, when the emulsion binder is added the pH can be reduced locally to a value below 9. Thus, the isoelectric points (IEP) of all powders must be shifted by a suitable dispersant to pH values below 8.5, which is the lower limit of the working range set by the pH of the binder.

The addition of an aminoalcohol (dispersant A) improves the stabilization of silicon nitride suspensions in the basic pH range. But A alone does not shift the IEP of the sintering additives and, therefore, can not prevent coagulation in the above mentioned pH range. Thus, a second dispersant, a polyacrylate (dispersant B), was added, which shifts the IEP of the sintering aids to lower pH values. Most stable suspensions could be achieved at a pH > 8 using a mixture of 90 wt.% A and 10 wt.% B at a concentration of 1 wt.% based on the powder amount (Fig. 2). The pH of the powder suspension is increased by the added dispersants to about 11. After addition of the binder still a high pH of around 10 is obtained, which results in a good electrostatic stabilization of the powder particles in the tape casting slurries. As it was found out in a similar system,[17] the binder emulsion has no influence on the electrostatic stabilization of the powder particles (Fig. 2).

The contents of water and organic additives in tape casting slurries should be as low as possible. Low amounts of water to be evaporated during drying and of organic additives to be burnt out reduce the risk of defect formation. This requires high particle loaded slurries which usually have high viscosities. On the other hand the viscosity of the slurries must be low enough in order to ensure a homogeneous mass flow under the blade during the casting process. At a low water content skin formation can occur in the reservoir hindering the tape casting process. Furthermore, if the viscosity is too high it is difficult to degas the slurry. To investigate the influence of the slurry composition on processing and properties of the cast tapes several slurries were prepared with binder contents (pure binder without water) between 10 and 15 wt.% based on solid plus binder amount (Table 2).

Because of the dominating influence of the highly shear-thinning binder emulsion,[21] the slurries exhibit distinctive shear-thinning behaviour, too (Fig. 3).

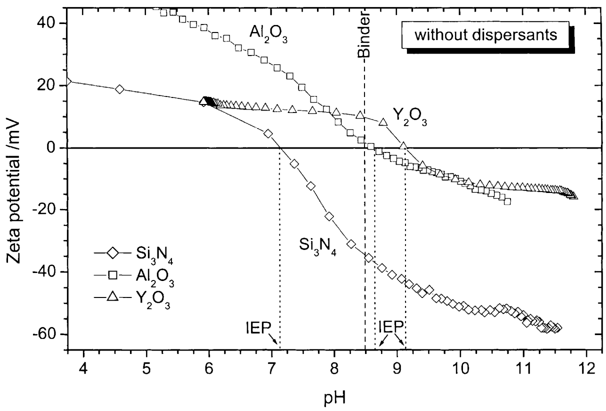

Fig. 1. Zetapotential versus pH of the single powders without addition of dispersants.

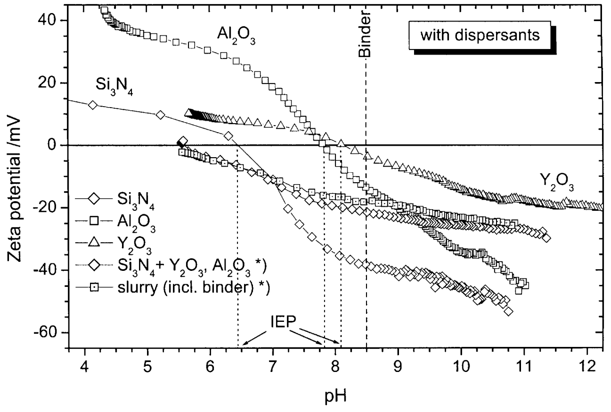

Fig. 2. Zetapotential versus pH of the single powders and the powder mixture with added dispersants and the binder-containing tape casting slurry. *) The zeta-potential of the powder mixture can only be approximated due to the different powder properties; however, the deviation to exact values is small because the concentration of sintering aids is only 7 vol.%.

Table 2
Composition and rheological properties of tape cast slurries

| Composition | Powder (vol.%) | Organic[a] (vol.%) | Water[b] (vol.%) | Binder content[c] (%) | $\eta$ (7 $s^{-1}$) (Pa s) | $P$ |
|---|---|---|---|---|---|---|
| S1 | 38.9 | 21.8 | 39.3 | 14.0 | 6.4 | 4.7 |
| S2 | 33.6 | 20.2 | 46.2 | 15.0 | 4.7 | 4.3 |
| S3 | 34.7 | 20.9 | 44.4 | 15.0 | 1.1 | 4.5 |
| S4 | 39.0 | 20.0 | 41.0 | 13.2 | 2.3 | 4.3 |
| S5 | 34.0 | 21.0 | 45.0 | 15.4 | 1.1 | 3.6 |
| S6 | 38.3 | 21.4 | 40.3 | 14.0 | 3.8 | 4.6 |
| S7 | 34.9 | 20.8 | 44.3 | 15.0 | 1.6 | 3.4 |
| S8 | 39.2 | 15.1 | 45.7 | 10.0 | – | – |

[a] Pure binder without water + organic additives.
[b] Free water + water of binder.
[c] $\text{Mass}_{\text{binder}}/(\text{mass}_{\text{binder + powder}})$; (pure binder without water).

Negligible thixotropy was observed. The rheological behaviour of the slurries meets the needs for the tape casting process:[22] during passing the blade, the viscosity decreases due to shear forces, and immediately behind the blade the viscosity rapidly increases again. This suppresses uncontrolled flow and prevents sedimentation of the ceramic particles. Time dependent effects like thixotropy are therefore undesired. Small changes in the composition (Table 2) have a great effect on the viscosity of the slurries but have hardly no effect on the type of their rheological behaviour. The viscosity of the compositions S1 and S6, which both have the same binder content, differs between 6.4 and 3.8 Pa s, although their powder content only varies from 38.9 to 38.3 vol.%.

Except for composition S1, all slurries are suitable for the tape casting process due to their dispersion stability, shear-thinning behaviour and lack of thixotropy.

### 3.2. Casting and green tape characterization

Slurry S1 could not be cast. Because of its high viscosity and yield stress the slurry was not transported through the blades. Furthermore, a dry skin developed rapidly on the slurry surface in the reservoir.

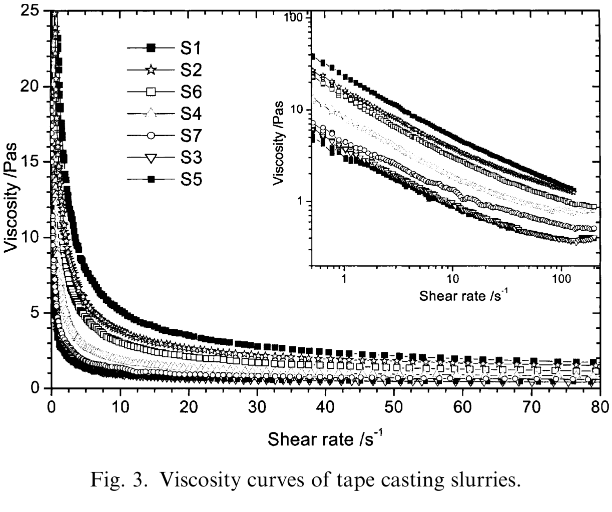

Fig. 3. Viscosity curves of tape casting slurries.

During casting of the other slurries no de-mixing of the organic components of the slurry was observed. Drying is a critical stage in tape casting. For some compositions cracks developed. During drying high capillary forces of the water can develop which cause cracks. Only after drying of the tape the binder molecules attribute to the strength of the tape by holding the powder particles together. With composition S6 a fine network of cracks was observed which had its origin in many small bubbles which could not be removed during degassing due to the high slurry viscosity (3.8 Pa s at 7 $s^{-1}$). Tapes obtained of comp. S2 did not show pinholes or bubbles, although its viscosity was very high (4.7 Pa s at 7 $s^{-1}$). Nevertheless, these tapes had cracks, which is due to a high porosity (42 vol.%) and therefore low green strength of the tapes: tape casting of thin films or of high viscosity slurries (e.g. because of a low water content or a high internal structure of the dispersed particles) leads to rapid drying of the tapes. This prevents the rearrangement of the powder particles after passing the blade and a low green density combined with a high sensitivity to crack formation is obtained. The binder content of comp. S8 was only 10 mass% resulting in a very coarse network of cracks. All tapes (even those with cracks) show high flexibility and good green strength after complete drying.

There was a significant dependency of the slurry composition on the green density: a high powder volume ratio in the slurry leads to a high green density (Table 3). The green density of S2 is very poor due to the high viscosity slurry which leads to a high porosity of the green tape as it was explained above. The highest green density was 1.65 g $cm^{-3}$ (comp. S8), i.e. 50% of the theoretical density, but the tapes had cracks. The best composition is that of S7 for which crack-free tapes with a slightly lower green density of 1.61 g $cm^{-3}$ were obtained. In the literature green densities above 1.9 g $cm^{-3}$ are reported for tape cast samples.[9] Thus, there is

Table 3
Properties of green tapes

| Composition | Green density (g cm$^{-3}$) | Powder (vol.%) | Organic (vol.%) | Pores (vol.%) | Thickness/μm (gap height) | Remarks |
|---|---|---|---|---|---|---|
| S2 | 1.37±0.10 | 36.0±2.6 | 21.6±1.6 | 42.4±3.1 | 255±10 (500) | Cracks |
| S3 | 1.52±0.03 | 39.9±0.8 | 24.1±0.5 | 36.0±0.7 | 185±5 (500) | |
| S4 | 1.53±0.03 | 41.1±0.8 | 21.2±0.4 | 37.7±0.7 | 140±5 (500) | |
| S5 | 1.56±0.03 | 44.4±2.6 | 27.6±1.6 | 28.0±1.6 | 200±10 (500) | |
| S6 | 1.58±0.04 | 42.0±1.1 | 23.4±0.6 | 34.6±0.9 | 245±5 (550) | Bubbles, cracks |
| S7 | 1.61±0.05 | 42.3±0.9 | 25.3±0.5 | 32.3±0.8 | 210±10 (500) | |
| S8 | 1.65±0.03 | 46.0±0.8 | 17.7±0.3 | 36.3±0.7 | 250±10 (500) | Cracks |

a great potential in optimising the aqueous slurries presented in this work.

The dried tapes had a smooth and homogeneous surface. Between top and bottom surface distinctive differences are found in roughness and particle arrangement (Table 4, Fig. 4). The bottom surface, which had contact with the carrier, is much smoother but shows regions with increased binder amount forming a continuous network. These regions seem to be responsible for the sticking of the tapes onto the polymer tape. Because of the low $T_g$ of the binder, which facilitates plastic deformation, the tapes could be easily laminated by compression at room temperature. The sticking behaviour of the binder-rich bottom surfaces helps to produce a good adhesion between the tapes. After lamination no single layers can be distinguished in a fracture surface neither in the green state (Fig. 5) nor sintered (Fig. 7). Lamination of two top surfaces was not possible with the used parameters because of their high surface roughness.

Table 4
Surface roughness of green and sintered tapes (composition S7)

| | Green tapes | | Sintered tapes | |
|---|---|---|---|---|
| | $R_a$ (μm) | $R_z$ (μm) | $R_a$ (μm) | $R_z$ (μm) |
| Top surface | 0.90±0.27 | 3.50±0.75 | 1.58±0.06 | 8.59±0.74 |
| Bottom surface | 0.052±0.004 | 0.27±0.05 | 0.46±0.07 | 2.36±0.82 |

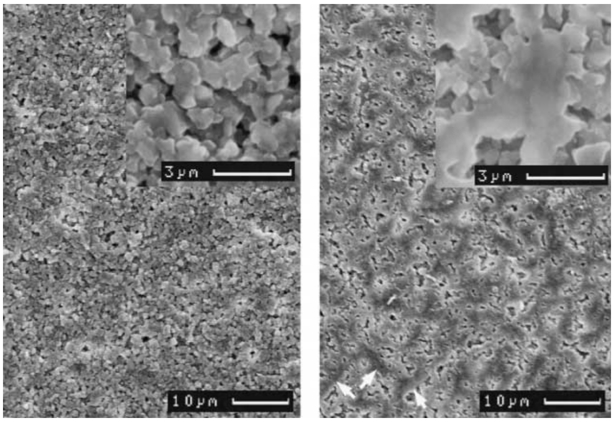

Fig. 4. Surface of green tapes (left: top; right: bottom surface) (SEM), (arrows point to darker regions with increased binder amount).

As can be seen from Fig. 4 the tapes have a high open porosity. By comparison the measured green density with the known composition of the tapes porosities of 30–40 vol.% were calculated (Table 3). Due to the porosity and the low thickness, binder burn out can be carried out with a relatively high heating rate of 5 K/

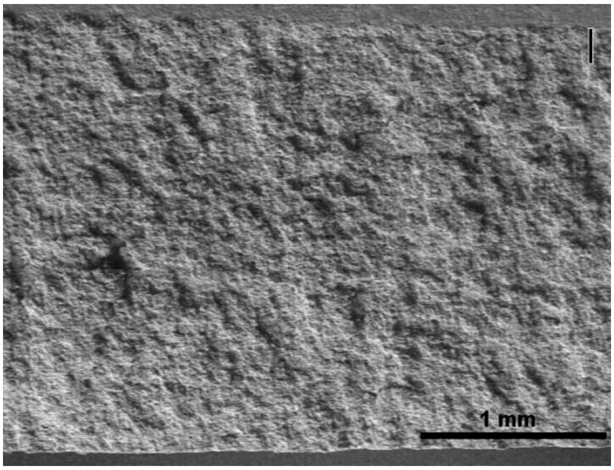

Fig. 5. Fracture surface of green tapes, laminated by compression at room temperature (13 layers) (SEM); bar in the right top corner represents thickness of single layers.

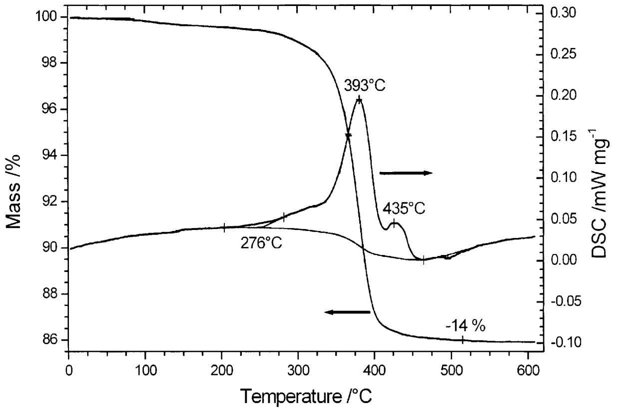

Fig. 6. Mass loss and DSC-signal of green tape (composition S6) during binder burn out in flowing nitrogen atmosphere with a heating rate of 5 K/min.

Table 5
Green and sintered densities and shrinkage anisotropy of cast tapes

| Composition | Green density (g cm$^{-3}$) | Sintered density (g cm$^{-3}$) | Sintered density (%th. density)[a] | Shrinkage anisotropy factor (%) |
|---|---|---|---|---|
| S2 | 1.37±0.10 | 3.17±0.14 | 95±4 | 7.7 |
| S3 | 1.52±0.03 | 3.26±0.12 | 98±3 | 8.6 |
| S4 | 1.53±0.03 | 3.21±0.12 | 97±4 | 5.3 |
| S5 | 1.56±0.03 | 3.27±0.06 | 98±2 | 3.2 |
| S7 | 1.61±0.05 | 3.24±0.06 | 98±2 | 5.4 |
| S8 | 1.65±0.03 | 3.25±0.10 | 98±4 | 7.6 |

[a] Estimated theoretical density: 3.32 g cm$^{-3}$.

min without any defects. Furthermore, during the binder burn out no warping occurs. The binder burns out in a narrow temperature range of 300 to 500 °C (Fig. 6). The total mass loss of the green tapes corresponds to the initial binder content (composition S6: 14% mass loss, Table 2). The different compositions, which only differ in the amounts but not in the type of the organic compounds, show the same behaviour during binder burn out. The DSC-signal shows the onset of decomposition at 276 °C. A strong endothermic peak is present at 393 °C which is combined with a rapid mass loss. At 435 °C a second endothermic peak indicates that a second, stronger type of binder molecule is burnt out at this temperature. Probably the copolymer of the binder emulsion is cracked into the two lower molecular species styrene and an acrylic polymer at the beginning of binder burn out. These two types of molecules decompose at different temperatures.

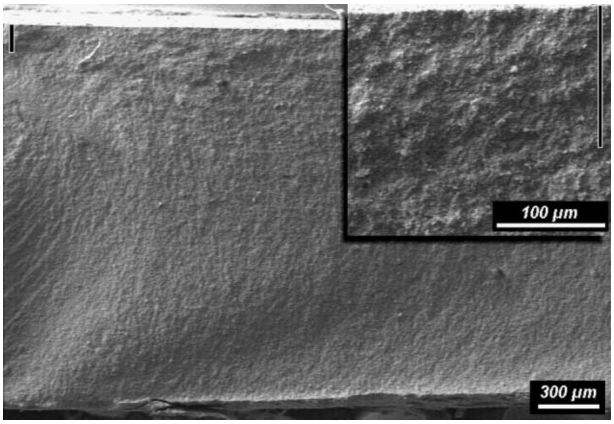

Fig. 7. Fracture surface of laminated tapes after sintering (13 layers) (SEM); bars represent thickness of single layers.

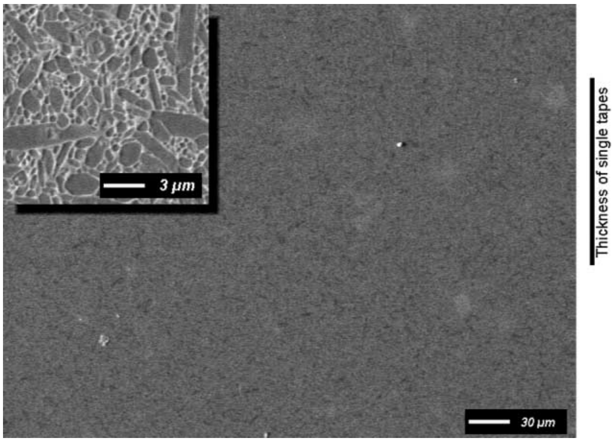

Fig. 8. Microstructure of sintered laminated tapes (composition S7): coarse β-Si$_3$N$_4$ grains surrounded by fine grains (light grey) and secondary phase (white) (SEM, plasma-etched).

### 3.3. Properties of sintered tapes

Because of the different quality of the top and bottom surfaces of the green tapes (see Section 3.3) the surfaces of the sintered tapes are also very different (Table 4, Fig. 9): the rough top surface consists of individual hexagonal crystals, whereas the bottom surface is much smoother. The hexagonal crystals look like α-Si$_3$N$_4$ needles which might be formed by a reaction of evaporated silicon and nitrogen during cooling.[23] Apart from the surfaces a dense material is obtained after sintering. The microstructure is typical for silicon nitride materials and consists of large β-Si$_3$N$_4$ grains surrounded by a fine-grained matrix and the secondary phase (Fig. 8). Some large pores (not shown) still remain because of the high porosity of the green tapes.

The densities of the sintered tapes measured by the Archimedes' principle were up to 98% of the theoretical

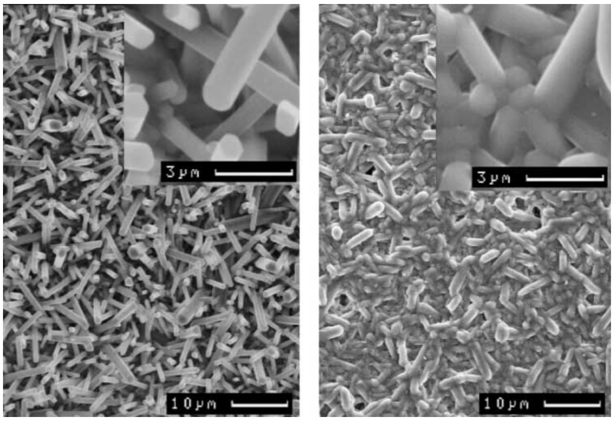

Fig. 9. Surface of sintered tapes (left: top, right: bottom) (SEM).

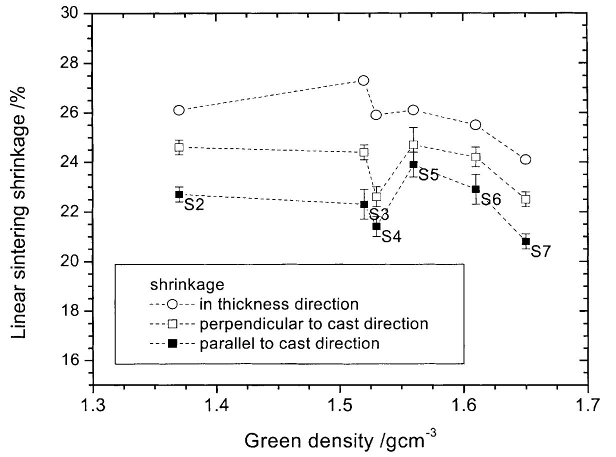

Fig. 10. Sintering shrinkage versus green density of the cast tapes showing anisotropy of shrinkage.

density (Table 5). The values have relatively great errors of about 4% due to the very thin and light samples. Above a green density of 1.5 g cm$^{-3}$ the sintering density of the different compositions is almost constant. Thus, the sintering shrinkage decreases with increasing green density above 1.5 g cm$^{-3}$ (Fig. 10).

An anisotropic sintering shrinkage parallel and perpendicular to the casting direction was observed. It can be characterised by a shrinkage anisotropy factor (1-*K*) with *K* being the ratio of the shrinkage parallel and perpendicular to the casting direction. Investigations in literature about the anisotropic shrinkage showed that the anisotropy factor greatly increases with increased solid loading of the slurry. The second most important influence was the shear rate during tape casting. Significant differences were also observed for different binder and powder types. But even tapes without any binder had anisotropic shrinkage concluding that the anisotropy originates from powder characteristics only. A correlation was found between anisotropic shrinkage and particle orientation caused by shape anisotropy.[24,25] In the present work the shear rate during casting was constant because of the constant gap height and casting velocity. The obtained values of the anisotropy (Table 5) show no correlation with the composition of the slurries. The anisotropy is believed to originate from a higher porosity parallel to the casting direction than perpendicular to it, due to the arrangement of particles caused by the shearing during casting.[25]

After sintering of laminated tapes the single layers could not be distinguished (Fig. 8) as it was already the case in the green state. Due to the compression during lamination the green density is increased which results in a sintered microstructure of high density. Because of the excellent joint it is suspected that the physical properties will be the same parallel and perpendicular to the layers. This will be proofed in further investigations on mechanical strength and thermal conductivity.

## 4. Summary

A powder mixture consisting of $Si_3N_4$ and the sintering aids $Y_2O_3$ and $Al_2O_3$ could be dispersed well in water in the alkaline pH range. A mixture of two dispersants was used to get the best results. Several slurry compositions with binder contents of 10–15 wt.% were prepared. The viscosity of the tape casting slurries is affected by solid and water content. Low variations of composition had a relative great effect on viscosity, whereas the shear-thinning rheological behaviour remained the same. No time dependent effects were observed.

It was possible to obtain crack free green tapes with a maximum thickness of approx. 250 μm with a binder content of 13–15 wt.%. The green density of optimised tapes was up to 1.61 g cm$^{-3}$. After sintering dense microstructures with relative densities of at least 98% were obtained. Due to the relatively low green density the linear sintering shrinkage was about 20–24%. Significant shrinkage anisotropy was observed with no correlation to the slurry composition. The green tapes could be easily laminated by compression with 14 MPa at room temperature. After lamination an excellent joint was obtained. In the green and sintered laminated components the single layers could not be detected.

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