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Extrusion of ceramic tubes with complex structures of non-uniform curvatures made from nano-powders

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Abstract

A computer-controlled extrusion technique was introduced for making ceramic tubes (with a wall thickness of 2 mm and external diameter of 8.0 mm) with tightly controlled bends from ceramic pastes prepared from nano-size boehmite powders. Firstly, the rheological flow behaviour of the paste and related flow parameters were calculated in order to show their effect on the curvature of the tubes. Secondly, an extrusion die with three adjustable pins set 120° apart, an extrusion device and a computer program were developed. The bending of the tube is adjusted automatically through stepper motor-driven pins and 2-D or near 3-D shapes are produced by altering the geometrical flow conditions during the paste extrusion. The computer program developed allows the extrusion time to be controlled for any desired die configuration, i.e. the time between the movement of the pins in any direction, therefore, this adjustment alters the geometrical configuration for flow, inducing bending in the tube. Finally, the effects of the extrusion speed and geometrical flow conditions on the curvature and shape of the tubes were reported. It is also shown that complicated shapes, such as near helical tubes or spiral ceramic tubes can be produced by moving the pins in an appropriate manner.

Keywords: Extrusion; Boehmite; Rheology; Tubes

1. Introduction

During the last decade, ceramic tubes have become fundamental components required by industry for variety of applications, such as single or multilayer structural/functional components for room/high temperature applications,[1,2] tubular electrolytes for use in solid oxide fuel cells (SOFC)[3,4] and in electrochemical energy storage batteries in the form of beta-alumina solid ceramic electrodes.[5] This new generation of batteries, so called "β-batteries" are designed for automotive applications in certain types of hybrid electric vehicles and load leveling applications. During service, the operation temperature could rise up to 350 °C under very corrosive conditions due to the composition of the electrolyte solution which may contain NaCl, H_2SO_4, KOH or NiOOH. The electrolyte materials suitable for this particular application should be stable and low resistance conductor for the related ions and a high resistance insulator for electrons.[5] All these requirements can only be met by ceramic electrolyte of tubular shape which makes the β-$A1_2O_3$ ceramic tubes the ideal candidate materials for that particular application. Ceramic tubes have also been identified as essential materials for dense ceramic membranes that can be used to separate gas at elevated temperatures.[6] For example, membrane tubes made of $SrFeCo_{0.5}O_y$ (SFC2) have been used for partial oxidation of methane to produce syngas ($CO + H_2$) in a methane conversion reactor operating at 850 °C leading to a significant cost reduction in oxygen separation.[7]

Extrusion technique has been widely used to produce such straight tubes in a cost-effective way. However, current extrusion technology is unable to produce ceramic tubes with varyingly controlled bends and shape flexibility. The mechanical wrapping technology used in industry today causes formation of high residual stresses that lower the mechanical and structural properties of the bent tube

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during operations. There are also issues with the retention of the tube cross-sectional uniformity. Therefore, the present work aims to make ceramic bend 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.[8,9]

2. Experimental work

2.1. Experimental equipment design

The computer controlled extrusion facility suitable for making ceramic tubes with varyingly controlled bends was designed to comprise four main features; (a) the die, (b) extrusion stand attached with three stepper motors and linear displacement transducers, (c) a displacement control electronic unit (universal motion interface, UMI) and (d) a software program (created within Labview™) that controls the extrusion parameters and die geometry. Small changes in the die alignment causes curvature in the extrudate and based on this principle, a die with changeable internal geometries and is capable of bending the extrudates into any desired shape while keeping a uniform cross-section was used as the main concept of making ceramic tubes with bends is shown in Fig. 1a. For this aim, an extrusion die was designed and the schematic diagrams are shown in Fig. 1b and c. The actual photo images of the developed die are shown in Fig. 2. The parts of the die are shown in Fig. 2a. An elastic tube forms the outer wall of the exit end of the tube-forming die, deformed by pins that can be moved in and out as shown in Fig. 2b. Note that the independent pins set 120° apart around the axis in the die land as shown in Fig. 2c.

The photo image of the designed extrusion stand with three stepper motors are attached around the stand is shown in Fig. 3a. The adjustable pins are driven by stepper motors (RSSM2, RS Components, UK), which are controlled through a motion interface driven by a computer program (Labview, National Instruments, UK). The linear displacement transducers (LDTs) which have a travelling distance of 2.5 cm (forward or backward) are inserted into a movable steel blocks and connected to the driving rods as shown in Fig. 3b. These transducers have a non-rotating spring return actuator running in a precision linear ball bearing. This arrangement provides a repeatability of measurement/movement of better than 0.15 μm. All gauging types are fitted with a 3 mm dia tungsten carbide ball end and the ball is carried in a removable stylus which is mounted in a deep female thread at the end of the actuator (see also Fig. 3b). The LTDs and the driving rods were accurately aligned to be on the same axis. The electronic motion interface used is connectivity accessory that can be used with motion control boards for up to four or six axes of simultaneous or independent control. This interface connects to the motion controller via a single interface cable and controls the movement of the stepper motors and LDTs based on the information given by the computer software. The experimental set up comprising the die, extrusion stand with stepper motors and LDTs as well as the motion interface is shown Fig. 3c.

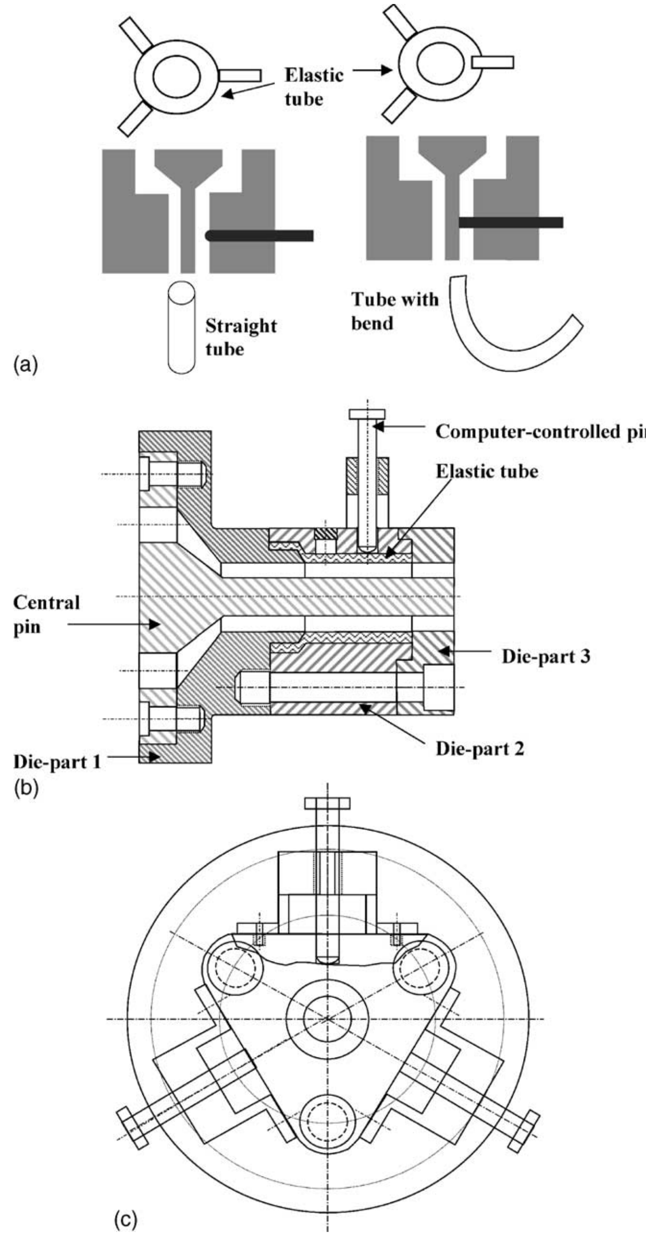

Fig. 1. Schematic representation of (a) basic concept of making ceramic tubes with bends; (b) longitudinal and (c) cross-sectional views of the die used.

The computer program developed allows the extrusion time to be controlled for any desired die configuration, i.e. the time between the movement of the pins in any direction. Using the software program each driving rod can be moved in or out as many times as required and at the same time the time between each step can be controlled and altered. The

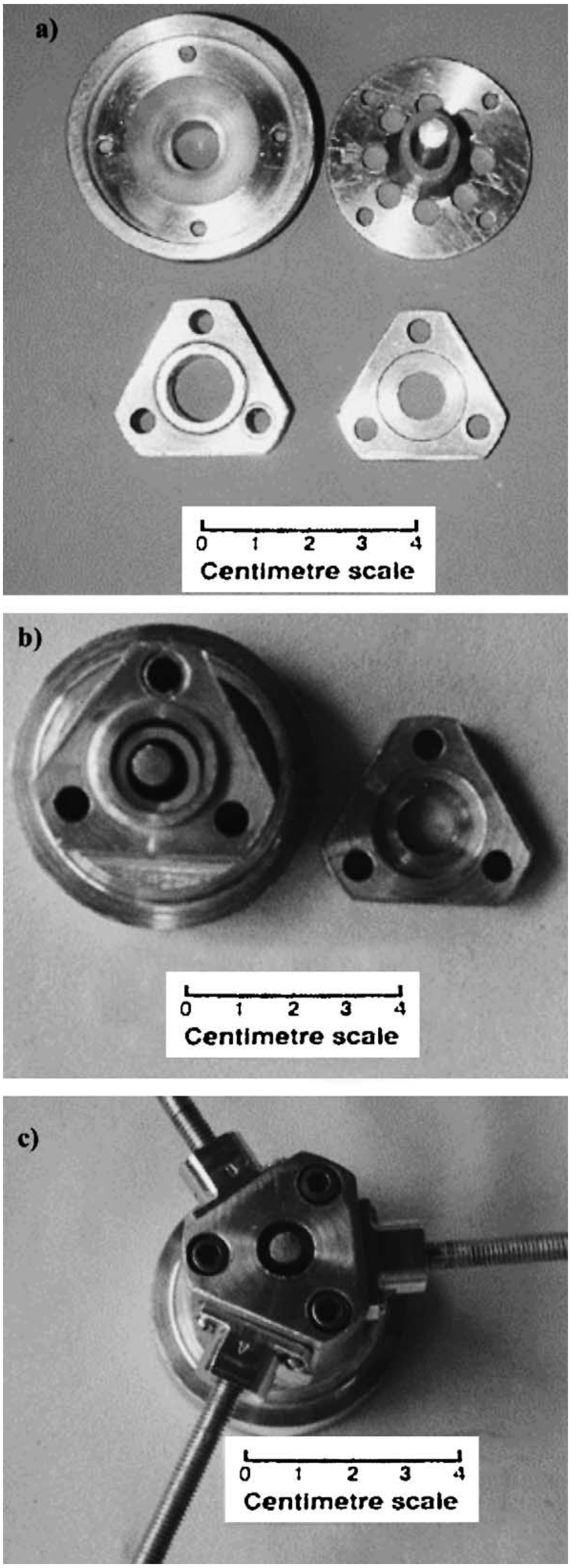

Fig. 2. Photographic images of (a) the parts of the die, (b) the die part assembled and location of the elastic tube, (c) the die fully assembled with driving rods in place.

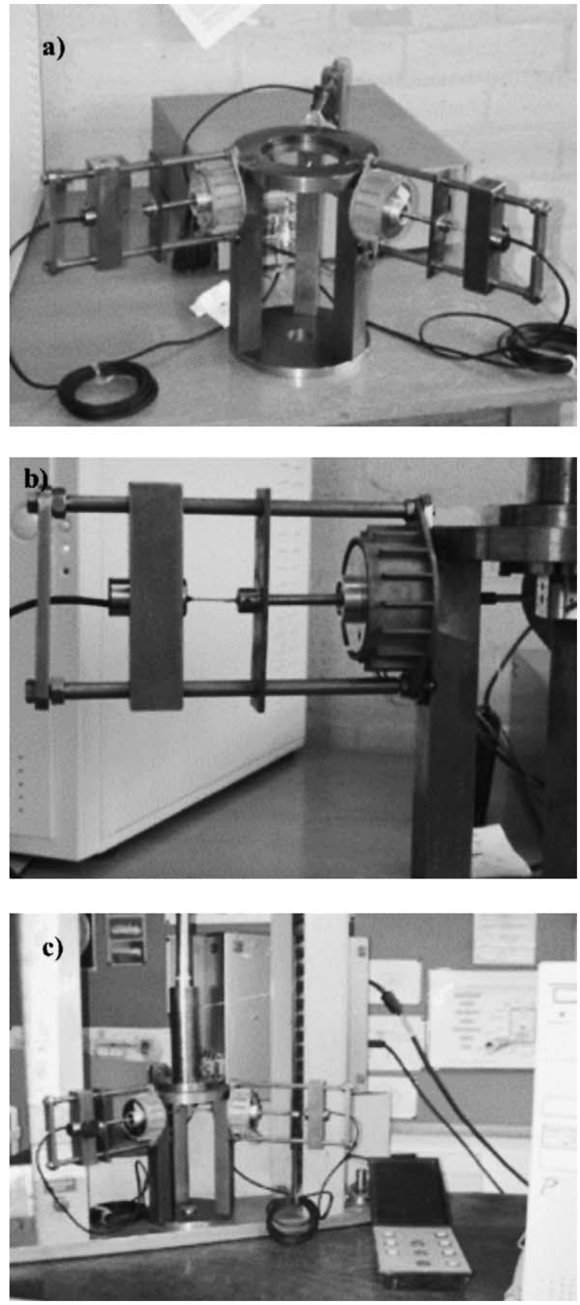

Fig. 3. Photographic images of (a) the designed stand with the stepper motors attached, (b) the location of the linear displacement transducers and (c) the assembled instrument showing the barrel, stepper motors and the location of the motors LDTs and stand.

speed of the movement of the pins between each cycle (in or out) can also be controlled with a very sensitive manner as milliseconds. All the pins can be returned to their original zero position (starting position when all the pins are out, i.e. when they do not touch the elastic tube) at any time. In summary, the travel distance, direction, waiting time and speed of each pin are all controlled very accurately by the software program. Three pins can also be moved altogether (in or out) or individually for any period of time required and to varying degrees. This adjustment alters the geometric configuration for flow, inducing bending in the tube. Thus, with the three adjustable pins set 120° apart, it should be possible to bend the tube in any desired direction, as shown in Fig. 1a. In these experiments the die produces extrudates with a wall thickness of 2 mm and external diameter of 8.0 mm assuming no die swell. The position of the pins was known by using miniature linear displacement transducers (LDTs) allowing the computer to reference the position of the pins as shown in Fig. 3b. In the construction of the die a complete rotation (360°) of the stepping motor moves the pin by 1.2 mm. Thus, rotating the pin by 180 or 90° moves the pin by 0.6 and 0.3 mm (in or out), respectively. The pins are named X, Y and Z.

2.2. Materials and paste preparation

The water-based paste was prepared using a very fine boehmite powder (Pural SB, Condea Chemie GmbH, Germany) with an average particle size of 50 nm and a cellulose ether based binder (Methocel K15M, Dow Deutschland Inc., Germany). During the manufacture of cellulose ethers, cellulose fibers are heated with caustic solution which in turn is treated with methyl chloride, yielding the methyl ether of cellulose. The fibrous reaction product is purified and ground to a fine and uniform powder. The binder solutions made of commercially available water soluble cellulose ethers have the unique property of forming a 3-D gel structure under elevated temperatures and the gelation is reversible and the solution liquefies upon cooling. At low temperatures, the molecules are hydrated with water and strong hydrogen bonds hold the polymer structure together. The binder (Methocel K15M) used in this work has a molecular weight of 120,000. Methocel cellulose ethers allow precise control of rheology in ceramic mixes, permitting broader operating ranges. Lubricity reduces energy consumption and die wear and promotes smoother surfaces. It also permits extrusion of extremely delicate, thin-walled shapes without sag or deformation. Glycerol and acetic acid were added (along with water) as lubricant and dispersant, respectively. The flow chart for the paste preparation is given in Fig. 4. Premixing of the pastes was carried out in a Kenwood planetary mixer to achieve bulk dispersion. The boehmite powder and binder were placed in the mixing bowl and liquid phases were added during mixing. The resulting paste-like dough was transferred to a water cooled Werner and Pfleiderer LUK 3 III-2 VAK double lobe mixer to wet the surface of the ceramic and introduce shear. The mixing time was set at 20 min to achieve a well-dispersed homogeneous mix with no agglomerates present. The resulting paste was immediately put in a plastic bag and sealed to avoid moisture loss until use. The aqueous boehmite paste prepared was very stiff and has a viscosity value of 7252 Pa s at a constant shear rate of 62 s^{-1}. The rheological behaviour of the paste prepared was characterised using a capillary rheometer (Rosand, UK). Three dies with different L/D (length/diameter) ratios were used. The ram speeds ranged from 125 to 0.5 mm/min and

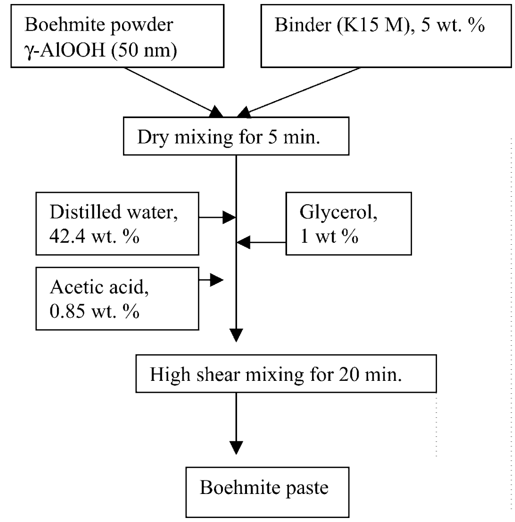

Fig. 4. Flow chart for the preparation of boehmite ceramic paste.

the load at each-pre-set velocity was recorded. For the purpose of this work the flow curve of the pastes was determined using conventional capillary flow practices. The data presented in the present work are corrected for entry effects (Bagley corrections), but not for flow behavior (Rabinowitsch correction to shear rate is not applied). Additionally the following equation was applied:[10]

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

where P is the pressure drop through a die of circular cross-section, σ_0 (the die entry or bulk yield stress), τ_0 (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.[10]

The degree of curvature of the tubes (k) was measured using the following equation:

$$k = \frac{8y}{L^2} \qquad (2)$$

where y and L are the deformation and the length of the extrudate.

3. Results and discussion

3.1. Rheological properties and modeling

The extrusion pressure (P) or pressure drop dependence on L/D ratio (length/diameter) of boehmite paste for different ram velocities is given in Fig. 5a. The Benbow–Bridgwater paste parameters (four-parameter model) were calculated using Eq. (1) and re-inserted into the equation and then the model curves obtained being plotted in Fig. 5b indicating the relationships between pressure and extrusion velocity

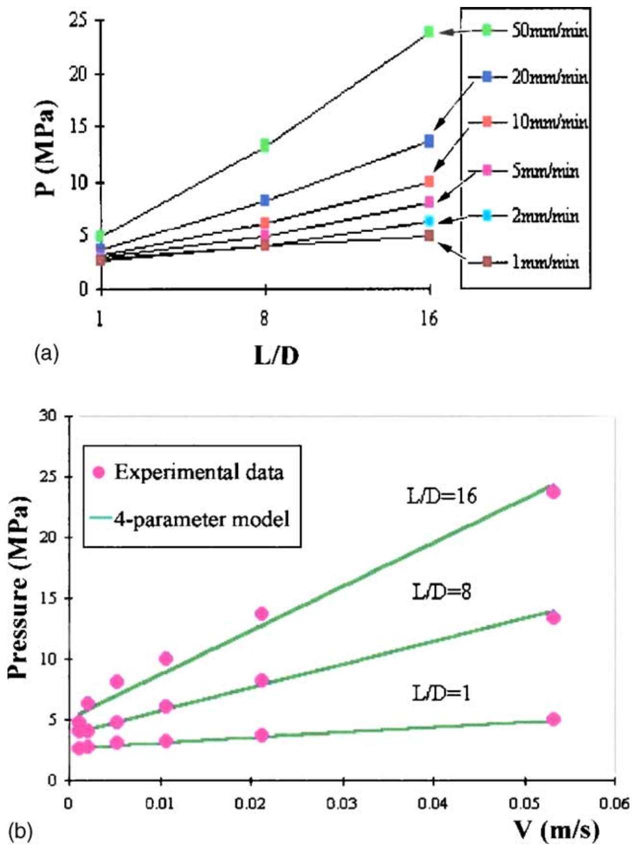

Fig. 5. (a) The extrusion pressure (P) or pressure drop dependence on L/D ratio (length/diameter) of boehmite paste for different ram velocities and (b) the model curves obtained from the Benbow–Bridgwater paste parameters calculated using Eq. (1) showing the relationships between pressure and extrusion velocity for three different L/D ratios.

for three different L/D ratios. As shown in Fig. 5b, the Benbow–Bridgwater model with four paste parameters provided a very good fit to the experimental data obtained from the extrusion trials. The calculated boehmite paste parameters are also given in Table 1. The data plotted in Fig. 5 represent compaction of the paste within barrel and die and also show that as the extrudate velocity increases, the extrusion pressure increases. This is due to the formation of the paste at the die entry and frictional shearing as it passes through the die land. Fig. 5 also shows that the gradient of extrusion pressure versus ratio of die length to diameter profile for a given die system increases with increasing extrudate velocity. It was also observed that the pressure increases steadily during extrusion for the slower extrudate velocities, indicating an increase in magnitude of the yield or shear stresses brought about by decreasing water content. At higher extrudate velocities, the extrusion pressures are fairly constant or steadily decrease due to decreasing contribution of the paste-barrel wall shear stress as the compact height decreases.

Table 1
Calculated Benbow–Bridgwater four-parameters using Eq. (1)

	σ_0 (MPa)	α (MPa s/m)	τ_0 (MPa)	β (MPa s/m)
Boehmite	1.02	4.97	0.32	4.18

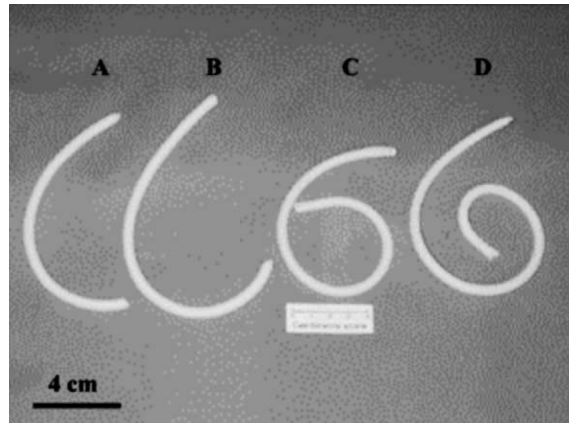

Fig. 6. Photo images of the boehmite tubes in green state showing the effect of the die geometry on the curvature of the bent tubes for a constant extrusion speed.

3.2. Extrusion of the tubes with bends

The effect of the die geometry on the curvature of the boehmite tubes in green state for a constant extrusion speed of 20 mm/min is shown in Fig. 6. The photograph marked A in Fig. 6 was produced by the movement of only one pin with various degree of turn whilst the other two pins were kept constant at their original starting position. Tubes marked A, B, C and D were extruded with rod Y set with rotations of 45° (0.15 mm forward), 90° (0.3 mm forward), 180° (0.6 mm forward) and 360° (1.2 mm forward), respectively. It is seen from Fig. 6 that as the degree of turn is increased forward the degree and nature of curvature becomes more significant and the shape of the extruded tubes changes from L shapes to G shapes for the movement of 45 and 360° turn of the pin, respectively.

The effect of the extrusion speed on the curvature of the C shapes boebmite tubes for a constant die geometry is shown in Fig. 7. The photographs of the C shape tubes in green state

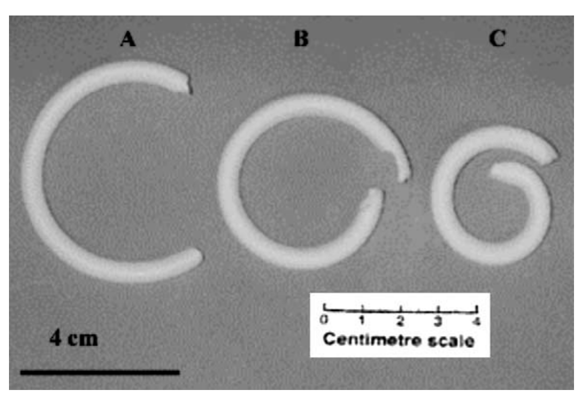

Fig. 7. Photo images of the boehmite tubes showing the effect of extrusion speed on the shape and curvature of C shape extrudates.

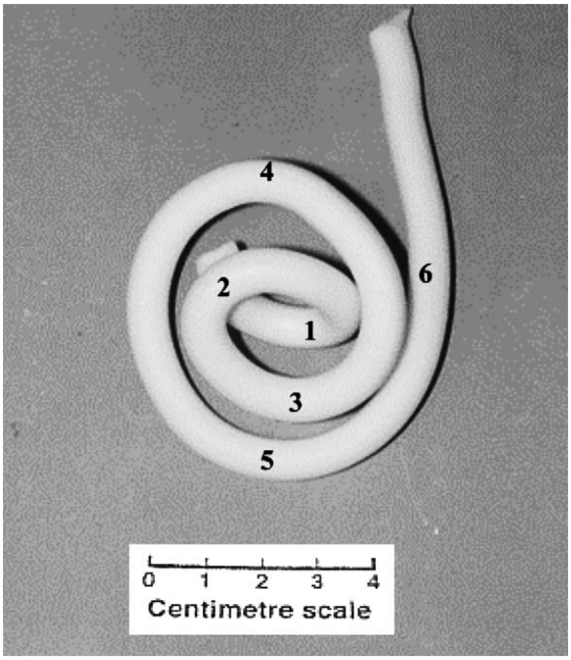

Fig. 8. Photo image of the boehmite tube with near spring helical shape showing the effect of sequential application of X, Y, and Z on the shape and curvature.

shown in Fig. 7 were produced by moving the Y pin 270° forward (whilst the other pins were kept constant) under different extrusion speeds. The first tube of C shape (marked A) was extruted with an extrusion speed of 30 mm/min while tubes of B and C were produced using extrusion speeds of 20 and 10 mm/min. It is seen from Fig. 7 that the curvature of the tubes becomes greater as the extrusion speed decreases. Fig. 7 also shows that the size and the shape as well as the degree of curvature of the boehmite ceramic tubes can easily be manipulated by altering the die geometry the effect of the paste rheology on the curvature of the tubes is presented elsewhere.[11]

The successful results in extruding boehmite tubes with near 3-D shapes using the three pins with different combinations are presented in Figs. 8 and 9. The tube with multidirectional curves shown in Fig. 8 was produced using the pin combinations detailed in Table 2 and an extrusion speed of 15 mm/min. At point 1, only one pin (Z) was moved 1.2 mm forward (equals to a 360° turn) and tube did bend opposite to the pin direction. During the second cycle (point 2), X and Y pins were moved forward 0.3 and 1.2 mm, respectively (whilst pin Z was returned to its zero position) resulting in the formation of near helical shape. At point 3, three pins were moved forward at the same time with different traveling distances for each pin as given in Table 2, in order to create 3-D tube as shown in Fig. 8. Different die geometries were created at the points 4 and 5 leading to the formation of helical shapes with different curvatures. It should also be noted from Fig. 8 and Table 2 that, straight boehmite tube was extruded when all the three pins were at their original starting point there is no contact between the pins and the plastic tube at this configuration, i.e. at the point 6. On the other hand, the degree and direction of the curvature of the tube can easily be changed and controlled using different pin combinations as shown in Fig. 9 indicating that greater bend was induced by greater insertion of the pin. By sequencing

Table 2
Positions of the pins for making complex boehrnite tube as shown in Fig. 8

Points on the tube in Fig. 8	Position of the pins, degree (mm)		
	X	Y	Z
1	0	0	360 (1.2)
2	90 (0.3)	360 (1.2)	0
3	0	90 (0.3)	180 (0.6)
4	45 (0.3)	180 (0.6)	90 (0.3)
5	45 (0.15)	45 (0.15)	180(0.6)
6	0	0	0

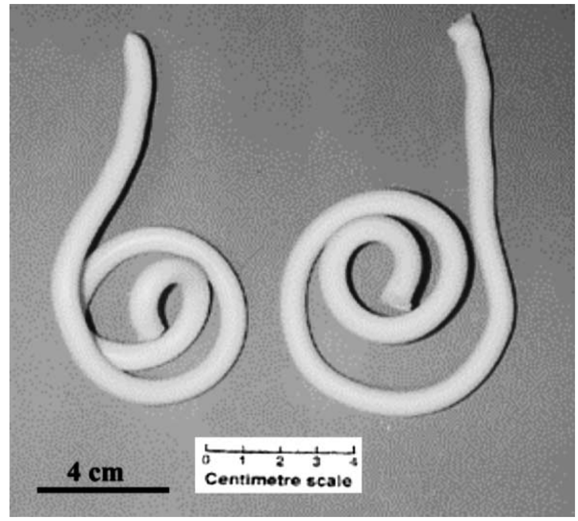

Fig. 9. Photo images of boehmite tubes with 3-D shapes showing the possibility of making ceramic tubes with very complex shapes.

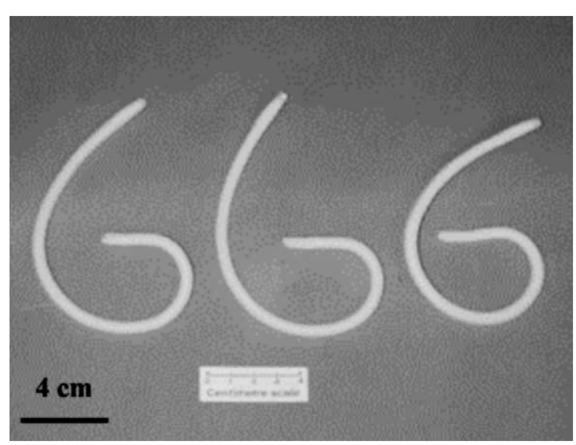

Fig. 10. Photo images of boehmite tubes showing the repeatability of making bend tubes using the developed extrusion technique.

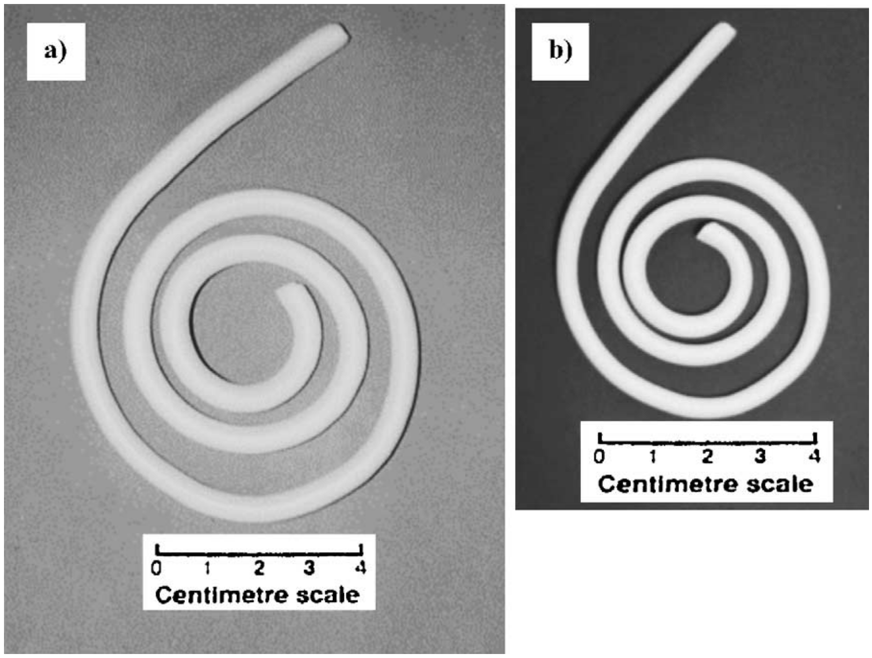

Fig. 11. Photo images of boehmite tubes with helical shape showing the effect of sintering on the structural integrity of the component produced; (a) green structure after air drying for 1 day and (b) sintered microstructure after sintering at 1500 °C for 2 h.

the motors Z–Y–X–Z, spiral geometries were produced as shown in Figs. 8 and 9.

When ceramic tubes with various curvatures are produced some critical issues, such as repeatability and structural integrity after sintering need to be addressed and effectively solved. The green microstructures of boehmite tubes shown in Fig. 10 were extruded using the same extrusion die geometry and speed leading to the formation similar curvatures and shapes. Only one pin (Y) was moved forward by 180° with an extrusion speed of 25 mm/min in order to produce the tubes shown in Fig. 10. Therefore, it can be concluded from Fig. 10 that the developed extrusion technique is able to produce repeatable products.

In order to investigate the effect of the sintering on the structural integrity of the boehmite tubes, a helical extruded was produced and sintered at 1500 °C for 2 h. The green and the sintered microstructures of the helical tube are shown in Fig. 11a and b, respectively. The overall shape in green state was maintained in sintered form as shown in Fig. 11b and there was no shape distortion or crack formation especially where the curvature formation has taken place due to high linear shrinkage of about 26%. However, the effect of the sintering on the curvature of the tube was also investigated and the k (1/mm) values for the tubes in green and sintered state were given in Table 3. It is seen from Table 3 that there is an increase in k value from green state ($k = 0.272$ 1/mm) to sintered form ($k = 0.373$ 1/mm). This is well expected as the density where the pin is touching the elastic tube during extrusion to make it bend to that particular direction is higher due to compaction than the other part of the tube leading to the higher k value where the curvature is formed in green state, on sintering.

It should also be noted that boehmite tubes with different geometries produced in this work exhibit very good surface finish with no damage due to wear indicating that the boehmite paste does not show any dewatering behavior (or significant liquid phase migration) and therefore the presence of homogeneous and well-mixed paste as the extrusion proceeds. This is very important because if water migrates into the extrudate, this will result in non-uniform of water content across the tube resulting in the formation of non-uniform green microstructure. On sintering, that kind of non-homogeneous green structure will deform and inevitably excessive sintering cracks will develop. But as shown in Fig. 11, although a boehmite tube that contains many bends did not contain any sintering deformation or cracks on the surface after sintering proving the effectiveness of the present technique in

Table 3
The influence of sintering on the degree of curvature (k) of the boehmite tube shown in Fig. 11 (the tube was sintered at 1500 °C for 2 h)

	Green state			Sintered		
	L (mm)	y (mm)	k (1/mm)	L (mm)	y (mm)	k (1/mm)
Boehmite	23	18	0.272	17	13.5	0.373

preparing homogeneous aqueous paste from nano-size powders and ceramic tubes with homogeneous structural integrity.

4. Conclusions

Boehmite ceramic tubes with tightly controlled bends and complex shapes were produced using a novel computerised-controlled extrusion technique. The influence of extrusion velocity and die geometry on the curvature of the bending tubes, where the bend was induced by a deformable die, was examined. It is shown that ceramic tubes with C, L or G shapes as well as more complicated shapes such as helical or near 3-D shapes can be produced through stepper motor-driven pins set 120° apart around the axis in the die land. Required shapes and the direction of the bending can then be controlled by altering the geometrical flow conditions during the paste extrusion. The shape of the tube and the degree of bend can be altered and controlled by changing the die geometry via pins that are inserted and withdrawn in a predetermined sequence and the speed of extrusion. The produced boehmite tubes with complex shape and curvatures are capable of maintaining their shape after sintering at 1500 °C for 2 h despite of the high shrinkage of 26%.

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