ISSUES AFFECTING THE MECHANICAL INTEGRITY OF SOFCs

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ABSTRACT

The elevated operational temperature of a solid oxide fuel cell (SOFC) means that the cell components are subject to a number of issues affecting their mechanical integrity within the composite structure. These include residual stresses due to thermal expansion mismatch of the components, thermally induced stresses, and material creep at the elevated temperature. Half cells made of a standard yttria stabilized zirconia (YSZ) electrolyte substrate coated with an anode or cathode were specially prepared for the residual stress and creep analysis, and a porous support material was tested to fracture under thermally induced stresses. The creep deflection of the coated material was observed to be greater than that of the corresponding plain YSZ under the same temperature and stress conditions. Results of residual stress measurements based on curvature measurement were also found to be significantly lower than the predicted Finite Element stresses. The porous support exhibited good resistance to thermal stresses.

INTRODUCTION

The present investigation arose from the observation that there is little information available on the mechanical behaviour of SOFC components. The bulk of the research work on fuel cells in general has focussed on the electrochemical performance rather than mechanical integrity. However, mechanical and electrochemical requirements in a cell can be in direct conflict. High working temperature can result in material constraints and integrity issues. For example, temperatures and stresses, which are within the conditions known to cause creep in these materials are known to be present.

The aim of this paper is to assess some of the factors affecting the mechanical integrity of a SOFC. The issues identified here are (i) residual stresses due to thermal expansion mismatch during cooling after manufacture; (ii) creep due to the high working temperature, and (iii) thermally induced stresses due to temperature variations.

The sintering of ceramic powders is a common route for making ceramic-based thin film components. Typically, one or more thin films are screen-printed on a rigid substrate and then sintered. Under these conditions, one or more of the thin films will undergo constrained sintering due to the constraint imposed on the films by the substrate. This can result in significant residual stresses, which can, in turn, cause distortion of the component upon cooling, micro-cracking, interface delamination or other undesirable
effects (1). In unsupported electrolyte/electrode situations encountered in fuel cells this effect can be seen by curvature of finished components. Curvature of such components is measured here.

At the high operating temperatures of SOFCs, some of these residual stresses can be relieved by material creep (2, 3). The creep behaviour of plain YSZ and anode-coated YSZ material was studied under constant temperature and stress regimes that might be encountered in SOFC operation and is reported here.

The chemical reactions and changes in electrical load influence the cell temperatures, and can be considerably non-uniform (4, 5). These temperature gradients generate stresses within the fuel cell components. Here a method of quantifying the effects of such stresses is presented.

**RESIDUAL STRESS**

The stringent electrochemical requirements for fuel cell materials make it difficult to select materials, which have well matched coefficients of thermal expansion (CTEs). When a thin film is printed on a rigid substrate and sintered, it will tend to shrink upon cooling, and in addition, there will be differential cooling strains due to materials with higher CTEs contracting more upon cooling. The issue is complicated, however, by the bonding between the different materials; the net result is the generation of residual stresses.

Actual residual stress values were estimated, in this instance, from curvature measurements of the specimen before and after the coating was applied (see (6)). Curvatures of the two-layer components were measured using a Talysurf profilometer in two orthogonal directions.

In a two layer structure, if the thickness of layer 1 is small compared to layer 2, which is often the case for electrodes applied in fuel cells, the mean stresses $\sigma_{M1}$ and $\sigma_{M2}$ in layers 1 and 2 can be given by the following expressions where $\kappa$ is the curvature of the structure (7):

$$\sigma_{M1} = \frac{-\kappa E_h h_2^3}{6h_1(h_1 + h_2)(1 - \nu_2)}; \quad \sigma_{M2} = \frac{\kappa E_h h_1^3}{6h_1(h_1 + h_2)(1 - \nu_2)}$$  \[1\]

Curvature measurements were conducted on anode–YSZ (Ceraflex plate) samples sintered at four different temperatures and cathode–YSZ (Ceraflex) sintered at two different temperatures. A second set of measurements was taken after removing the coating using sandpaper. The residual stress due to thermal expansion mismatch is relieved after the coating is removed and the curvature of the sample is altered. This change is used to calculate the residual stress. Tables I and II later show the residual stresses calculated from curvature measurement of the two-layer samples compared with FE predicted stresses assuming purely thermo-elastic conditions and a stress free condition at the sintering temperature.
The residual stress in the anode at room temperature due to its thermal expansion mismatch was calculated from equation [1] to be 46 MPa. This residual stress is generated upon cooling the structure after sintering to room temperature. The stress free temperature was calculated by Atkinson & Selcuk for these materials (8), to be 1200°C. This is the temperature above which the stress is relieved plastically (and hence equivalently zero). It is clear therefore that much of the residual stress evident at room temperature is caused by thermoelastic cooling, and disappears on reheating. Tables I & II show that the residual stresses obtained from the Finite Element models assuming a purely thermoelastic cooling process from the sintering temperature to room temperature overestimate the residual stresses derived from curvature measurements. This indicates a stress relief has taken place by some sort of plastic deformation, and the next section is an attempt to account for the creep component of this.

Table I. Estimated residual stresses from curvature measurement and FE analysis of a cathode-YSZ bi-layer.

| Sintering | Residual | Estimated |
|-----------|----------|-----------|
| 1025°C    | 0.44     | 49.8      |
| 1125°C    | 0.91     | 54.8      |

Table II. Estimated residual stresses from curvature measurement and FE analysis of an anode-YSZ bi-layer.

| Sintering | Residual | Estimated |
|-----------|----------|-----------|
| 1150°C    | 4.4      | 143       |
| 1250°C    | 13.55    | 156       |
| 1350°C    | 22.4     | 169       |
| 1450°C    | 19.3     | 182       |

It is notable that the measured residual stress, on the anode-YSZ samples, is at its greatest at 1350°C. This could indicate that at this temperature the interfacial bond is stronger, and that sintering is best achieved at this temperature. This is reinforced by the observation that rubbing off the coating was more difficult for samples sintered at 1350°C, indicating a stronger bonding.
CREEP

Ring-on-ring creep experiments of 28-days duration under constant load were conducted on plain YSZ samples and anode-coated YSZ samples subjected to biaxial stresses representative of the SOFC service conditions. The experimental work was conducted in conjunction with appropriate finite element analysis to study the deflection-time curve and characterize the creep properties of the materials.

Square YSZ specimens of size 50 mm square and 200 μm thickness and the same specimens coated with a CeO-NiO cermet anode 25 μm thick were used. The specimens were loaded in a ring-on-ring arrangement of 40 mm diameter supporting ring and a 4 mm diameter loading ring (see Figure 1). A dead weight of 150 gm rested on top of the loading ring to generate a bi-axial stress of 55 MPa within the loading radius. A displacement LVDT transducer was mounted on top of the dead weight to measure the deflection over time. Measurements of deflection, time and furnace temperature were recorded using a computerized ("Maclab") data acquisition system.

![Figure 1. Schematic diagram of creep test rig.](image)

Typical time-deformation curves are shown by the dotted lines in Figure 2. The curves show that significant creep occurs in YSZ electrolytes even at 1000°C, relatively low since it is only approximately 0.4 of the melting point temperature. At such temperatures the creep mechanism is most likely to be Coble creep, i.e. creep by diffusion along the grain boundaries (9). A general steady state creep law, as given below, was used where the creep strain rate is proportional to a power of the experienced stress:

\[ \dot{\varepsilon}_c = A\sigma^n \]  

For Coble creep, the stress exponent will be \( n = 1 \).
A finite element analysis of the ring-on-ring loading condition was conducted to simulate the stress state and predict the vertical deflection at the center of the sample. The material constant \( A \) of equation [2] was determined by matching the measured and predicted deflection values, bearing in mind that \( A \) is temperature dependent. Figure 2 shows the match of the result where \( A \) was found to be \( 5.3 \times 10^{18} \) and \( 15 \times 10^{18} \) for the plain YSZ and anode-coated YSZ respectively.

For coatings deposited on a relatively thick substrate and then cooled to room temperature after sintering, the stresses in the substrate are small. However, there are much more significant stresses in the coating, and these may be relieved by creep (2), leading to permanent strain.

![Figure 2. Deflection of YSZ and anode-coated YSZ in a ring-on-ring biaxially loaded creep test.](image)

While temperature remains constant, since the total strain in the coating remains constant, then as the creep strain increases the elastic strain decreases thereby relieving the residual stress. The total strain is then given by

\[
\varepsilon = \varepsilon_e + \varepsilon_{cr} = \text{const}
\]  

where \( \varepsilon \) is total strain, \( \varepsilon_e \) is elastic strain, and \( \varepsilon_{cr} \) is creep strain.

Differentiating (3) with respect to time, assuming a biaxial stress, and substituting from (2), this gives

\[
\frac{d}{dt} \left( \frac{1-v}{E} \sigma \right) = -A \sigma^n
\]  

Solving, and using \( n = 1 \), the final stress \( \sigma \) can be given as a function of the initial stress \( \sigma_0 \) and material constants:

\[
\ln \sigma = -AEt + \ln \sigma_0
\]
From this, it is possible to predict the time required to relieve the stress by a given factor. The difference in the recorded deflection between the YSZ and anode-coated YSZ is due partly to the stress relaxation in the anode layer. It is important to quantify what extent of the difference in deflection is attributed to stress relaxation due to creep and what extent of the difference is accounted for by other factors such as difference in creep properties of the two materials or the effect of chemical reaction between the two at their interface.

The residual stress on the substrate is calculated assuming a thermoelastic heating/cooling regime below the onset of creep at 900°C. After heating up from room temperature to 1000°C at the start of the creep experiment, this gives an anticipated stress present of 1.18 MPa. The final stress after relaxation due to creep for 660 hrs and before cooling is 0.094 MPa. A relaxation of only 2.4% of the room temperature residual stress (1.086 MPa) appears to have been caused by creep. There is therefore some other mechanism, which accounts for this relaxation. This may be due to the highly porous nature of the electrodes.

![Figure 3. Schematic diagram of the thermal shock test.](image)

**THERMALLY INDUCED STRESS**

Heat is generated by the electrochemical reaction in the cell and is transferred between stack components by convection, radiation and conduction. The rate of the cell reaction depends on the concentration of reactant gases and on temperature. Heat generation or sink in a localized area in a cell causes a hot or cold spot giving rise to stress generation. It is useful to assess the seriousness of the stresses caused in this manner.

In this experiment, 50 mm square samples of a Magnesia-Magnesium Aluminate porous ceramic support (MMA) were tested with different temperature profiles across the surface. The samples were initially heated to a temperature of 950°C in a furnace and a cold air blown to the center of the specimen to generate a temperature profile (see Figure 3). The air flow is increased gradually to enlarge the temperature difference between the center point and the sample edge. This was increased until failure occurred. The
temperature at every stage was measured by thermocouples. The technique is an enhancement of a simpler test of Busso et al. (10, 11). However, in that case the material samples were thin (200 microns) in the sense that through-thickness temperature variations could be ignored. Here a much greater sample thickness was required, and is more representative of supported SOFC designs and so this simplification is no longer valid, and the method was modified to allow measurement of temperature on each side, and thereby deducing the temperature variation throughout the sample.

The thermal stresses, which develop during the test, were calculated numerically using finite element technique with the temperature distribution at the time of failure established from thermocouple measurements. In each case the samples were tested to destruction, and were found to fail by fracture normal to the sample surfaces. From the crack paths, it is apparent that the cracks initiated at the cold spot in each sample. In the most severe cases, the samples fractured into two halves, with a crack roughly symmetrical about the center. A typical crack observed in the samples is shown in Figure 4.

Fracture detection on the previous study (7) was performed by attaching an LVDT to the rod carrying the cold air, which rested on the sample. Fracture then resulted in sudden drop of the rod making it possible to detect the time and conditions of failure. In this work, however, the sample did not move as anticipated at failure and no rod drop was detected from the LVDT. However, the temperature readings give a sharp change just below the center of the sample, giving a clear indication of when failure occurred.

Failure occurred when temperature at the cold spot was approximately 800°C. Temperature profiles at the point of failure were used as a load in the finite element analysis and resulting stress distribution obtained. Figure 5 shows the stress distribution on the specimen at failure. The model is based on a quarter of the plate due to symmetry therefore the cold spot is in the lower left corner of the figure. The stress at fracture compared well with strength values from four-point bend tests. The stresses seen using the material in practice in fuel cells are well within the bounds indicated by this test.

![Figure 4. A typical crack on the specimen.](image)

![Figure 5 Stress distribution at failure.](image)
CONCLUSIONS

Several factors influencing the mechanical integrity of SOFCs have been investigated in this work. In particular, residual stresses of electrode-coated YSZ were evaluated. They are considerably less than what a simple thermoelastic analysis would suggest. Secondly, the time dependent deflection of anode-coated YSZ material was observed to be significantly greater than the corresponding plain YSZ under the same stress and temperature conditions. The residual stresses on the anode-coated YSZ samples at room temperature were observed to reduce, and some of this stress relaxation was caused by creep. However, predictable Coble creep does not appear to account for majority of the stress relaxation. It is concluded therefore that either there is some other stress-reduction mechanism apparent between YSZ and anode layers in SOFCs. Finally, a method for establishing material properties under thermal stress is briefly presented, and a porous substrate is shown to withstand designed temperature distributions.

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