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Differential sintering in ceramic injection moulding: particle orientation effects

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Abstract

The sintering shrinkage in three orthogonal directions was measured in sections cut from large rectangular injection moulded ceramic blocks. Two powders were used: a comminuted alumina and a chemically-derived zirconia. Pronounced anisotropy of shrinkage was observed in the former whereas the equiaxed zirconia showed uniform shrinkage throughout the moulding. The pattern of shrinkage anisotropy was consistent with that observed by other investigators and indicates that slight particle anisotropy can introduce differential sintering. The sintering shrinkage in the alumina powder was found to be most pronounced perpendicular to the main flow direction.

Keywords: Al_2O_3; Anisotropy; Injection moulding; Shrinkage anisotropy; Sintering; ZrO_2

1. Introduction

Powder injection moulding is used in industrial production of small ceramic components of complex shape and offers high dimensional precision.[1,2] Thus non-uniform shrinkage during sintering may cause deformation and loss of shape in otherwise precise components.[2] Differential sintering might be caused by local differences in packing efficiency, by agglomeration or by faster densification near the surface caused by temperature gradients during sintering.[3] Deformation in some sintered ceramic mouldings, however, indicates a relationship with flow-induced alignment of plate-like or anisotropically shaped powders.

There are many reports of preferred orientation caused by particles with grossly anisotropic shape such as fibres, whiskers or platelets. Indeed by using flow-induced fibre alignment in open-ended and double-gated modulated pressure injection moulding, a preferred fibre orientation can be obtained in ceramic- and metal-matrix composites.[4,5] Conventional injection moulding produced an orientated layer parallel to the flow direction in the subskin area comparable to orientation patterns in polymer composite mouldings. By imposing a reciprocating melt-flow during solidification, the oriented area increased. In the remaining central area the fibres were found to be mainly perpendicular to the flow direction.

Cox and Williamson[6] studied the microstructure, drying- and firing-shrinkage of ball-clay and earthenware with reference to particle orientation and found greater firing-shrinkage perpendicular than parallel to the laminar orientation. Stedman et al.[7] reported a high rate of sintering in the direction perpendicular to the plane of silicon carbide platelets or whiskers and restricted sintering in the directions parallel to them. Watanabe et al.[8,9] and Ohara et al.[10] investigated the microstructure development during sintering of plate-like bismuth titanate powder and found an influence of particle orientation on sintering rate and preferred densification of particles with face-to-face contact in the initial stage of sintering. Taruta et al.[11] reported non-uniform densification in plate-like alumina.

Roosen and Bowen[12] studied the unfired microstructure of alumina powder and the relationships between microstructure and sintering behaviour. There was a strong influence of pore-size distribution on the initial and intermediate stages of sintering. The sintered microstructure also showed the effects of initial pore-structure differences. The significance of their work is

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that different sintered densities and different microstructures can be obtained from the same starting powders using the same sintering schedule as a consequence solely of different forming techniques.

Zhang et al.[13,14] used two different alumina powders and investigated the influence of particle morphology on defects and differential shrinkage during sintering. There was a large effect of particle shape, mould geometry and gate position on the shrinkage behaviour in ceramic injection moulding. They attributed the former to particle orientation caused during mould filling. Like the observed orientation in fibre-composites[4,5] the platelike alumina particles tended to align parallel to the mould wall at the surface and to be perpendicular in the moulding centre. There was less shrinkage parallel than normal to the plates.

In contrast to these studies of unambiguously anisotropic powders, Uematsu et al.[15,16] present a problem that is slightly different. For their powder, there is no obvious particle shape anisotropy; it appears to be an equiaxed alumina. Conventional characterisation methods do not disclose orientation effects. Yet these are unmistakably present and can be detected by an optical method using immersion in liquids of matched refractive index. The implication is that in alumina powder with only very slight deviations from spherical symmetry, the slightly elongated axes of particles will, in suspension flow, align parallel to the flow direction. They draw attention to the possibility of anisotropic shrinkage during sintering caused by particle alignment. Uematsu's work has implications for the design of powders for injection moulding.

The mechanisms which lead to differential shrinkage of aligned particles can be quantitatively modelled if a series of geometrical assumptions is made. Thus, densification during sintering is usually described by the approach of particle centres neglecting anisotropies of surface energy, assuming a uniform array of contacts between particles and hence a uniform initial pore distribution in the assembly. These assumptions do not hold in an assembly of oriented anisotropically shaped particles.

In the present work, two sub-micron powders, namely a near-spherical zirconia and a comminuted alumina, were processed in the same way to investigate the influence of the powder on differential sintering in ceramic injection moulding. This work maps the differential sintering in the final components onto flow and filling behaviour in ceramic injection moulding.

2. Experimental

2.1. Materials

Two different ceramic powders were used in this study. The alumina powder was grade CT 3000 SG (Alcoa Chemie GmbH, Ludwigshafen, Germany) being a fine pure α-alumina with average particle size (d_{50}) of 0.6–0.8 μm and BET specific area of 6–8 m^2g^{-1} (Fig. 1a). The zirconia powder was grade TZ 3YS (Tosoh Corporation, Tokyo, Japan) with average particle size (d_{50}) of 0.3 μm and BET specific area of 6–7 m^2g^{-1} (Fig. 1b). Both powders were provided in suspension in a powder injection moulding grade of polyoxymethylene at 56 vol.% for CT 3000 SG and 47 vol.% for TZ 3YS and were prepared by high shear mixing. Both ceramic injection moulding suspensions are commercially available: the alumina under the designation Catamold AO-F and the zirconia under the designation Catamold TZP-A from BASF AG, Ludwigshafen, Germany.

2.2. Processing conditions

The suspensions were injected into a 25×45×60 mm rectangular mould. The cavity was direct-gated from a

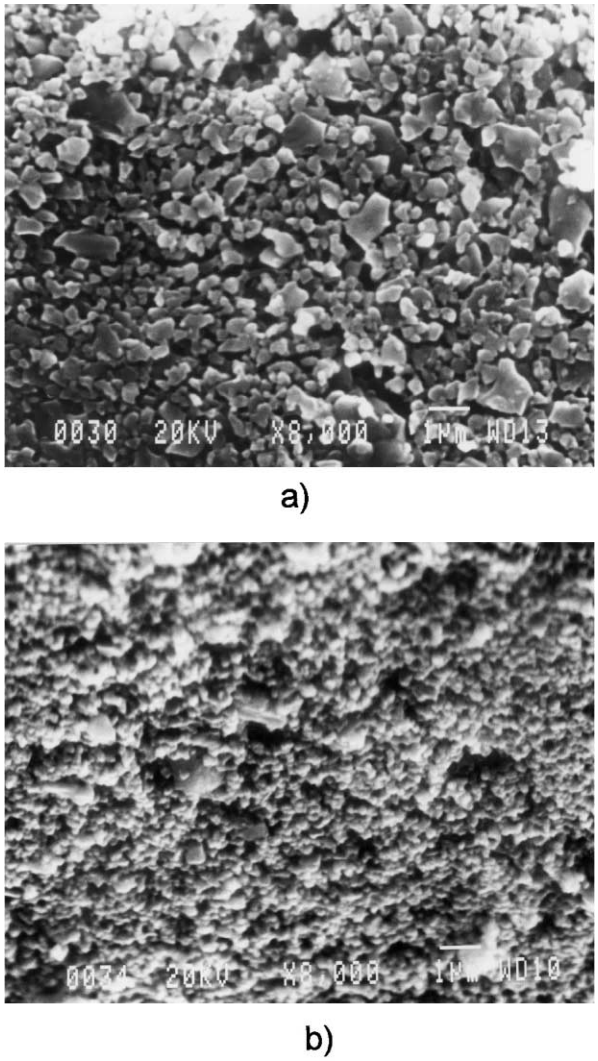

Fig. 1. Scanning electron micrographs of (a) Alcoa CT 3000 SG alumina, (b) TZ 3YS zirconia.

12 mm thick insulated sprue. A Negri Bossi NB90 injection moulding machine was used operated with the settings given in Table 1.

The polyoxymethylene was removed by catalytic degradation in the solid state at 110°C in an oven (Model VT6060-MU-2 Heraeus Instruments, Hanau, Ger.) The furnace was supplied with oxygen-free nitrogen at 500 l/h and liquid fuming nitric acid at a rate of 30 ml/h from a metered pump (Constrakron3, Kron-lab Sinsheim, Germany). The mouldings were sliced into 6 mm thick bars as described below and were catalytically degraded for 5 h and afterwards sintered in air. The alumina samples were sintered at 1600°C for 2 h and the zirconia samples at 1500°C for 2 h. The temperature ramp was 2°C/min to 400°C with a 1 h hold at 270°C, 5°C/min to 1500°C/1600°C with a 2 h hold and cooling at 2°C/min to 400°C.

2.3. Sample preparation

A 12×6×45 mm bar was cut from each of a series of 25×45×60 mm thick alumina and zirconia mouldings (Fig. 2a). The samples were notched to give reference marks for the measurement of shrinkage along the z direction. The x and y directions were measured at the centre and the ends of the bar. One 25×45×60 mm alumina moulding was cut into 200 equally sized cubes to provide a map for the differential sintering distribution throughout the moulding (Fig. 2b). To investigate the influence of the melt flow on differential sintering further a melt stream extruded from the nozzle was cut into equal length cylinders of approximately 10 mm diameter and 9 mm long (Fig. 2c). The longitudinal and radial shrinkages were measured. All measurements were taken using a digital vernier at ±0.01 mm accuracy.

Table 1
Injection moulding conditions

Parameter	Settings
Barrel temperature profile	170–170–170–175°C (nozzle)
Mould temperature	135°C
Injection speed	8×10^{-5} m^3 s^{-1}
Maximum injection pressure	95 MPa
Hold pressure	5–120 MPa for 400 s

3. Results and discussion

3.1. Powder morphology and microstructure

Fig. 1a shows a scanning electron micrograph of the fine alumina powder in a fracture surface of a moulding broken after binder removal. The alumina has a narrow particle size distribution, the particles are mainly submicron and angular. A few particles show plane surfaces and have noticeable anisotropy of shape but after careful observation of images like that in Fig. 1a it was not possible to give an unambiguous assessment of preferred orientation. Fig. 1b shows a fracture surface of a zirconia moulding broken after binder removal. In contrast to the alumina powder, the particles are more spherical, having no plane surfaces and no apparent

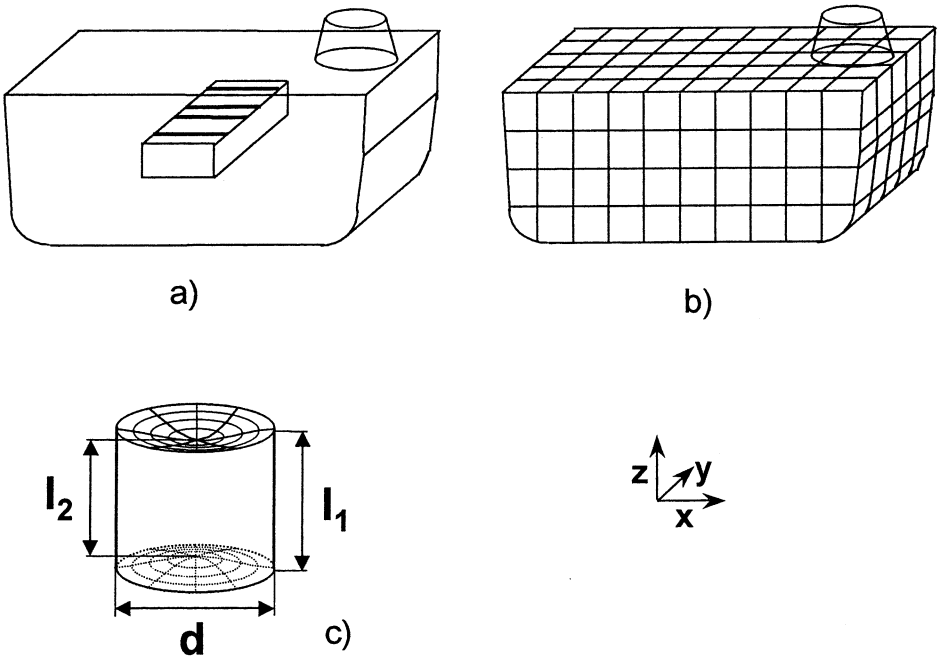

Fig. 2. Sectioning plan for (a) bars, (b) 200 cubes, (c) melt extrusion.

anisotropy of shape. The powder is finer with some larger but still sub-micron particles.

Fig. 3a shows the corresponding alumina grain structure in a fully sintered moulding. The moulding has been cut, polished and thermally etched. The microstructure reveals a fairly homogeneous grain size distribution with little development of abnormal grain growth. There is some evidence of preferred elongation in the grain structure typical of alumina, but study of such micrographs did not yield an unambiguous relationship to a characteristic direction in the moulding. The zirconia microstructure, in contrast, which is shown in Fig. 3b, reveals a homogeneous grain size with no preferred anisotropy of shape and no preferred orientation.

3.2. Mould filling and particle orientation

To visualise mould filling, a series of short shots with gradually increasing shot volume was made.[17] Fig. 4 shows schematically the melt front profile deduced from the short shots as it fills the mould cavity. In the early stage of mould filling, the melt jets into the cavity, collides with the opposite wall and folds up in order to build up a melt front. A substantial fraction of the melt front becomes uniform as it fills the cavity but the remainder of the coil can still be seen. The asymmetry of the moving melt front is conspicuous: the melt streams preferentially along the die wall opposite the gate. This indicates pressure differences in the melt which are caused by the gate position. As the melt front enters the mould, a layer of solid develops on the mould walls.[18] The thickness of this solid and stationary layer depends on mould and melt temperature, on filling time and injection speed.[18] Studies with open-ended moulding[4] and modulated pressure moulding[5] reported an increase in preferred particle orientation from the moulding walls inwards. In open-ended moulding, the melt flows continuously through the moulding during solidification and in modulated pressure moulding an oscillating hold pressure creates a reciprocating melt flow as the moulding solidifies. In both cases, particles became aligned as the melt flowed adjacent to the stationary solid layer.

By using optical methods, particle orientation in unfired mouldings made from a commercial alumina powder has been found. Uematsu et al.[15] applied several examination techniques for the microstructural characterisation of unfired alumina injection moulded bodies. They observed the consequences of preferred particle orientation by using a liquid immersion method with optical microscopy. Powder X-ray diffraction analysis and scanning electron microscopy (SEM) were unable to detect preferred orientation. The measurements of differential shrinkage during sintering in injection mouldings that are presented below lend weight to this accumulating evidence of particle alignment in particle assemblies where conventional methods do not readily detect preferred orientation.

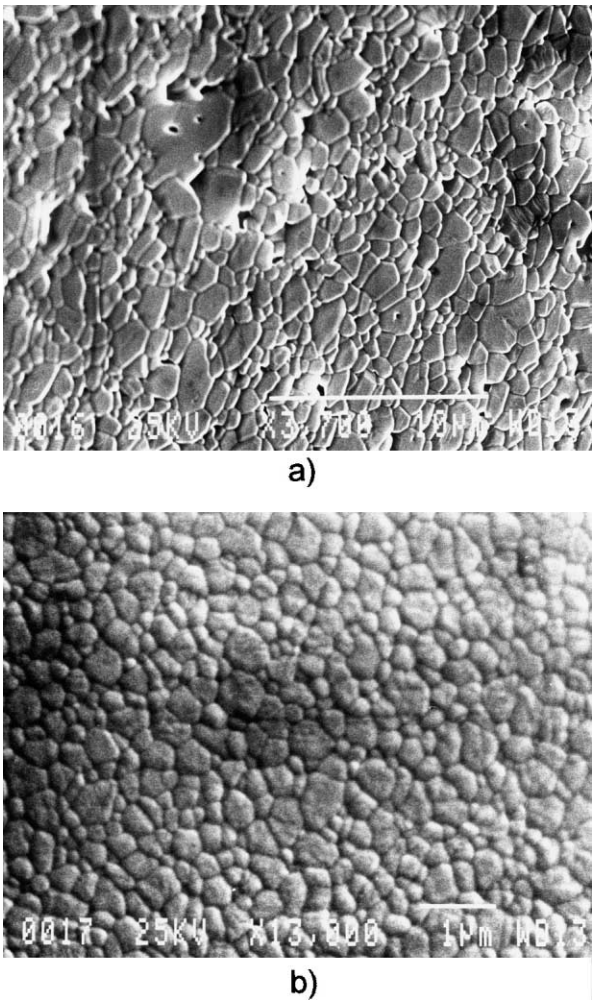

Fig. 3. Scanning electron micrographs of thermally etched sintered mouldings taken close to the moulding surface: (a) alumina, (b) zirconia.

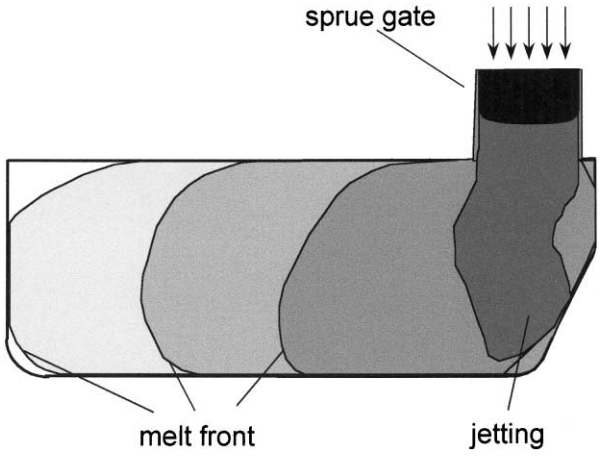

Fig. 4. Schematic profile of the melt front during mould filling.

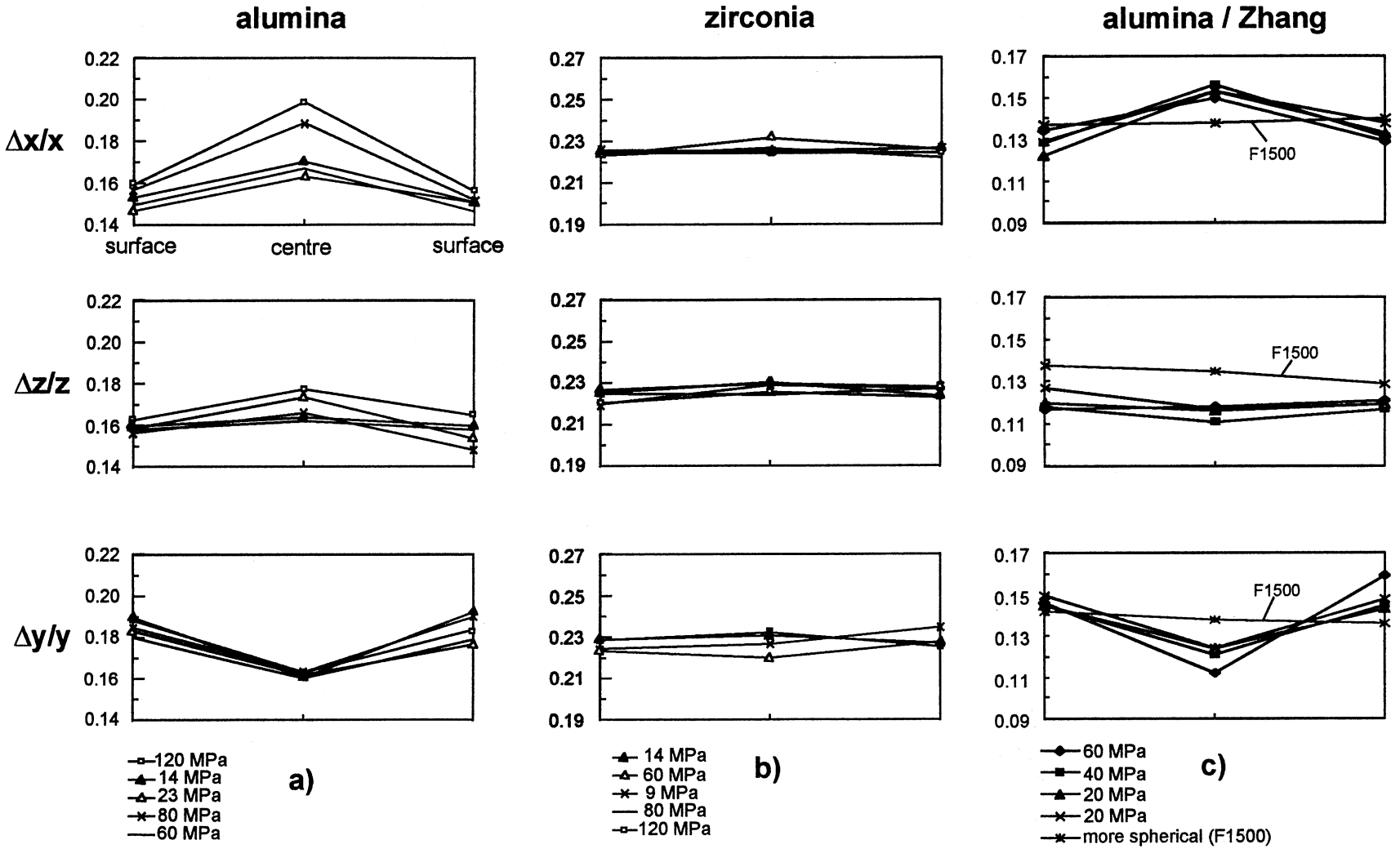

Fig. 5. Linear shrinkage in the x-, y- and z-directions (defined in Fig. 2) for bars of alumina and zirconia cut from large mouldings according to the sectioning protocol in Fig. 2a. The results from Zhang et al. (Ref. 14) are plotted for comparison.

3.3. Differential shrinkage

Fig. 5a and b show the linear shrinkage during sintering in alumina and zirconia mouldings. The shrinkage was measured on a 12×6×45 mm slotted bar (shown in Fig. 2a) in the moulding centre and also close to each moulding surface. Pronounced differential shrinkage during sintering was found in bars cut from alumina mouldings. The linear shrinkage varied between 15 and 20%. The biggest sintering differences were measured in the x-direction which is the main filling direction. A maximum shrinkage was measured in the moulding centre and a minimum along the surface. Similar results were found in the z-direction but were less pronounced. In the y-direction, the results are reversed: a minimum was found in the moulding centre and a maximum along the moulding surface. In the zirconia mouldings (Fig. 5b) no noticeable differences were found. The average linear shrinkage of $\Delta l/l_0 = 22.6 \pm 0.6\%$ was seen over the whole range of holding pressure, independent of location and direction.

Similar results were reported by Zhang et al.[14] Fig. 5c shows the linear shrinkage in their injection moulded alumina bars of 15×20×45 mm plotted on axes for direct comparison with the present work. They used two different grades of alumina powder: a plate-like powder and a more spherical powder. The results are in surprisingly good agreement with those of this study. The plate-like alumina powder produced significant differential shrinkage when ceramic injection mouldings were fired while the more spherical or equi-axed powders (marked as F1500) produced homogeneous densification during sintering. The implication is that there is enough shape anisotropy in the powder used in this work to provide differential sintering even though, as in Uematsu's work, it cannot be unambiguously detected by conventional means.

The data in Fig. 5 can be combined to give the volume shrinkage at each position in each moulding. This indicates the extent to which the orthogonal shrinkages combine to preserve uniform density. The volume shrinkage in zirconia mouldings during densification calculated from the dimensional changes is consistent between mouldings with an average value of $\Delta V/V_0 = 53.6$ and a 95% confidence interval of 0.4% for the 12 cases (three positions in each of four mouldings). This is quite close to the theoretical value of 53.3% based on the powder volume fraction in the moulding suspension.

In the case of alumina mouldings, the linear shrinkage variation of 15–20%, if assumed isotropic, would correspond to volume shrinkages from 39 to 49% but the volume shrinkage calculated by combining orthogonal dimensions has an average of $\Delta V/V_0 = 42.1\%$ with a 95% confidence interval of 0.5%. The expected volume shrinkage for this composition is 42.5%. A directional variation in linear shrinkage with consistency in volume shrinkage is characteristic of differential sintering caused by aligned anisotropically shaped particles.

In order to relate differential shrinkage to the flow and filling behaviour in injection moulding, the transverse and longitudinal shrinkages in an extruded ceramic cylinder were measured (Fig. 2c). The cylinder was extruded through a 10 mm thick nozzle into air and afterwards cut into sections. Fig. 6 shows the shrinkage calculated from the deformation measured across the base of the extruded ceramic cylinder which appears as a concave hollow after sintering. The measured linear shrinkage across the diameter $\Delta d/d_0 = 0.179 \pm 0.003$ is significantly higher than the isotropic linear shrinkage of 16.8% associated with the final 98.2% density of an assembly of initially relative density 55.7 vol.%. The longitudinal linear shrinkage at the cylinder surface $(\Delta l/l_0)_1 = 0.153 \pm 0.003$ was about 1.5% lower than the isotropic shrinkage. The shrinkage at the centre of the cylinder was $(\Delta l/l_0)_2 = 0.1984 \pm 0.0017$ and was about 3% higher than the isotropic shrinkage. The parabolic-like shrinkage distribution in the extruded cylinder can be related to the velocity profile of the melt. Thus a relationship to the flow characteristics and to the suggested particle alignment emerges. In Uematsu's work[15] the packing arrangement of an apparently equiaxed alumina powder which showed no shape anisotropy in the scanning electron microscope was investigated. They found particle alignment in a 5–6 mm diameter sprue, with the slightly elongated axes parallel to the flow direction. This is consistent with a preferred particle alignment along the cylinder surface which causes the lower firing shrinkage observed. The higher longitudinal shrinkage at the centre of the cylinder may be caused by particle alignment perpendicular to the flow direction which corresponds with the orientation expected from other studies.[4,5]

In an extension of this work, the shrinkage distribution throughout a 25×45×60 mm thick insulated sprue

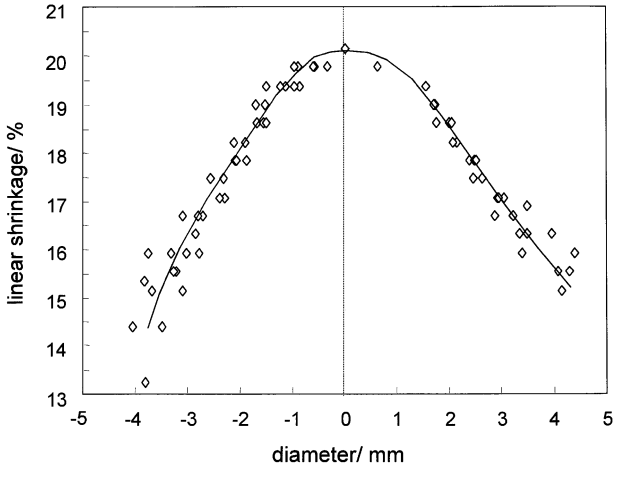

Fig. 6. Shrinkage across an extruded ceramic cylinder after sintering.

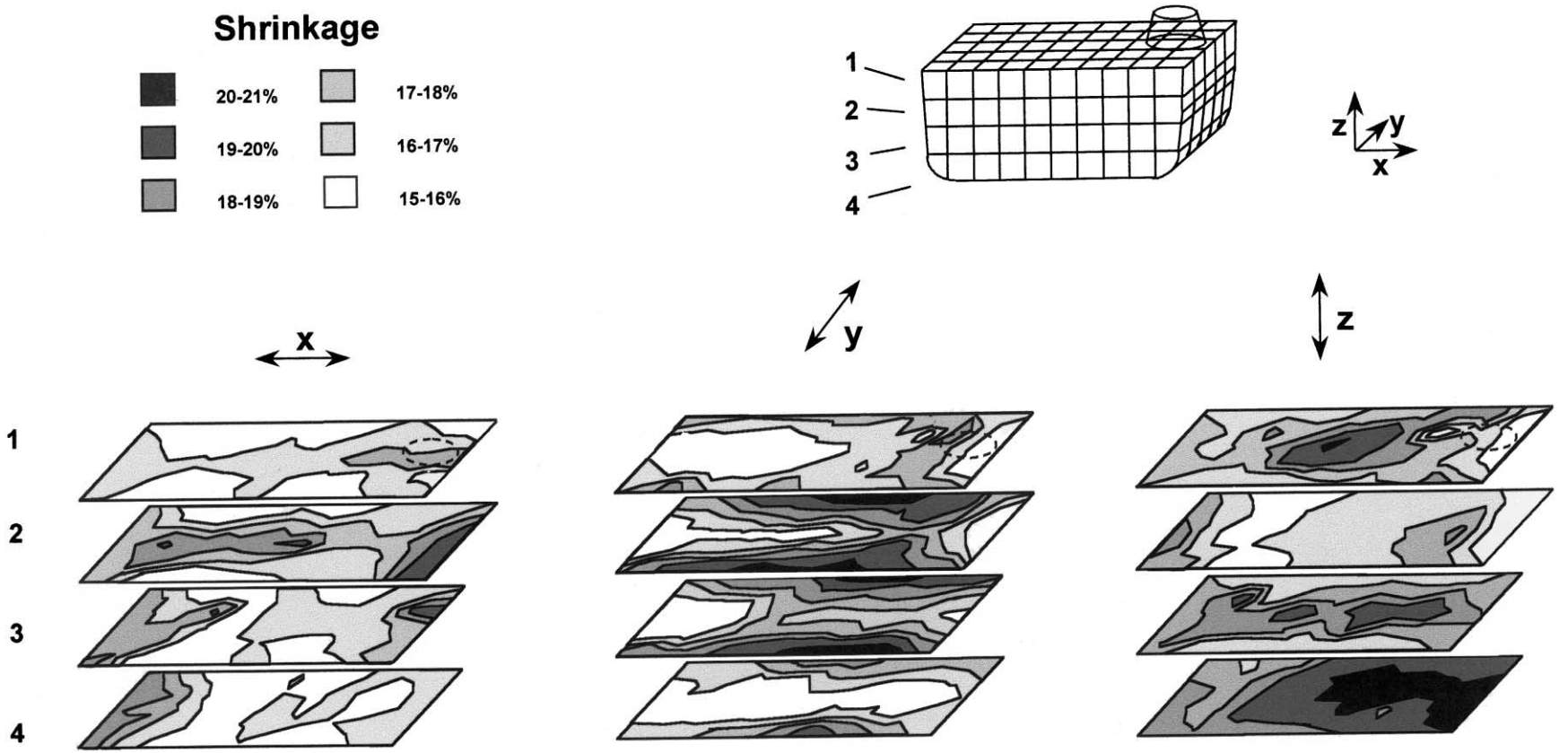

Fig. 7. Maps of linear sintering shrinkage throughout an alumina moulding for the three directions.

alumina moulding made using 60 MPa hold pressure was investigated using cube-shaped samples cut according to Fig. 2b. Fig. 7 is a map of the linear sintering shrinkage throughout an alumina moulding giving a pictorial visualisation of the shrinkage in x-, y- and z-directions. These results reveal a systematic pattern of behaviour consistent with the observations reported above. A high linear shrinkage was always found perpendicular to the die walls. In the y-direction for example, a maximum appears along the middle of the front and back face of the moulding. In the z-direction the maxima are mainly along the bottom-face opposite the gate, associated with a smaller maximum on the top-face. In the x-direction, the maxima are along the right and left faces and are associated with a maximum in the moulding centre. In each case, a high shrinkage appears perpendicular to the die wall corresponding to the alignment of particles parallel to the die wall.

Fig. 4 shows enhanced melt flow on the side opposite the gate caused by the asymmetry established early in mould filling. As a result, an asymmetric shrinkage in the z-direction is observed (Fig. 7) with a maximum shrinkage opposite the gate. The particle alignment also caused a maximum shrinkage in the y-direction located at the front and back face of the moulding. This symmetrical linear shrinkage in the y-direction indicates the gate position in the moulding as preferred alignment appeared on the front and back face close to the gate.

If particle orientation is the cause[6–11,13,14] of the observed differential sintering and flow-induced alignment of particles occurs,[4,5,15,16] the results present a sound correlation between mould filling and differential sintering in ceramic suspensions with slight anisotropy of particle shape. The melt stream enters the mould cavity having already acquired preferred particle alignment in the runner system (Fig. 6). When the melt touches the die wall, a thin layer quickly solidifies.[18] As the suspension continues to flow, a gradually increasing solid layer with occluded particle alignment develops. However, as mould filling takes less then 2 s, only a thin layer solidifies during mould filling and the majority of the moulding contents solidify after mould filling. The orientation effects continue to be seen at much greater depth. It must be velocity gradients, no matter how small, both during mould filling and during the packing stage that are responsible for the preferred particle orientation. In insulated sprue moulding, flow at low shear rates continues as solidification progresses and the mould is packed to compensate for shrinkage.

4. Conclusions

The injection moulding of a chemically-derived equiaxed zirconia powder and a comminuted alumina powder were compared. In the case of the alumina mouldings, there was pronounced differential sintering which was detected by linear shrinkage measured on samples cut from mouldings in three orthogonal directions. Despite these differences, volume shrinkage was consistent with the initial and final relative densities. In the case of the zirconia mouldings, the orthogonal shrinkages were identical within experimental error. These results are remarkably similar to results in other published work using different powders, binder systems, moulds and moulding conditions and with work on the optical microscopy of particle alignment in an injection moulding sprue. The pattern of shrinkage anisotropy was correlated with the mould filling as deduced from short shots. These effects are attributed to shape anisotropy in the alumina and it is argued that mould filling even at low shear rates produced preferred particle orientation throughout the mouldings.

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