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A novel method for the evaluation of thin ceramic membranes

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In order to test both the integrity and the mechanical strength of thin ceramic membranes, a novel testing technique which uses gas pressure to provide a uniform loading to a thin disc of material has been developed. The validity of this technique has been demonstrated by a series of tests on as-received and abraded glass specimens. Thin ceramic membranes have been produced by film blowing a polymer filled with ceramic powder, followed by pyrolysis, to remove the organic constituents, and sintering. Membranes of both alumina and samaria-doped ceria have been investigated during this study. Comparative testing of these materials was carried out to investigate the effects of processing conditions, and hence the resulting microstructure, on their mechanical strength and uniformity.

1. Introduction

There is currently considerable interest in the processing and properties of thin ceramic membranes. Self-supporting membranes of ceramics with high oxygen ion conductivity (for example yttria-stabilized zirconia or samaria-doped ceria) and with thickness in the range 50 to 200 μm are suitable for use as the electrolyte in solid oxide fuel cells (SOFCs) [1, 2]. It is essential that such electrolytes are capable of forming a gas-tight barrier to prevent the mixing of gases from the air and fuel sides of the fuel cell during operation. This implies that the electrolyte membrane should have well-characterized and reproducible mechanical properties sufficient to withstand the thermal and mechanical stresses to which it is subjected during cell fabrication and operation [2]. The work described here forms part of an ongoing project in the Department of Materials Engineering at Brunel University on the processing and properties of ceria-based ceramics for use in SOFCs [3].

The conventional methods for the biaxial testing of ceramic membranes have been described by Ritter *et al.* [4] and by de With and Wagermans [5]. The ring-on-ring test uses concentric rings to apply the loads and is experimentally difficult to set up so as to minimize wedging and friction effects. This test also requires very flat specimens to avoid uneven loading under the rings. The presence of a stress concentration under the loading ring for this test causes uncertainty in both the measured fracture stress and the volume of material subjected to the fracture stress. Although the piston-on-three-ball experimental arrangement allows the testing of warped specimens, the stress under the piston cannot be determined exactly so that the calculation of the fracture stress is uncertain and this test is best used as a comparative method. The ball-on-ring test again requires flat plate specimens but provides a very low friction between the specimen and the loading apparatus. However, the stress distribution in the specimen in the region of the central loading ball is not fully understood and is usually approximated, with the approximation becoming less certain as the thickness of the specimen decreases [4]. The problems of testing thin ceramic membranes by these conventional techniques are compounded when investigating experimental materials and/or processes at an early stage in their development when it may be difficult to obtain a sufficient supply of flat, uniform plates.

Gorham and Rickerby [6] first described a hydraulic strength test for glass and ceramic discs which was improved by Matthewson and Field [7] who used it to study the impact properties of hot-pressed silicon nitride discs of 25 mm radius and 3 mm thickness. Recently this technique has been modified by Newton *et al.* [8] for use with large specimens of clay-based materials with coarse microstructures. In this hydraulic bursting technique the circular disc specimen is supported by a steel ring close to its edge and hydraulic pressure is applied to one side of the disc via a neoprene diaphragm. The fracture stress is calculated from the bursting pressure and the position of the site of initial failure using plate bending theory assuming that the disc is simply supported [6, 7]. In order to avoid spurious failure due to contact stresses between the support ring and the specimen, even for specimens with parallel, flat faces, paper or polymer gaskets have to be inserted between the specimen surface and the support ring. Also the requirement for the site of failure to be known means that the pieces of the specimen have to be held in place after fracture has

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occurred and this is achieved by the application of a self-adhesive polymer sheet to the upper surface of the specimen before testing [7, 8]. Although this technique appears to work well for specimens with a thickness of 3 mm and above, the presence of a neoprene membrane between the pressurizing fluid and the specimen, the necessity for intermediate gaskets to eliminate contact stresses and the use of a backing sheet on the specimen make this technique impractical for thin ceramic membranes such as those of interest for SOFC electrolytes.

An alternative technique was therefore developed for the evaluation of ceramic membranes, using gas pressure to provide a uniform loading to a circular disc of material, which would allow the comparative testing of materials to investigate the effects of processing and the resulting microstructure on their mechanical strength and uniformity.

2. Experimental details

2.1. Mechanical testing apparatus

A novel apparatus was designed and evaluated to develop a new technique to test thin ceramic membranes. The design of the machine is shown in Fig. 1. In this apparatus one side of the thin film sample was subjected to a uniform loading caused by the pressure of gas which was introduced using a needle valve. The as pressure was monitored using a P445 Digitron pressure transducer situated as close as possible to the specimen. The output from the transducer was recorded during the whole of the pressurization cycle on a calibrated chart recorder (Instrumentation Potentiometric Recorder R.E.511.20). Fracture of the specimen caused a drop in pressure at the transducer and the value of the applied pressure at fracture was read from the chart recorder trace. It was also possible to detect any gas leaking through the specimen due to cracks or open porosity by monitoring the output of this transducer with the system sealed under pressure.

A fast cold-curing epoxy resin, Araldite grade Lecoset 7007 supplied by Leo Corporation, UK, was used to seal the specimen to one end of a 21 mm outside diameter, machined stainless steel tube which fitted into a vacuum fitting connected to the rest of the apparatus. The end of the tube was beveled as shown in Fig. 2 to improve the adhesion of the specimen to the tube.

Samples were uniformly loaded with an input pressure of 200 kPa at a flow rate of 1.67×10^{-6} m^3 s^{-1}.

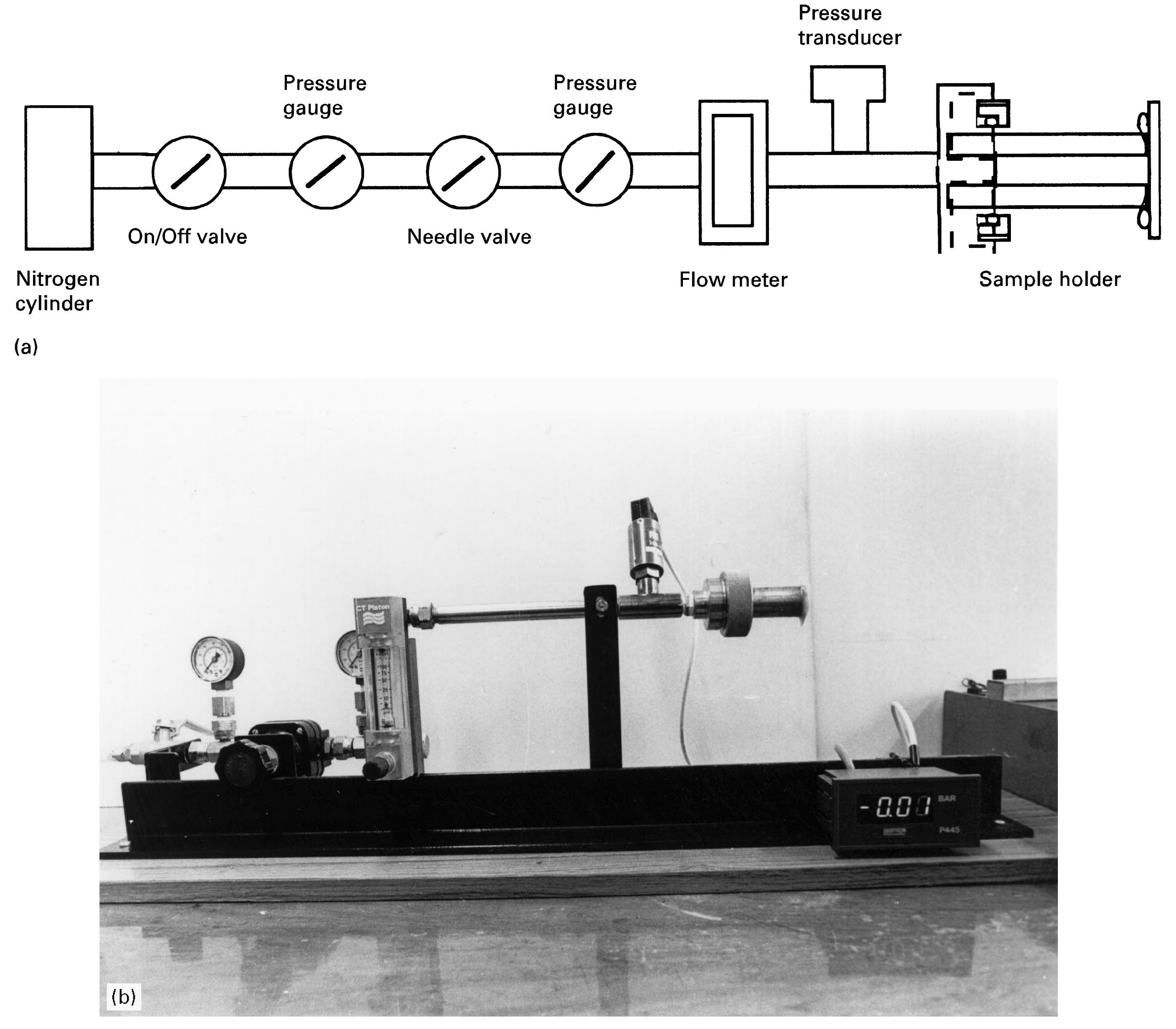

Figure 1 Adhesive seal test apparatus, (a) schematic diagram and (b) general view.

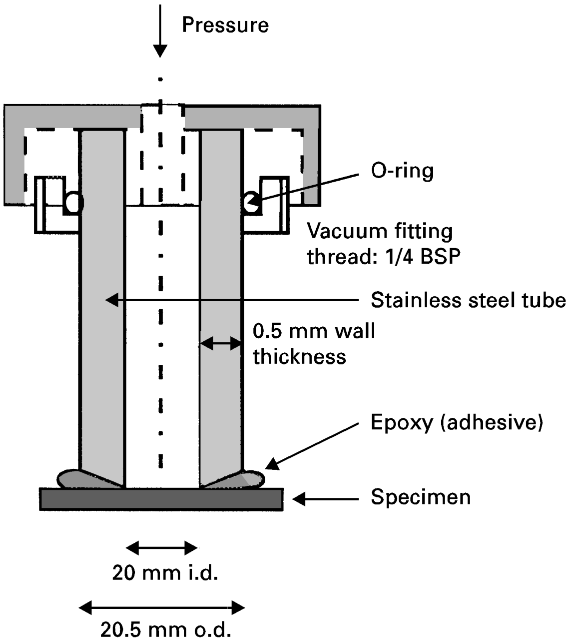

Figure 2 Schematic diagram of sample holder for adhesive seal tests.

Strength values were calculated according to Equation 1. For a circular plate, with clamped edges and uniform loading [9]:

$$\sigma_f = 3Wr_0^2/4t^2 \tag{1}$$

where σ_f is the strength at fracture, W is pressure at fracture, t is the thickness of the sample and r_0 is the radius of the sample. The maximum tensile stress (σ) in this case occurs at the high pressure surface of the fixed edge of the plate.

2.1.1. Mechanical testing of glass coverslips

In order to establish the validity of the testing technique developed here, initial measurements were carried out using uniform, standard specimens of a brittle material, i.e. glass microscope coverslips.

Two hundred microscope coverslips of glass quality CM5, were supplied by Chance Propper Ltd. (West Midlands, UK). This glass is formulated to withstand humid conditions without excessive surface deterioration. This was chosen to provide a narrower distribution in fracture strengths than would be the case for a simple soda-lime-silica glass [10].

Samples were cleaned with industrial methylated spirits (IMS), fully dried at 100 °C in a vacuum oven and stored in a dessicator until required for mechanical testing.

Individual thickness measurements on the coverslips were not carried out as the micrometer anvil might have scratched the glass surface and weakened the specimen. In order to avoid this, 10 batches to 5 coverslips were arbitrarily selected, cleaned and dried using the same procedure. Measurements were then accurately made for each batch using a Mitutoyo digital micrometer. The mean value for the 10 batches was then taken as the thickness for all the coverslips tested here.

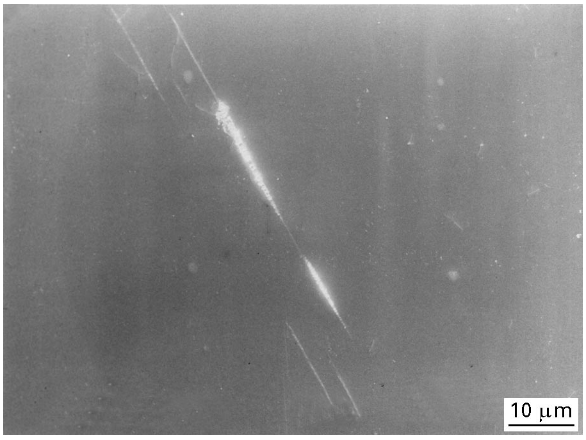

Figure 3 SEM micrograph of abraded glass coverslip showing induced surface damage.

2.1.2. Abrasive test on glass coverslips

In order to provide a comparison between different sets of strength data, surface defects were introduced in some of the coverslips. A total of 38 samples were scratched twice with 90 μm silicon carbide powder to induce reproducible surface defects larger than any accidental damage in the as-received specimens.

Samples were cleaned with IMS and dried as above. Scanning electron microscopy (SEM) examination, before mechanical testing, was undertaken for both scratched and non-scratched samples in order to compare both surfaces. Induced defects were clearly observed under the microscope, Fig. 3, for the abraded specimens.

2.2. Processing of thin ceramic films

2.2.1. Preparation of filled polymer

The formulation of the filled polymer used for film blowing experiments had four constituents: polymer, ceramic powder, plasticizer and dispersant. The matrix polymer was polystyrene, grade HF555, density 1060 kg m^{-3} supplied by BP Chemicals, UK. Two different ceramic powders were used; alumina and samaria-doped ceria. Alumina (Al_2O_3) grade RA6, with a density of 3987 kg m^{-3} and average particle size of 0.90 μm was supplied by Alcan Chemicals Ltd., UK. Doped-ceria was prepared from 90 : 10 (Ce : Sm) mixture of CeO_2 of 99.5% purity (7132 kg m^{-3} density and 6.90 and 0.59 μm average particle size for unmilled and milled, respectively) and Sm_2O_3 of 99.9% purity (8347 kg m^{-3} density with a median particle size of 3.33 μm) both supplied by Rhone Poulenc, France. The as-received CeO_2 powder was milled for 24 h in water and dry mixed with Sm_2O_3 to give a 90 : 10 composition. Subsequently samples were calcined at 950 °C for 8 h and then milled for a further 24 h in water and for 1/2 h in propan-2-ol to break up any agglomerates. Trimetilate ester OTM (grade Hexaplas, density 989 kg m^{-3}), supplied by ICI Chemicals & Polymers, UK, was used as the plasticizer and stearic acid (99% purity and 941 kg m^{-3} density), supplied by BDH Chemicals, UK, was used as the dispersant.

Formulations containing 50 vol % alumina powder (plus polymer, plasticizer and dispersant) and 45 vol % doped-ceria powder (plus polymer, plasticizer and dispersant) were prepared with weight ratios of organic constituents in the mixtures of 6:3:1 and 7:2:1, respectively. The alumina formulation was compounded at a temperature of 125 °C using a twin roll 30 cm × 15 cm Shaw Robinson single geared mill (Joseph Robinson & Co. Ltd, Manchester, UK). The doped-ceria formulation was twin screw extruded at 125 °C (Betol TS40, Luton, UK). The extrusion process was repeated to ensure a uniform distribution of constituents throughout the filled polymer.

2.2.2. Tubular film blowing

Thin films of filled polymer were prepared by the film blowing technique developed by Greener and Evans [11]. A specially constructed die was fitted to a Davenpont Capillary Rheometer with the gas inlet attached to a nitrogen cylinder set at a pressure of 14 kPa. The granulated filled polymer was dried overnight under vacuum at 40 °C before extrusion through the die and subsequent inflation with nitrogen gas. For the alumina samples the initial rheometer barrel temperature was set at 120 °C and the charge was left to warm up for a period of 10 min before film blowing. Both rheometer barrel temperature and piston speed were varied in order to improve the quality of the film blown material. The optimum barrel temperature was found to be 125 °C. Faster piston speeds appeared to give better results due to the shorter die residence time during film blowing. Doped-ceria samples were film blown at a barrel temperature of 135 °C following the same procedure as for alumina films.

2.2.3. Film pressing

After film blowing, specimens of the filled polymer film were cut to approximately 50 mm × 50 mm and flattened by placing between heated plates in a hydraulic press (Geo E. Moore & Son (Birminghan) Ltd). A pressure of approximately 16 MPa was applied for 30 s at a temperature of 80 °C followed by a cooling cycle at 20 °C under 10 MPa pressure.

2.2.4. Binder removal and sintering

Alumina films were pyrolized and sintered in air in a chamber furnace (Lenton Thermal Design Limited). The furnace temperature was increased from room temperature to 900 °C at a rate of 1 °C min^{-1} and from 900 °C to the sintering temperature at a rate of 5 °C min^{-1}. After sintering, specimens were furnace cooled to room temperature.

Several methods were tested for maintaining flatness while pyrolizing the films. The most successful one was found to be sandwiching the film between two special high purity alumina Saffil fibre boards (100 mm × 50 mm × 10 mm, Slate Vernaware, Bolton, UK) capable of withstanding continuous use at 1700 °C. It was found that, by placing three or four additional boards on top of the upper Saffil board, the extra weight helped to flatten the films more thoroughly. Specimens were sintered at 1560 °C for 3 h.

For the film blown doped-ceria samples a partial removal of the polymer was carried out at 310 °C in a nitrogen atmosphere. Specimens were then sintered in air at 1525 °C for 2 h using the same heating cycle as for the alumina films.

2.3. Characterization of thin ceramic films

Cross-sections of thin ceramic films were mounted in an epoxy resin, polished on successive diamond laps down to 1 μm and gold-coated for examination using a Jeol 840 scanning electron microscope to determine the film thickness and microstructure [12].

3. Results

3.1. Mechanical tests on glass coverslides

The results of the mechanical tests on the as-received and abraded glass coverslides are summarized in Table I. A plot of $\ln\{\ln[1/S_j]\}$ versus $\ln \sigma_j$ (where S_j is the probability of survival at an applied stress of σ_j) was used to obtain the value of the Weibull modulus [13–15] in each case, as shown in Figs 4 and 5.

3.2. Observation of ceramic films

3.2.1. Alumina

Fracture surfaces of film blown alumina ceramic films sintered at 1560 °C for 3 h are shown in Fig. 6.

The sintered films were highly non-uniform with thickness variations of up to 64% across a single specimen (25 mm × 25 mm) . Typical sintered film thicknesses were in the range 60 to 150 μm. The sintered microstructure consisted of grains less than 1 μm diameter with a large volume fraction of residual porosity. Typically the pore size was in the range 1 to 10 μm, Fig. 6b.

3.2.2. Doped-ceria

Fracture surfaces of film blown doped-ceria films sintered for 2 h at 1525 °C are shown in Fig. 7a and b. As with the alumina films, the sintered film thickness showed great variability over a single specimen; typically a 72% variation in thickness was observed by

TABLE I Summary of mechanical test results on glass coverslips

Specimen type	Number of specimens	Mean fracture stress (MN m^{-2})	Standard deviation (MN m^{-2})	Weibull modulus, *m*
As-received	38	398	132	3.3
Abraded	38	103	21	5.3

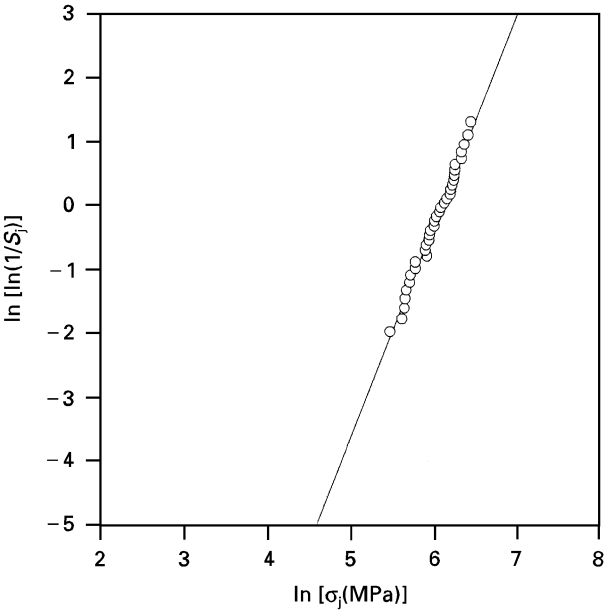

Figure 4 Weibull plot for as-received glass coverslips, Weibull modulus (m) = 3.3.

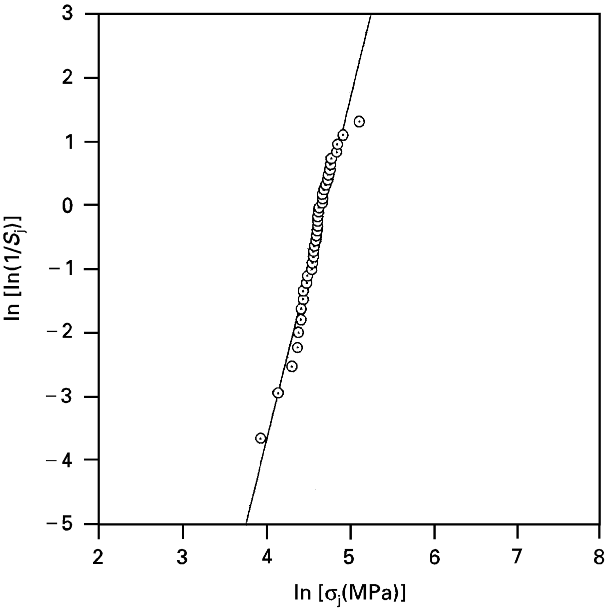

Figure 5 Weibull plot for abraded glass coverslips, Weibull modulus (m) = 5.3.

SEM examination. The range of sintered film thicknesses was found to be approximately 40 to 250 μm. The sintered microstructure consisted of grains less than approximately 4 μm diameter with a large volume fraction of residual porosity. Typically the pore size was less than 2 μm, Fig. 7b.

3.3. Mechanical tests on ceramic films

The results of the preliminary mechanical tests on the film-blown alumina and doped-ceria ceramics are summarized in Table II.

In all cases the ceramic films appeared to be gastight prior to fracture, i.e. there was no detectable pressure drop under static conditions. However, the

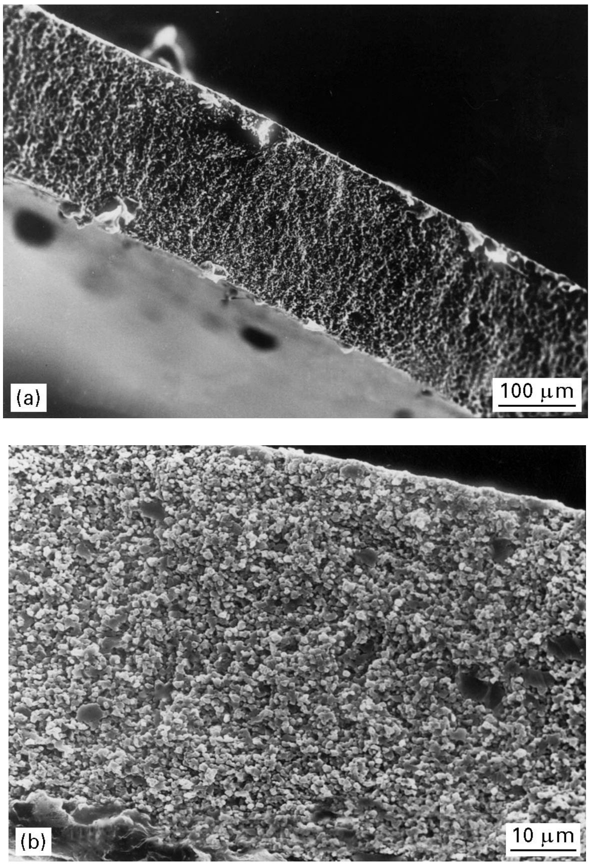

Figure 6 SEM micrographs of fracture surfaces of alumina specimens sintered at 1560 °C for 3 h, (a) magnification = 204x, (b) magnification = 680x.

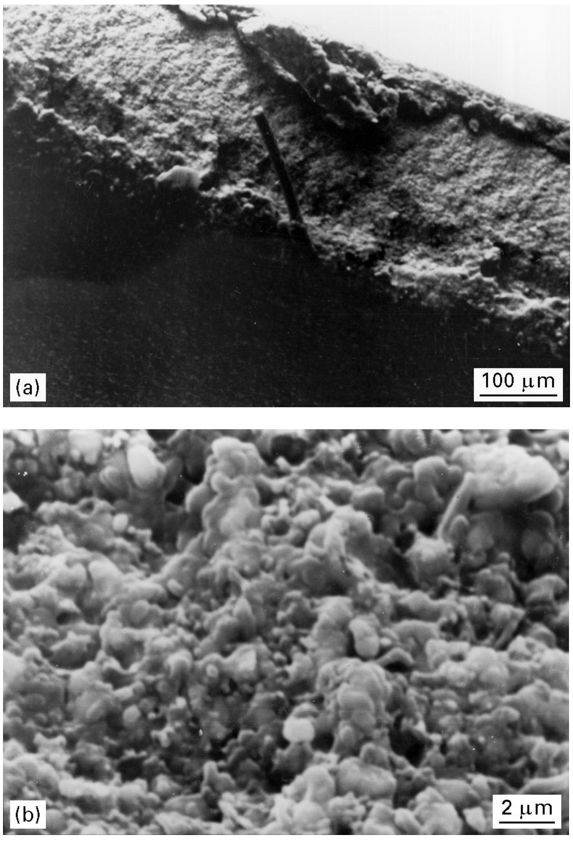

Figure 7 SEM micrographs of fracture surfaces of doped-ceria specimens sintered at 1525 °C for 2 h, (a) magnification = 224x (showing a Saffil fibre which adhered to the specimen during sintering), (b) magnification = 6800x.

TABLE II Summary of mechanical test results on ceramic membranes

Specimen type	Number of specimens	Mean fracture stress ($MN\,m^{-2}$)	Standard deviation ($MN\,m^{-2}$)	Weibull modulus, m
Alumina	22	464	179	2.2
Doped-ceria	5	316	279	–

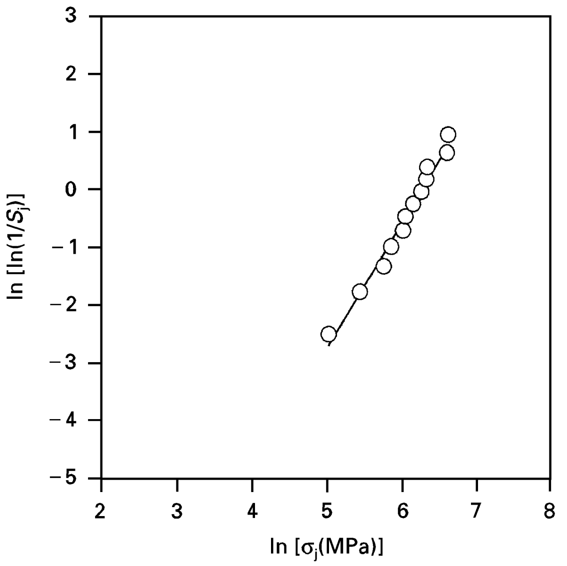

Figure 8 Weibull plot for alumina specimens sintered at 1560 °C for 3 h. Weibull modulus (m) = 2.2.

variability in the film thickness across the specimen for both alumina and doped-ceria films prevented a reliable measurement of the true thickness of the ceramic at the point-of-fracture initiation. The results presented here are therefore calculated on the basis of the mean film thickness found by measuring the thickness of the film fragments after fracture by SEM [12]. Sufficient alumina specimens sintered under nominally identical conditions (1560 °C for 3 h) were available to allow a Weibull analysis, Fig. 8, but only five doped-ceria specimens in total were tested so no Weibull modulus could be obtained in this case.

The apparent fracture strengths, calculated using the average specimen thickness measured by SEM in each case, are plotted against the average specimen thickness in Figs 9 and 10. In these figures the horizontal error bars indicate the spread of specimen thicknesses (t) measured and the vertical error bars the spread in the resulting calculated fracture strengths (σ) from Equation 1.

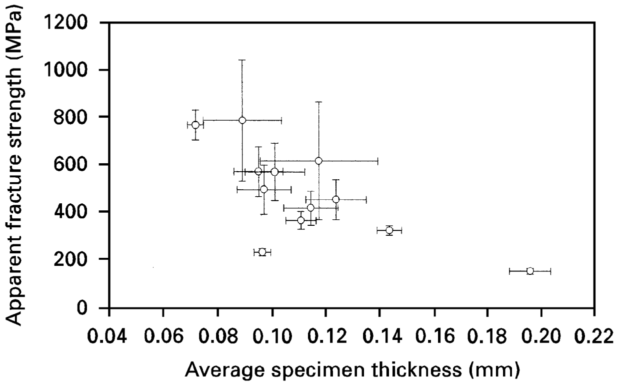

Figure 9 Effect of specimen thickness on the apparent fracture strength of alumina specimens sintered at 1560 °C for 3 h.

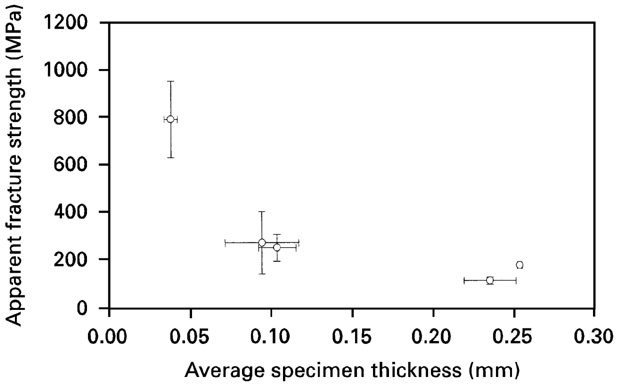

Figure 10 Effect of specimen thickness on the apparent fracture strength of doped-ceria specimens sintered at 1525 °C for 2 h.

4. Discussion

4.1. Testing technique

The Weibull plots obtained for the as-received and abraded glass coverslides are given in Figs 4 and 5. Each plot is typical of a set of specimens of a brittle material with a single population of flaws, in this case surface defects due to damage. The Weibull modulus (m) is greater for the abraded samples and this set of specimens has a lower average strength than the as-received glass coverslides. This is consistent with the behaviour of glass when comparing a set of specimens with accidental surface damage, which will give rise to a wide spread of surface defect sizes, with a set which has been treated to produce surface damage of a more severe but also more uniform type [16–21].

These results suggest that the technique developed in the present investigation is capable of characterizing the fracture behaviour of thin films of brittle materials. It is not possible to determine from the results whether the test is accurate in determining the absolute strength value for a thin brittle specimen. Equation 1 is based on a simplified theory [9] which assumes that the deflection (ω) of the specimens on loading is small compared to its thickness (t) .

This theory also allows the maximum deflection (ω_m) of the specimen at fracture to be estimated as:

$$\omega_m = \sigma_f r_0^2(1 - v^2)/4Et \tag{1}$$

where σ_f is the fracture strength, r_0 is the radius of the specimen under load, v is the Poissons ratio and E is the Young's modulus or modulus of elasticity for the material.

Using a value of $E = 70$ GPa [22] for glass, ω_m for the as-received coverslides was found to be in the range $1.0 \times t$ to $10.5 \times t$. For the abraded specimens, ω_m was $0.5 \times t$ to $1.4 \times t$. This suggests that Equation 1 can only be considered to be an approximate solution in this case. A more detailed analysis of the loading system (using finite element methods) may be required to obtain absolute strength values from this testing technique. However, the Weibull plots for both types of glass specimens, Figs 4 and 5, appear to be well behaved and the values of the Weibull moduli obtained are consistent with the known behaviour of brittle solids [16–21]. This demonstrates that the testing technique is capable of producing self-consistent results which can distinguish between groups of specimens of brittle materials with different flaw types and/or populations. Therefore, this technique can be used to investigate the effects of composition and processing conditions on the fracture behaviour of thin films of glasses or ceramics.

4.2. Fracture of ceramic thin films

The Weibull plot obtained for the film-blown alumina specimens, Fig. 8, gave a low value for the Weibull modulus. This indicates that the processing technique used in this investigation produced specimens which were highly variable despite the nominally identical film blowing and sintering conditions employed.

The processing technique also produced specimens which were of inconsistent thickness and work is continuing to resolve these problems by improvements in die design and control of the film blowing process parameters. Despite the inherent variability in the materials, the fracture strength of both alumina and doped-ceria thin films appear to increase slightly as the average specimen thickness decreases, Figs 9 and 10. This effect may be an artefact of the approximate solution used to calculate the strength values, Equation 1. For the alumina specimens (E taken as 380 GPa [22]) deflections at fracture were in the range $0.2 \times t$ to $17.0 \times t$ and for the doped-ceria specimens (E taken as 172 GPa [22]) deflections were $0.2 \times t$ to $85 \times t$ with the large deflections occurring for the thinnest samples. Equation 1 then seems to become a worse approximation to the true fracture strength as the specimen thickness decreases.

However, there may also be a real effect of specimen thickness on fracture strength for these materials. These thin membranes were tested in the as-sintered condition with no surface machining or polishing prior to testing. The materials were also of relatively low final density and contained a high proportion of pores, typically with a size equal to or larger than the mean grain diameter, Figs 6 and 7. This suggests that the pores may act as fracture-initiating flaws in these materials. Thinner specimens may be those which have sintered to high density and therefore contain fewer, smaller pores. Also specimens which had a greater final thickness may have been poorly sintered due to constrained sintering arising from adherence of the ceramic film to the Saffil support boards. Another possible explanation is that the thicker fired specimens were produced from sections of the filled polymer which had not expanded uniformly during film blowing due to the presence of agglomerates of ceramic powder in the polymer. Such agglomerates would hinder the subsequent sintering of the ceramic film and may lead to regions of high residual porosity within the specimen.

5. Conclusions

The novel testing apparatus developed in this study was shown to provide reproducible fracture strengths and Weibull moduli for standard glass specimens. The expected reduction in fracture strength and increase in Weibull modulus in abraded glass specimens was observed using this testing technique.

Despite the problems with the processing of the film blown membranes, at an early stage in the development of this technique, specimens were produced which had acceptable fracture strengths at room temperature. The specimens were also found to be gas tight, an important requirement for an electrolyte in solid oxide fuel cells.

Although the problems in measuring the actual thickness of the specimens at the point of fracture led to uncertainties in the absolute values of the fracture strengths obtained here, the result did suggest that there may be a real increase in fracture strength as the specimen thickness decreased. This implies that there may be differences in the microstructure of the fired ceramic in thinner and thicker regions, possibly due to either less constraint on the sintering of the thinner regions or the presence of ceramic powder agglomerates in the thicker regions of the ceramic membrane before firing.

Acknowledgements

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