COMPARISON OF STRENGTH AND MICROSTRUCTURE OF THIN FULLY STABILISED ZIRCONIA AT ROOM TEMPERATURE AND 950°C

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ABSTRACT

Samples of fully stabilised zirconia made by the tape-casting process were broken at room temperature and 950°C using a biaxial flexure test. The fracture stress values were corrected to allow for the stress distortion which occurs as a result of the test geometry, and the mean strength, Weibull modulus, and fracture microstructure compared at each temperature. It was found that there was only a slight decrease in strength at 950°C, yet the Weibull modulus decreased significantly. Also there was a change in the appearance of the fracture surface at the higher temperature, indicating that a change in the fracture mechanism could be occurring.

INTRODUCTION

Fully stabilised zirconia is used as the electrolyte in the solid oxide fuel cell (SOFC) on account of its good ionic conductivity properties (1). However, the mechanical properties are also important since microcracking or failure of the electrolyte would degrade functional performance. Thus the mechanical properties of FSZ must be sufficient to maintain integrity at the operating temperature of 950°C. Also, to ensure that conduction
can be maintained over a long period of operation time, it is vital that the electrolyte's mechanical properties do not deteriorate as a function of time during service.

Both the electrical and the mechanical properties of the electrolyte will depend on its microstructure, and this is a product of the manufacturing process. Thus the limited data available on thick, bulk, FSZ specimens (2) may not be relevant to the thin, tape-cast material employed for SOFC.

In this paper, biaxial flexure strength tests and fractographic studies are used to compare the strength and fracture behaviour at room temperature and 950°C of specimens of 8 mol% YSZ, made by the tape-casting process.

EXPERIMENTAL PROCEDURE

Material

All the specimens tested were discs of cubic zirconia, stabilised with 8 mol% yttria. They were tape-cast in Germany by Kerafol, using powder supplied by Tosoh.

Biaxial Flexure

The biaxial flexure test used was the ring-on-ring design. The support ring, on which the sample was positioned, consisted of a ring of polished sapphire balls, and the loading ring was made of polished silicon nitride; this was to minimise friction between the specimens and the rig (3).

During a test, force versus deflection plots were produced as the loading ring was pushed into the centre of the specimens, at a speed of 1 mm/min., until failure occurred. The breaking force, plus the specimen dimensions, were used to calculate the failure stress, $\sigma_f$.

The dimensions of this rig were selected so that the membrane stresses produced in the specimens as a result of their comparatively large deflections were reduced (4), but the $\sigma_f$ values calculated are still distorted because they are obtained from standard expressions which are used for bulk specimens. Thus FEA was used to modify these standard equations, displaying the change in the stress distribution experienced across the specimens as the test proceeds, and to calculate a more accurate $\sigma_f$ value (5) (6).
Nominal specimen dimensions were diameter of 22mm and thickness of 0.15mm. 15 specimens were broken at room temperature and 15 at 950°C, and from the corrected $\sigma_f$ data the mean fracture stress $\sigma_0$ was calculated and a Weibull plot produced for each test temperature.

**SEM Analysis**

The fracture faces of the weakest and strongest specimens broken at each temperature were examined, in order to locate the source of failure. By studying the microstructure across each fracture face, close to and far from this source, the mode of crack propagation through FSZ at room temperature and 950°C could be compared.

EDAX was also used to obtain information concerning the type and quantity of impurities present, and their distribution across the specimen surfaces.

**RESULTS**

**Biaxial Flexure**

The Weibull plots for each temperature are shown in figure (1), and the results summarised in table (1). There is little change in $\sigma_0$, but the Weibull modulus, m, which is an indication of the scatter in the strengths, decreased significantly at the high temperature. There was no change in the shape of the force versus deflection plots for the two temperatures, and in all cases the failure initiated from the region where the loading ring had been placed, and hence the applied stress was greatest.

| Test temperature | $\sigma_0$  | m   |
|------------------|------------|-----|
| 20°C             | 266MPa     | 7.7 |
| 950°C            | 258MPa     | 4.6 |
SEM Analysis

SEM analysis of the specimens tested at room temperature showed that the source of failure of the weaker specimens were large defects sited on or very near to the tensile face. Such a defect is shown in figure (2). Around these defects, and across the rest of the fracture face, the failure was transgranular, as shown in figures (2) and (3). It was also observed that these defects were distributed throughout the microstructure, as shown in the fractograph of figure (3).

For the stronger specimens broken at room temperature, the precise location of the failure site often could not be detected due to multiple fracture of the specimen, but similar defects as those shown above were noticed to be distributed throughout the structure.

Analysis of the weaker specimens broken at 950°C showed again that the source of failure was due to large defects at the tensile face in the region of the loading ring. Around the defect the crack path was transgranular, but further away the structure changed, with individual grains being clearly seen, indicative of intergranular failure - see figure (4). The failure appeared to be intergranular from the tensile edge through almost to the compressive edge, at which point it merged into a transgranular structure.

This phenomenon was repeated for the stronger samples. Again the actual failure initiation site could not be exactly located, but around the area from whence the crack began the structure was transgranular, whereas the rest of the fracture face away from the defect clearly displayed individual grains, consistent with an intergranular crack path.

The EDAX results showed that there were very low levels of alumina and silica impurities distributed throughout the tensile surfaces of the specimens.

DISCUSSION

The negligible difference in the mean fracture stress between room temperature and 950°C is encouraging; at both of these temperatures the fracture stress seemed to be determined by the presence of relatively large (approximately 35μm wide) defects. However, the changes observed in the Weibull modulus and the fracture mode suggest that the mechanical behaviour of FSZ is modified at the higher temperature.

The appearance of the fracture surface for the 950°C tests could be due to (i) the high temperature directly affecting the fracture mechanism, (ii) microstructural changes which
occur at 950°C affecting the fracture mechanism, or (iii) modification of the fracture surface on cooling from the test temperature, by, for example, thermal annealing. Possibility (ii) was investigated by heat treating a specimen at 950°C for 1 hour and then testing it at room temperature. The fracture surface was essentially the same as that described for the other specimens tested at room temperature, but with the occasional area of intergranular failure. Thus there is some evidence for microstructural change at 950°C, but this change is insufficient when considering the time scale of the flexure test to account for the high temperature fracture path. A specimen fractured at room temperature which had been examined previously in the SEM was heated to 950°C, cooled, and re-examined; its appearance did not change. It is therefore concluded that the intergranular failure observed in the 950°C tests is mainly a direct effect of temperature on fracture mechanism.

The fracture was not intergranular over the complete section of the sample and this suggests that 950°C may be close to the temperature at which the high temperature fracture mechanisms begin to operate. This is consistent with the values for Weibull modulus; the lower value at 950°C represents the slightly different behaviour occurring within the batch of specimens, caused by the different processes associated with the low temperature transgranular and high temperature intergranular failure mechanisms.

In addition to these findings, earlier work had been performed using tape-cast specimens containing approximately 1.2% alumina. The fracture surfaces of these specimens showed the same difference in crack path at the two temperatures as has been described above. However the mean strength at 950°C, of 119MPa, was less than half the room temperature strength of 276MPa; this drop in strength is attributed to the significant presence of alumina impurity at the grain boundaries.

At this stage it is not known why there was a change in the crack path observed between the two temperatures in the present work. The previous study on the specimens containing 1.2% alumina suggests that it is associated with impurities at the grain boundaries but, if this is the case, the EDAX results demonstrate that only very small quantities are required.
CONCLUSIONS

The work performed so far has shown:

(i) an impurity content of 1.2% alumina in FSZ can cause the strength at 950°C to be less than half the room temperature value,

(ii) tape-cast specimens of high purity do not show a significant strength loss between room temperature and 950°C. The strength seems to be determined by relatively large defects introduced during manufacture,

(iii) at 950°C a change in failure mode seems to be occurring, indicated by a significant decrease in the Weibull modulus, and the fracture showing intergranular as well as transgranular characteristics.

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REFERENCES

1. N. Minh, J. Am. Ceram. Soc., 76, 563 (1993).
2. D. J. Green, R. H. J. Hannink, M. V. Swain, Transformation Toughening of Ceramics, p.138, CRC Press Inc, Florida, (1989).
3. D. K. Shetty, A. R. Rosenfield, W. H. Duckworth, P. R. Held, J. Am. Ceram. Soc., 66, 36 (1982).
4. R. Kao, N. Perrone, W. Capps, J. Am. Ceram. Soc., 54, 566 (1971).
5. H. Greiner, E. Keim, W. Kleinlein, E. Weiss, / F. Grosz, P. Zegers, et al, Editors, p.705, Proceedings 2nd International Symposium SOFC, Athens (1991).
6. E. Keim, Interner Bericht, KWU E121/90/87.
Figure (1) - a graph showing Weibull plots of FSZ specimens tested at room temperature and at 950°C.
Figure (2) - a SEI of the tensile face of a FSZ specimen fractured at room temperature, showing a large defect and a transgranular structure.

Figure (3) - a SEI of the central area of a FSZ specimen fractured at room temperature, showing a transgranular structure, and a pore cluster.

Figure (4) - a SEI of the tensile face of a FSZ specimen fractured at 950°C, showing an intergranular structure.