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Journal of the European Ceramic Society 30 (2010) 3397–3406

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Effect of powder, binder and process parameters on anisotropic shrinkage in tape cast ceramic products

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Received 14 April 2010; received in revised form 3 August 2010; accepted 9 August 2010
Available online 1 September 2010

Abstract

The effect of powder, binder and process parameters on the properties of cast alumina tapes and their anisotropic shrinkage were investigated. Three alumina powders with different particle shapes (platelets, spherical, standard) and three PVB binders with different chain lengths were used. In addition, casting velocity and blade gap height were varied. The orientation of the particles in the tape was detected quantitatively by image analysis of micrographs. The shrinkage anisotropy is more than 12% for the platelet shaped powder and 8% for the standard powder, whereas the spherical particles lead to almost isotropic shrinkage. The influence of the organic binder chain length proved to be minor compared to the influence of the particle morphology. The variation of casting speed and blade gap height has no effect on anisotropic shrinkage in the investigated parameter range. This is explained by theoretical considerations of particle rotation in a sheared fluid.

Keywords: Tape casting; Sintering; Shaping; Al_2O_3; Shrinkage anisotropy

1. Introduction

Tape casting is an established low cost ceramic forming technique for the manufacture of large areas of thin ceramic sheets of controlled thickness.[1,2] These ceramic green tapes can be punched, metalized and laminated to build up complex multilayer components, like, e.g., capacitors, inductors, high integrated circuits, actuators, and gas sensors.[3,4] There is a strong trend towards denser packaging and higher integration of circuits within the devices. The punched and printed structures already have dimensions smaller than 100 μm. During firing, the exact position of vias or other circuitry details in different layers must be maintained relative to each other, even though the green tapes exhibit a linear shrinkage of 15–20%. Already a small deviation in shrinkage can lead to device failure of interconnected multilayer ceramics. The control of position becomes even more complicated due to the anisotropic shrinkage of tape cast sheets. Therefore, a better understanding of the causes for anisotropic shrinkage of green tapes will also allow to better understand shrinkage deviations of specified shrinkage values of green tapes and finally to keep the accepted tolerance values in tape manufacture.

Anisotropic shrinkage has been described in several studies with different materials.[5–7] It is caused by the formation of an anisotropic microstructure of the green tapes.[8–15] During casting, the slurry is sheared while passing the blade of the casting head. Anisotropic particles and binder molecules are supposed to be oriented in the shear field. Because of the high viscosity of the slurry and its pseudoplastic rheological behaviour, such an alignment will be frozen in after passing the blade. The subsequent drying step is another anisotropic process. The solvent used evaporates only at the top surface of the cast tape. The capillary forces transport the solvent to the surface. Therefore, increased amount of dissolved binder can be deposited at the top surface of the tape.[16] When the liquid film retracts to the inner parts of the drying tape structure, particle rearrangement by capillary forces takes place. Because the cast film adheres to the tape carrier, drying shrinkage can only occur in the z-direction. Removal of the dried tape from the carrier can result in another stretching effect in the casting direction. In addition, aging also influences the anisotropy of the green microstructure.[17] Because of this anisotropic green tape microstructure, many tape cast products show anisotropic shrinkage behaviour, which means that the shrinkage in the x-, y-, and z-directions of the cast tape

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doi:10.1016/j.jeurceramsoc.2010.08.012

Table 1
Composition of Al_2O_3 slurries.

	wt%
Al_2O_3 powder	63.87
Solvent	25.65
Dispersant agent	1.28
Binder	4.73
Plasticizer	4.47

differs.[18,19] Shrinkage in the z-direction is typically larger than the in-plane shrinkage.[6] The main reason for the anisotropic in-plane shrinkage is the particle orientation during the tape casting process.[9,20,21] Besendorfer and Roosen[13] and Rauscher and Roosen[22] determined the interrelation between particle shape and size on in-plane shrinkage anisotropy of an LTCC system quantitatively.

In order to determine the respective influence of particle shape and molecular length of the binder on tape properties and anisotropy development in tape casting, three different alumina powders and polyvinylbutyral binders were used for tape casting. A powder of spherical and plate-like shape was chosen for tape casting and compared with a milled standard powder. A powder with spherical particles allows to eliminate the influence of particle shape on shrinkage anisotropy and therefore to investigate just the effect of binder molecules. Such a powder was only available with a particle size of about 4 μm. To assure comparability of all powders, the platelet shaped and standard powders are chosen in the same particle size range. These coarse powders do not possess sufficient sintering activity for complete densification during firing, but shrinkage anisotropy occurs already in the initial states of sintering.[18] The powders can be used to investigate shrinkage combined with particle orientation, which would not be possible for completely densified microstructures.

Three PVB binders with a wide range of molecular weights were used for tape casting to investigate the influence of binders on shrinkage anisotropy. The effect of the process parameters on anisotropy was investigated by varying the casting velocity and blade gap height and thereby the shear rate beneath the blade. The interrelation between green tape microstructure and shrinkage was investigated by determination of the particle orientation of the cast structure. For this purpose, micrographs of the tapes were characterized by means of an automatic image analysis.

2. Experimental

2.1. Powder characterization

As starting materials for the tape casting process, three different alumina powders of similar particle size, but different particle shape were chosen. The powder CL 3000 exhibit platelet shaped particles, whereas the powder WRA FG is a ground standard alumina powder. Both powders are from Almatis GmbH, Frankfurt, Germany. In contrast, the particles of the powder DAW 05 (Denka, Tokyo, Japan) are of spherical shape. The particle size distributions of all powders were determined by laser granulometry (Mastersizer 2000, Malvern Instruments, Worcestershire, U.K.) after powder dispersion by ultra sonic treatment and addition of branched ethoxylated octylphenol (Igepal CA-630, Sigma–Aldrich, St. Louis, USA) as a dispersant. The particle shape was measured by a flow particle image analysis system (Sysmex FPIA 3000, Malvern Instruments, Worcestershire, U.K.) and by scanning electron microscopy (Quanta 200 FEI Company, Hillsboro, USA). The FPIA system allows to take pictures of individual particles of a powder and to generate geometric data of these particles. The exact functionality of the system is described elsewhere.[22] For each powder, 50.000 particles were analyzed. Additionally, the specific surface area was measured by BET method (ASAP 2000, Micromeritics Instruments Corp., Norcross, USA).

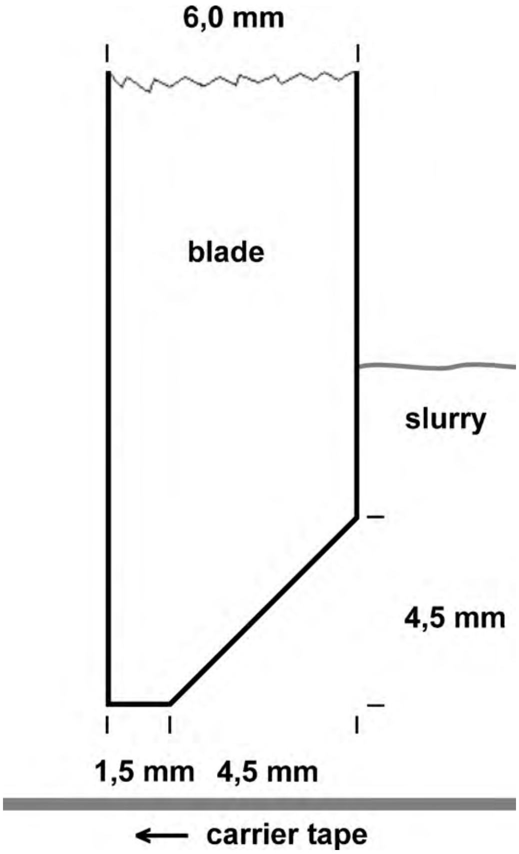

Fig. 1. Blade geometry of the casting head.

2.2. Slurry preparation and tape casting

From these powders, slurries with a solid content of 28 vol% were prepared. As a solvent, an azeotropic mixture of 68 wt% ethanol and 32 wt% toluol was used and Menhaden Fish oil (Kellogg Co., Buffalo, USA) was added as a dispersant. For a complete deagglomeration of the powder particles, the suspensions were milled in a ball mill for 24 h. After addition of a polyvinylbutyral binder (B-98, Solutia Inc., St. Louis, USA) and the plasticizer alkylbenzylphtalate (Santicizer S261A, Ferro Corp., Cleveland, USA) the slurries were homogenized by another milling step for 24 h. The exact composition of the tape cast slurries is given in Table 1.

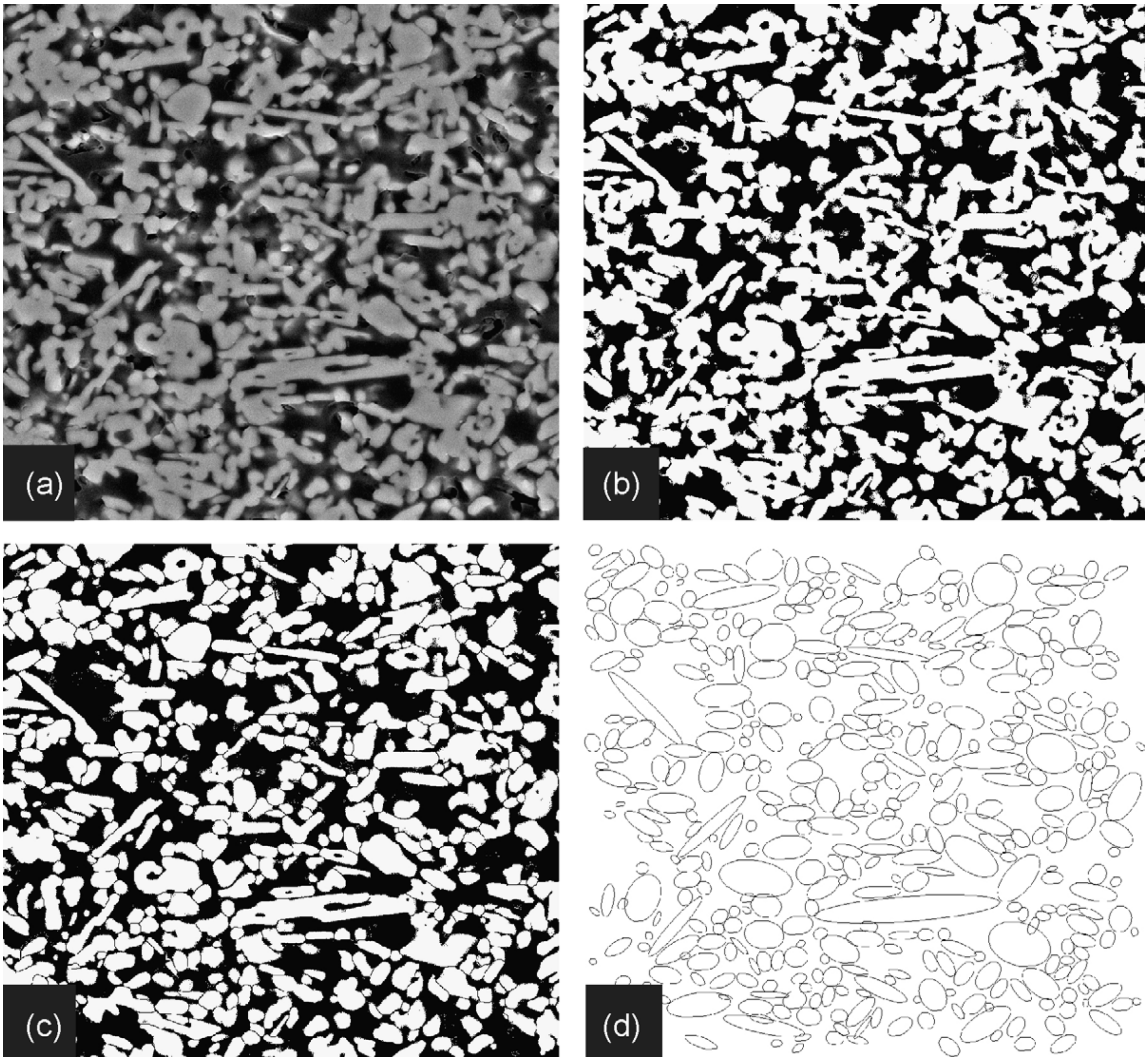

Fig. 2. Procedure of image analysis. (a) SEM image, (b): binary image, (c): separated particles, (d): best-fit ellipses.

In addition to the standard binder B-98 with a molecular weight of 40–70 × 10^3 g/mol, the binder BL-1 (Sekisui Chemical Co., Tokyo, Japan) with a molecular weight of only 19 × 10^3 g/mol and the binder B-74 (Solutia Inc., USA) of very high chain length with 120–150 × 10^3 g/mol were used. For these slurries, the spherical powder DAW 05 was chosen to eliminate particle shape influences. Their composition and preparation were identical to the other slurries. To characterize the binder properties, the viscosity of a 10 wt% solution in an azeotropic ethanol/toluol solvent mixture was measured (Anton Paar, Graz, Austria).

Before casting, the slurry was degassed, and characterized concerning their rheological behaviour (UDS 200, Anton Paar, Austria). Each slurry was tape cast with a casting speed of 10, 50 and 250 mm/s, respectively. The adjusted blade gap height was 150 μm or 450 μm. A fixed single blade casting head and a moving tape carrier was used. The average reservoir height was about 10 mm in all cases. The slurries with the two additional binders were cast with 10 mm/s and 450 μm. A single blade casting head was used. The blade geometry is shown in Fig. 1. The cast slurry was dried at room temperature.

2.3. Sample preparation

After drying, for each set of parameters, six square samples (30 mm × 30 mm) were cut with a hot knife (Groz-Beckert KG, Albstadt, Germany). For each sample, thickness was measured by means of a micrometer screw and the green density was calculated. The tapes were fired using the following temperature–time profile: heating rate of 3 °C/min up to 300 °C, of 1 °C/min up to 450 °C, of 5 °C/min to the maximum temperature of 1600 °C, 30 min dwell time, cooling rate of 5 °C/min. For the sintered samples, again density and thickness were determined. With the thickness values in the green and sintered state, the shrinkage in *z*-direction was calculated.

2.4. Analysis of shrinkage anisotropy

For an exact determination of the lateral shrinkage, hardness indentations by Vickers pyramid, Zwick GmbH & Co. KG, Ulm, Germany) were introduced into the green tapes at the four corners. The distances between these indentations were measured before and after sintering on six samples for every tape

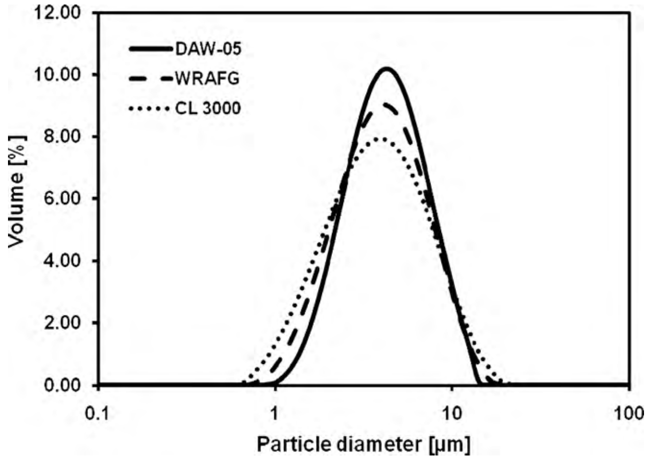

Fig. 3. Particle size distribution of the alumina powders.

by means of a laser scanning microscope (UBM Messtechnik GmbH, Ettlingen, Germany) with an accuracy of 2 µm. Thus, the shrinkage in casting direction ε_x and transverse direction ε_y could be determined accurately. With these two parameters, the shrinkage anisotropy factor K_{xy} was calculated:

$$K_{xy} = 100 \times \left(1 - \frac{\varepsilon_x}{\varepsilon_y}\right) \tag{1}$$

2.5. *Particle orientation analysis*

The degree of particle orientation after tape casting was measured by analyzing cross-sections of the sintered samples. It could not be measured directly in the green state, because the mechanical strength of the green tapes was not sufficient for the preparation of polished cross-sections. At the chosen sintering temperature of 1600 °C the sintering process is in an early stage and so the microstructure remained almost unchanged. The sintered specimens were embedded into a polymeric resin and polished. SEM micrographs of polished sections of the *x*–*z* plane (*x*: casting direction, *z*: thickness direction) were taken in the backscattering mode to ensure a high contrast. For image analysis, the free software Image J (National Institute of Health, Bethesda, USA) was used. In a first step, the original SEM micrographs (Fig. 2a) were converted into binary pictures (Fig. 2b). Overlapping particles and particles in contact were separated manually by black lines (Fig. 2c). Now, the shape of the particles could be detected automatically. Particles at the edge of the picture, and particles smaller than 100 square pixels (ca. 0.4 µm^2) were not taken into account. The evaluation of particle orientation was accomplished by circumscribing a best-fit ellipse to every single particle (Fig. 2d). The angle between the major axis of the ellipse and the horizontal axis (casting direction) is equivalent to the orientation angle of the particle. If that angle was between ± 45°, the particle was considered as orientated in casting direction. The particle orientation of four tapes was evaluated. For both, the CL 3000 and the ground WRA FG powder, the tapes cast 10 mm/s and 250 mm/s with blade gap height of 450 µm were used for this investigation. At least 1000 individual particles were evaluated from each tape.

Table 2
Medium particle size d_{50} and specific surface area of the Al_2O_3 powders.

Powder	d_{50} (µm)	Specific surface area (m^2/g)
CL 3000	3.8	0.81
WRA FG	4.0	0.89
DAW 05	4.2	0.57

3. Results

The dispersed powders have similar medium particle sizes d_{50} of 3.8 (CL 3000), 4.0 (WRA FG) and 4.2 µm (DAW 05). The particle size distributions gained by laser granulometry are shown in Fig. 3. The distribution width is similar for all three powders. The results of the pyknometer and BET measurements can be obtained from Table 2.

3.1. *Particle size and shape of the powders*

The SEM micrographs of cross-sections of slightly presintered tapes (Fig. 9) still show the different particle shapes of the three alumina powders. The CL 3000 powder contains a high amount of flat platelets with about 1 µm in thickness. In contrast, the DAW 05 powder comprises nearly perfect spherical particles. The WRA FG powder shows an irregular particle shape which is typical for a ground material. Besides, the flow particle image analysis delivered the particle shape distribution of all three powders. In this analysis the particle shape is expressed by the width to length ratio (*w*/*l*) of the individual grains. The average *w*/*l* values of the three powders were determined as 0.77 (CL 3000), 0.79 (WRA FG) and 0.86 (DAW 05), indicating clearly the most isotropic shape for the spherical DAW 05 particles. Additionally, it has to be taken into account, that the FPIA system always pictures the largest area of a particle, due to the alignment of irregular particles in the flat flow chamber. Therefore, the smallest dimension, e.g., of a CL 3000 platelet is ignored at the shape calculation via the *w*/*l* ratio.

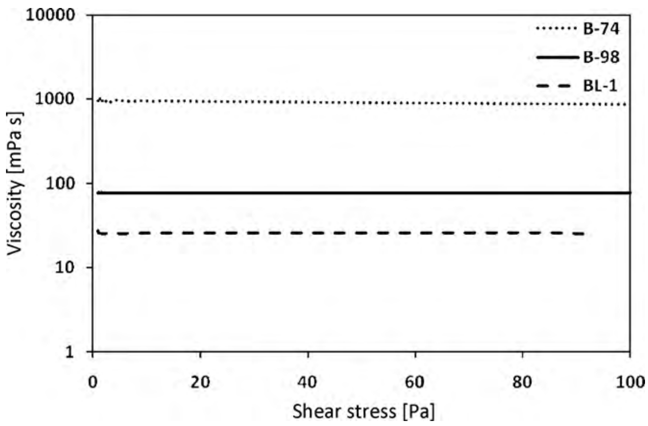

Fig. 4. Viscosity of 10 wt% binder solutions.

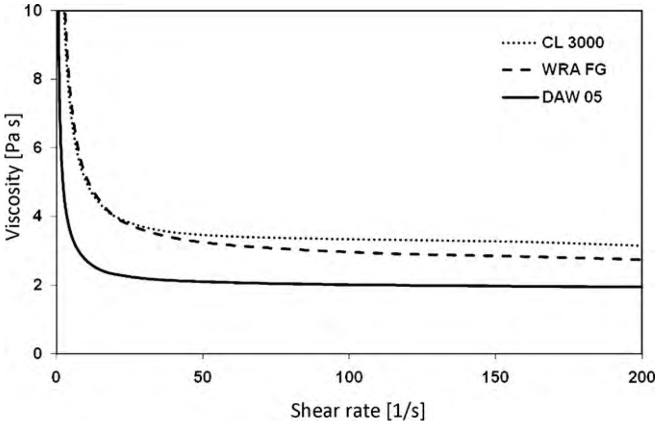

Fig. 5. Shear rate dependent slurry viscosity.

3.2. *Rheological behaviour of slurries and binder solutions*

The viscosities of the binder solutions are shown in Fig. 4. The binder BL-1 with the lowest molecular weight shows a viscosity which is reduced by 50% compared to the standard binder B-98. The long-chain binder B-74 leads to a 10 times higher viscosity than the standard binder. All tape casting slurries exhibit shear thinning behaviour (Fig. 5). At a shear rate of $100\,s^{-1}$, the slurry CL 3000 shows the highest viscosity of 3.3 Pa s followed by WRA FG with 3.0 Pa s. The DAW 05 slurry exhibits a significantly lower viscosity of 2.0 Pa s.

3.3. *Green tape properties*

The green density and tape thickness were determined after drying for all tapes (Figs. 6 and 7). The values of the green densities range from 52% of the theoretical density of alumina (%TD) to 66%TD. The tapes from the isotropic DAW 05 powder always exhibit the highest density values, the tapes derived from the anisotropic CL 3000 powder, always the lowest ones. Besides, tapes cast with a blade gap height of 150 μm always show lower densities than the 450 μm cast tapes. Compared with the blade gap height during casting, the dried green tapes posses a relative thickness of 32–46%. The tape thickness was always uniform across the width of the tapes. In accordance with the density measurements, the thickness of the DAW 05 tapes is always on the low side, due to the high green densities. The CL 3000 tapes exhibit the highest thickness values. The lowest casting speed of 10 mm/s leads to green tapes with a slightly increased tape thickness, compared to those green tapes which had been cast at higher speeds.

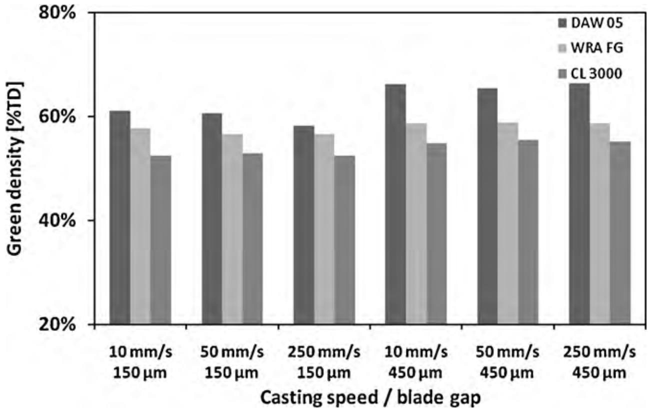

Fig. 6. Density of green tapes in dependence on casting speed and blade gap.

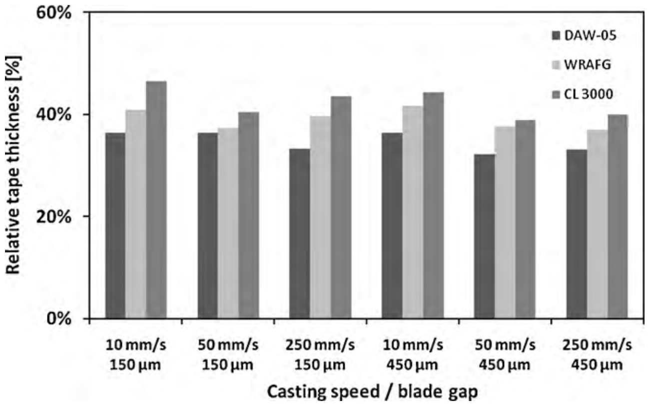

Fig. 7. Green tape thickness relative to blade gap height in dependence on casting speed and blade gap.

3.4. *Properties of sintered tapes*

The green tapes were sintered at 1600 °C and 30 min dwell time. The SEM micrographs in Fig. 8 show, that the coarse powder particles were only slightly sintered at this temperature, but complete densification was not the goal of this investigation anyway. The original shape of the particles is still existent which is important for the particle orientation analysis. The tapes are highly porous, but possess sufficient mechanical strength for sample preparation. The density is between 53%TD and 65%TD. Tapes from the spherical DAW 05 powder still possess the highest density values. Contrary to the green tape density, the sintered density is independent of casting velocity and blade gap height. The differences in particle packing have been balanced during thermal treatment.

3.5. *Linear shrinkage and shrinkage anisotropy*

Shrinkage in casting direction (x) and transverse direction (y) was determined accurately by measuring the distance of hardness indents before and after firing by means of laser scanning microscopy. All samples made from the three powders exhibit linear shrinkage values between 2.7% and 3.9% in casting direction and between 3.0% and 4.0% in the transverse direction. The ground WRA FG powder causes the highest in-plane shrinkage. The shrinkage in thickness direction, determined geometrically with a micrometer screw, is much higher. Tapes cast with 150 μm blade gap height shrink approx. 11% on average, a blade gap height of 450 μm results in a z-shrinkage of only approx. 6%, due to the higher green density of these tapes.

The anisotropy factor K_{xy} was determined for six samples of each tape (Fig. 9). K_{xy} is always bigger than zero, indicating that there was less shrinkage in casting direction (x) than in transverse direction (y). The influence of the particle shape on

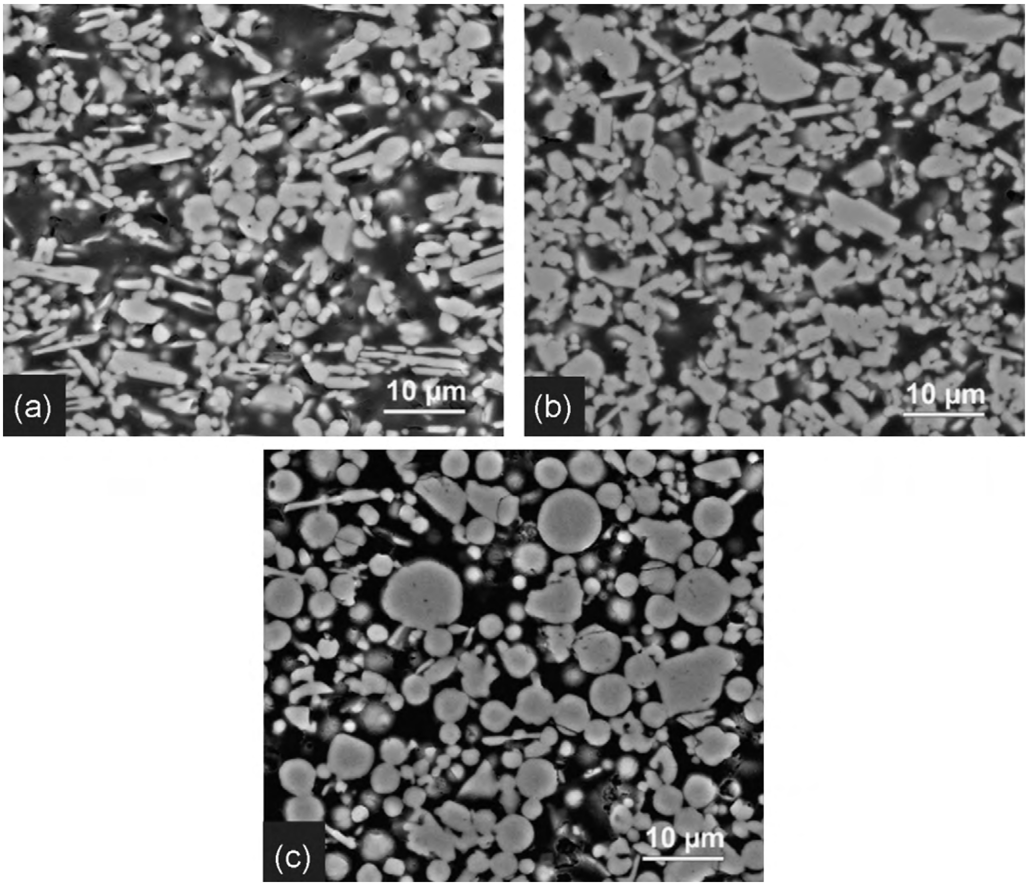

Fig. 8. SEM micrographs of sintered tapes. (a) CL 3000, (b) WRA FG, (c) DAW 05.

K_{xy} is clearly visible. The average K_{xy} value is 1.9 for the DAW 05 tapes, 8.4 for WRA FG tapes and 12.7 for CL 3000 tapes. That means tapes containing the spherical powder shrink almost isotropic. The larger the anisotropy in particle shape, the larger becomes the shrinkage anisotropy of the sintered tapes.

K_{xy} was also calculated for the tapes containing an alternative binder. The short-chain binder leads to an anisotropy factor of 0.87 ± 1.81. Taken into account the high standard deviation, it is a similar value than the accordant tape with the standard binder. The tape with the long-chain binder exhibits a slightly increased K_{xy} value of 3.59 ± 2.25.

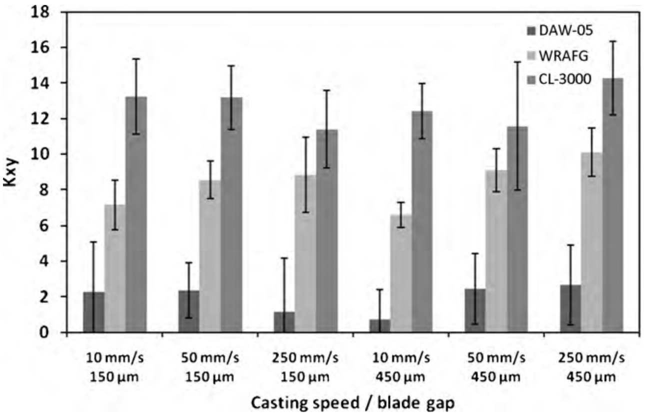

Fig. 9. Shrinkage anisotropy factor K_{xy}.

3.6. Particle orientation in cast tapes

The orientation of particles was determined by analyzing SEM micrographs of cross-sections of sintered tape samples. Two CL 3000 and two WRA FG tapes were examined. For each tape, more than 1000 individual particles were evaluated. In all four tapes the fraction of oriented particles lays above 50%, which clearly indicates the orientation of particles in the shear field. In the CL 3000 tapes, significantly more particles (70%) are oriented than in the WRA FG tapes (62%). The tape DAW 05 was not investigated, because an orientation angle cannot be assigned practically to a spherical particle.

The degree of orientation depends particularly on particle shape and size. The bigger a particle is, the more likely it remains in an oriented state after tape casting (Fig. 10). Also, a more anisotropic shape, characterized by a high *w*/*l* ratio *r* leads to a higher fraction of oriented particles (Fig. 11).

4. Discussion

4.1. Influence of particle shape on green properties

It was shown by DLS, SEM and FPIA that the selected powders have about the same size and differ only in shape. Therefore, the powders are comparable and suitable for this investigation. The particle shape of the ceramic powders used for tape casting

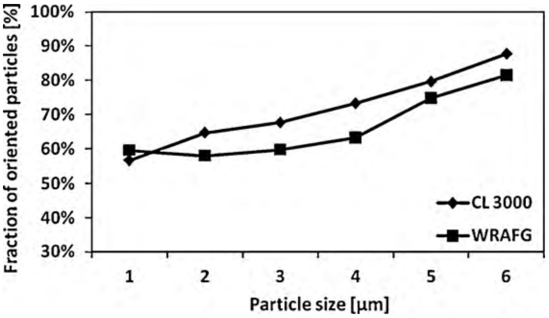

Fig. 10. Fraction of oriented particles depending on particle size.

had a significant influence on both, processing and tape properties. The spherical powder led to a lower slurry viscosity and higher packing density in the green tape. The globular particles can more easily slide against each other and rearrange to a denser packing under shear stress compared to anisotropic particles/platelets. Latter get stuck and hinder one another's movements.

The particle morphology does not only influence the slurry rheology, but also the casting step itself and therefore the green tape properties. The powder with the isotropic particles causes the highest drying shrinkage and therefore yields the highest green density and the lowest tape thickness. The reason is again the small resistance against rearrangement of the particles under the influence of capillary forces in the drying film. The DAW 05 spheres pack comparatively dense while anisometric particles of the CL 3000 and WRA FG powders hinder each other and build less dense structures. This effect is also described in literature.[23] Besides, the spherical powder does not form any noteworthy agglomerates, which would decrease the green density. The existence of agglomerates cannot be completely excluded for the other two powders.

4.2. *Influence of process parameters on green properties*

The slowest applied casting speed of 10 mm/s results in higher tape thickness compared to the tapes cast with 50 and 250 mm/s. This is especially visible for the tapes, which had been cast with a gap height of 450 µm. Because this increase in thickness is not reflected in the green density values, the higher tape thickness cannot be explained by less dense packing. Instead, a higher wet film thickness must be the reason. This can be caused by the hydrostatic pressure, which affects the volume flow under the blade at low shear rates. At higher casting speeds and therefore higher shear rates, the proportion of the pressure-induced flow is negligible. A calculation of the proportion of hydrostatic pressure-induced flow and shear flow confirms this conclusion for the parameters used. A higher throughput at low casting velocities was also calculated and experimentally confirmed by Tok et al.[24] and Chou et al.[25]

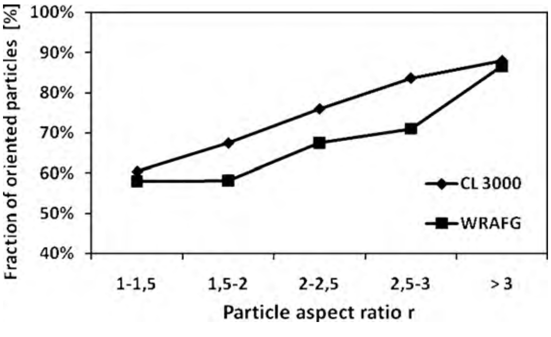

Fig. 11. Fraction of oriented particles depending on particle shape ratio *r*.

The green density of the tapes cast at a gap height of 450 µm is higher than the density of the 150 µm tapes for all casting velocities. This is especially true for the DAW 05 tapes. A possible explanation would be that particle rearrangement during drying is easier in the larger volume of the thicker tapes. Also, the drying time is much longer for the 450 µm tapes, thus there is more time for particle rearrangement. The lower shear rate for the higher blade gap height seems not to be an influencing factor, because the variation in shear rate by different casting velocities does not affect the green density.

4.3. *Shrinkage anisotropy*

In this investigation all determined K_{xy} values are positive, meaning the shrinkage in casting direction is minor than in transverse direction. Numerous studies come to the same conclusion.[8–10,22,26] Regardless of the very low absolute shrinkage values of the sintered alumina tapes, the anisotropy occurs clearly, because it develops already in the initial stage of sintering as demonstrated by Raj and Cannon.[18] The shrinkage behaviour can be influenced by particle shape and process parameters. Their impacts are discussed below.

4.3.1. *Influence of particle shape on shrinkage anisotropy*

The comparison of the anisotropy factors of the alumina tapes shows clearly the interrelation between particle shape and shrinkage behaviour. Independent of casting velocity and blade gap height, the non-isometric CL 3000 powder causes the highest discrepancy between shrinkage in *x*- and *y*-direction with K_{xy} values >10. The K_{xy} values are lower for the ground WRA FG powder but still indicate significant shrinkage anisotropy. By contrast, there is nearly no anisotropy observed for the tapes derived from the spherical DAW 05.

The main reason for the development of anisotropic shrinkage is the alignment of the solid particles due to shear forces during the casting process.[8–11,22,26] Particle orientation can also be analyzed in terms of the voids between the particles. Non-spherical particles lead to non-isometric pore geometries and aligned particles possess different contact points or rather different contact areas and radii to the particles nearby in *x*- and *y*-direction. At these contact points sintering begins with neck growth. Both effects cause a divergence in densification rate in different spatial directions.

Compared to platelets and needles, spherical particles cannot align. Hence they lead to an isotropic contraction. Therefore, the minor shrinkage anisotropy of the tapes with the isometric powder DAW 05 indicates a small degree of particle alignment caused by a small amount of non-spherical particles.

According to Greenwood et al.[6] particle alignment is also responsible for the relatively high shrinkage in z-direction due to a high number of contact points between the particles in this direction.

The theoretical background for the particle orientation and alignment beneath the casting blade is described by Jeffery.[27] His equations state that the current particle angle Φ, i.e. the angle between shear direction and major particle axis at a time t can be described by particle shape r and the shear rate $\dot{\gamma}$. Eq. (2) defines the rotation in the plane given by the direction of the shear gradient and the casting direction, which is in the existing case the x–z plane.

$$\Phi(t) = \mathrm{arc\ tan}\left(r \tan \frac{\dot{\gamma}t}{r + (1/r)}\right) \quad (2)$$

From this equation can be derived that particles rotate with the highest velocity if they are aligned perpendicular to the casting direction. The angle speed becomes minimal when the particle is aligned in flow direction. This is true as long as the viscous forces dominate over the force of inertia, which is described by the Reynolds number. Therefore, the particle remains longer in the oriented position. This is more pronounced if the particle is of elongated shape. As a result, after the forming process more particles are oriented in casting direction than perpendicular to it. Due to the cycling rotation speed, not all particles can be aligned. Note that slurry viscosity does not affect this behaviour as long as the viscous forces dominate. In our case the Reynolds numbers are in the range of 10^{-7} and 10^{-5} which assure these assumptions.

4.3.2. Influence of binder chain length on shrinkage anisotropy

In comparison with particle shape, the molecular weight of organic additives has a minor effect on anisotropic shrinkage. The molecular weight of the binders does affect the viscosity of the slurry and the shear stresses acting during tape casting. But the applied forces on a particle in a shear gradient and the resulting particle rotation and alignment are independent of the slurry viscosity, so latter cannot be the reason for the slightly increased shrinkage anisotropy of the tape with the long-chain binder. The higher K_{xy} is probably caused by elongation and alignment of the binder molecules in casting direction. Partially, these stretched molecules relax, but they leave behind anisotropic pores after binder burnout and can thus influence the shrinkage behaviour. But the effect is quite small compared to the impact of the particle shape and the fluctuations are very high. The effect is only visible for very high chain lengths like in the binder B-74. Binders used in established formulations should therefore not differ too much.

4.3.3. Influence of process parameters on shrinkage anisotropy

Whereas the particle shape has a significant effect on the degree of shrinkage anisotropy, no clear dependence of the variation of casting velocity and blade gap height could be found (Fig. 9). On average, both blade gaps lead to similar K_{xy} values for all three powders. The average K_{xy} values are also comparable for all the casting speeds.

The influence of a variation of process parameters and the resulting shear forces were also discussed by other authors. Raj and Cannon[18] examined aqueous alumina suspensions with high solid contents. They observed an increase in shrinkage anisotropy with rising casting velocity. This effect was stronger at low velocities and weakens at higher ones. Watanabe et al.[8] reported that a shear rate above $12.5\,\mathrm{s}^{-1}$ has no further effect on the orientation degree of the analyzed particles, in this case $Bi_4Ti_3O_{12}$ platelets with 4 μm in diameter. For an aqueous alumina system, a shear rate limit of $100\,\mathrm{s}^{-1}$ was determined, above which no further increase of shrinkage anisotropy could be observed.[10] The study on an LTCC system of Besendorfer and Roosen[13] showed only a minor effect of the casting velocity. Because the deviations observed by others occur at low shear rates where the shear forces are small, non-uniform flow profiles caused by hydrostatic pressure might be reason for these results.

In summary it seems likely that there is a critical shear rate from that on a constant maximum particle alignment is achieved. The exact value of this limit depends on the system used and the solids content in particular. In the present investigation the high casting velocities lead to high shear forces. These dominate the flow profile. Therefore no dependencies of casting velocity on particle alignment and shrinkage anisotropy could be observed in our study.

4.4. Particle orientation in the tapes

In order to examine the correlation between particle alignment and shrinkage, the orientation of the ceramic grains inside the sintered tapes was determined. Both, in the CL 3000 and in the WRA FG tapes more than 50% of the particles are oriented in casting direction. That indicates that a preferred orientation exists. A comparison of particle orientation and shrinkage anisotropy reveals this correlation. The CL 3000 tapes have the highest fraction of aligned particles and lead to distinct shrinkage anisotropy. The tapes from ground WRA FG powder exhibit a lower degree of particle orientation and show lower K_{xy} values.

According to the theoretical considerations of Jeffery it is not possible to reach one hundred percent orientation. All particles are rotating as long as the shear forces are applied, not only until they are aligned. But due to their changing angular speed depending on their orientation (slow when oriented, fast when perpendicular) they get an overall average orientation in shear direction. This average orientation depends only on the particle shape, because in this theory interparticulate interactions are not considered. The calculated values for the CL 3000 tapes would be 71% and for the WRA FG tapes 68%.

The results of the image analysis also confirm the mathematical description of Jeffery that the probability for a particle to orientate in casting direction is dependent of particle shape. The more elongated a particle is, the more likely it is aligned. This also explains the higher degree of particle orientation within the CL 3000 tapes which contain an especially large number of highly non-isometric particles.

5. Conclusion

In the present paper, the influence of raw materials and process parameters on tape properties and shrinkage behaviour of tape cast alumina was described quantitatively. The investigations showed that slurries from spherical particles exhibit lower viscosities at similar particle loading than platelet shaped particles. Green tapes from spherical powders lead to higher drying shrinkage and higher green density compared to ground powder and especially to platelets. They allow easier particle rearrangement and pack more densely. A higher blade gap height also causes an increased packing density. Additionally, at the slowest casting velocity, a higher green tape thickness was observed. This is caused by higher slurry throughput initiated by the hydrostatic pressure.

It was found, that the particle morphology has the predominant effect on shrinkage anisotropy of tape cast products. The influence of the molecular weight of binders is only very minor. Particles start to rotate beneath the blade. The rotational speed is dependent on the current particle orientation and leads to an unbalanced rotation. On average, this leads to an alignment of the particles in casting direction. But because the particles rotate continuously, not all particles are completely oriented in the casting direction. Strongly non-isometric and large particles align more likely than smaller and spherical ones. Tapes consisting of the platelet shaped powder showed a fraction of oriented particles of 70% and therefore high shrinkage anisotropy, whereas tapes made from ground powder had 62% oriented particles and lower shrinkage anisotropy. The tapes with spherical particles showed nearly isotropic shrinkage. Thus, in this study it could be shown, that the assumptions of Jeffery applied to powders of different particle shape are valid. But due to the non-constant rotational speed of the particles and their continuous rotation, a 100% alignment of the particles in a shear field is not possible.

Very long organic binder molecules, which are uncommon for tape casting, also align under shear stress and can lead to additional shrinkage anisotropy. But the effect is very small compared to the influence of the particle shape. In contrast to particle shape, casting speed and blade gap height have only minor effect on the development of shrinkage anisotropy. Higher shear forces cannot increase the degree of particle orientation in the tapes when the casting is already done with a linear shear profile below the blade. This is the case, when the contribution of the hydrostatic pressure to the throughput is negligible. For our experiments, this negligible hydrostatic pressure is the reason why our results are independent of the processing parameters. For a higher hydrostatic pressure an influence of the casting speed on the particle orientation is expected, because at low casting speeds the influence of the hydrostatic pressure on throughput is then not negligible anymore.

Acknowledgments

The authors wish to thank the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), Bonn, Germany, for the financial support and Dr. Torsten Kraft, Dr. Andreas Wonisch and Dipl.-Ing. Pit Polfer from the Fraunhofer IWM, Freiburg, Germany for fruitful discussions.

References

1. Mistler RE, Twiname ER. *Tape casting, theory and practice*. Westerville, OH: The American Ceramic Society; 2000.
2. Hellebrand H. Tape casting. In: Brook RJ, editor. *Processing of ceramics, Part 1.*, vol. 17A. Weinheim: VCH Verlagsgesellschaft mbH; 1996. p. 190–265.
3. Schwartz B. Review of multilayer ceramics for microelectronic packaging. *Journal of Physics and Chemistry of Solids* 1984;**45**(10):1051–68.
4. Gongora-Rubio MR, Espinoza-Vallejos P, Sola-Laguna L, Santiago-Avilés JJ. Overview of low temperature co-fired ceramics tape technology for meso-system technology (MsST). *Sensors and Actuators A: Physical* 2001;**89**(3):222–41.
5. Wu M, Messing GL. Fabrication of oriented SiC-Whisker-Reinforced Mullite Matrix Composites by tape casting. *Journal of the American Ceramic Society* 1994;**77**(10):2586–92.
6. Greenwood R, Roncari E, Galassi C. Preparation of concentrated aqueous alumina suspensions for tape casting. *Journal of the European Ceramic Society* 1997;**17**(12):1393–401.
7. Ozer IO, Suvaci E, Karademir B, Missiaen JM, Carry CP, Bouvard D. Anisotropic sintering shrinkage in alumina ceramics containing oriented platelets. *Journal of the American Ceramic Society* 2006;**89**(6): 1972–6.
8. Watanabe H, Kimura T, Yamaguchi T. Particle orientation during tape casting in the fabrication of grain-oriented bismuth titanate. *Journal of the American Ceramic Society* 1989;**72**(2):289–93.
9. Raj PM, Odulena A, Cannon WR. Anisotropic shrinkage during sintering of particle-oriented systems – numerical simulation and experimental studies. *Acta Materialia* 2002;**50**(10):2559–70.
10. Patwardhan JS, Cannon WR. Factors influencing anisotropic sintering shrinkage in tape-cast alumina: effect of processing variables. *Journal of the American Ceramic Society* 2006;**89**(10):3019–26.
11. Chantaramee N, Tanaka S, Uematsu K. Development of packing structure of powder particles in tape casting. *Journal of the Ceramic Society of Japan* 2007;**115**(1338):136–40.
12. Rauscher M, Roosen A. Influence of low-temperature co-fired ceramics green tape characteristics on shrinkage behavior. *International Journal of Applied Ceramic Technology* 2007;**4**(5):387–97.
13. Besendorfer G, Roosen A. Particle shape and size effects on anisotropic shrinkage in tape-cast ceramic layers. *Journal of the American Ceramic Society* 2008;**91**(8):2514–20.
14. Chantaramee N, Tanaka S, Uematsu K. The effect of packing structure of powder particles on warping during sintering. *Journal of the European Ceramic Society* 2008;**28**(1):21–5.
15. Chantaramee N, Tanaka S, Uematsu K. The dependence of particle alignment on processing parameter (H_{slurry}/L) in alumina tape. *Journal of the Australian Ceramic Society* 2008;**44**(2):23–6.
16. Roosen A. Tape casting of ceramic green tapes for multilayer device processing. In: *Ceramic transactions*. Columbus, OH, USA: The American Ceramic Society; 1999. pp. 103–121.
17. Nahass P, Pober RL, Rhine WE, Robbins WL, Bowen HK. Prediction and explanation of aging shrinkage in tape-cast ceramic green sheets. *Journal of the American Ceramic Society* 1992;**75**(9):2373–8.
18. Raj PM, Cannon WR. Anisotropic shrinkage in tape-cast alumina: role of processing parameters and particle shape. *Journal of the American Ceramic Society* 1999;**82**(10):2619–25.
19. Pohle D, Wagner M, Roosen A. Effect of friction on inhomogeneous shrinkage behavior of structured LTCC tapes. *Journal of the American Ceramic Society* 2006;**89**(9):2731–7.
20. DiMarcello FV, Key PL, Williams JC. Preferred orientation in Al_2O_3 substrates. *Journal of the American Ceramic Society* 1972;**55**(10):509–14.
21. Raj PM, Dunn SM, Cannon WR. Measurement of particle orientation in tape cast ceramic microstructures. *Journal of Computer-Assisted Microscopy* 1998;**10**(1):33–51.

22. Rauscher M, Roosen A. Effect of particle shape on anisotropic packing and shrinkage behavior of tape-cast glass–ceramic composites. *International Journal of Applied Ceramic Technology* 2009;**6**(1):24–34.
23. Reed JS. *Introduction to the principles of ceramic processing*. New York: Wiley-Interscience; 1988.
24. Tok AIY, Boey FYC, Lam YC. Non-Newtonian fluid flow model for ceramic tape casting. *Materials Science and Engineering A – Structural Materials Properties Microstructure and Processing* 2000;**280**(2):282–8.
25. Chou YT, Ko YT, Yan MF. Fluid flow model for ceramic tape casting. *Journal of the American Ceramic Society* 1987;**70**(10):C280–2.
26. Chantaramee N, Tanaka S, Takahashi T, Uematsu K. Evolution of discontinuity in particle orientation in ceramic tape casting. *Journal of the American Ceramic Society* 2008;**91**(10):3181–4.
27. Jeffery GB. The motion of ellipsoidal particles immersed in a viscous fluid. *Proceedings of the Royal Society of London* 1922;**102**:161–79.