Shaping ceramics by plastic processing

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Abstract

Ceramic products have been formed from plastically deformable bodies for many millennia. A well-formulated paste can be shaped easily but this masks the complexity of the physical process and the choices involved in designing the material. Over recent years considerable effort has been applied to understand these aspects and that progress is reported here along with some of the difficulties encountered in defining the behaviour. The ability of plastic processing to produce complex structures is reviewed, concentrating on composite and honeycomb structures in technical ceramics. Two of the difficulties in continuous processing of these materials are considered, namely the long-term stability of the paste during flow through phase migration and monitoring of these processes for control.
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1. Introduction

Ceramics have been prepared from plastic bodies from Neolithic times, for example they are well documented at Çatalhöyük[1] Turkey, 6500 BC. The natural plasticity of clays when mixed with water lends itself to the forming of vessels for domestic use. Over the centuries the process and formulations have been refined to create truly magnificent objects in earthenware and porcelain.[2] On the time line of ceramic history, it is only relatively recently that extrusion has emerged to take advantage of the plasticity of clay bodies to make utilitarian products for industrialisation.[3] Clays, whilst creating plasticity in a body, limit the properties of the material and technical ceramics normally require the use of cleaner, often synthetic materials. In order to achieve the same plasticity in technical ceramics, polymeric or other chemical additives are incorporated into the mix but clays may still be incorporated to impart or improve plasticity if the formulation can accommodate them. Thus, ceramics of almost any composition can be formed by plastic-based processes and, with the introduction of thermoplastic or thermosetting binders, can also be injection moulded,[4] press moulded[5] and calendered.[6] Here we briefly review some developments in ceramics plastic forming focussing on formulation, characterisation of flow and the development of complex microstructures by composite and co-processing. The importance of control is evident throughout much of the reviewed work and developments in process control for pastes are described.

Many workers report that they have used extrusion or injection moulding to shape their test components. It is impractical and unnecessary to review them all here but[7–12] are examples. Plastic processing is commonly applied to shape new formulations and in these circumstances there is little attention paid to the practicalities of the forming process itself and its optimisation. However, there is also abundant evidence that the way in which the body is prepared, processed and shaped is critical to the performance of the finished component. In the development of their plastic body process, viscous polymer processing (VPP), Clegg et al.[13] showed that the selection of powders and the mixing process are critical in reducing defects and ensuring the performance and reliability of the finished component. Where particular care has been taken in the preparation of materials to optimise the formulation and the plastic shaping process, the properties of the finished component are comparable to any other forming process, if not better. Zirconia-toughened alumina extrudates with strengths in excess of 1 GPa and toughness greater than 8 MPa m$^{1/2}$ have been produced by extrusion[14,15] of hydrothermally derived sols, the sol being seeded and conditioned to allow high-pressure filtration and the formation of an extrudable filtrate. The superior properties were due to the exclusion of hard agglomerates in the process. With advancing nano-processing

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technologies, particularly in the preservation of fine grain size during sintering,[16] it should be possible to develop structural components with even better mechanical properties.

2. Paste formulation

Plastic bodies formulated for ceramics can be considered as two phase systems, comprised of solid particles surrounded by a continuous liquid phase. This is, of course, an oversimplification as the particulates may be multi-phase (here referring to size and/or composition) in order to optimise the packing behaviour and the final component properties. The liquid phase often also comprises several components. In aqueous systems the liquid viscosity is increased with polymeric or mineral binder additions and lubricating agents are frequently added to aid flow at high solid loadings. With organic continuous phases there will normally be a solvent combined with a binder, lubricant and plasticiser. It is not uncommon to find that industrial paste systems evolve into complex mixtures as the practitioner tweaks the formulation to overcome processing issues; 10 or more component systems are not unknown. There are almost as many formulations in the literature as there are papers on plastic processing: Table 1 lists some examples.

The microstructural requirements of the finished component will often limit flexibility in powder selection for the ceramicist but it is important to understand how particle size, size distribution and morphology also influence the behaviour of the plastic body. These bodies, doughs or pastes represent just a section along the spectrum of the possible material states as powder is added to a liquid. Fig. 1 shows the relationship between relative viscosity, η_r ($\eta_r = \eta/\eta_0$, where η is the apparent (shear) viscosity of the suspension and η_0 is the apparent viscosity of the pure liquid phase). In his review, Rutgers[29] identified over 100 equations which attempt to describe the form of this curve. One commonly found in the ceramics literature is that by Chong et al.[30] and another popular among chemical engineers as well as ceramicists is the Krieger–Dougherty relationship[31]:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-|\eta|\phi_m} \qquad (1)$$

where ϕ is the solids loading (volume fraction) and ϕ_m is the solids loading at infinite viscosity (equivalent in practical terms to the maximum packing fraction): $|\eta|$ is the intrinsic viscosity and is a hydrodynamic shape factor (=2.5 for spheres and greater for elongated particles). Pastes would normally occupy a narrow region just below ϕ_m such that their 'viscosity' is sufficient to retain shape but not large enough to prevent flow or damage process equipment. As a result they are characterised by a high apparent yield stress and shear-thinning behaviour once flow is initiated.

As ϕ_m is dictated by the packing behaviour of the solid it is clear that changing the packing behaviour of the powder will therefore influence the flow significantly. Packing theories for powders are numerous and well reported.[32] For randomly distributed mono-sized spheres we can expect a maximum packing fraction of 0.64 irrespective of their chemical composition (unless colloidal interactions arise).[33]

Pastes of this form have only a small amount of liquid in excess of that required to fill the interstices of the powder bed. Typically this excess will be between 2 and 5 vol.%. They exhibit little shrinkage on drying or debinding (typically 1–5 linear % for dense particulate systems) with good mixing.[34,28] This will generate high green densities for a given powder system and largely accounts for why extruded products often exhibit good mechanical properties.

The component green density can be increased by blending powders as this will change ϕ_m. Examining Fig. 1 it is clear that an increase in ϕ_m, indicated by the dashed line, will lead to reduced η_r for the same solids loading or require less liquid to achieve the same η_r. This has been demonstrated systematically for bimodal[35] and trimodal systems.[36,37] Fig. 2 shows the reciprocal of the bulk yield stress (determined experimentally by application of Eq. (2), paste flow section) as a function of mois-
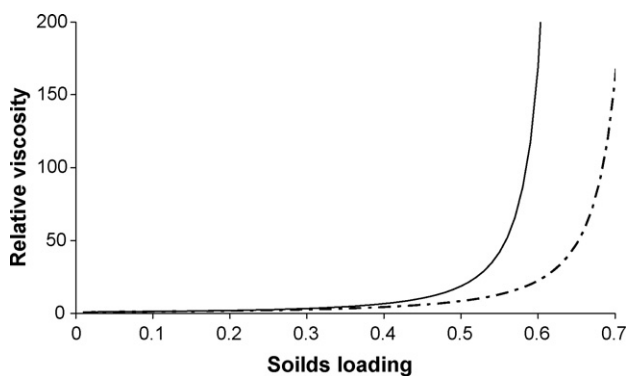

Fig. 1. Influence of solids loading on relative viscosity. Solid line calculated using Eq. (1) with $\phi_m = 0.64$ (random packed mono-dispersed spheres); dashed line $\phi_m = 0.75$ (bimodal mixture of mono-dispersed spheres of infinitely different size in the ratio ~40:60 or 20:80, coarse to fine), $|\eta|\phi_m$ set to 2.
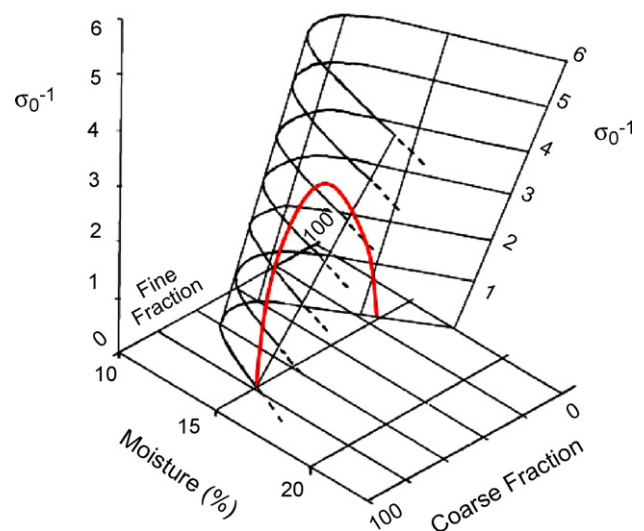

Fig. 2. Effect of liquid content (moisture vol.%) and mixture composition on reciprocal of paste bulk yield stress for a bimodal mixture of alumina particles: coarse fraction median size 29 μm and fine fraction 2.9 μm. The thicker line on the 15% moisture plane indicates the paste behaviour at that moisture level (with modifications from Ref. [36]).

Table 1
Examples of published formulations for plastic processing of ceramics

Particulate (s)	Binder system	Application	References
Clay	Water	Pipes and catalyst supports	17
Talc, kaolin, alumina	Methyl cellulose, water	Catalyst support	18
Alumina	Bentonite, starch, water	Model pastes	19
Alumina	Polyethylene glycol, vegetable fat	Injected alumina components	20
Alumina	Boehmite, nitric acid, water	Catalyst supports	21
Alumina	Ammonium polyacrylate, water (coagulated with γ-lactone)	Structural ceramic extrudates	22
Zinc oxide	Polyvinyl alcohol, glycerine, paraffin, polyethylene ethanol	Templated ceramics	23
Alumina	Hydroxypropylmethyl cellulose, water	Structural ceramics	24,25
Alumina	Stearic acid, polyethylene glycol, polyvinylbutyral	Structural ceramics	26
Zirconia	Ethylvinyl alcohol, stearic acid	Structural ceramics	27
Zirconia	Paraffin wax, oleic acid	Structural ceramics	28

ture content and particle blend. From such a plot it is possible to predict the behaviour of intermediate compositions without having to resort to multiple experiments. Ceramicists in conventional processing use continuous particle size distributions and the packing of these can be estimated[38] to allow predictive formulation.

Particle shape has an important influence on packing behaviour. Most ceramic powders are not spherical and for a single powder size the larger the aspect ratio, the lower the packing density.[39,32] However, if powders of two different morphologies and size are mixed together the packing behaviour may improve.[40] Fig. 3 summarises the packing behaviour for mixes
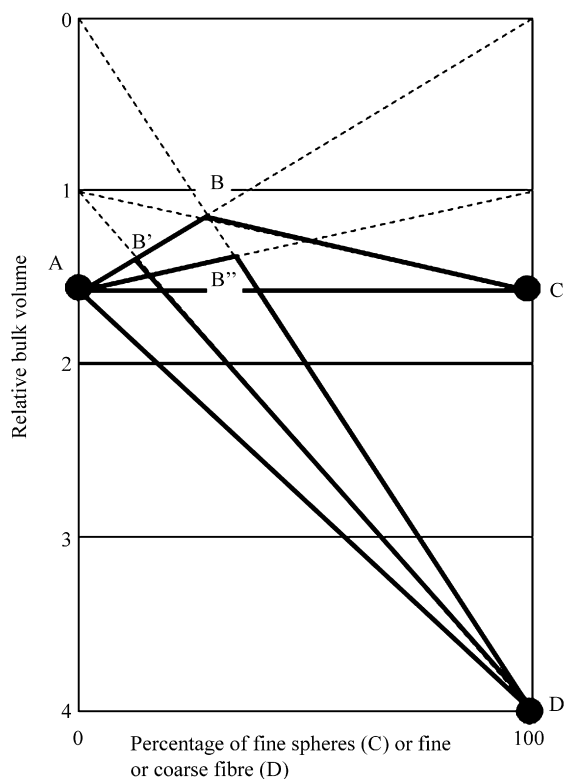

Fig. 3. Plot of relative bulk volume for spheres mixed with spheres (region ABC) and spheres mixed with fibres where the packing fraction in 100% fibres is 0.25 and in 100% spheres is 0.64. AB′D—fine fibres, coarse particles; AB″D—coarse fibres, fine particles.

of two spheres of different diameter alongside spheres mixed with fibres of different size for comparison. Packing density in Fig. 3 is represented by relative bulk volume which is the reciprocal of the packing fraction (this been applied to give straight lines in the figure).[40] The packing density of the pure fibre is influenced by the fibre length—the longer the fibre the lower the packing density. For fibres in combination with spheres two solutions exist as the fibres may be larger or smaller in diameter than the spheres.

For mixtures of two spherical powders the ratio of coarse fraction to fine fraction, R, governs where in the triangle ABC the mixture will lie. If R is infinite, packing will follow line ABC, while if R is unity it will follow AC. For the fibre-sphere system R' is the ratio of fibre diameter to sphere diameter and can range from 0 to ∞. For fine fibres in coarse spheres, the permissible packing behaviour is denoted by the triangle AB′D, while for coarse fibres in fine spheres it would be AB″D. Where the fibre and sphere diameters are infinitely different in diameter packing is denoted by loci AB′D or AB″D, and where they are the same by diameter AD. It is interesting to note that the maximum packing in the two fibre-sphere systems is the same but occurs at different volume ratios. The behaviour of the materials with intermediate values of R or R' can be calculated[41,42] and is now commonly performed numerically. These principles have been applied to fibre and platelet composite extrusion.[43,44] Thus, by combining knowledge of packing behaviour with understanding of the behaviour of selected pastes, intermediate compositions can be formulated with relative ease. This becomes particularly useful when developing composite or co-processed materials (see later).

The majority of ceramic paste bodies are formed by combining a relatively inert ceramic precursor powder with a liquid phase but they may also be formed by chemical interaction between particles in inviscid liquid to form plastically deformable gels. Examples of the latter are common in the preparation of ceramic catalyst supports[45,46] and will not be considered in great detail here. Intermediate forms lying between these extremes are widespread; clay bodies, for example, derive their plasticity from the combination of fine particle size and electrochemical particle–particle interactions whilst gels can be used as binders for particulate systems.[10,21]

While pastes can be formulated using the principles outlined above it is important that they are well mixed if reliable components are to be produced. The paste preparation methods described in the literature can be classified as either (i) build-up or (ii) break-down processes. In the former the powder is dispersed in the fluid at low concentration, normally by extended milling, and converted to a paste by liquid removal or gelation. This could be said to be the traditional approach for clay-based products. In the latter, large shear forces are applied to bring the liquid phase into direct contact with the powder, dispersing and distributing the ingredients at or close to the final composition. This is the most common approach for technical ceramics. There is insufficient space to discuss selection and optimisation of the mixing process in detail, suffice to note that large strains rather than high stain rates appear to be key to generating well prepared pastes.[47–52]

3. Paste flow

At first inspection the paste forming process appears to be simple. Under a sufficiently high load a well-formulated paste will flow to form the desired shape. However, the complexity of the formulation is also reflected in the mechanisms operating in the paste during flow and has led to much debate on how to evaluate the behaviour. Two recent papers have highlighted the difficulties of analysing these complex multi-phase systems: Chandler et al.[53] discuss the underlying constitutive laws of deformation and review the common test methods employed in paste analysis, while Wilson and Rough[54] describe irregular features arising in their extrusion. Structurally, pastes bear many similarities to saturated soils and it is therefore not surprising that soil mechanics methodologies have been widely applied to the study of ceramic pastes. Notable among these are those which come close to having ideally defined boundary conditions and movement. If these conditions are satisfied it is possible to define the material characteristics fully. Simple compression tests come close to this ideal and are often used when commenting semi-qualitatively on plasticity[55] but the test suffers from uncontrolled distortion, making full analysis difficult.[53] Triaxial tests, where the specimen is fully confined, although more complex can be used to generate highly reliable data for modelling. Torsional tests can be used but data reported in the literature are scarce and difficulties arise with attachment and defining the boundary conditions.[56,53] Oscillation tests are reported to offer some promise[53] but little data are in the public domain to date.

Other, less rigorous soils tests have been applied to ceramic paste evaluation. Indexing methods such as the 'Atterburg limits' have been used to characterise clay-based pastes but are useful only as go/no-go tools for extrudability.[57] Likewise, cone penetration tests can be used to estimate bulk yield strengths but provide no indication of flow properties and are prone to error due to the assumptions made in the analysis.[58]

The above methods are small displacement tests whereas during shaping macro-deformation and flow occur. It would therefore be appropriate to test the materials under similar conditions. This may be performed by squeezing a film of paste between parallel plates or by capillary flow (i.e. ram extrusion)

but both of these methods suffer from a need to quantify slip at the wall. We concentrate here on extrusion and the reader is referred to Adams et al.[59] and Basterfield[60] for a description of the squeeze technique.

For extrusion analysis Benbow assumed plug flow during his studies through the later part of the 20th Century. Visualisation experiments[61–63] confirmed that this assumption is a good description when pastes suitable for shape forming pass along a capillary. He recognised the link to soil mechanics in describing pastes using engineering plastic models and published 'Paste Flow and Extrusion'[58] with Bridgwater, which introduced a systematic framework for understanding paste structure and enabled design of paste processes. For ram extrusion they developed the following relationship for the extrusion pressure, P, developed at the ram:

$$P = P_1 + P_2 = 2(\sigma_0 + \alpha V^m)\ln\left(\frac{D_0}{D}\right) + 4\frac{L}{D}(\tau_0 + \beta V^n) \quad (2)$$

Here P_1 and P_2 are the pressure drops associated with the die entry (convergent flow) and flow along the die capillary, respectively. For barrels and dies of circular cross-section and 90° entry angle, σ_0 is the bulk yield stress (MPa), α the die entry velocity factor (Pa(s m^{-1})^m), m the die entry velocity index, τ_0 the die wall initial yield shear stress (MPa), β the die wall shear stress velocity factor (Pa(s m^{-1})^n) and n is the die wall velocity index: V is the average paste velocity as it exits the die, L the die length, and D and D_0 are the die and barrel diameter, respectively.

Eq. (2) has been widely applied to many classes of paste materials[54] and is popular because of its ease of use. It can be used to characterise pastes,[18,20] guide formulation development[64,65] and design process equipment[66–69] and dies.[70,71] However, there are some failings in its predictive capacity, particularly as the complexity of the extruder geometry increases. This results from some of the parameters being predicted without direct measurement and some evaluations[72–74] have proposed developments of Eq. (2) which yield parameters with more physical meaning.

An example is the use of the Herschel–Bulkley constitutive function[75] to describe the paste (bulk) rheology: Basterfield et al.[73] developed the following analogous relationship for P_1 initially assuming no slip at the wall:

$$P_1 = 2\sigma_0'\ln\frac{D_0}{D} + Ak_u\left(\frac{2V}{D}\right)^{m'}\left(1 - \left(\frac{D}{D_0}\right)^{3m'}\right) \quad (3)$$

with A given by

$$A = \frac{2}{3m'}(\sin\theta_{max}(1 + \cos\theta_{max}))^{m'} \quad (4)$$

where k_u is the flow consistency (Pa s$^{m'}$) in uniaxial extension and θ is the angle of the cone formed by the slip planes as the paste enters the die. It is noteworthy that σ_0' and m' are similar in magnitude to σ_0 and m (Eq. (2)) for many experiments.

Rheological models such as the Herschel–Bulkley model, whilst being more appropriate for numerical modelling,[76] require knowledge of the wall boundary condition and particularly slip or partial slip for their application. Quantification

of slip in conventional rheology is an involved process. The Mooney[77] approach has been the preferred route for many years but there are numerous cases in the literature of the approach failing to yield meaningful solutions, as analysed by Martin and Wilson[78]. Hatzikiriakos and Dealy[79] developed a simpler approach and there is some evidence of its applicability to ceramic pastes.[80] Other slip laws – often non-linear functions – have been reported (e.g. Ref. [81]) but reliable characterisation and prediction of this critical facet of paste extrusion is very much in its infancy (see, for example Ref. [82]). This knowledge is needed before simulation of the shear-dominated part of Eq. (2), i.e. P_2, can be performed *in silico*.

One shortcoming of the above approaches is that the paste is treated as a uniform plastic material even though these are multi-phase materials. Fundamental modelling of pastes as discrete particles surrounded by fluid, as now practised in simulation of suspensions, has been attempted by Yuan et al.[83]: particle motion was calculated using discrete element modelling (DEM) and linked to flow of the liquid through the particle matrix. This approach is hindered by computational complexity as current computing power limits us to simplified systems with significantly fewer particles than in practice so it is unlikely to be of practical use in the short term. An alternative approach is to modify soil mechanics models to accommodate the large strains experienced during extrusion and this has been demonstrated by Patel et al.[84]: the shortcoming is the need to generate material parameters but its power lies in being able to predict phase separation or difference in solid/liquid concentrations.

Some degree of phase separation is essential for paste flow as wall slip is often caused by the presence of a liquid-rich layer of material at the wall which deforms preferentially to the bulk material (sometimes called *apparent* slip: the layer is thin as evidenced by imaging[62,63]).

Phase separation at the macro-scale, often termed phase migration, is highly undesirable: in the extreme case the solid can act as a filter and the pressure developed in the liquid during extrusion causes it to drain from the material, leading to
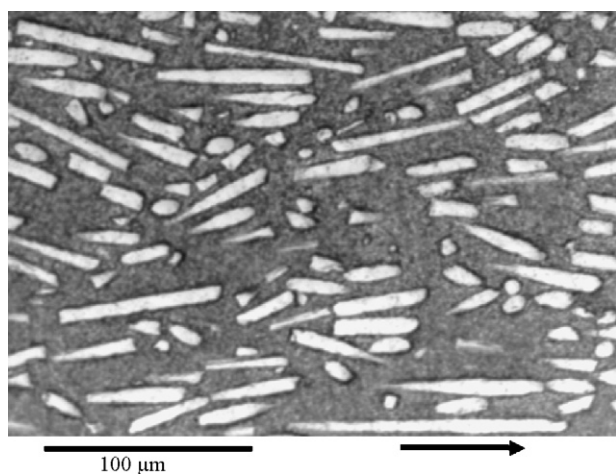

Fig. 4. Optical micrograph of Al_2O_3 matrix containing SiC fibre (20 vol.%) following ram extrusion through concentric cylindrical dies (barrel diameter 25 mm, die diameter 3 mm) at a ram velocity of 20 mm/min. Arrow shows direction of extrusion (from experiments described in [93]).

catastrophic failure. The propensity for phase migration is determined by formulation, with high solid loadings reducing the permeability of the particulate matrix and shear-thinning liquids reducing the flow rate at the relatively slow shear rates involved. However, these parameters also determine the pressures developed during extrusion and therefore the driving force for phase migration: there is therefore a need to optimise formulations for stable, non-separating flow. Testing of formulations propensity for phase migration can be performed by capillary extrusion[85] and squeeze flow[86]: linking the results to performance in complex geometries is not straightforward. Extrusion has been analysed by critical state theory[87] to develop threshold criteria and this is now being applied to detailed simulations[84] to link formulation, die geometry and operation to design out phase migration.

4. Composite extrusion of 0-3/3-0 form (notation defined in Ref. [88])

During convergent flow, the paste will experience various degrees of shear and extension depending on the configuration of the die.[89] This leads to alignment of non-spherical components in the paste and anisotropy in product properties. For example, shrinkage is often lower in the direction of extrusion and distortion through differential shrinkage is common with injected products.[90] Exploiting this alignment can be used to derive strongly textured grain growth by templating fine structures using plates or fibres. Messing's group at Penn State have pursued this approach with tape casting[91] and have mentioned extrusion[92] as an alternate fabrication route. In another example, rod-like ZnO particles have been extruded to create textured microstructures with reduced electrical resistivity compared to uniformly textured samples.[23] This alignment is most apparent when extruding fibre-loaded composite formulations[93] as shown in Fig. 4. The stresses developed by differential shrinkage in the composite formulation must be considered to avoid the normal issues which beset ceramic composite processing after forming.

This process has recently been used to create aligned porous materials by extruding carbon or polymer (nylon 66) fibres within a ceramic matrix with subsequent removal during the sintering cycle.[94,95] The porosity of these materials was up to ~40%[96] and they demonstrated good mechanical properties for this degree of porosity. Porosity exhibited strong directionality, as might be expected, and influenced permeability. Using a similar approach but replacing the fibre with deformable polymer particles allowed permeable structures with directional pore structures to be generated.[97]

5. Co-extrusion and co-injection processing

Virtually all practical paste processes exhibit laminar flow (Reynolds numbers well below unity), allowing co-extrusion and co-injection moulding to be considered for the manufacture of complex multi-component structures. Several papers have appeared over the past decade describing the manufacture of composites by plastic processing (1-3/3-1 composites[98,99] and 2-2[100–102]) for both structural and functional applications. Many
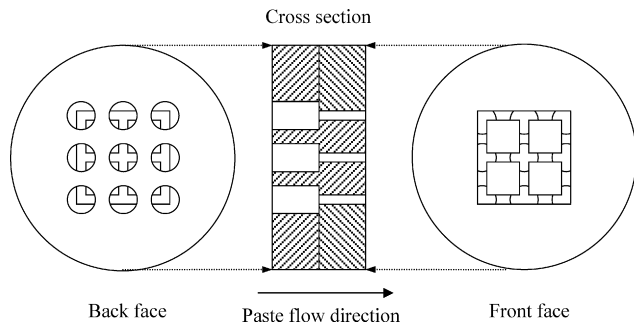
Fig. 5. Simplified honeycomb die structure.

Fig. 6. Honeycomb structure giving 2D negative Poisson ratio.

are prepared by the 'Rock Candy' approach,[103] whereby the structure is assembled on the macro-scale by hand and then swaged down using a ram extruder with an appropriately shaped barrel and die. The process can be repeated to gain even finer structures.[104] The method is labour intensive and prone to operator variance. As a result few examples of commercial application exist and the technique is only generally considered for high added value applications, e.g. manufacture of SOFCs[105] or ultra high cell density honeycombs.[106] A second method is available where the pre-form to be reduced is formed in a complex die in which continuous paste streams are brought together into the desired structure[107]; this is sometimes called the multi-billet process.[25]

The formation of high cell density honeycombs can be used to identify the limits of both the conventional and co-extrusion processes and illustrate the issues which may arise during manufacture. The conventional process for ceramic honeycomb manufacture was developed for the mass production of cordierite supports for the automotive catalyst market but is now additionally used to produce a wide variety of compositions for numerous applications.[108] A conventional honeycomb die is schematically illustrated in Fig. 5. It is possible to spark erode the entire assembly but in most cases the die is fabricated by a combination of conventional machining and wire cutting by spark erosion. Improved micro-machining technologies[109] allow much finer structures to be produced and our laboratory has recently achieved a cell density of 240 cells/cm^2.

With high precision dies the paste formulation must be considered carefully and mixtures free of large agglomerates to prevent flow related failure. For many applications there is a balance between the function of the structure and the pressures required to form it. As a result of these considerations and the difficulty of operating high cell density dies (blockage, cleaning and wear), cell densities of 140 cells/cm^2 or less are most common.[110]

In the conventional die manufacturing process the pin shape is limited to either squares, rectangles or triangles; these simple geometries suffice for most applications. One patent[111] refers to the improved thermal shock properties that can be achieved in honeycomb structures which develop a negative Poisson ratio. Fig. 6 shows an example of such a structure. Huang and Blackburn[112] manufactured a nylon die using rapid prototyping (selective laser sintering, SLS) and produced lengths of zirconia extrudate which demonstrated negative Poisson ratio. The cell
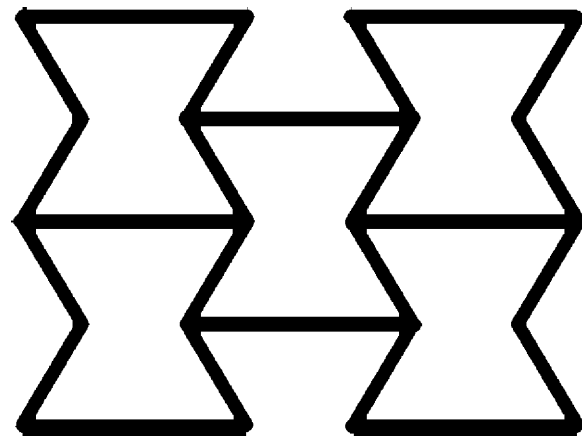
density was low (3.9 cells/cm^2) but with improved resolution in solid freeform fabrication, dies with greater wear resistance and finer structures should be possible.[113,114]

Van Hoy et al.[104] and Crumm and Halloran[115] showed that honeycomb structures can be formed by the lay-up and reduction extrusion process. By combining the required ceramic formulation with carbon-based formulations with similar rheology they formed a macro-unit cell of the desired honeycomb structure. Thermoplastic formulations are used to produce extended workability. The pre-form 'unit cell' is then reduced in cross-section by ram extrusion and the now long extrudate cut and re-assembled. The assembly is then re-extruded to form the green honeycomb. The process is shown schematically with simplified geometries compared to the original papers in Fig. 7. Increasing the reduction ratios or multiplying up the stacking process can give very fine structures. Crumm and Halloran[116] subsequently demonstrated that fine scale negative Poisson ratio structures can be produced by increasing the complexity of the original lay-up process. The lay-up process is time consuming and Buchtel and Earl[117] demonstrated a simplification for conventional honeycombs. They first extruded a cordierite formulated honeycomb using conventional procedures and then, after re-hydration of the extrudate, back-filled the holes with a deformable wax. The assembly was then re-extruded to reduce the dimension and increase the cell density. They achieved cell densities up to 432 cells/cm^2 by this route. In principle there appears to be no limit to the resolution of the cell structure that can be produced. However, with successive reductions, the honeycomb wall thickness approaches the particulate size and defects start to appear. A recent review[110] suggests that structures with around 1240 cells/cm^2 can be formed by modification of the Buchel and Earl route. By substituting glass for the particulate and drawing down while hot, structures of 2015 cells/cm^2 were reported: it should be noted that the glass must be inclusion free.

The above methods rely on the use of plug and laminar flow. Ram extrusion allows this process to occur with relative ease, as the contents are moved by the ram displacement. For the body to be uniform in cross-section, both crossways and lengthways, the co-extruded materials have to be rheologically matched. If
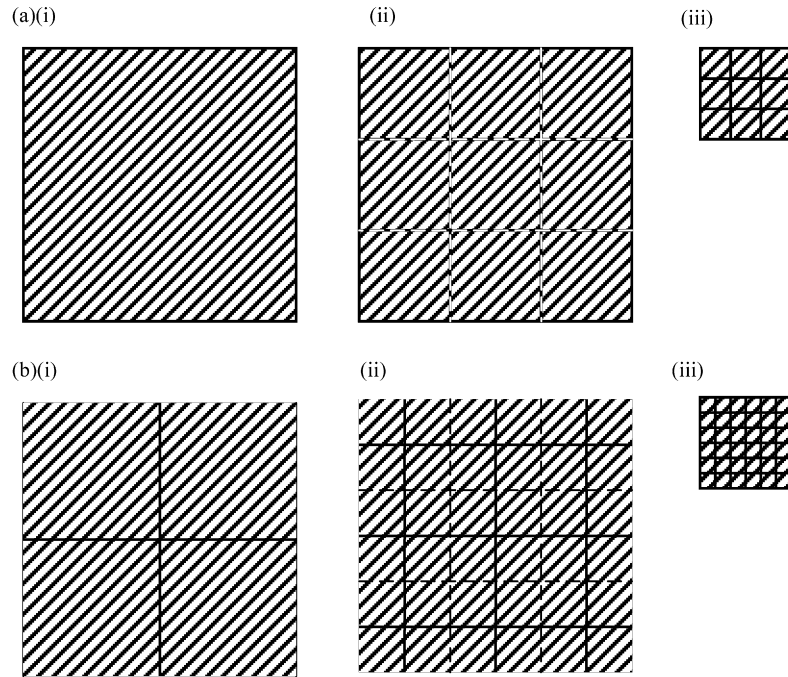
Fig. 7. Multi-billet route to manufacture of honeycombs: (a) type A, outer walls of ceramic paste (black) surrounding inner core of carbon paste; (b) type B, cross of ceramic paste (black) constructed with carbon paste support (hatched). (i) Original lay-up; (ii) second lay-up after first extrusion reduction; (iii) final structure after second extrusion (based on Refs. [104,115,117]).

one material is stiffer (more competent)[118] than another then flow instabilities can occur at the interface. In ceramics these defects have not been widely reported but uneven layer distributions have been observed when material with higher stiffness has exited the barrel preferentially.[100,119] It is also possible to develop fractures in the stiff layer due to the greater extensional flow of the less stiff material that surrounds it.[120] This process can be likened to that of boudinage formation in metamorphic rocks.[118] Some interesting defects have been observed in the co-extrusion of non-ceramic materials by deliberately employing different rheologies. An example is the 'Ovaici Necklace' observed in cold extrusion of chocolate.[121] Two chocolate polymorphs (forms IV and V) were co-extruded and in the process the outer shell of the stiffer material fractured to give a 'bead on a string' structure. We have attempted to replicate this defect in our laboratory with ceramic formulations but have only achieved spiral fracture to date.

The above defects are generated at the extrusion stage but one must remember that the post-extrusion processes of drying and sintering can also cause the growth of defects. Co-processed materials must either have matched drying and sintering characteristics or the structure must be able to withstand the stresses that develop during these stages. Defect-free structures are achievable by reducing the difference between the coefficients of thermal expansion of the layers. This is commonly achieved in the alumina–zirconia system by replacing the zirconia with zirconia-toughened alumina[122] or by using high toughness zirconia in thinner layers, as shown in Fig. 8.[123] Successful defect-free co-extrusion of ceramics is only possible if the microstructure, rheology, extrusion process, drying and sintering behaviour are all well defined. Fortunately many of the compo-
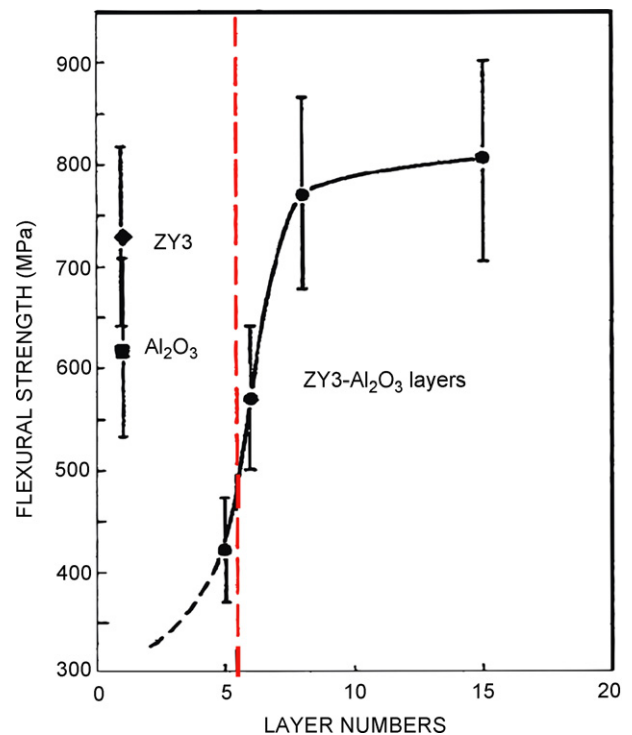

Fig. 8. Flexural strength as a function of number of layers in a 0.25 mm wall thickness tube with outside diameter 2.5 mm for interleaved 3 mol% yttria-stabilised zirconia and alumina. More than six layers gives strains below the critical strain required for zirconia layer failure. Long dashed vertical line indicates the number for defect-free structures predicted by theory (with modifications from Ref. [119,123]).

nents that might be made by co-processing are small and this naturally alleviates some of the difficulties in formulation matching as the magnitude of the interlayer stresses are much reduced.

The above discussion has centred on batch ram extrusion. A co-extrusion die offers the potential for continuous manufacture but if the die is to be fed by screw extruders the control of formulation becomes even more critical. In most screw extruders the flow rate is governed by the formulation as well as the extruder geometry and screw speed; the rate of delivery to the die can vary greatly, causing significant structural inhomogeneity when multiple streams are joined. This added complexity means that to the authors' knowledge no continuous co-extrusion of advanced ceramics is practiced commercially although co-extrusion of brick clays does occur.[124]

6. Control

Most industrial extrusion machines are operated by skilled personnel who rely on visual inspection methods to monitor the process. Some of the gross defects described above can be identified visually at the extrusion stage but micro-scale defects present in the green body can go undetected and are only evident post-drying, sintering or even at the test stage. Standard statistical process control methods monitoring extrusion speeds, pressures and temperatures can indicate deviant operating conditions that give rise to gross defects arising from poorly mixed pastes but not micro-scale features. The density of most technical ceramics precludes the use of many imaging techniques for on-line analysis of the green state so alternative methods for control and defect identification are required. West et al.[125] have reported the use of electrical impedance tomography to identify large voids or liquid zones in ceramic extrudates but more development is required to achieve the resolution required for ceramic products. Benchtop X-ray tomography[52] is now available for microstructural analysis but the imaging and reconstruction timescale preclude its use on-line.

Russell et al.[126,127] have demonstrated that analysis of die pressure sensor signals can be used to monitor the performance of extrusion of ceramic and other paste materials. They applied signal processing methods to filter out machine noise and track particular characteristics associated with surface fracture, agglomerate break-up, escape of air pockets and changes in paste homogeneity on both ram and continuous (screw) machines. The methods were demonstrated in real time on an industrial screw extruder[128] and indicate a promising route for monitoring product quality at relatively low cost compared to the time-consuming analysis of dried and fired products.

7. Conclusions

It is clear that plastic processes have much to offer in the development of complex high performance ceramic structures. Methods exist to aid in the development of new formulations and to predict the behaviour of the materials to allow process design and optimisation. These methods are, however, often semi-empirical with compromises aimed at supporting practical application. Full constitutive definitions of the behaviour are complex and still incomplete. Highlighted in this respect is the definition of slip behaviour. Additionally pastes are multi-phase and these phases may de-mix during processing leading to equipment and product failures. Instability in paste flow is not often studied, yet it is critical to performance, and reference to new work developing understanding in this area is reported. Despite these limitations understanding of the process has allowed the development of increasingly complex structures including high cell density monoliths and composite structures. The limitations of the methods used in their formation are discussed. The flexibility of the process and the fine structures that can be prepared are inspiring and the next stage must be to implement them in manufacture and to do this further understanding will be essential for process modelling and control.

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