MECHANICAL PROPERTIES OF CERAMIC MATERIALS FOR SOLID OXIDE FUEL CELLS

A. Atkinson and A Selçuk
Department of Materials
Imperial College
London SW7 2BP UK

ABSTRACT

Mechanical properties (Young’s modulus, Poisson’s ratio, mean fracture strength and Weibull modulus) of yttria-stabilised zirconia, gadolinia-doped ceria, lanthanum strontium manganate, NiO/YSZ composite and laminated ceria/zirconia structures were measured. The techniques included sonic excitation and “ring on ring” biaxial flexure at room temperature and 800°C. The “composite sphere model” was used to interpret the effect of porosity on elastic properties. Fracture of the materials was found to be initiated at the sample surface under the maximum tensile stress.

INTRODUCTION

The key electrochemical components of Solid Oxide Fuel Cells (SOFCs) are mostly brittle ceramic materials that are subjected to mechanical stresses arising from fabrication and assembly (residual stresses), and from cell operation. The ability of the cell stack to cope with these stresses is an important issue in achieving the target operational life time of an SOFC system (e.g. of $10^4$ to $10^5$ hours). However, comparatively little research has been carried out on the mechanical properties of SOFC components and their impact on the lifetime of SOFC operation.

A fundamental component in planar SOFCs is the integrated PEN structure (Positive electrode - Electrolyte - Negative electrode), which is produced by ceramic powder processing routes such as tape casting, screen printing or calendering. The mechanical properties of the individual layers in the integrated PEN will depend on their microstructures and hence on the way in which they are fabricated. Since at least three individual layers of different ceramic materials are joined together in PENs, the overall reliability of the PEN structures will also depend on the interfaces between these layers. The main electrolytes currently being developed are yttria-stabilised cubic zirconia (YSZ) and gadolinia-doped ceria (GO). The most common cathode material is strontium-doped lanthanum manganate (LSM) and the anode is usually a Ni/YSZ cermet formed by reduction of a NiO/YSZ ceramic composite. In order to analyse how the PEN
will respond to residual and operational stresses it is necessary to have data for the elastic and fracture properties of the individual materials in the form in which they are fabricated for the PEN (not as single crystals or bulk ceramics formed by a different route such as powder pressing).

Literature data for the mechanical properties of the SOFC components are limited. Scafe et al. (1) measured the porosity dependence of Young’s modulus of tape-cast YSZ containing 8 mol% yttria, determined by the ultrasonic “pulse-echo” technique at room temperature. Lowrie et al. (2) measured the biaxial flexure strength and Weibull modulus of similar electrolytes at room temperature and 950 °C. Sammes and Zhang (3) recently reported measurements of four-point flexure strength and indentation toughness of pressed and sintered specimens of Ce0.8Gd0.2O1.9 at 25, 500 and 800 °C. In the present paper we report studies of the elastic moduli, Poisson’s ratio, biaxial flexure strength and Weibull modulus of YSZ, GCO, tetragonal zirconia polycrystal (TZP), LSM and NiO/YSZ at room temperature and 800°C and in forms that are representative of their use as components in fuel cells. We also report measurements of room temperature biaxial fracture of YSZ/GCO laminated bilayers.

**EXPERIMENTAL**

**Materials**

The general characteristics of the materials studied are given in Table 1. They were produced in the form of circular disks by a polymer vehicle ceramic fabrication process, in which a viscous ceramic powder-binder mixture was prepared and then shaped into a green tape by extrusion. Circular discs 21 mm in diameter were cut from the green tapes, and, after binder burnout at 400°C, densified by sintering in air at the

| Material code | Composition | Sintering condition | Thickness (µm) | Relative density (%) |
|---------------|-------------|---------------------|---------------|---------------------|
| 10GCO         | Ce₀.₉Gd₀.₁O₁₀₅⁵ | 1500°C, 1 h         | 190 - 205     | 95 - 98             |
| 20GCO         | Ce₀.₈Gd₀.₂O₁₀₉₀ | 1500°C, 1 h         | 200 - 215     | 94 - 98             |
| YSZ1300       | 8 mol%Y₂O₃ - ZrO₂ | 1300°C, 3 hrs.     | 175 - 190     | 93 - 99             |
| YSZ1350       | 8 mol%Y₂O₃ - ZrO₂ | 1350°C, 3 hrs.     | 175 - 190     | 93 - 99             |
| LSM           | La₀.₈₅Sr₀.₁₅MnO₃ | 1300°C, 3 hrs.     | 500 - 550     | 85 - 90             |
| NiO-YSZ       | 75 mol% NiO-YSZ  | 1300°C, 2 hrs.     | 515 - 550     | 86 - 92             |
| TZP           | 3 mol% Y₂O₃ - ZrO₂ | 1500°C, 1 h.      | 165 - 175     | 90 - 95             |
temperatures given in Table 1. The density of each specimen was determined by a geometrical method (4) and the range of measured geometrical densities for each set of specimens is given in Table 1.

The objective of the GCO/YSZ laminate was to create an electrolyte suitable for "intermediate" temperature operation (650 - 800°C) by co-firing at 1500°C a thin layer of YSZ (5 microns) with a 180 micron layer of 10GCO. The YSZ acts as a blocking layer to the electronic conductivity of GCO which is induced at low oxygen chemical potentials and degrades the PEN performance.

Measurements

The Young's and shear moduli, E and G, and Poisson's ratio, ν, were determined at room temperature by the impulse excitation resonance technique (4), except for LSM which did not give a sharp resonance. The high temperature (800°C) Young's modulus and fracture in biaxial flexure at both room temperature and 800°C were measured using the ring-on-ring loading configuration (5). The outer ring (stationary) had a diameter of 17 mm and comprised 24 sapphire balls each 2 mm in diameter. The inner ring (driven) was made from reaction bonded silicon nitride with a radius of 3.4 mm and a cross sectional profile radius of 0.6 mm at the contact with the specimen. All experiments were carried out at a crosshead speed of 1 mm/min. Finite Element Modelling (FEM) with the commercial code “ABAQUS” was used to relate the stress distributions in the specimens to the measured load-displacement curve because the central displacement of the specimen at fracture was usually an appreciable fraction of its thickness, under which conditions the load-deflection relationship is not linear (5). Young's modulus was also measured from the load-deflection relationship at room temperature (RT) and the value from this method was found to be lower than that measured by the resonance method by between 2 and 6%. This was probably the result of a contribution to the deformation of the specimen arising from it not being perfectly flat before loading. (Specimen flatness and roughness were measured using a stylus profilometer.) Suitable resonances could not be obtained at 800°C and so Young's modulus at this temperature was measured from the load-displacement curve and then increased by 4% to be consistent with the resonance measurements at RT. Poisson's ratio at 800°C was assumed to have the value 0.313; equal to that measured on single crystals at RT (6). For most specimens, fracture was initiated within the circle of the inner loading ring and thus the biaxial fracture stress was taken to be the average stress within this region at the tensile face of the specimen. In a few GCO specimens, when they were significantly non-planar, the fracture was initiated outside this region and therefore these results were discarded.

The GCO/YSZ bilayer laminates were curved after fabrication in response to residual stresses induced by the thermal expansion mismatch between the two materials. The curvature of the specimens at room temperature was measured using a surface profilometer. Thermal expansion was measured by dilatometry and the averages for
Table 2. Average coefficient of thermal expansion ($x10^{-6}$ K$^{-1}$) for cooling from T to the test temperature

| From T (°C) | 10GCO to RT | to 800°C | YSZ to RT | to 800°C |
|------------|-------------|----------|-----------|----------|
| 1500       | 13.61       | 15.46    | 11.25     | 12.49    |
| 1400       | 13.38       | 15.54    | 11.19     | 12.54    |
| 1300       | 13.17       | 15.02    | 11.11     | 12.58    |
| 1200       | 12.96       | 14.83    | 11.00     | 12.62    |

cooling the specimens from high temperature to the test temperature are given in Table 2. The residual stress distribution and the expected curvature after cooling from a high temperature to 800°C and RT was calculated by fully elastic FEM. Good agreement with the experimentally measured curvature at RT was found when the temperature below which stress relaxation by creep was negligible was assumed to be 1200°C. The calculated residual stress distribution is shown in Figure 1 and indicates large compressive stress in the YSZ layer. The mechanical behaviour of these asymmetrical laminates in the ring-on-ring test depends on which surface is under tension. The total stress distribution under the combined residual thermal expansion mismatch and applied testing loads was calculated using FEM and the results for the case where the applied load puts the YSZ layer in tension is shown in Figure 2. In this loading configuration the maximum tensile stress occurs in the GCO at the interface with the YSZ and inside the inner loading ring.

RESULTS AND DISCUSSION

Elastic Properties

The dependence of Young’s modulus, shear modulus and Poisson’s ratio on volume fraction of porosity, $p$, is illustrated in Figure 3. The measured results are fitted well (solid curves) by the composite sphere model of Ramakrishnan and Arunachalam (9) in which the only adjustable fitting parameters are the moduli at zero porosity. The porosity dependence of the moduli according to this model are given by

\[
E = E_0 \frac{(1 - p)^2}{(1 + b_E p)} , \quad G = G_0 \frac{(1 - p)^2}{(1 + b_G p)} , \quad \nu = 0.25 \frac{4\nu_o + 3p - 7\nu_o p}{1 + 2p - 3\nu_o p} \quad [1, 2, 3]
\]
where \( b_E = 2 - 3 \nu_o \) and \( b_G = \frac{11 - 19 \nu_o}{4 + 4 \nu_o} \). \([4, 5]\)

The porosity dependence of elastic moduli of all the materials were fitted well by this model, except the NiO/YSZ composite \([4]\). It is suggested that the model is not applicable to this composite because the two solid constituents have significantly different elastic constants. The fitted values of Young’s modulus and Poisson’s ratio at zero porosity are given for each material in Table 3.

**Biaxial Flexural Strength of Single Materials**

The Weibull modulus, \( m \), and the Weibull characteristic strength, \( \sigma_o \), were calculated by the least square method using the estimator

\[
W = \frac{(j - 0.5)}{n},
\]

\([6]\)

where \( j \) is the ranking of the strength, \( \sigma \), and \( n \) is the number of specimens in the set, and the Weibull distribution function

\[
F = 1 - \exp \left[ -\left(\frac{\sigma}{\sigma_o}\right)^m \right]
\]

\([7]\)

The fitted parameters are summarised in Table 3. The Weibull modulus for most of the materials is in the range 3.5 to 7 which is typical of monolithic ceramics in which no special precautions have been taken to narrow the spread of fracture strengths. The YSZ material sintered at 1300°C displays a higher mean strength than that sintered at 1350°C which could reflect a finer grain size in the material sintered at the lower temperature. The fracture strengths of the two types of material were combined in a single set (of 20 specimens) and analysed by the same method and the result is shown in Figure 4. The data show reasonable consistency with a common distribution for the two materials; indicating that the strength-determining flaws are the same in both. The plots show deviation from the fitted distributions at lowest strengths which could indicate an upper limit to the flaw size. The strength at 800°C is significantly lower than the RT strength but the Weibull modulus is unchanged; indicating that the same flaws initiate fracture at both temperatures. This is different from the behaviour reported by Lowrie et al. \([2]\). They found a Weibull strength of 266 MPa and modulus of 7.7 (15 specimens) at RT; which are similar to the results on YSZ1300 found in the current study (Table 3). However, Lowrie et al found that the flexural strength remained approximately the same at 950 °C, but the Weibull modulus was reduced to 4.6. The reasons for the different behaviour at high temperature found in the two studies are not clear and are the subject of continuing experiments. The fracture surfaces (Figure 5) show that fracture was initiated at flaws on or near the surface of the specimens. Typical surface defects revealed by profilometry were in the range 5 to 10 microns deep.
Table 3. Summary of mechanical properties

| Material code | $E_0$ (GPa) | $v_0$ | Mean strength (MPa) | Weibull module | Sample size |
|---------------|-------------|-------|---------------------|---------------|-------------|
|               | RT 800°C    | RT 800°C | RT 800°C | RT 800°C | |
| YSZ1300       | 187         | 0.334  | 157             | 0.313         | 108         |
| YSZ1350       | 186         | 0.311  | 153             | 0.313         | 108         |
| LSM           | 161         | 0.317  | 180             | 0.313         | 108         |
| NIO-YSZ       | 161         | 0.317  | 180             | 0.313         | 108         |
| TZP           | 161         | 0.317  | 180             | 0.313         | 108         |
TZP showed the highest strength at RT which is consistent with the transformation toughening of this composition. However, its mean strength at 800°C was approximately the same as YSZ reflecting the fact that the toughening mechanism becomes less effective as the unconstrained transformation temperature (approximately 900 °C) is approached. The LSM cathode material is significantly stronger at 800°C than at RT, which probably reflects some continuing microstructural change (sintering) occurring at 800°C during preparation for testing.

The RT strength of 10 GCO and 20GCO is similar to that reported by Sammes and Zhang (3), bearing in mind the fact that different loading configurations were used. However, the 10GCO material in the present study has higher flexural strength at 800°C than at RT, whereas Sammes and Zhang found a slight decrease in their material with a porosity in the range 5% to 12%. As discussed for YSZ, there is no satisfactory explanation currently for the different responses to temperature exhibited by similar materials in different studies. Nevertheless, the modulus values ($E = 200$ GPa) for 10GCO being the same at both test temperatures suggest that, for the same critical defect size and distribution, the high temperature strength should be as high as the RT strength.

Biaxial Flexure and Fracture of GCO/YSZ Laminates

Weibull plots for these laminates are shown in Figure 6 in which the applied load was generating a tensile strain component in the YSZ. The fracture stress plotted is the estimated maximum tensile stress and occurs in the GCO at the interface with the YSZ (section 4 in Figure 2). These results suggest that the GCO in the laminate is approximately twice as strong as a single GCO layer. This might be explained if the interface between the two materials had smaller flaws than an external surface (i.e. some of the incipient large surface defects were “filled in” during the lamination of the bilayers). Alternatively, it might be that there has been some limited stable cracking in the GCO that has partially relieved the stress near the interface so that the assumption of a fully elastic analysis to calculate the stress would not be valid. However, although some features were seen on the fracture faces in this region, no evidence of yielding by cracking was evident in the load - displacement curves. We therefore conclude that the GCO probably did not fail until these high estimated stresses were reached. This is potentially important for the use of GCO in SOFCs because GCO is generally regarded as being a significantly weaker material than YSZ.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the funding provided by the Commission of the European Communities (Contract BRE-CT93-0578), and the supply of samples by the Netherlands Energy Research Foundation and DSM of The Netherlands, and Siemens AG Corporate Research and Development of Germany.
REFERENCES

1. E. Scafe, M. Musicanti, and S. Mercuri, in Proceedings of the First European Solid Oxide Fuel Cell Forum, Vol. 2, p. 789, ed. U. Bossel, Druckerei J. Kinzel, Germany (1994).
2. F.L. Lowrie, R.D. Rawlings, B.C.H. Steele and W. Kleinlein, in Proceedings of the Fourth International Symposium on Solid Oxide Fuel Cells, Edited by M. Dokiya, O. Yamamoto H. Tagawa and S.C. Singhal, p. 318, The Electrochemical Society, Pennington (1995).
3. N.M. Sammes and Y. Zhang, in the Second European Solid Oxide Fuel Cell Forum Vol. 2, p. 697, Edited by B. Thorstensen, U. Bossel (1996).
4. A. Selçuk and A. Atkinson, accepted for publication in J. European Ceram. Soc.
5. H. Greiner, E. Keim, W. Kleinlein and E. Weiss, in Proceedings of the Second International Symposium on Solid Oxide Fuel Cells, p. 705, Edited by F. Grosz et al. (1991).
6. R.P. Ingel and D. Lewis III, J. Am. Ceram. Soc., 71, 265, (1988).
7. A.J.A. Winnubst, K. Keizer, and A.J. Burggraaf, J. Mater. Sci., 18, 1958 (1983).
8. J.D. Buckley and D.N. Braski, J. Am. Ceram. Soc. 50, 220 (1967).
9. N. Ramakrishnan and V.S. Arunachalam, J. Mater. Sci., 25, 3930 (1990).

Fig. 1 The residual stress distribution predicted in a 10GCO (180 micron) / YSZ (5 micron) bilayer laminate assuming no creep below 1200°C and complete stress relief above 1200°C. Note the different distance scales in the two materials.
Fig. 2 The calculated total stress in a 10GCO/YSZ bilayer laminate when loaded to apply tensile strain to the YSZ layer. (a) shows the location of the section through the stress distribution in the laminate and (b) shows the variation with radial position for each section.

Fig. 3 Young’s modulus, shear modulus and Poisson’s ratio of YSZ measured at RT using the resonance method. The solid line is calculated using the “Composite Sphere Model” (9). Also shown are data from other workers (1, 6, 7, 8).
Fig. 4
Weibull plots of biaxial flexure strength for the YSZ1350 and YSZ1300 materials analysed as a single set.

Fig. 5
Scanning electron micrograph of the fracture surface of a YSZ1300 specimen after fracture at room temperature.

Fig. 6
Weibull plots for GCO/YSZ bilayer laminates testing with the applied load generating a tensile strain component in the YSZ. The fracture stress plotted is the estimated maximum tensile stress and occurs in the GCO at the interface with the YSZ.