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Fabrication of zirconia- and ceria-based thin-wall tubes by thermoplastic extrusion

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Abstract

Thin-wall tubes made of zirconia stabilized by 8 mol% of yttria and of ceria doped by 10 mol% of gadolinia were prepared by thermoplastic extrusion. The rheological behaviour of the ceramic mixtures prepared and the effect of rheological properties on the deformation of tubes were studied. After sintering, the diameter of tubes was 10.5 mm and their wall thickness ranged from 270 to 420 μm. The deformation and shape irregularity of sintered tubes were determined. The tubes, which were sintered at a temperature of 1500 °C, had a relative density of more than 98% t.d. Flexural strength and fracture toughness of sintered ceramics were determined on test bars prepared by injection moulding from thermoplastic mixtures identical to those used for extrusion. The fracture toughness established was 1.7 MPa $m^{0.5}$ for yttria-stabilized zirconia, and 1.1 MPa $m^{0.5}$ for gadolinia-doped ceria.

Keywords: CeO_2; Electrolyte; Extrusion; Suspensions; ZrO_2

1. Introduction

Tubular geometry is one of the possible variants of the design of solid oxide electrolyte in applications such as fuel cells and other electrochemical reactors. It is mainly small and thin-wall ceramic tubes that have a good resistance to thermal stresses appearing in cyclic rapid heating and cooling of reactors.[1–3] Designs of tubular fuel microcells have therefore been proposed and tested that utilize self-supporting tubular electrolyte without a support electrode.[3–5] Also in these cases, when the tubular electrolyte has the function of supporting the fuel cell, the electrolyte must be of sufficiently thin wall to ensure a sufficient passage rate of oxide anions. In the above-mentioned cases the thickness of tubular electrolyte ranged from 200 to 300 μm, with the tube diameter being about 2.5 mm.

Yttria-stabilized zirconia (YSZ) is the most frequently applied solid oxide electrolyte in fuel cells. Electrolytes that would allow reducing the operation temperature necessary for the YSZ electrolyte (800–1000 °C) would reduce the production cost of cells since they would allow using cheaper structural materials. Solid electrolytes for intermediate temperatures (600–800 °C) are currently tested that are based on ceria doped by rare earth elements.[6,7] They are used either as such or in combination with YSZ. Another much-promising material that could be used as ion conductor of oxygen at intermediate temperatures is strontium- and magnesium-doped lanthanum gallate (LSGM).[8]

The extrusion of thin-wall tubes is an economically advantageous method of manufacturing tubular electrolytes, which enables producing dense thin-wall ceramic tubes whose properties are comparable with or better than those obtained by the other shaping methods (cold isostatic pressing[8] and vacuum casting[9]). Although a few publications have appeared that describe the design and properties of fuel cells with tubular electrolyte,[2–5,10,11] the extrusion method itself is only sporadically described in detail in the literature. Du et al. described the preparation and optimization of thin-wall tubes made of YSZ[12] and LSGM.[8] Bellon et al.[13] described tube extrusion from gadolinia-doped ceria with a binder that uses an organic solvent while Hatchwell et al.[14] reported on the preparation of identical tubes with an aqueous binder. In all these cases the tubes were up to 3 mm in diameter and 200–400 μm

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thick. The main problem in extruding thin-wall tubes can be seen in the tendency of the thin-wall profile to collapse. The rheological properties of the mixture being extruded must be such that no deformation of the plastic green body can occur due to own weight or to the necessary handling. When a thermoplastic mixture is used, the extruded green body solidifies (i.e. mixture viscosity increases abruptly) immediately the tube is cooled below the shaping nozzle. This enables the preparation of thin-wall tubes of larger diameters, which would otherwise be deformed. Such tubes can be utilized even in applications such as protective layers for plastic shafts, filters, thermowells and heat exchangers. Clemens and Graule[15] applied thermoplastic extrusion to prepare from tetragonal zirconia thin-wall tubes of 5 mm in diameter and 200 μm wall thickness.

The aim of the present work was to prepare thin-wall tubes from two types of solid oxide electrolyte, namely yttria-stabilized zirconia and gadolinia-doped ceria. The tube diameter, 10.5 mm, had been chosen in order that the tubes could be used as experimental tubular electrolyte and also in order that the potentials of the method of thermoplastic extrusion in preparing thin-wall tubes of larger diameters could be assessed.

2. Experimental

Zirconia stabilized with 8 mol% of yttrium oxide (YSZ) and ceria doped with 10 mol% of gadolinium oxide (GDC) were used for the preparation of ceramic tubes. Yttria-stabilized zirconia (TZ-8YS, Tosoh, Japan) was used as supplied. Ceria (99.95% purity, Guangzhou Zhujiang Refinery, China) was ball-milled and doped with gadolia (99.99% purity, Guangzhou Zhujiang Refinery, China). Ceria was refined and doped in an attrition mill with zirconia balls in xylene with dissolved stearic acid. After milling, the powder was dried at 90 °C. Apart from ceramic powders the thermoplastic mixtures contained ethylene–vinyl acetate (EVA) copolymer (Elvax 250, Du Pont de Nemours, USA), paraffin wax (54/56, Slovnaft, Slovakia) and stearic acid (1.0067, Merck, Germany). The composition of mixtures is given in Table 1. The powder loading of the two mixtures was identical, i.e. 52.9 vol.%. The ceramic mixtures were prepared by mixing ceramic powders with the other organic components in a heated two-blade kneader (HKD 2.5, IKA-Werke, Germany) at a temperature of 100 to 120 °C for 2 h. Prior to cooling, the mixture was granulated manually. Continuous tube extrusion was performed on a twin-screw extruder (BS-30, Betol Machinery, UK) at temperatures between 80 and 130 °C. The tubes were extruded through a nozzle of 13 mm outer diameter and 12 or 12.3 mm inner diameter (i.e. a wall thickness of 500 or 350 μm, respectively) vertically into the cooling water. The cooling water had a temperature of 35 °C and its level was 30 mm below the nozzle. The rate of tube extrusion was 7–10 mm s^{-1} and the tubes were cut into pieces of 500 mm in length. For heat treatment they were shortened to 260 mm.

Table 1
Composition of ceramic mixtures

	YSZ powder (wt.%)	GDC powder (wt.%)	EVA (wt.%)	Paraffin wax (wt.%)	Stearic acid (wt.%)
YSZ mixture	87.8		6	4	2.2
GDC mixture		89.7	4.6	3	2.7

To establish strength and fracture toughness, bars of 3.5 mm × 4.65 mm × 60 mm were prepared by injection moulding. The same mixture was used for injection moulding as for tube extrusion. A detailed description of the parameters of injection moulding can be found in previous work.[16] The binder was removed in a nitrogen atmosphere at a heating rate of 10 °Ch^{-1} up to a temperature of 500 °C and then at a heating rate of 120 °C/h^{-1} up to a temperature of 800 °C. In the case of bars the temperature increase in the temperature range from 100 to 200 °C was slowed down in view of their larger cross-section. During the binder removal, all the bodies were embedded in granulated active carbon (AY-5 12×30, Carbon Link, UK). Sintering took place in an air atmosphere at a temperature of 1500 °C for 2 h. The increase to the sintering temperature was at a rate of 300 °Ch^{-1} up to a temperature of 800 °C and then at a rate of 100 °Ch^{-1} up to 1500 °C. During sintering, the tubes were suspended vertically on a hook that was thermally moulded at the end of the thermoplastic tube after extrusion.

The size distribution of powder particles was established on a laser diffraction analyser (LA-500, Horiba, Japan). The shape of ceramic particles and the microstructure of sintered ceramic specimens were examined by scanning electron microscopy (XL-40, Siemens, the Netherlands). The rheological behaviour of ceramic mixtures was investigated on a capillary rheometer (Galaxy V, Kayeness, USA) with a nozzle of 1 mm in diameter and 30 mm in length. The measurement was conducted at shear rates between 10^2 and 10^3 s^{-1} and temperatures of 90–140 °C. The shear rate values were corrected to the non-Newtonian behaviour of the mixture by the Weissenberg–Rabinowitsch method.[17] The density of sintered tubes was determined by the Archimedes method (EN 623-2), always on at least three specimens. The wall thickness of sintered tubes was measured by an optical measuring microscope on tube sections and, the same as tube deformation, it was determined on a minimum of three specimens. The average grain size was established by the linear intercept method from microphotographs of sintered ceramics.

The flexural strength of sintered test bars was established by four-point bending (in the "B" arrangement according to EN 843-1). The specimens were tested in non-machined condition, which simulated the conditions of tubes, whose surface will also be non-machined. The parameters of the Weibull strength distribution were calculated numerically in accordance with the ENV 843-5 standard. Fracture toughness was determined on four specimens, using the SEVNB method.[18]

3. Results and discussion

3.1. Ceramic powders and ceramic mixture rheology

The size distribution of the particles of the ceramic powders used, which was determined by laser diffraction, is shown in Fig. 1. It is obvious from the graph that the two powders, YSZ and GDC, had particles of roughly the same size, with median $d_{50}=0.5$ μm. However, from the microphotographs in Figs. 2 and 3 it follows that the particles measured were aggregates (i.e. clusters of predominantly chemically bonded particles) formed from smaller dense primary particles of 0.1–0.3 μm in size. In comparison with zirconia, ceria was made up of finer primary particles and formed a less regular structure with many big dense aggregates of as much as 1 μm in size.

Figs. 4 and 5 show the dependence of viscosity on shear rate for the studied ceramic mixtures at temperatures from 90 to 140 °C. Over the whole range of the temperatures examined the ceramic mixtures exhibited pseudoplastic behaviour, i.e. their viscosity decreased with increasing shear rate. The dependence of viscosity on shear rate was described by the power law[19]

$$\eta = K \cdot \dot{\gamma}^{(n-1)}, \quad (1)$$

where η is the mixture viscosity, K is the constant, $\dot{\gamma}$ is the shear rate and n is the exponent giving the deviation from Newtonian behaviour. The chosen model was in very good correlation with the values measured ($r^2>0.99$). The power law exponent, n, ranged for the individual temperatures of YSZ mixture from 0.57 to 0.70, its average value was 0.63. The GDC mixture exhibited a substantially higher level of pseudoplasti-

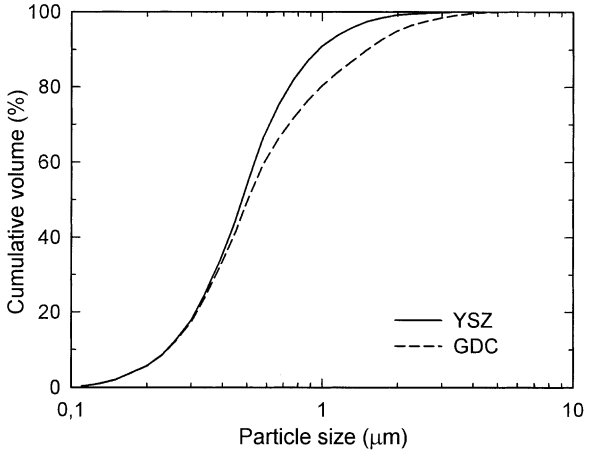

Fig. 1. Particle size distribution of YSZ and GDC ceramic powders.

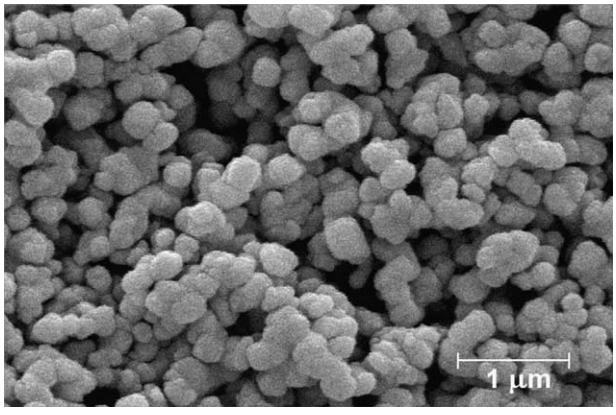

Fig. 2. Microphotograph of the YSZ powder (8 mol% Y_2O_3 stabilized ZrO_2).

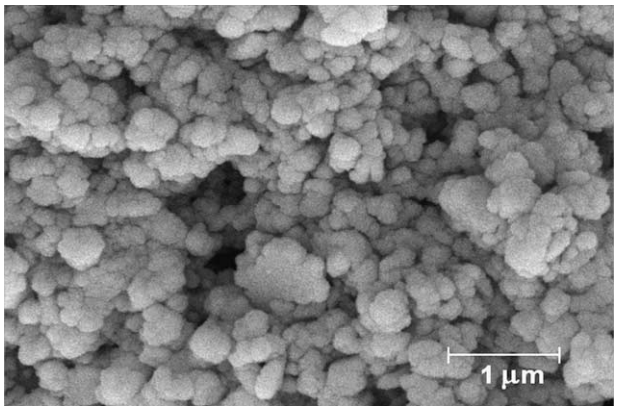

Fig. 3. Microphotograph of the GDC powder (10 mol% Gd_2O_3 doped CeO_2).

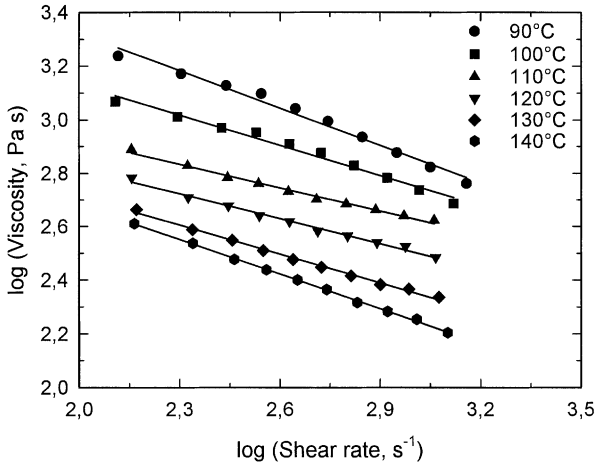

Fig. 4. Rheological behaviour of the YSZ mixture at different temperatures.

city, the power law exponent ranged between 0.30 and 0.33 and its average value was 0.31. The temperature dependence of ceramic mixture viscosity at shear rates of 200 and 1000 s^{-1} is shown in Figs. 6 and 7. The activation energies of viscous flow were determined by means of the Andrade relation[19]

$$\eta = A \cdot \exp\left(\frac{E}{RT}\right), \quad (2)$$

where A is the constant, E is the activation energy of viscous flow, R is the universal gas constant, and T is the absolute temperature. For the YSZ mixture the activation energy was 39.9 kJ mol^{-1} at a shear rate of 200 s^{-1} and 35.1 kJ mol^{-1} at a shear rate of 1000 s^{-1}. For the GDC mixture the respective activation energies were 17.6 and 17.1 kJ mol^{-1}. The activation energy of viscous flow expresses the steepness of the temperature dependence of viscosity of a ceramic mixture. From the viewpoint of thermoplastic extrusion of thin-wall tubes, mixtures with higher activation energies appear to be of greater advantage. With such a mixture a smaller deformation during the cooling of extruded thermoplastic tube can be expected since the mixture viscosity increases with decreasing temperature more quickly than in a mixture with lower activation energy. The differences in rheological behaviour of the two mixtures consisted in the different nature of the particles of the two powders used. Both mixtures were prepared on the basis of the results obtained earlier for injection moulding of thermoplastic ceramic mixtures. The ceramic mixtures prepared had therefore rheological properties and behaviour similar to the mixtures used in earlier works for injection moulding of zirconia[16] and ceria.[20] For the extrusion of thin-wall tubes, Du et al.[12] also used the same zirconia powder as we did. However, for their method of cold extrusion the powder had first to be calcined to a temperature of 900 °C to make the particles coarser and to reduce the specific powder surface.

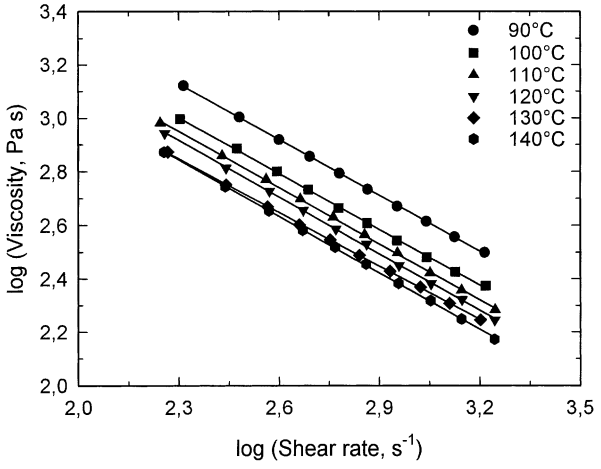

Fig. 5. Rheological behaviour of the GDC mixture at different temperatures.

3.2. Extrusion of tubes

Thermoplastic extrusion of tubes in vertical direction and their subsequent cooling immediately below the nozzle made it possible to prepare non-deformed thin-wall tubes of 13 mm in diameter. The sag and ovality of tubes depended in the first place on correct nozzle alignment, i.e. on uniform tube-wall thickness. Non-uniform wall thickness made the tube bend in the direction of the thinner wall either immediately after extrusion or later during sintering. A disadvantage of thermoplastic extrusion in the vertical direction was the narrowing of tubes with increasing length of extruded tube. The weight of extruded tube loaded the plastic region of the tube just below the nozzle and thus reduced its diameter. This narrowing increased with increasing temperature of the mixture being extruded. The lowest applicable temperatures were therefore

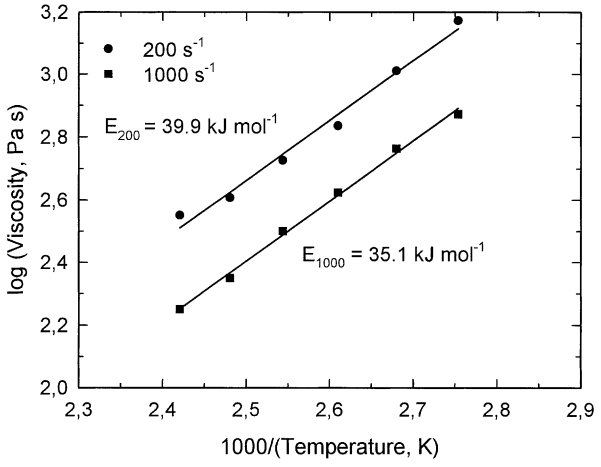

Fig. 6. The temperature dependence of viscosity of the YSZ mixture at shear rates of 200 and 1000 s^{-1}.

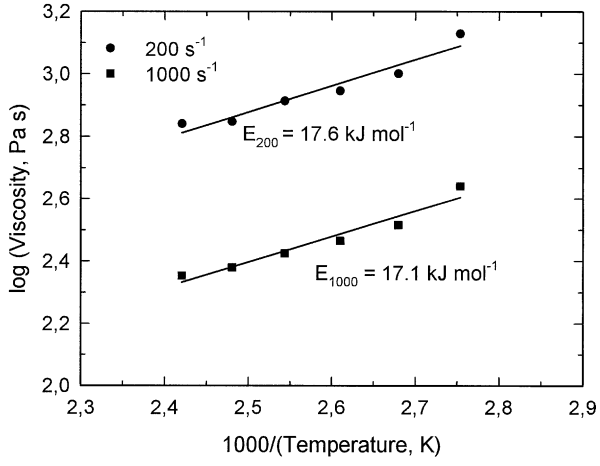

Fig. 7. The temperature dependence of viscosity of the GDC mixture at shear rates of 200 and 1000 s^{-1}.

chosen for extrusion. For the YSZ mixture a temperature of 80 °C was chosen as optimum while for the GDC mixture it was 120 °C. At lower temperatures there appeared excessive contamination of ceramic mixture caused by wear in the extruder, and also increased torque on the screws, which could eventually block the extruder. The reduction in the green-body diameter of YSZ tubes of 260 mm in length and 500 μm nominal wall thickness (denoted YSZ-500) was 0.3 mm. The narrowing of green-body tubes of nominal wall thickness 350 μm (YSZ-350 and GDC-350) was for both materials identical and for a length of 260 mm it amounted to 0.2 mm. A section through an extruded YSZ-350 tube can be seen in Fig. 8.

3.3. Properties of sintered tubes

To prevent deformations during high-temperature treatment due to a non-homogeneous temperature field or due to non-uniform placement in the furnace, the tubes were sintered in suspended position. That is why prior to removing the binder a hook was thermally moulded on extruded thermoplastic tubes. Fig. 9 shows an extruded tube with suspension, a sintered tube with suspension and a sintered tube subsequent to separating the suspension and cutting the tube to a length of 160 mm. The outer diameter of sintered tubes was about 10.5 mm and the average wall thickness was 400 μm for the YSZ-500 tube and 290 μm for the YSZ-350 tube. The average wall thickness of GDC-350 tubes was 280 μm. The deformations and irregularities in sintered tubes were determined on specimens 160 mm long. The subject of investigation was the largest and smallest wall thickness, the tube sag (i.e. deflection from the straight line at the tube centre), the tube narrowing (i.e. the difference between the diameters at the beginning and end of the tube) and the tube ovality (i.e. the difference between the largest and the smallest diameter of the tube). The average values of deformations and irregularities of sintered tubes are given in Table 2. It was possible to prepare tubes of uniform wall thickness. The difference in the wall thickness of thin-wall YSZ-350 and GDC-350 tubes did not exceed 20 μm. For the YSZ-500 tube the difference was larger, namely up to 30 μm. The maximum tube ovality, 0.43 mm, was established for GDC-350 tubes. The irregular ovality along the tube length was responsible for the maximum deflection of 0.40 mm measured for these tubes. The other YSZ tubes had a deflection of not more than 0.25 mm. The larger deformation (ovality and deflection) in GDC tubes was probably due to the less favourable rheological properties of the GDC mixture compared with the YSZ mixture, above all the low activation energy of viscous flow (as stated earlier).

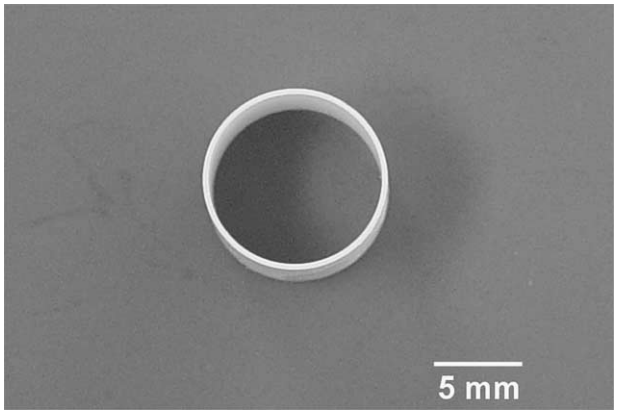

Fig. 8. Cross-section of an extruded YSZ-350 tube.

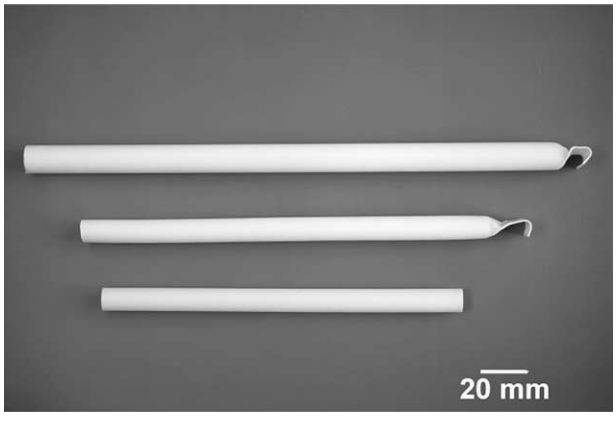

Fig. 9. Photograph of an extruded tube with suspension, a sintered tube with suspension and a sintered tube after separating the suspension.

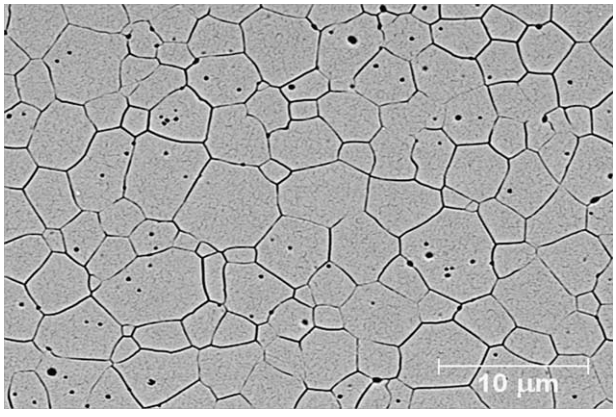

Fig. 10. SEM microphotograph showing the microstructure of a sintered YSZ tube.

Table 2
Average values of deformation of sintered tubes

Tube	Deflection (mm)	Narrowing (mm)	Ovality (mm)	Smallest/largest wall thickness (μm)
YSZ-500	0.25	0.14	0.21	390/420
YSZ-350	<0.25	0.10	0.32	280/300
GDC-350	0.40	0.04	0.43	270/280

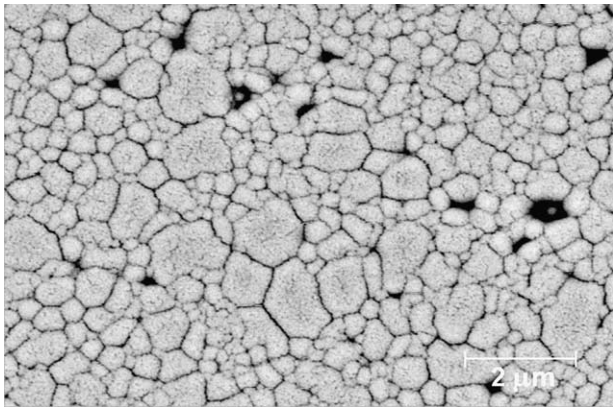

Fig. 11. SEM microphotograph showing the microstructure of a sintered GDC tube.

The relative density and strength of sintered tubes and test bars are given in Table 3. The theoretical density of cubic YSZ was assumed to be 5.99 g cm^{-3} and it was calculated on the basis of the lattice parameter ($a = 0.513$ nm) given in a survey elaborated by Lee and Rainforth.[21] The theoretical density of GDC, 7.25 g cm^3, was determined with the aid of the lattice parameter ($a = 0.5419$ nm) calculated from a relation that Kim gives for doped ceria in his work.[22] The lattice parameter calculated in this way is in good agreement with data given by other authors.[6,7] In the case of YSZ tubes and bars a high density was obtained after sintering, approximately 99% t.d. Fig. 10 shows a photograph of the microstructure of a sintered YSZ tube. The YSZ ceramics contained only tiny round pores (<0.5 μm), mostly enclosed within the grains. The enclosed pores in grain centres point to a rapid growth of grains and a considerable microstructure coarsening during sintering. The average grain size was 2.8 μm. The relative density obtained after the sintering of GDC ceramics was roughly 97.5% t.d., with the bars exhibiting slightly higher values. In the microphotograph of the structure of a sintered GDC tube (Fig. 11) a more frequent occurrence of pores of up to 1 μm and small grains of an average size of 0.43 μm can be observed. The grains were however of different sizes. Along with grains of about 1–2 μm in size the structure also exhibited a number of very small grains under 0.2 μm. By contrast, Maca et al.[20] found for sintered non-doped ceria ceramics prepared from the same powder by the same sintering mode an almost theoretical density and an average grain size of 4.6 μm. The difference in the microstructures obtained was probably due to gadolinium doping. Rahaman and Zhou[23] showed that doping the ceria ceramics with cations larger than Ce^{4+} (radius ratio $Gd^{3+}/Ce^{4+} = 1.086$) led to a suppression of grain growth and a more difficult sintering process, i.e. to the sintering curve being shifted towards higher temperatures. This explanation is also confirmed by the fact that when the holding time at sintering temperature was increased from 2 to 4 h, the density of GDC ceramics increased from 97.5 to 98.3% t.d.

Table 3
Relative density, ρ_{rel}, of sintered tubes and bars and mechanical properties (flexural strength, MOR, Weibull modulus, m, fracture toughness, K_{IC}) of sintered bars

Material	Tube	Bar			
	ρ_{rel} (% t.d.)	ρ_{rel} (% t.d.)	MOR (MPa)	m (–)	K_{IC} (MPa $m^{0.5}$)
YSZ	99.02	98.86	216	9.5	1.7
GDC	97.50	97.64	144	4.1	1.1

Flexural strength and fracture toughness were determined on test bars that had been prepared from the same ceramic mixture by injection moulding and sintered simultaneously with tubes. The average strength in four-point bending for the YSZ test bars was 216 MPa with the Weibull modulus $m = 9.5$. GDC bars had a lower strength, 144 MPa, and a very low Weibull modulus $m = 4.1$. Although the values established for GDC ceramics may be influenced by the lower number of specimens tested (10 GDC bars, 30 YSZ bars), it is obvious that the strength and reliability of GDC ceramics are lower than in the case of YSZ ceramics. The low strength and its large scatter reduce the possibility of using GDC ceramics as self-supporting tubes. The strength values found for ceramic electrolytes, GDC in particular, were low in comparison with current structural ceramic materials. This was due to the very low values of fracture toughness. The YSZ ceramics had a fracture toughness of 1.7 MPa $m^{0.5}$ while the GDC ceramics had only 1.1 MPa $m^{0.5}$. The fracture toughness of structural ceramics based on zirconia (tetragonal zirconia polycrystals) currently ranges between 5 and 7 MPa $m^{0.5}$, i.e. approximately five times higher than in the case of the ceramic electrolyte specimens tested. Since the strength of tetragonal zirconia[16] is also approximately five times higher than the strength of YSZ and GDC ceramics, it can be assumed that both the nature and the size of defects in ceramic electrolytes are similar to those in structural tetragonal zirconia. The low strength values of YSZ and GDC ceramics are thus given by the properties of the materials used, which are characterized by low fracture toughness and not by the technology used in preparing the specimens.

4. Conclusion

The method of thermoplastic extrusion enabled the preparation of regular thin-wall tubes from yttria-stabilized cubic zirconia and gadolinia-doped ceria. It was possible to produce sintered tubes of 10.5 mm in diameter and with a wall thickness of below 300 μm without significant deformations or irregularities. After

sintering, the ceramic tubes had a relative density of more than 98% t.d. The low strength and its large scatter limit the utilization of gadolinia-doped ceria as self-supporting tubular electrolyte.

Acknowledgements

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