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Control of Texture in Al_2O_3 by Gel-casting

T. Carisey, A. Laugier-Werth & D. G. Brandon

Department of Materials Engineering, Technion, Israel Institute of Technology, Haifa 32000, Israel

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Abstract

Small alumina platelets were distributed in an alginate-containing alumina slip and oriented by tape-casting using a water-based doctor-blade process. The tape was gelled at the exit from the doctor-blade by a cation-exchange reaction. The tape thickness could be controlled from 0·2 to 2 mm and there appeared to be no limit to the laminate thickness which could be produced by tape lay-up and filter-pressing. The platelets were aligned parallel to the green tape to better than 10°. Several cation reactions were investigated and both their gelling behaviour and their effect on the sintering characteristics were studied. The large-grained sintered products were highly textured and showed pronounced anisotropy in their crack propagation resistance.

1 Introduction

In many engineering materials microstructural or crystallographic anisotropy (texture) can be used to inhibit crack propagation. The control of crystalline texture is a frequent objective in metal working processes but is seldom applied to conventional ceramic processing technology. Nevertheless, the production of a crystallographically and microstructurally oriented monolithic ceramic could be a useful alternative to the introduction of aligned second-phase reinforcement. Within limits, the control of crystalline texture could result in a beneficial mechanical anisotropy, avoiding the aligned two-phase microstructural geometries characteristic of a composite material, many of which have problems associated with mismatch of the chemical, thermal or elastic properties of the two phases.

Reinforcement of a ceramic matrix with semi-aligned SiC platelets has already been shown to give improved mechanical properties with pronounced mechanical anisotropy. For example,[1] the addition of 30% of SiC platelets to an Si_3N_4 matrix powder prior to hot-pressing has led to significant increases in the fracture toughness, the Weibull modulus and Young's modulus. The mechanical anisotropy was also demonstrated in indented samples, for which the extent of crack propagation in the two directions parallel and perpendicular to the direction of hot-pressing was markedly different.

The tape-casting process has been used to produce ceramic tapes, 25 to 300 μm in thickness,[2] for electronic applications, and alumina is one of the commonest tape-cast materials.[3] Particle alignment during tape-casting has also been studied[4] and it was shown that, providing the pressure gradient is neglected, the orientation of the particles depends only on their concentration and shape, while the effects of slip viscosity, trolley velocity and tape thickness on the particle alignment were minor. The flow behaviour of a ceramic slip during tape-casting has been analysed based on the principles of fluid dynamics.[5] The fluid flow process can be considered a linear combination of Poisseuille pressure flow and Couette drag, so that the velocity distribution in a slip flowing between an extended 'doctor-blade' and a moving substrate carrier is given by:

$$V_z = -\rho g H(x^2 - hx)/2\mu l + V_0 x/h$$

where ρ is the density (1750 kg/m^3), g is the gravity acceleration (9·81 m/s^2); H is the height in the container (10 mm); h is the 'blade' gap (2 mm); μ is the slip viscosity (10 Pa.s); l is the length of the 'blade' (30 mm); V_0 is the trolley velocity (200 mm/s) and V_z is the slip velocity at a distance x from the 'blade' surface.

The first term in the equation is the pressure effect component and the second is the drag effect, while the dimensions given in parentheses are appropriate for the geometry used in the present work. From this equation and with these dimensions, it is obvious that pressure flow can be neglected and the platelets should orient in the uniform shear field of the dominant drag flow.[4] The authors have previously prepared alumina/alumina platelet composites by conventional tape-casting[6] and found that the shear forces acting during tape-casting could orient the platelets to better than 15°. However, the laminate thickness which could be prepared by subsequent tape layup was limited by the long times required for burn-out if the large amount of organic plasticizer present was not to cause bloating and delamination.

Far smaller quantities of organic additives have been reported[7] for a water-based tape-casting process which uses a cellulose ether binder. The process involved a compromise between the requirements for a high green density (a high ratio of inorganic to organic components) and a high green strength (a high ratio of binder to plasticizer). The liquid to solid (sol–gel) transformations used in green moulding can be achieved by a number of routes of which solidification of a plasticizer or solvent evaporation are two of the commonest. An acrylic polymerization reaction has been shown to give a flexible gelled slip in aqueous solution at concentrations of organic additives of only 5% with up to 60% solids loading.[8] This process has been patented under the name of *gel-casting*, although irreversible polymerization is just one gel-formation process.

A sol–gel route has been developed for the production of a gelled thread containing aligned whiskers. An early report[9] described the production of a Ca alginate fibre containing aligned whiskers but gave no experimental details. More recently[10] it was shown that extrusion of a Na alginate-containing water-based Al_2O_3 or Si_3N_4 slip with SiC whisker additions could give good whisker alignment. Extruded thread was gelled to form a flexible 'spaghetti' on exiting an extrusion needle immersed in gelling solution. Whisker alignment was retained after filter-pressing and sintering, and the small amount of organic additives present (less than 2%) did not require any especial burn-out schedule.

The sol–gel reaction between water-soluble Na alginate and polyvalent cations yields an insoluble cation cross-linked alginate and is used in many food and pharmaceutical applications.[11] The reaction is based on ion exchange,[12] for example:

$$Na_n \text{ alginate} + n/2\ Ca^{2+} \longrightarrow nNa^+ + Ca_{n/2} \text{ alginate} \quad (1)$$

Smidsrød & Haug[13,14] showed that many divalent cations could be used to obtain the gel reaction and could be ranked according to their efficacy in precipitating the alginate. In the present application, some cation will remain as a dopant in the ceramic, so that the gelling cation should be a good sintering agent rather than a deleterious impurity.

In the present contribution a process for water-based tape-casting of a platelet-containing slip by the sol–gel route, followed by tape layup and filter-pressing to yield a green body with well-oriented platelets is reported. A number of polyvalent gelling cations have been investigated.

2 Experimental

2.1 Machine design

The tape-casting unit was based on a conventional design for the tape-caster trolley, but with an additional section for gelling (Fig. 1). The conventional sections comprise an extended doctor-blade, which controls both the thickness of the tape and the alignment of the platelets, and the slip reservoir. The new section consists of a flexible tube which is attached to the exit from the extended doctor-blade and controls the supply of the gelling solution from a reservoir. During casting the tape-caster trolley is pulled at a fixed speed up an inclined teflon-covered support plate, the inclination being necessary to drain away the gelling solution and prevent gelling of the slip beneath the doctor-blade (Fig. 2). As in conventional tape-casting, the blade gap (the tape thickness), the trolley velocity and the slip viscosity can be independently varied, together with, in the present case, the flow rate of the gelling solution.

2.2 Composite fabrication

The alumina powder used for the present study was Sumitomo AKP50 and the alumina platelets were supplied by Elf-Atochem in three different sizes: 3–7 μm, 10–15 μm and 15–25 μm. A solution of Na alginate was prepared with 4 wt% of alginic acid sodium salt. This solution was diluted with distilled water (2 : 3) and a dispersant was added (Dolapix PC85). After adding the platelets (typically 5 wt% in the final green body), the pH was adjusted to 10 by adding NH_4OH and ultrasonic agitation was used to break up any soft platelet agglomerates. The alumina powder was then incorporated and, after 18 to 20 h of ball-milling, the slip was tape-cast onto the teflon substrate. On inverting the substrate in a water bath, the cast tape detached from the teflon under its own weight and was then washed to remove excess cation. The tape was cut into squares (31 × 31 mm) which were stacked and compacted by filter-pressing before drying and sintering. The sintering programme comprised three stages: 600°C for 2 h, to burn out the small amount of organic

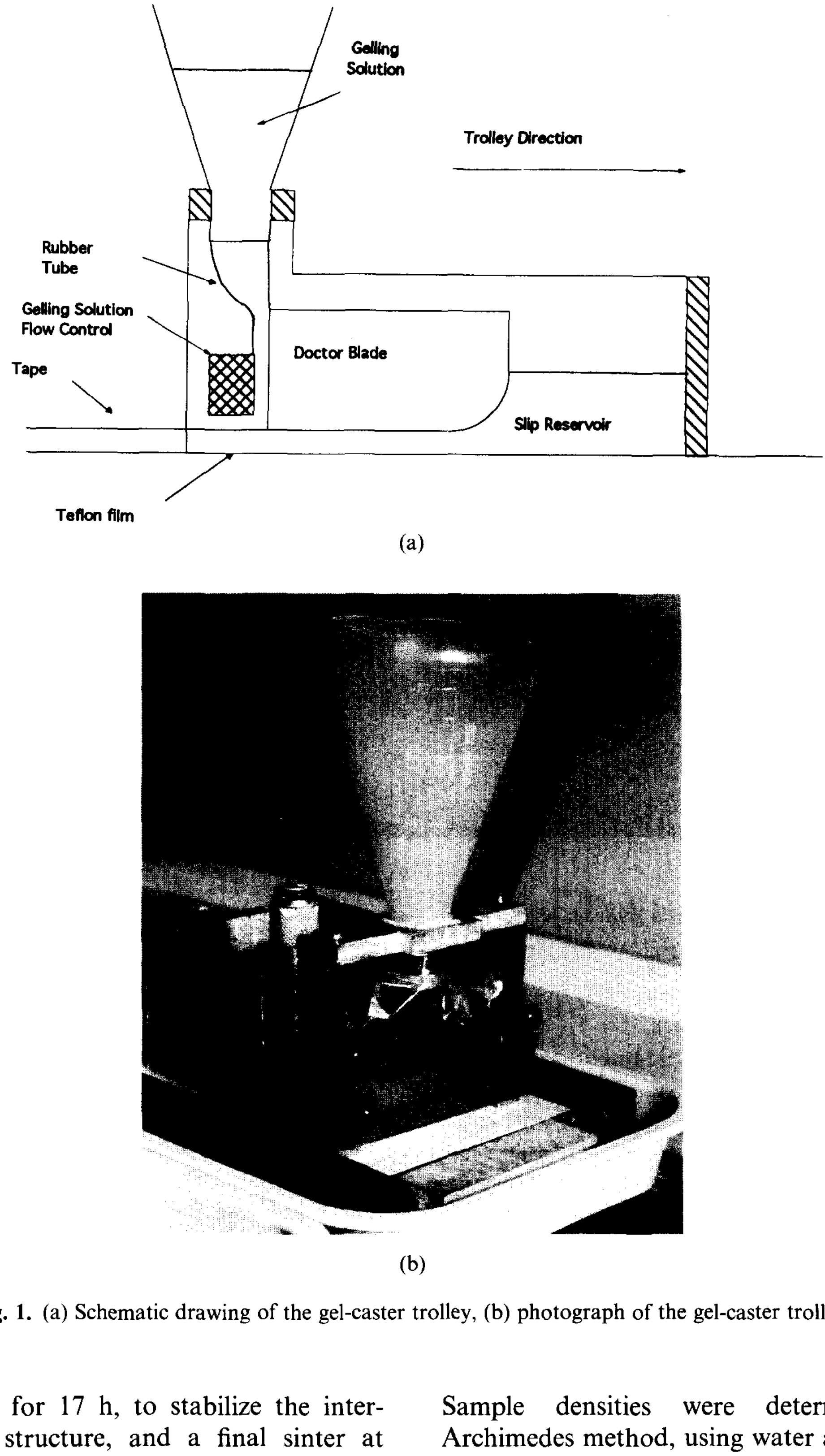


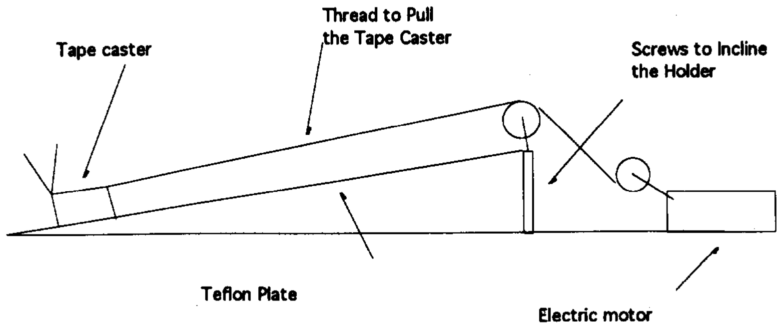
Fig. 1. (a) Schematic drawing of the gel-caster trolley, (b) photograph of the gel-caster trolley.

additives, 900°C for 17 h, to stabilize the interconnected pore structure, and a final sinter at 1475 to 1550°C for 3 to 15 h, to collapse the pore structure and reach the final sintered density. The heating rate was 2°C/min and the final cooling rate was 5°C/min.

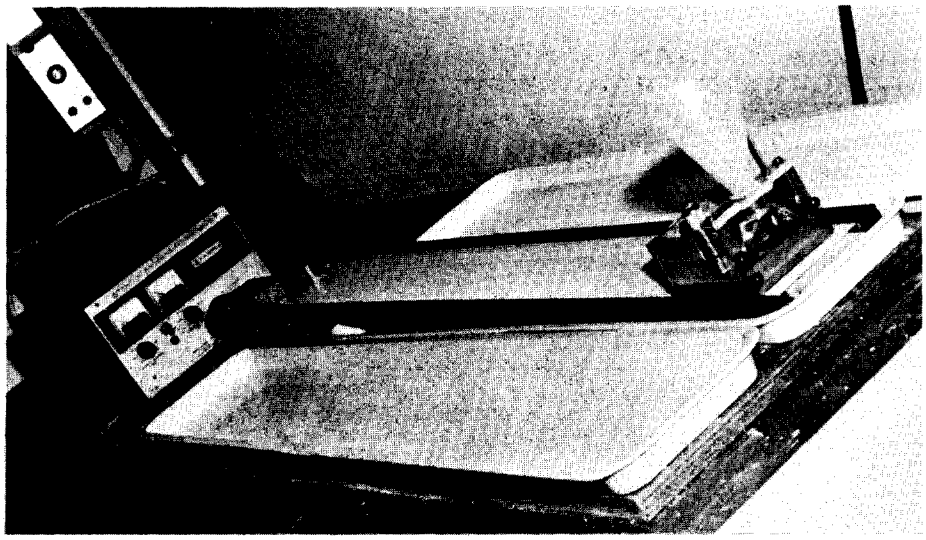
The shrinkage on sintering was markedly anisotropic, with the through thickness shrinkage appreciably greater than the lateral shrinkage. Typical sample dimensions after sintering at 1500°C for 9 h were 26 × 26 mm, with a sample thickness of 3–5 mm, depending on the number and thickness of the tape layers used in the layup. Sample densities were determined by the Archimedes method, using water as the immersion medium.

2.3 Characterization

Optical and scanning electron microscopy (SEM) were used to characterize polished and thermally etched (1450°C for 30 min) sintered samples cut parallel and perpendicular to the original tape surface. Optical microscopy was used to characterize the platelet distribution in cross-sections of the dry green body which had been vacuum impregnated with epoxy resin. Crack propagation



(a)



(b)

Fig. 2. (a) General layout of the gel-caster system, (b) photograph of the gel-caster system.

was studied by Vickers indentation on polished sections of the sintered samples.

The degree of platelet alignment was determined by X-ray diffraction using the (0006) reflection ($2\theta = 41{\cdot}65°$) wth CuK_α radiation and rotating the sample about the normal to the plane defined by the incident and diffracted beams. The integrated intensity of the (0006) peak was measured as a function of the angle of tilt of the original tape surface in the diffractometer. The range of tilt angles available with the diffractometer geometry and samplé size used was −10 to +15°, and peak intensity measurements were taken at 5° intervals of sample tilt.

3 Results

Figures 3 and 4 show the (0006) integrated diffracted intensities for sintered samples containing 3–7 μm and 15–25 μm platelets respectively. These 'rocking curves' were taken from both the 'top' and 'bottom' of the samples, as well as both parallel (0°) and perpendicular (90°) to the tape casting direction (where 'top' is here the surface formed by the extended doctor-blade and 'bottom' is that in contact with the teflon substrate). In all cases the samples were strongly textured parallel to the original tape surface with most diffracting grains (full-width, half-maximum of the curves) aligned within ±5°. In these samples, and as might be expected,[4] the larger platelets gave a stronger texture than the smaller platelets, but the difference was not large. The curves are symmetrical about the 0° position and there is very little difference between the top and bottom of the samples or between the texture parallel and perpendicular to the casting direction. The largest differences were for the smallest platelets, for which the texture at the interface with the teflon substrate was significantly greater parallel to the casting direction (Fig. 3). In all cases, few grains have a c-axis which is tilted more than 10° to the specimen surface. It should be noted that the tape thickness in the case of Fig. 4 was 2·25 mm, which was the maximum studied.

Figure 5 shows transverse sections of the green tape, dried in alcohol (to avoid cracking) and epoxy impregnated. The first two micrographs contain 5 wt% of the small (Fig. 5(a)) and large platelets (Fig. 5(b)). In both cases the platelets are seen to be uniformly aligned and distributed

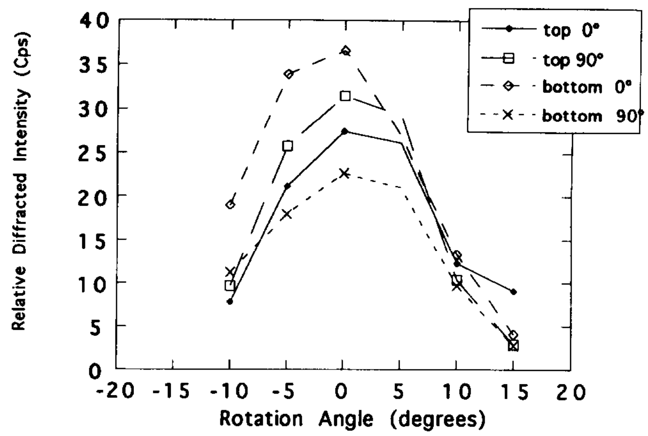


Fig. 3. Diffracted intensity versus tape surface tilt angle for a sintered sample made from 1 mm thick green tape containing 5 wt% of 3–7 μm platelets.

throughout the tape thickness. In Fig. 5(c) the sample contains 10 wt% of the small platelets, which again are uniformly aligned and distributed.

The maximum achievable tape thickness is determined both by the requirement to align the platelets in the shear stress field under the extended doctor-blade, and by the rate of diffusion of the ion-exchange cation through the tape as it exits from the doctor-blade. In general, good alignment for the small platelets was retained for tape thicknesses up to 2 mm, while the larger platelets were well-aligned at even larger tape thicknesses. The gelling reaction was always sufficiently fast to prevent further flow of the slip once it had exited from the doctor-blade, but the thicker tape had to be kept in contact with the gelling solution for several minutes in order to complete the gelling reaction through the full tape thickness. Typically, 10 layers of gelled tape could be stacked to produce a filter-pressed green sample 4–6 mm thick. Filter-pressing was accompanied by some loss of water and increase in green density.

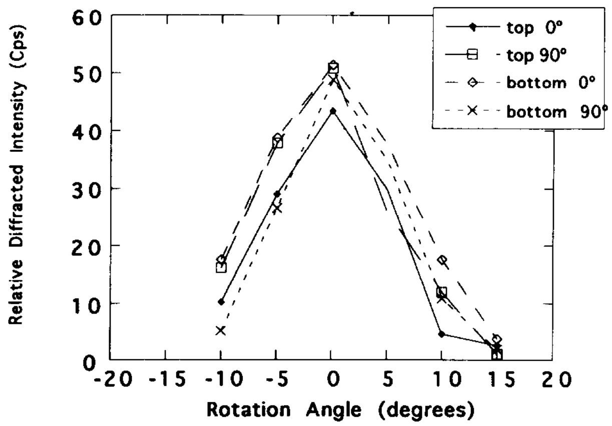
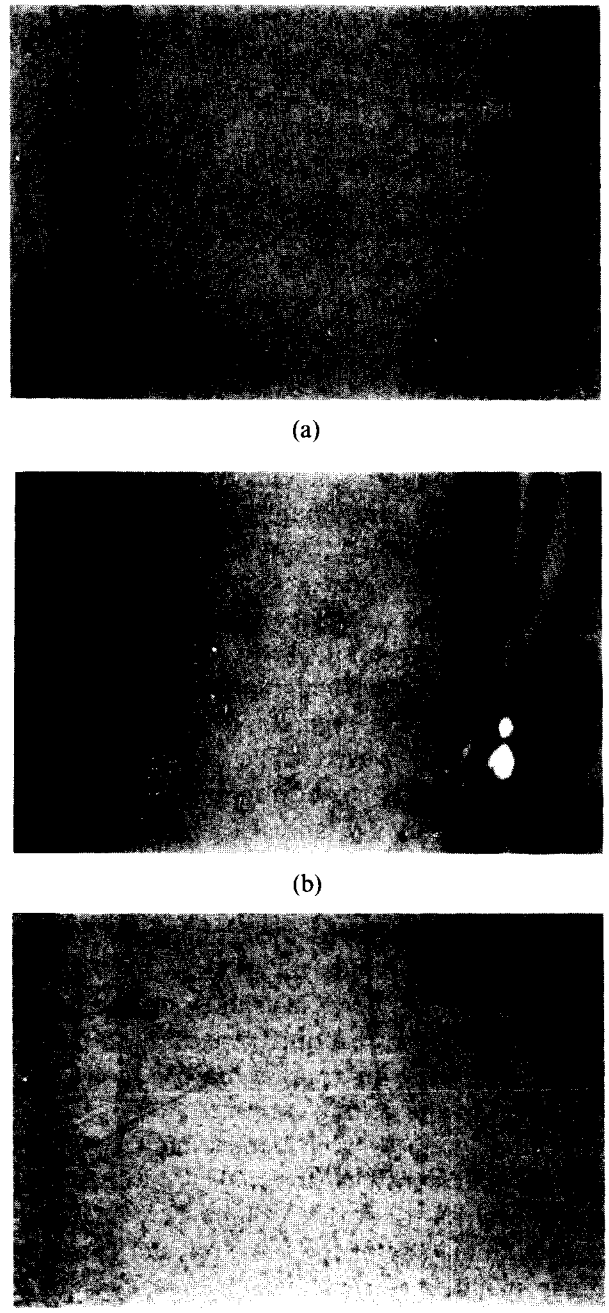


Fig. 4. Diffracted intensity versus tape surface tilt angle for a sintered sample made from 2·25 mm thick green tape containing 5 wt% of 15–25 μm platelets.



(a)

(b)

(c)

Fig. 5. Polished transverse sections of epoxy resin-impregnated green tape, showing the platelet distributions: (a) 5 wt% of 3–7 μm platelets, (b) 5 wt% of 15–25 μm platelets, (c) 10 wt% of 3–7 μm platelets.

As already noted, shrinkage on sintering was markedly anisotropic and the final sintered sample thickness was 3–5 mm.

There appeared to be no limit to the number of layers which could be bonded by filter-pressing, and no evidence for any delamination was observed either before or after sintering. Neither was there any microstructural indication of the position of the original tape surface in the polished and thermally etched cross-sections cut from the sintered product.

Six gelling cations were compared: 2+—Ca, Sr and Ba; 3+—Y and La; 4+—Ce. All these cations have an ionic radius of about 0·1 nm, which appears to be that necessary to coordinate and ionically crosslink the negatively charged polysaccharide chains.[14] The minimum concentration of alginate and the maximum volume fraction of solids which still gave a strong, flexible tape were determined approximately for Ca and found to be 1·6 wt% of alginate with 68 wt% of powder. The strengths of the gels formed using the other cations were then compared at this same slip composition, and the following rank order was observed:

$$Ba > Sr > Ca > Ce > Y > La$$

This is completely consistent with the results of Smidsrød & Haug,[13] who investigated only divalent cations. The lanthanum gelled tapes were too weak to be detached from the teflon substrate without tearing, so that a higher alginate concentration would be necessary with this cation. The yttrium and cerium gelled tapes were easily handled at the 1·6 wt% alginate level, while in the case of calcium the alginate concentration could be reduced to 1·4 wt%. The minimum alginate concentrations for strontium and barium gelled tapes were about 1·2 and 1·0 wt% respectively. Previous work has shown that the ion-exchange reaction for calcium is complete when about 20 wt% of Ca is bonded to the alginate, so 1·4 wt% of alginate corresponds to about 0·3 wt% of Ca added to the 68 wt% of solids in the slip. It follows that the gel reaction, as used in the present process, will result in an alumina product with up to 0·5 wt% of the gelling cation.

The filter-pressed green bodies made from these tapes all had densities about 47% of theoretical, significantly less than that obtained by filter-pressing an alumina slip of the same powder containing neither platelets nor alginate (57%). The highest green density was obtained for the calcium gel—50% of theoretical. The variation of sintered density with sintering temperature (9 h, in each case) is shown in Fig. 6. The rapid sintering in the presence of calcium at only 1500°C is associated with excessive grain growth. As expected, the presence of the platelets introduces local constraints which inhibit shrinkage. Nevertheless, densities exceeding 97% are readily attainable.

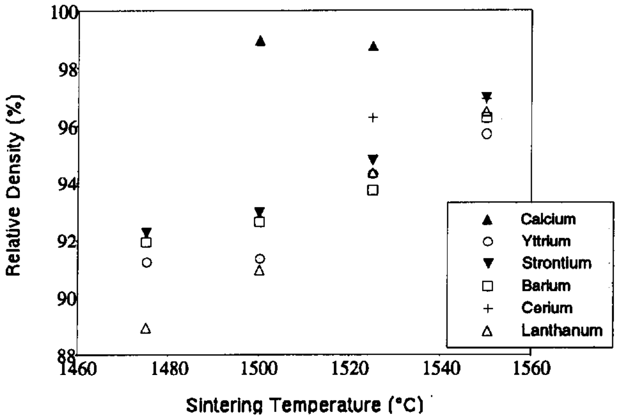
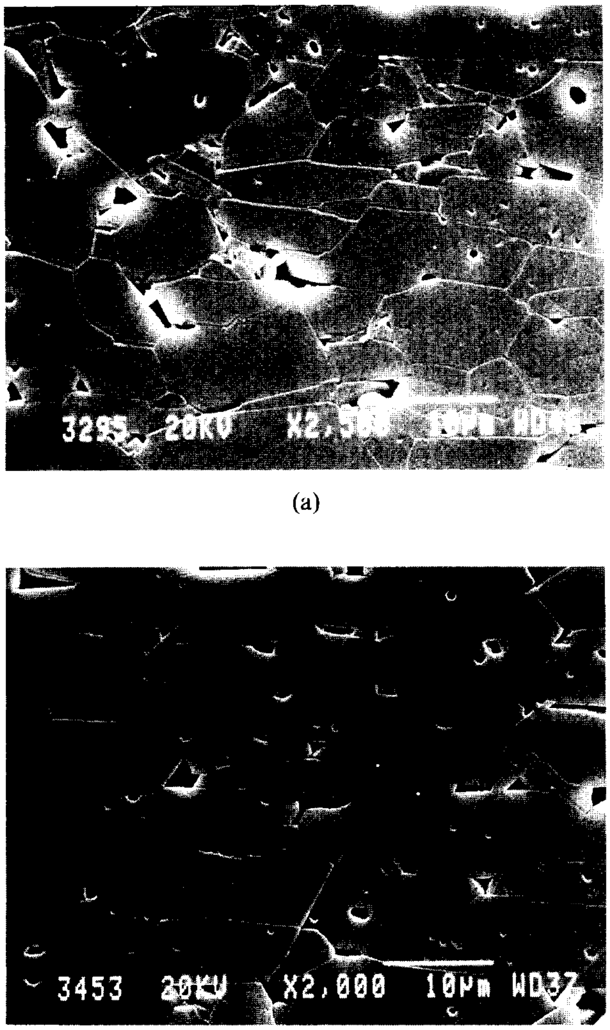


Fig. 6. Effect of sintering temperature on the relative density for different gelling cations (5 wt% of 3–7 μm platelets).

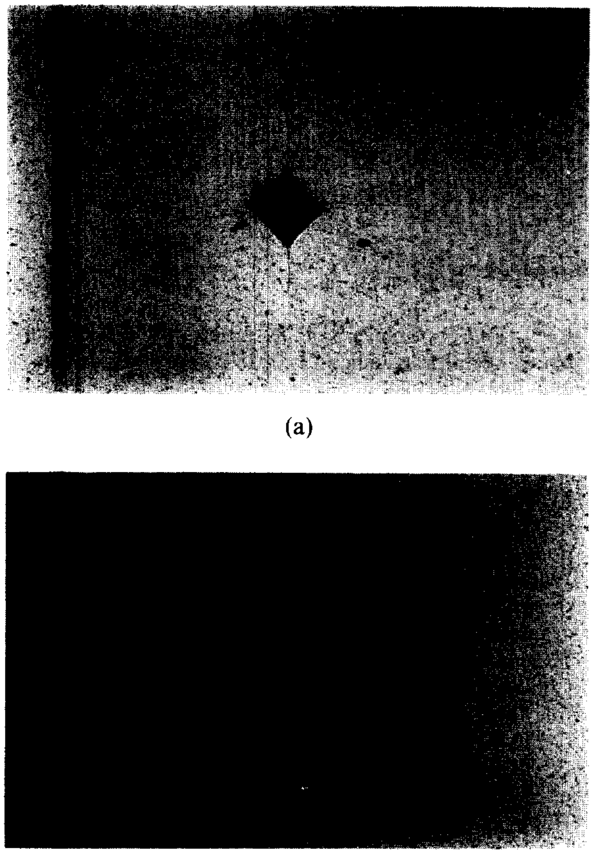


(a)

(b)

Fig. 7. SEM micrographs of thermally etched sintered samples: (a) 3–7 μm platelets at 5 wt%, (b) 10–15 μm platelets at 5 wt%.

The microstructural anisotropy of these monolithic aluminas is evident in Fig. 7. The platelets have acted as seed crystals to develop the strong (0001) crystalline texture (*c*-axis perpendicular to the surface) as well as significant grain-size anisotropy (flattened grains, foreshortened perpendicular to the surface). This microstructural anisotropy and texture has been found to lead to anisotropic crack propagation resistance. Figure 8 compares a 200N Vickers hardness indentation in two samples prepared by the gel-casting route. The first sample (Fig. 8(a)) contained no platelets, while the second (Fig. 8(b)) contained aligned platelets. The crack propagation resistance in the through-thickness direction is clearly superior in the platelet-containing alumina.



(a)

(b)

Fig. 8. Vickers indentation cracking at 200 N; (a) sintered gel-cast alumina containing no platelets, (b) sintered gel-cast alumina containing 5 wt% of 3–7 μm platelets.

4 Discussion

The present results have demonstrated the practical feasibility of producing gel-cast tape preforms of alumina containing aligned seed platelets. This tape can be compacted and sintered to yield a laminated and textured product. The mechanical properties of these materials, which will be reported elsewhere, reflect the microstructural anisotropy of the product and show improved through-thickness crack propagation resistance.

The gelling cation used in the ion-exchange reaction plays a critical role, since this cation is subsequently introduced into the final ceramic product as a dopant. Calcium is known to promote grain growth and for this reason is generally considered to be deleterious. The remaining cations which have been studied are considered to be either beneficial sintering aids (Y, Ce and La), or else harmless (Sr and Ba). All these additions should lead to some second-phase formation, which is generally expected to be undesirable. The gelling response of the alginate solution should depend on the pH, so that pH control of the gelling solution, independent of the pH of the slip, offers one possibility for reducing the amount of gelling cation required for the process. The addition of an alcohol derivative could also affect the gelling response favourably and will be investigated, as will the use of other organic additives aimed at modifying either the gelling reaction, or the surface reactivity of the powder, or both.

The density of the final product is a major parameter controlling the mechanical properties. The values currently achieved (better than 97% of theoretical) are insufficient for many applications and are in part related to the comparatively low green densities of the filter-pressed layup made from the wet, gelled tape. The best way of improving the green density is probably by increasing the volume fraction of solids in the slip, which can only be done by reducing the casting velocity (for a more viscous slip) or reducing the slip viscosity. More viscous slips are difficult to handle (and may contain entrained gas bubbles), while suitable additives to reduce slip viscosity have not yet been found.

The aligned alumina platelets exercise an appreciable constraint on the shrinkage during the sintering process, and result in higher through-thickness shrinkage perpendicular to the sample surface. The relative rates of shrinkage in the transverse and radial directions change during the sintering reaction: initially the rates are approximately uniform, but the rate of transverse shrinkage then slows down while the through-thickness shrinkage continues. The sintering constraints due to the aligned platelets depend not only on the aspect ratio and volume fraction of the platelets, but also on the homogeneity and isotropy of the platelet distribution in the gelled sample. In general, the oriented platelets are not randomly distributed, but are more closely spaced in the through-thickness direction. The shrinkage anisotropy is then less than would be expected on the basis of a random, isotropic distribution of the platelets, while the aspect ratio of the final grains is appreciably less than 1.

The gel-casting process for the production of a water-based tape preform could have some interesting manufacturing potential. For example, the tape could be slit and spirally wound to form tube. Tape layups to form plate or bar products should be straightforward. Tapes of different composition (for example, alumina/zirconia slips) could be laminated to any desired thickness in any desired combination, for example to form graded structures. Tape could also be cast and fired on a substrate as a coating or enamel, and in this case control of the transverse sintering shrinkage by the aligned platelets could be used to improve the coating integrity and inhibit cracking during sintering. It should also be possible to cast onto a rotating drum or moving band from which the tape could be stripped and collected continuously.

5 Conclusions

(1) A water-based tape of alumina containing aligned alumina platelets can be formed by gelling an alginate-containing slip in a modified design of doctor-blade tape-caster.
(2) Flexible wet tapes of 0·2–2 mm thickness can be produced in which the platelets are uniformly distributed and aligned to better than ±10°.
(3) The wet, gel-cast tape can be cut, layed up and compacted by filter-pressing into a green body with no detectable processing defects in the interface regions.
(4) The filter-pressed and dried green body can be sintered to near theoretical density to yield a strongly textured product with a high degree of microstructural anisotropy.
(5) The crystalline texture and microstructural anisotropy inhibit crack propagation in the through-thickness direction, as demonstrated by a Vickers indentation test.
(6) Several polyvalent cations are suitable gelling agents for this gelling reaction, but their effect on the microstructure and properties of the sintered product have yet to be studied.

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