Extrusion of alumina ceramic tubes with controlled bends

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An extrusion die was introduced in which the internal geometry of the die could be controlled through a simple computer interface to produce alumina tubes with varyingly controlled bends. The relationship between the paste rheology and the bending behaviour is addressed through a detailed analysis of the rheological flow behaviour, such as paste composition and viscosity as well as the nature of the liquid binders. It is shown that the curvature of the tube is controlled by paste composition and binder rheological properties and the degree of bend increases with increasing viscosity of the paste (the greater the solids loading the greater the curvature).

1. Introduction

Extrusion is an effective technique to produce ceramic or metal tubes to be used as multilayer structural/functional components for room/high temperature applications [1, 2], tubular electrolytes for use in solid oxide fuel cells (SOFC) [3, 4], in electrochemical energy storage batteries in the form of beta-alumina solid ceramic electrodes [5] as well as dense ceramic membranes that can be used to separate gas at elevated temperatures [6]. However, current extrusion technology is unable to produce ceramic tubes with varyingly controlled bends and shape flexibility. The mechanical wrapping technology (in green state) used in industry today causes formation of high residual stresses that lower the mechanical and structural properties of the bent tube during operations. Therefore, the present work introduces a new extrusion technique for making bent ceramic tubes using a single-step extrusion process to overcome the problems outlined above and to extend the capabilities of this type of processing to allow production of complex structures of non-uniform curvature with tightly controlled dimensional tolerances by the introduction of three computer-controlled independent pins set 120° apart around the axis in the die land [7, 8]. The effect of some rheological parameters, such as paste composition/viscosity, binder solution and rheological flow parameters on the curvature of the tube is investigated and some limitations of the process suitable for making such tubes have also been identified.

2. Experimental work

2.1. Die design and construction

The schematic diagram and the photo of the die used are shown in Fig. 1. The detail information of the design procedure is presented elsewhere [7, 8]. Briefly, the die and barrel were constructed largely from stainless steel. The outer diameter of the die orifice was 8 mm and the mandrel diameter was 4 mm (see also Fig. 1a and b). The position of the push rods along the die land could be changed. The die was fed from a 25 mm diameter barrel and ram assembly. Drive was achieved using a conventional screw driven load frame (Instron or Avery Denison). The die drive mechanism plays a significant role in making ceramic tubes with controlled bends. The push rods were driven by stepper motors (RS Components) with a low friction coupling between rod (non-rotating) and drive shaft (rotating). The paste flow pressure and the elasticity of the polymer liner ensured that the original die geometry was obtained when the pins were returned to zero position. Movement was controlled by motion control electronics (National Instruments) and Labview® software (National Instruments). Linear displacement transducers (RS components) working in parallel with step registration controlled the position of the pins. Bending in any direction was achieved by having three independently drivable pins set 120° apart around the die (see Fig. 1b and also c). By driving them partly or fully in, the obstruction caused the paste to flow around it and the tube to bend towards the inserted pin. Note, curvature in the

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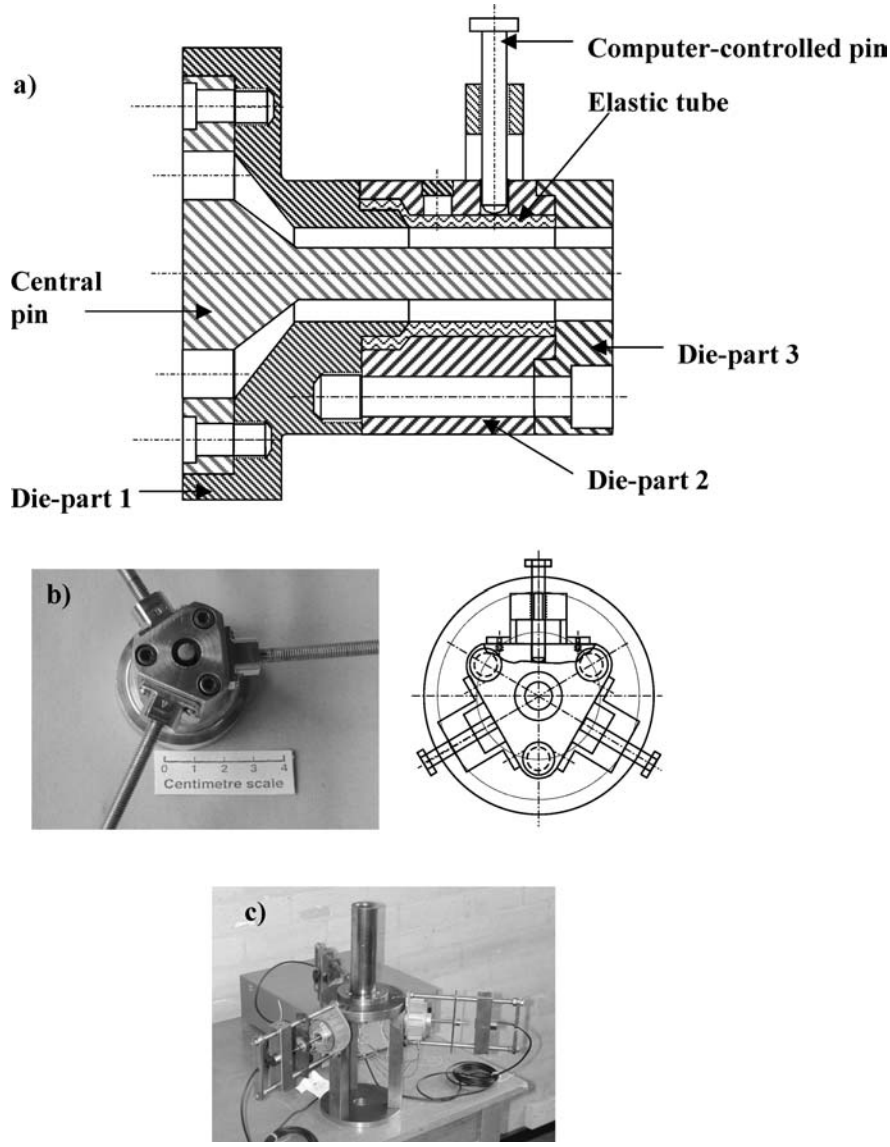

Figure 1 (a) Schematic (b) the assembled die and (c) the assembled extruder and drivers.

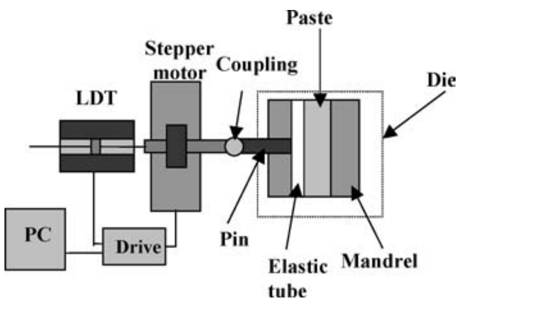

Figure 2 Drawing of one of the pin drive systems indicating the working principal for making bending tubes.

direction between two pins was achieved by inserting both pins to the desired degree. A 360° rotation of the stepper motor (73 steps) moved the pin 1.2 mm and rotating the motor 1.666 turns caused the pin to go from completely open to completely closed. A schematic of the drive chain on a single pin is shown in Fig. 2.

2.2. Rheological analysis

The rheology of the paste, as expected, proved to be a critical factor in curvature development [7, 8]. Two methods were employed to determine the character of the paste from data gathered by capillary flow. Conventional capillary practices were used to determine apparent viscosity and shear rate. Additionally the following Benbow-Bridgwater approach [9] was applied:

$$P = 2(\sigma_0 + \alpha\nu)\ln\left(\frac{D_0}{D}\right) + 4(\tau_0 + \beta\nu)\frac{L}{D} \qquad (1)$$

where P is the pressure drop through a die of circular cross-section, σ_o(the die entry or bulk yield stress), τ_o (the die wall shear stress), α (the die entry velocity coefficient) and β (the die land velocity coefficient) are the "four paste parameters" representing flow through a die of length L and diameter D from a barrel of diameter D_0 and V is the extrudate velocity. Elasticity was thought to be a possible influencing parameter in the development of curvature and here the elasticity of the binder systems was evaluated using oscillatory measurements. We were unable to measure the elasticity of the pastes directly and this is now an area of investigation.

TABLE I Paste formulations (w%)

Paste	Powder	%	Binder	%	Additive	%	Water (%)
1	Alumina F280	26.3	Clay	3	–	–	15.2
	Alumina F600	26.3	Starch	3			
	Alumina F1500	26.3					
2	Alumina RAC45B	78.9	Agar	1.9	Glycerol	0.2	19.0
3	Alumina RAC45B	78.9	Alginate Collatex A/RN	1.9	Glycerol	0.2	19.0
4	Alumina RAC45B	78.8	Methocel HPM50DS	1.3	Glycerol	0.2	19.7
5	Alumina RAC45B	78.8	Methocel HPM500DS	1.3	Glycerol	0.2	19.7
6	Alumina RAC45B	78.8	Methocel K15M	1.3	Glycerol	0.2	19.7
7	Boehmite Pural SB	49.9	Methocel K15M	5.0	Acetic acid	0.7	44.4

2.3. Paste compositions

During the experimental work, many paste compositions were evaluated. The majority was based around alumina or boehmite powders with different binder additions. The binders selected were agar, alginates, methylcelluloses and hydroxypropylmethulcellulose (HPMC) of different molecular weights and substitutions and clay. The boehmite compositions contained a proportion of methylcellulose and were peptized with acetic acid to develop the required plasticity. The key formulations are shown in Table I.

Pastes were prepared by premixing the formulation in a planetary mixer, followed by high shear mixing in a double lobe mixer to wet the surface of the ceramic and form a uniform paste. Mixing was standardized so that the pastes were comparable to one another. It was found that better mixing led to more stable flow and consistent curvature.

2.4. Curvature of the tubes

Curvature (k) of the extruded tubes (in both green and sintered form) was determined using $k = 8y/L^2$, where y is the deflection and L is distance over which that deflection has occurred (when L is not very small compared to k, curvature was calculated using $k = 2/y + 8y/L^2$). For direct comparison the measurements were made on the same component after the extrusion of a fixed length in the green state, after drying and after sintering, where appropriate. Curvature of the green tubes is reported in Table II for the pastes tested.

3. Results and discussion

The apparent viscosity of the pastes prepared and the Benbow-Bridgwater parameters are shown in Table II. The elasticity of the binder systems is recorded in Table II as the ratio between G' and G'' at 1 and 10 Hz and η* is recorded at the angular frequency of 62 rad/s to give an impression of binder viscosity (G'/G'' characterizes the stiffness of the paste). As shown in Table I, as the apparent viscosity increases, the value of the curvature increases. Pastes with higher binder viscosities provide higher k values and therefore result in higher die wall shear stresses (τ_o). For example, paste 4 (the softest paste) with lowest apparent viscosity value of 639 Pas, binder viscosity of 2 rad/s and binder elasticity of 0.24 (at 1 Hz) show a die wall shear stress of 0.02 MPa and the tube obtained from this paste provides a k value of 0.02 1/mm whilst paste 7 (the hardest paste) with a viscosity value of 7252 Pas, binder viscosity of 200 rad/s and binder elasticity of 2.30 (at 1 Hz) results in a die wall shear stress value of 0.32 MPa and provides an extruded tube with a k value of 1.44 1/mm as shown in Table II. It can be concluded from the Table II that the curvature of the tube is affected by the apparent viscosity of the paste which is controlled by the rheological properties of the binder system used.

The effect of the solids content of the paste on the curvature of the ceramic tube is also investigated. For this aim, a separate experimental procedure using pastes with different amount of binder concentration is followed and the results are presented in Fig. 3. The curvature of the tube and the stiffness of the paste (G'/G'') are plotted as a function of binder concentration. As shown in Fig. 3, the stiffness of the paste increases rapidly with increasing solids loading of the binder as predicted by the Kreiger-Dougherty equation (the curvature of the tube also increases with increasing binder solution concentration). Further experiments are being conducted to clarify this effect. Changing the molecular weight of the celluloses did not appear to change the curvature significantly even though the elasticity and viscosity of the binder changed markedly (the molecular weights of HPM50DS,

TABLE II Rheological and some physical data for the pastes prepared as well as the curvature values of the tubes in the green state

Paste	Binder	Apparent viscosity η_a (Pas)	σ_0 (MPa)	α ($MPasm^{-1}$)	τ_0 (MPa)	β ($MPasm^{-1}$)	G′/G″ (1 Hz)	G′/G″ (10 Hz)	$\eta*$ (Pas) at 62.5 rad/s	k (1/mm)
1	Clay + starch	680	0.25	1.48	0.03	0.47	3.24	4.55	400	0.26
2	Agar	910	0.17	1.70	0.01	1.01	5.25	6.00	–	0.04
3	Alginate	1818	0.22	2.37	0.03	1.25	0.03	0.26	–	0.08
4	HPM50DS	639	0.19	0.01	0.02	0.20	0.24	0.50	2	0.027
5	HPM500DS	906	0.32	0.03	0.02	0.30	0.75	1.95	40	0.032
6	K15M	2187	0.70	3.49	0.05	1.96	1.28	2.00	47	0.31
7	Boehmite	7252	1.02	4.97	0.32	4.98	2.30	2.48	200	1.44

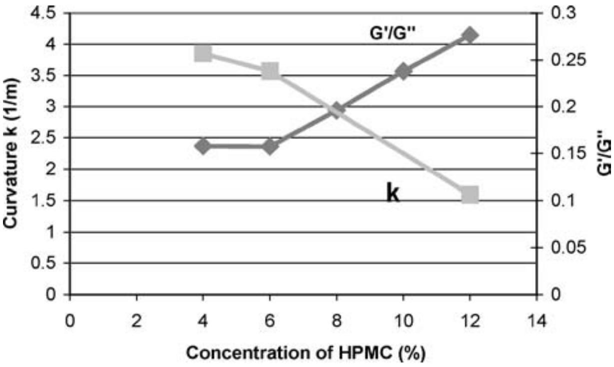

Figure 3 Curvature (k) of the tube in green form and G'/G'' (stiffness of the paste or elasticity of the binder used) dependence on the binder phase concentration in an HPMC bound alumina paste.

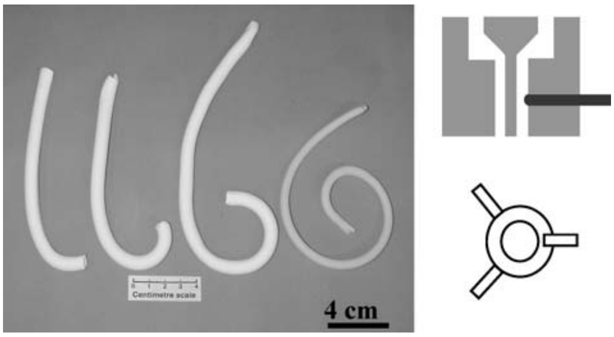

Figure 4 Extruded tubes with a pin inserted 50% and apparent viscosity increasing left to right. From left to right paste numbers in Table II: 2, 3, 6 and 7.

HPM500DS and K15 are 22,000, 100,000 and 120,000, respectively).

It should however be noted, that where the binder and paste properties are similar to those listed in Tables I and II, the behaviour lies close to the curvature values reported for the Methocel pastes as might be expected. Fig. 4 shows tubes extruded from the die with a constant pin insertion for various compositions increasing in stiffness from left to right. It can be seen that the stiffer paste shows more retained bending. The effect of gravity also plays an essential role during extrusion and the influence of gravity can be countered to a limited degree by progressive insertion of the pin during extrusion. Fig. 5 illustrates how this can be applied to produce a spiral. All three pins are inserted and withdrawn

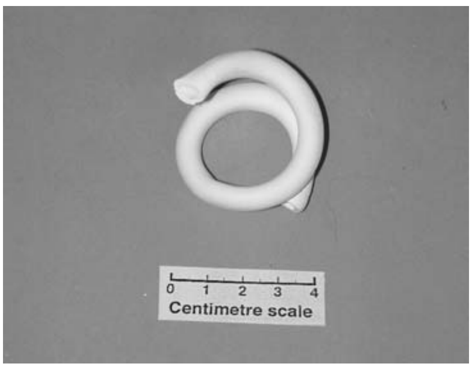

Figure 5 Spiral formed by progressive and cyclic pin insertion.

in sequence with progressive further penetration. The relationship of curvature with degree of pin insertion was also demonstrated elsewhere [7, 8] and it is found that the further the pin is inserted the greater the curvature. However, it should be noted that curvature is controlled by many factors, including time and rate of extrusion, paste formulation and die setting (the relationships between curvature and Benbow-Bridgwater parameters are also presented elsewhere [8]).

It is also noted from this work that the process leads to some difficulties with respect to dimensional tolerances that are not commonly found in other tube processing solutions. The deceleration of the tube on the concave side tends to lead to thinning of the wall on that side of the tube (pin side). The inner walls are typically 20% thinner in alumina and 27% in the boehmite materials in the green state. The clay bound pastes show almost no differences in wall thickness. The degree of bend (k) increased by typically 0.05 in the aluminas during drying. During sintering there is a tendency for the material to bend further. In the alumina materials k increased by 21% and in the boehmite materials by 37%. The linear shrinkage in the wall thickness was 13% in the alumina and 43% in the boehmite materials in the thicker section and 15 and 57% respectively in the thinner section.

The process was also modelled using CFX-4, where only one pin obstruction was placed into the tube flow as a typical plot from CFX-4 is shown in Fig. 6. The paste flow was modelled using a Herschel-Bulkley non-Newtonian model. The boundary wall conditions were no slip but better solution for the wall conditions are also being investigated. The results were calculated for full and partial insertion of the pin. Velocity vectors were plotted for the flow. For the system developed here, the flow is seen to be much reduced on the pin side of the tube, particularly just down stream of the pin. Flow becomes more uniform the further down stream from the pin and so one would predict that curvature would be greater the closer the pin to the die exit. In reality this proved to be true, but when the pin was too close to the end of the die, the tube would not fully re-form and a compromise was required.

From the experimentation carried out, it seems that if the process variables are controlled in an exacting way the process is capable of giving reproducible results. When soft pastes are used (such as paste 1) the major difficulty faced in the process is gravity. A suggested solution was extrusion into a mutually buoyant suspension. One possibility for this is bromoform but this was not a practical solution to the problem due to the carcinogenic nature of the material and even then the density is rather low compared to that of the alumina pastes being extruded. As an alternative setting mechanism, the pastes prepared with ammonium alginate were extruded into $CaCl_2$ solution in order to gel the binder phase. This showed promise but the reaction rate was too slow and the resultant material was unable to support its own weight. The solution may be to move to a thermoplastic binder system and this is the subject of a future work.

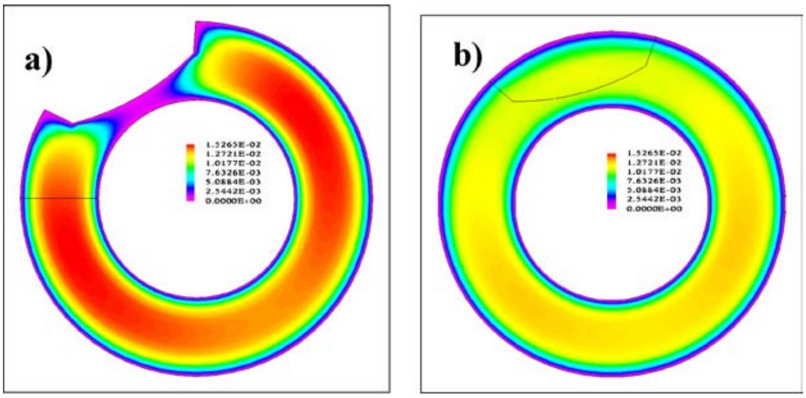

Figure 6 CFX-4 velocity images of flow through a partially blocked die, on the left the point of blockage and on the right the velocity profile at the exit showing slowing in line with the pin.

4. Conclusions

A die was manufactured in which the internal geometry of the die could be controlled through a simple computer interface to produce bent tubes. The tubes could be bent in any direction and thus a wide variety of shapes are produced. The relationship between the paste rheology and the bending behaviour is addressed. It is shown that the curvature of the tube is directly related to the nature of the paste which is controlled by binder rheological properties. It is also shown that there are some simple rules to be followed when ceramic tubes with controlled bends are extruded: (a) the greater the solids loading the greater the curvature and (b) the curvature is influenced by the binder solution concentration. If very soft pastes are used, the influence of gravity needs to be overcome in some way and this is the subject of the current work. It is also noted from this work that the process leads to some difficulties with respect to dimensional tolerances that the deceleration of the tube on the concave side tends to lead to thinning of the wall on that side of the tube (pin side).

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