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Optimisation parameters for the extrusion of thin YSZ tubes for SOFC electrolytes

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Abstract

Thin wall thickness (0.25–0.35 mm) tubes, as tubular electrolytes of solid oxide fuel cells, were successfully fabricated from yttria stabilised zirconia (YSZ) by way of extrusion. Water-based additives and organic additives were studied. An economic and practical process was developed to achieve smooth, linear, and dense ceramic tubes with 2.7–2.8 mm diameter. The microstructures of the selected tubes were examined. This paper describes the fabrication procedure, formulations and optimisation parameters for successfully extruding thin YSZ tubes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Extrusion; ZrO_2; Fuel cells; Tubular electrolyte; Microstructure-final

1. Introduction

Yttria-stabilised zirconia (YSZ) is a typical electrolyte material for use in solid oxide fuel cells (SOFC).[1–3] Extruded thin walled tubes have been examined as possible electrolyte configurations by a number of authors.[4,5] Extruded tubes have a number of advantages over traditional tubular electrolytes in that they have superior mechanical properties, withstand thermal shock, and they are very cheap and relatively easy to fabricate. The bending strength of the YSZ tubes with 2.4 mm diameter and a wall thickness of 0.2 mm, was reported [6] as 407 MPa, while the strength of 0.56 mm rods was 734 MPa. Although tubular electrolytes made of YSZ can be purchased from several companies, such as Viking Ceramics Limited (Denmark), Coors Ceramics (USA), and Zircoa (USA), little information appears in the literature about the manufacturing technique in detail.

Extrusion is a very economic process for making objects with constant cross section such as rods and tubes. The selection and use of additives play an important role in the extruding process. Chevalier et al.[7] modelled the behaviour of the paste made of a ceramic powder (TiO_2). The organic removal process was investigated by Sproson and Messing.[8] For binders to be useful in extrusion, their rheology, burnout behaviour, and green strength properties must be known. This research report describes the optimisation fabrication procedure and parameters for successfully extruding thin YSZ tubes.

2. Materials and experimental procedure

Eight mol% yttria stabilised zirconia (8YSZ) powder (TOSOH Corporation, Japan) was used in this work. Other materials used were B-1501 and B-1502 (Dramax™, Rhom and Haas Formulation Chemicals), PEG-400 (Union Carbide Co., Danbury, CT), and AMP-95 (Angus Chemical, Buffalo Grove, IL); HYPERMER® KD1 (ICI, America), acetone, PVB (Polyvinyl butyral, Aldrich Chemicals, USA), and Octanol-1 (BDH, UK).

The procedures used to extrude YSZ tubes involve various processing steps as shown in Fig. 1. The commercial YSZ powder was heat treated at 900°C for 2 h to reduce the powder surface area which adsorbs the additives required for the extrusion to occur. The calcined powders were then milled either by hand using a mortar and pestle, or by roller mill in a 250 ml Neglene container with acetone and 10 mm diameter zirconia grinding media. The effect of the milling time on the particle size was investigated. Particle size analysis was performed using a laser diffraction particle sizer (Malvern

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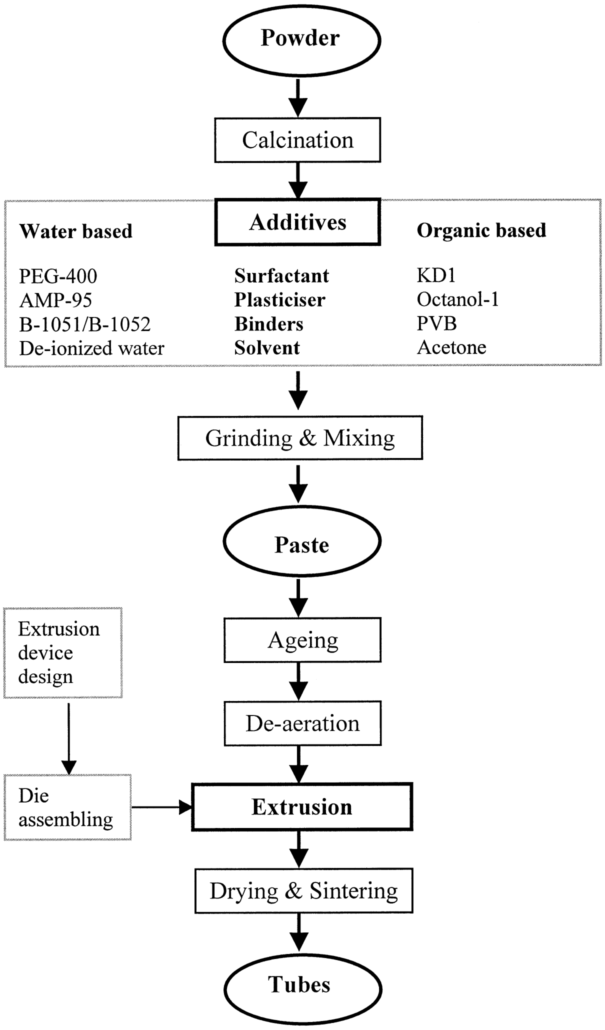


Fig. 1. The procedure developed for extrusion of thin YSZ tubes.

Masterizer). The desired powders were mixed/ground with the surfactant, plasticiser, binders, and/or solvent (if ball milling). The ball milled slurry was tape cast onto an acetate sheet. The mixtures were then aged in plastic bags overnight to produce pastes.

Workable pastes were extruded into tubes, using an in-house designed high strength steel piston extruder, as shown in Fig. 2. The die-head surfaces in contact with the extrudate were polished to a 1 μm finish, to reduce friction between the die wall and extrudate. The piston was moved down slowly and the extrudate was then forced through the die to form a tube using a standard LLOYD LR100K tensile testing machine coupled to a personal computer. The effect of piston speed on extrusion quality was determined, and in most cases the piston speed was set at 4 mm/min.

After drying, the green tubes were sintered in air in a chamber furnace (Ceramic Engineering). A slow heating rate (1°C/min) under 500°C was used to burn-out the polymer, and sintering was performed at a ramp rate of 6°C/min to 1500°C, followed by a dwell time of 2 h at

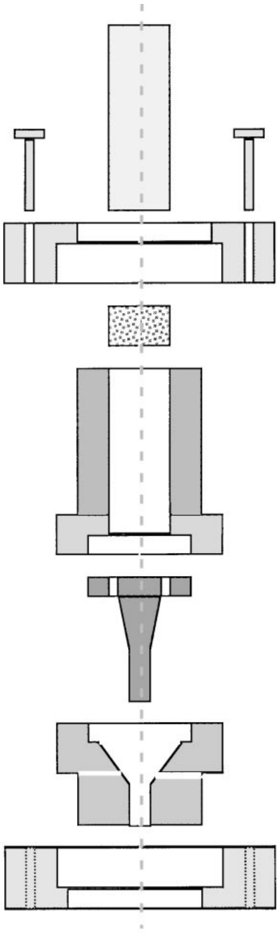


Fig. 2. Schematic diagram of the extrusion device.

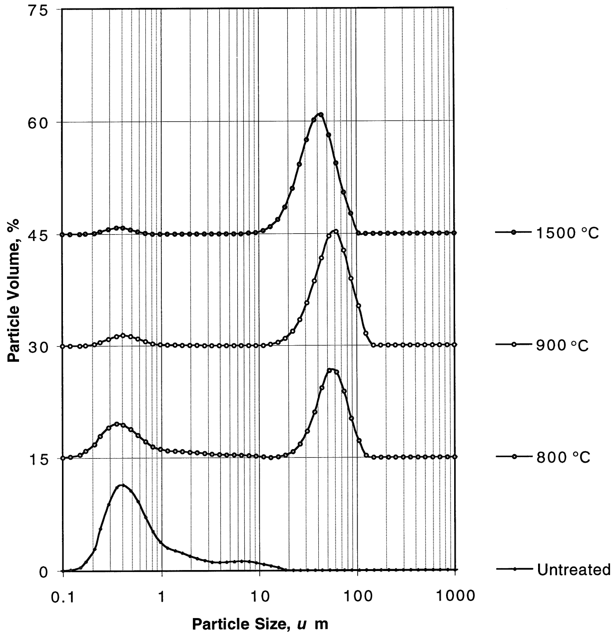


Fig. 3. Effect of calcination temperature on particle size distribution.

1500°C. The tubes were placed horizontally on a V-shape holder or vertically hung on a specially designed sample holder, to enable the tubes to remain straight during drying and firing. Sample holders were made either from zirconia or alumina. The microstructure of the sintered tubes was examined, using a Hitachi S4000 scanning electron microscope (SEM). The samples (fracture, cut or polished surfaces) were platinum coated for surface investigation at higher magnification.

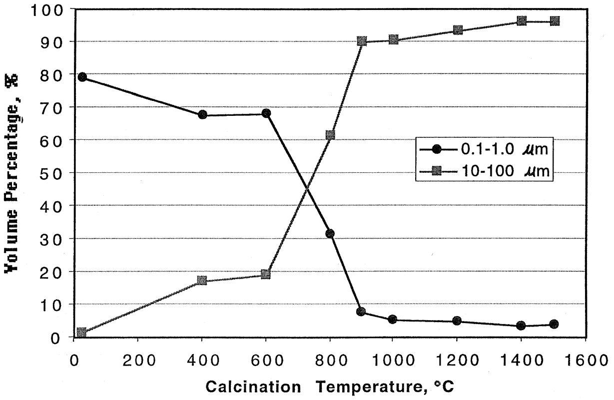


Fig. 4. The particle volumes covered by the two major distributions.

3. Results and discussion

3.1. Powders treatment and particle size analysis

One of the most important parameters for ceramic green body extrusion is the particle size of the powder. As most non-clay ceramic powders are non-plastic, powder particle size of greater than 5 μm may present problems in batch formulation. For powders with particle size below 1 μm, extrusion problems are generally not so severe.[9] However, powders with smaller particle size have higher surface areas, which require significant amounts of organic additives to produce workable ceramic pastes for extrusion. With a large quantity of additives, it can be very difficult to obtain high sintered densities. Therefore, to understand the relationship between particle size, amount of additives and the characteristics of the

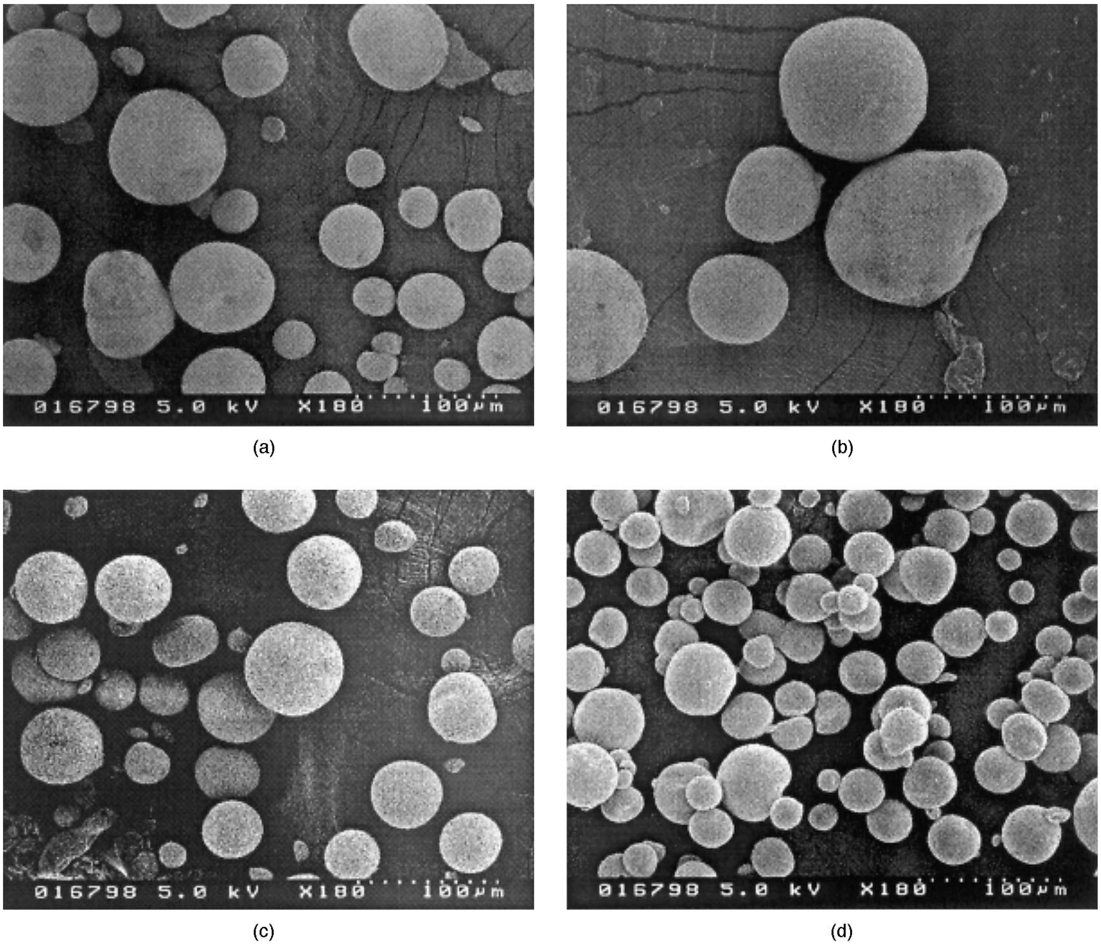


Fig. 5. Micrographs of the powders: (a) powder as received; (b) powder calcined at 900°C for 2 h; (c) powder calcined at 1200°C for 2 h; (d) powder calcined at 1400°C for 2 h.

final product, the as-received powder was calcined and ground.

Fig. 3 shows the particle size distribution of the powders as-received and calcined at 800, 900, and 1500°C, respectively. It can be seen that the particle size distribution shifted from a mean of 0.4 to 40–50 μm with calcination up to 1500°C. The particle volumes covered by these two distributions are plotted in Fig. 4. For the as-received powder, most (80 vol%) particle sizes were between 0.1 and 1.0 μm with a high specific surface area. After high temperature calcination, at 900°C for example, the particle surface area reduced significantly. The largest particle size of the powder, calcined at 1400–1500°C, is 90 μm, which is 25% smaller than that formed with calcining at 900°C. SEM micrographs of the powders as-received and after calcination are shown in Fig. 5. It can be seen that the agglomerates after calcination at 1400°C are much smaller, and this indicates that the powder has partially sintered. Overall, 900°C is the optimal calcination temperature. The powder calcined at 900°C had a lower surface area and was easier to grind.

In order to obtain the maximum packing density, the calcined powders were ground. Hand grinding, using a mortar and pestle for 15 min, was necessary to produce

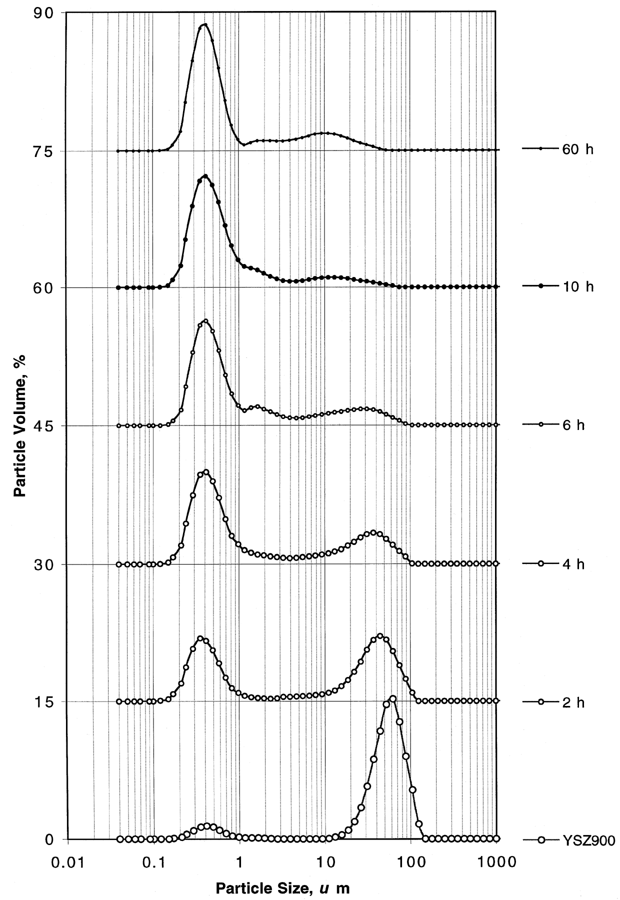


Fig. 6. Particle size contribution after different dry ball mill durations.

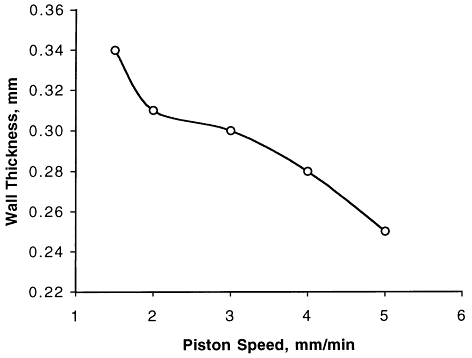


Fig. 7. The effect of piston speed on the wall thickness of the sintered tubes.

Table 1
Extrudate formula of water based additives

Sample No	Powder treatment	Additives[a]					Ageing time and paste	Green/sintered tubes	Comments
		PEG-400	AMP-95	B-1501	B-1502	H_2O			
YSZ3a	Untreated	0.6%	3.6%	8.3%	9.2%	27%	24 h, very sticky		Too sticky to be extruded
YSZ3b	900°C, 2 h	0.6%	3.6%	8.3%	4.6%	27%	24 h, not sticky[b]	Rough surface	Porous tubes
YSZ5a	100%-900°C, 2 h	6.6%	1.8%	8.3%	4.6%	25%	3 days, workable[b]	Good shape[b]	Similar surface, porous
YSZ5b	80%-900°C, 2 h 20%-fine powder	6.6%	1.8%	8.3%	4.6%	25%	3 days, workable[b]	Good shape[b]	
YSZ9	100%-fine powder	6.6%	1.8%	8.3%	4.6%	25%	2.5 h, very plastic	worm-shape	Paste plastic
YSZ10	50%-900°C, 2 h 50%-fine powder	6.6%	1.8%	8.3%	4.6%	25%	20 h, a little sticky[b]	Straight[b]	Paste de-aired Green tubes dried 4 days[b]
YSZ11	50%-900°C, 2 h 50%-untreated	6.6%	1.8%	8.3%	4.6%	25%	20 h, easy to extrude[b]	Straight[b]	
YSZ12	900°C, 2 h	6.6%	1.8%	8.3%	4.6%	20%	24 h, easy to extrude[b]	Straight[b]	Ball mill 8 h in Acetine[b]
YSZ13	900°C, 2 h	6.6%	1.8%	8.3%	4.6%	25%	44 h, workable	Not smooth	Ball mill 12 h in Ethanol
YSZ14	Untreated	6.6%	1.8%	8.3%	4.6%	133%	40 h, loose	Cracked after extruding	Ball mill 10 h in Ethanol

[a] Wt percentage related to the powder.

[b] Satisfied at that stage.

a fine powder. Longer duration of grinding time, although it reduced the particle size, was deemed inefficient. Fig. 6 shows the particle size distribution after different dry ball mill durations. It can be seen that at milling times less than 10 h, increasing the dry ball mill time greatly reduced the amount of agglomerates. After 10 h, however, prolonging the ball mill time did not show a significant effect on the particle size distribution. From this study, it was learned that the agglomerates (with an average particle size of 10 μm) could not be completely eliminated, although the amount of the agglomerates could be significantly reduced through the variation of the grinding techniques (by hand, dry ball mill and wet ball mill), or optimising the grinding duration.

3.2. Formulation of extrudate

The function of the additives used in producing the YSZ extrudates including binders, dispersants, lubricants and pH control agents, was studied. PVB, one of the most popular binders, and the specific extrusion binders B-1501 and B-1502, have at least two roles to play: namely they thicken the solvent phase and give the green body wet and dry strength.

Table 1 gives the extrudate formulae tested for the water-based system. The additives were mixed with the powder using a mortar and pestle. Particle size contribution and character of the powder played an important role in producing straight, dense and smooth-surface finished tubes. Tubes extruded from 100% of untreated (as-received) powder are very porous and coarse (see sample YSZ3b, YSZ5a and YSZ5b in Table 1). The consistency of the pastes, made of 100% fine powder, was too plastic to be successfully extruded (sample YSZ9). Those with certain particle contributions (samples YSZ10 and YSZ11) were extrudable and the tubes showed a symmetric tubular shape. It should be noted that dense, straight and even-shaped tubes were obtained from formula YSZ12, in which the powder was calcined at 900°C for 2 h, and where the additives were ball milled in acetone for 8 h.

Table 2 lists the formulae investigated for the organic system. Obtaining extrudable pastes was largely dependent upon the particle size of the YSZ ceramic powders. Pastes produced using 100% untreated (as-received) powder were either too adhesive (samples YSZ1 and YSZ3), or too stiff (sample YSZ80s) to be extruded. The pastes, made of 100% calcined power, were too soft and loose (samples YSZ7b and YSZ89s). However, the mixture of the pastes made from YSZ7a and YSZ7b with particle contribution similar to samples YSZ10 and YSZ11 in Table 1 (50% powder calcined at 900°C and 50% fine powder), showed good workability. The resulting tubes were smooth, dense and straight.

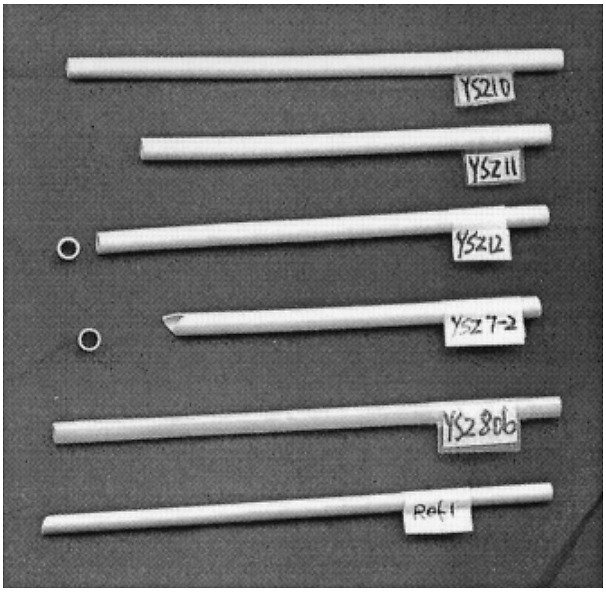


Fig. 8. Photograph of sintered tubes in this study, and a commercial one labelled Ref. 1.

Table 2
Extrudate formula of organic additives

Sample No	Powder treatment	Additives[a]				Mixing and grinding	Paste	Green/sintered tubes	Comments
		KD1	Acetone	PVB	Octanol-1				
YSZ1	Untreated	3%	96%	6%	24%	Ball mill 24 h			Too sticky to be extruded
YSZ3	Untreated	3%	52%	6%	9%	Stirring 9 h		Extruded rods	Too sticky to be extruded
YSZ7a	900°C, 2 h	6%	60%	6%	6%	Ball mill 8 h	Rigid, plastic	Using (a + b), tubes with smooth surface[b]	The particle size distribution[b] 50%-900°C, 2 h 50%-fine powder
YSZ7b	900°C, 2 h	6%	60%	6%	6%	Stirring 8 h	Dry, loose, soft		
YSZ80s	Untreated	5%	50%	6%	6%	Stirring 4 h	Rigid, plastic	Cracked while drying	Unworkable
YSZ80b	Untreated	4%	50%	6%	6%	Ball mill 4 h	Soft, plastic	Workable[b]	
YSZ89s	900°C, 2 h	5%	50%	6%	6%	Stirring 4 h	Dry, soft, loose	Unextrudable	Particles too coarse
YSZ89b	900°C, 2 h	4%	50%	6%	6%	Ball mill 4 h	Loose, plastic	Cracked while drying	Ball mill times should > 4 h

[a] Wt percentage related to the powder.

[b] Satisfied at that stage.

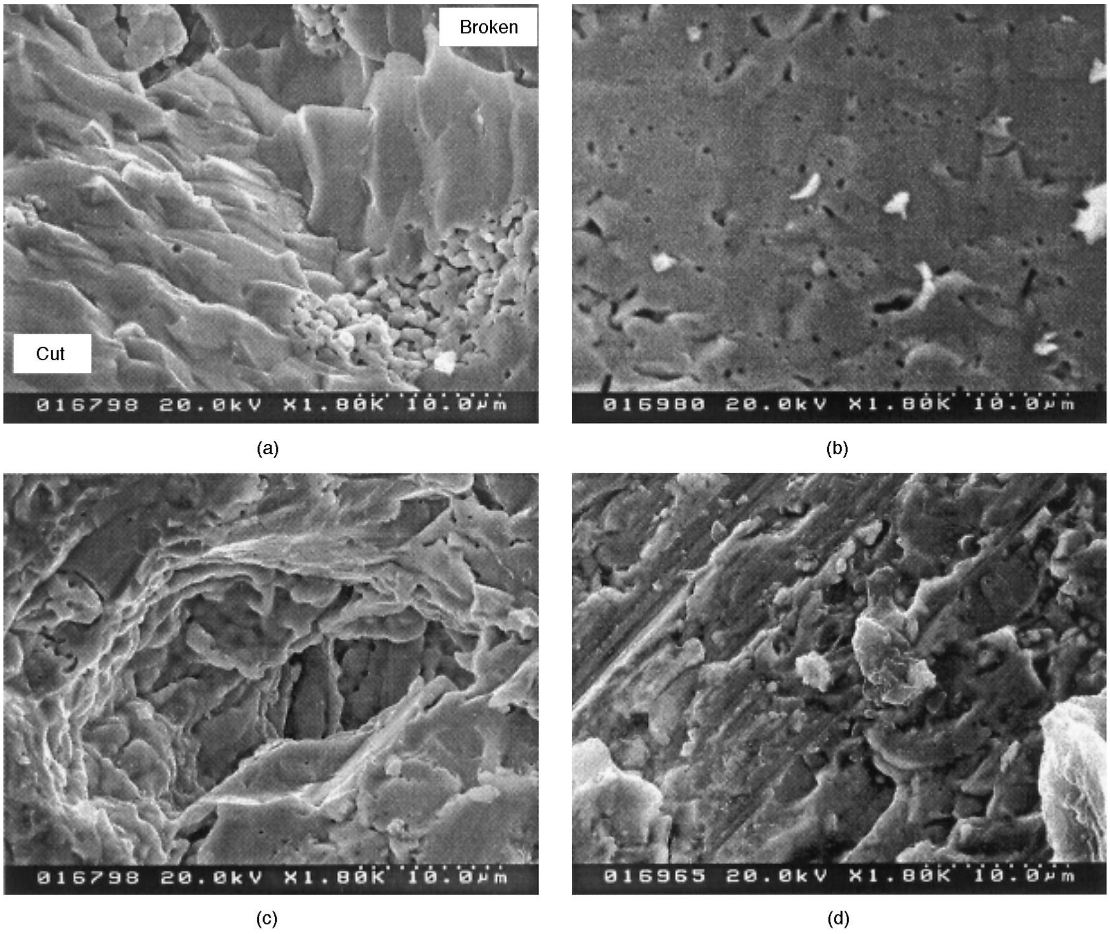
3.3. Extrudate paste preparation

Providing extrudable pastes is the most important step in the process. Powders were mixed with additives by means of roller mill, or manually with a mortar and pestle. The fundamental purpose of mixing is to produce a uniform extrusion batch. Pockets of binder and powder form inhomogeneities, which may become voids in the final fired object. Poor mixing often leads to dilatant flowing behaviour. This occurs because of the occluded binder that resides within the agglomerates.

For the organic-based system, the milled powder with solvent (acetone) was poured onto a plastic sheet and dried until the consistency of the mixture allowed it to be easily removed from the sheet. The drying process of the tape-cast slurry was a decisive step. If the slurry is under-dried, the consistency is too sticky and soft; conversely over-drying produces a paste that is too stiff to be extruded. The drying time is largely dependent upon the thickness of the cast tape, solvent level, and the ambient temperature. Ten to thirty minutes was recorded for the slurry prepared in this study for a tape-cast layer of 1–2 mm. For the water based system, the pre-dispersed PEG-400 in distilled water (PEG-400: $H_20 = 1: 10$), and AMP-95 were manually mixed with YSZ powder for 15 min using a mortar and pestle. Binders B-1051 and B-1052 were then added and mixed for a further 15 min. By varying the ratio of B-1051 and B-1052, the rigidity and flexibility of the paste can be adjusted. The ratio of B-1051: B-1052 was kept at 1.8 to produce rigid extrudates. Addition of solvent (water or acetone) is necessary to adjust the workability of the paste. The resultant mixtures were placed inside polyethylene bags to retain the solvent content, and for ageing overnight. It was necessary to knead the pastes properly just before performing the extrusion process. Rheological properties, plasticity, flexibility, rigidity, and stiffness could be used to evaluate the extrudability of the pastes.

3.4. Extrusion

As a plastic forming method, there exist certain mechanical requirements [9] for extrusion to occur. The first requirement is flow. During the extrusion process, the paste must be plastic enough to form the desired cross-section under the application of pressure. The second



(a) (b)
(c) (d)

Fig. 9. Microstructure of the cross-section of the selected tubes: (a) YSZ 7; (b) YSZ 9; (c) YSZ 10; (d) YSZ 12.

requirement is wet strength. After the material is extruded, the green body must be strong enough to resist deformation due to its own weight or due to handling stresses. If either of these conditions is not met, an optimum extrusion will not be obtained.

It was found that the wall thickness of the resulting tubes was affected by the velocity of the die piston. Fig. 7 shows the results obtained from sample YSZ7(a + b) and a die gap of 0.115 mm. It can be seen that the faster the piston speed, the thinner the tubes formed. Thin-wall electrolytes have lower cell resistances. However, there is a limitation to how thin a wall thickness can be produced, because it is very difficult to avoid green-tube deformation. Secondly, the sintered tubes may not have significant strength to be a self-supported electrolyte in a fuel cell assembly.

The load required to produce an optimum extrusion quality was recorded at 1–7 kN for water based pastes, and 15–30 kN for organic based pastes, which depended on the stiffness of the extrudates. To avoid flattening of the tube during extrusion, the end of the remaining part of the tube was kept open after cutting, to retain the air pressure balance between the inside and outside of the tube.

3.5. Drying and sintering

The resulting green tubes were dried in air for at least 24 h and then in an oven at 105°C for 2 h before sintering. The firing regime was determined according to the thermal gravimetric analysis (TGA). A slow ramp of 1°C/min up to 500°C was utilised to burn out the organic components, and a ramp rate of 6°C/min to 1500°C for 2 h was undertaken. With this sintering regime, no micro-sintering cracks were detected using the SEM. Linear sintering shrinkage of the tubes was measured at 20% for the water based system and 25% for the organic based system.

3.6. Microstructure determination

Fig. 8 shows a photograph of the sintered tubes, and Fig. 9 shows the micrographs of the cross-sections of selected tubes. The microstructure and density of the sintered tubes were largely dependent upon the preparation method of the green tubes. Tubes made from organic additives have a dense structure and a smooth surface finish. Breaking of the tubes occurred in a brittle manner as can be seen in sample YSZ7 in Fig. 9. In comparison, tubes made from water-based additives exhibited superior mechanical integrity, although micropores with approximate diameter of 1 μm were observed using SEM (sample YSZ9 in Fig. 9). In both cases, holes with approximate diameter of 5–10 μm caused by inhomogeneities were detected (samples YSZ7 and YSZ10). The presence of porosity or porous regions in sintered ceramic objects may be the major strength-controlling defect. This microstructure can be improved by using an optimally prepared paste, with observation of a dense cross-section shown in sample YSZ12 in Fig. 9.

4. Conclusions

Using the procedure developed in this study, dense, smooth finished and straight, thin YSZ tubes could be extruded with either water-based additives, or organic additives. With the water based additive system, the degree of success in producing well-shaped tubes was higher than that of the organic system. The particle size distribution played an important role in achieving extrudable pastes, and thus even-shaped tubes. The microstructure of the sintered tubes exhibited a well-sintered body with micro-pores.

Holes, caused by inhomogeneities in the sintered objects, could be removed by using the optimized extrudate formulae and procedures.

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