Finite element analysis of the fracture behaviour of multi-layered systems used in solid oxide fuel cell applications

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Abstract
This work investigates the fracture behaviour of a multi-layered system typically used in solid oxide fuel cell applications, namely the lanthanum strontium manganite (LSM) and lanthanum strontium cobaltite oxide (LSCoO) films on a yttria stabilized zirconia (YSZ) substrate. The fracture is caused by excessive residual stresses during manufacture due to a large property mismatch of the layers within the system. The fracture modes observed are surface, channelling and interfacial cracking. Finite element analysis is used to determine the crack driving force (energy release rate) for the surface and interfacial cracks. It is found that by inserting an LSM layer between the LSCoO film and the YSZ substrate, the energy release rates for all the crack types can be alleviated compared with the system with a homogeneous LSCoO film. To reduce the crack energy release rates further, an additional LSM–LSCoO composite layer can be inserted between the LSM and LSCoO films.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices, which convert the chemical energy of a fuel directly into electrical energy without an intermediate step of conversion to heat. It has, in recent years, attracted much research interest due to the fact that they have high energy conversion efficiency and are considered clean and efficient power systems as opposed to traditional fossil fuel-based ones. Their applications include utility power generation, small scale combined heat and power and transportation [1, 2].

The active part of an individual fuel cell is a three-layered structure, which consists of two electrodes, namely anode and cathode, separated by an electrolyte, and is often called a positive–electrolyte–negative (PEN). The fuel, e.g. hydrogen, is supplied to the anode and is
oxidized, releasing electrons to an external circuit. The oxidant, e.g. oxygen, is supplied to the cathode, where it receives electrons from the external circuit and then reduces to oxygen ions, which move through the electrolyte and react with the H₂ fuel. The electrolyte conducts ions between the two electrodes and the electrons flow through the external circuit, giving the electrical current.

The choice of the PEN materials depends on the SOFC operating temperature. Within the range of 500–700°C, ceria-based electrolytes are commonly used, whereas zirconia-based electrolytes are used at higher operating temperatures, i.e. within the range of 700–1000°C, due to the high conductivity of the zirconia at high temperatures [3]. Typical materials used for the latter are yttria stabilized zirconia (YSZ), lanthanum strontium manganite (LSM) as the cathode and a NiO/YSZ composite as the anode. However, alternative cathode materials with a higher conductivity are constantly being sought for improvement of the cell electrical performance. These include a promising lanthanum strontium cobaltite oxide (LSCoO), which has eight times the conductivity of LSM’s [4]. Nevertheless, the main limitation in using LSCoO is due to the fact that its thermal expansion coefficient differs greatly from that of YSZ, resulting in large thermal residual stresses during manufacture. These stresses, if large enough, can cause cracking within the layers.

The mechanical properties of the ceramic components of the SOFCs are very important for ensuring the successful manufacture and reliability of the system. Despite this, a great deal of the research in this field has been concentrated on the electrochemical rather than the mechanical aspects of the SOFC materials, and one of the most serious problems in the study of the SOFCs is the lack of data for the ceramic components. Relatively few studies on the mechanical behaviour and failures of the SOFC components have been reported to date. Most of the work focused on the mechanical properties of individual materials that constitute the SOFC rather than the integrity of the multi-layered PEN structure, despite the experimental findings which show that the PEN structure is weaker than anticipated from the known properties of the constituent materials [5, 6]. Examples of the work are those investigating the fracture strength and fracture toughness of zirconia-based electrolytes [7–12], and those studying the mechanical aspects of the LSM cathode and Ni/YSZ anode [13–15]. To the best of the author’s knowledge, there is no published work to date on the mechanical behaviour of LSCoO.

The lack of understanding of the mechanical behaviour and manufacturing-related failures of the multi-layered PEN structures lead to the selection of the constituent materials and their thicknesses by trial and error such that, while giving maximal conductance, the layers do not fail during manufacture. This is costly, time consuming, often unreliable and results in a long product development cycle. This work is aimed at gaining a deeper understanding of the mechanical and fracture behaviour during manufacture of such structures. It is focused on the cathode–electrolyte system, i.e. LSM and LSCoO-based multi-layered systems, since it was found experimentally that the cathode–electrolyte system is more susceptible to fracture than the anode–electrolyte system [5, 6]. It first examines the types of fracture found within the multi-layers. Then numerical study using finite element analysis is carried out to determine the driving force for various crack types observed. The better understanding of such behaviour is of great benefit for a systematic way of optimizing the design of an SOFC.

2. Multi-layered samples and their fracture behaviour

Six multi-layered samples were studied. A photograph of one of the samples and its schematic representation are shown in figures 1(a) and (b), respectively. On the whole, two different sets of samples were considered. The first set of samples (samples 1–3) are three-layered systems consisting of a 50 × 50 mm², 10 mm thick dense YSZ substrate, a 20 µm thick LSM film and an
LSCoO film of various thicknesses (see figure 1(c)). The second set of samples (samples 4–6) are four-layered systems, also consisting of a YSZ substrate, a 20 µm thick LSM film and an LSCoO film of various thicknesses, as well as an additional 20 µm thick composite film between the LSCoO and LSM films (figure 1(d)). The composite film is made up of 50% LSM and 50% LSCoO in composition. The films were deposited the screen printing technique and the samples were sintered at 1100˚C and then cooled down to room temperature.

Observations showed that there was no substrate cracking in any of the samples after the samples were cooled down. No delamination was observed in the films except in sample 6 where the entire film was found to have delaminated from the substrate. Close examination of the samples revealed that only samples 2, 3 and 5 had developed multiple cracks on the film surface. These cracks will greatly reduce the electrical performance of the system, and therefore are undesirable. No such damaging cracks were seen in samples 1 and 4, and hence they are considered to have ‘survived’ the manufacture. The observed cracking patterns were multiple surface cracks running normal to the film surface, as well as channelling cracks running laterally across the film surface, surrounding islands of uncracked film.

Figure 2(a) shows an image of the film surface of sample 2 taken with an optical microscope. Qualitatively similar characteristics of the film surface were observed in samples 3 and 5. The delaminated film from sample 6 is shown in figure 2(b). The summary of the configurations and observations after manufacture of the samples is listed in table 1.

3. Determination of driving force for surface, channelling and interfacial cracks

In order to determine the driving force (energy release rate) for cracks within the multi-layered systems, the elastic properties of the materials are required. Very few elastic property data for LSM films have been reported in the literature. Adamson [16] reported the Young's modulus...
of thin layers of screen-printed LSM films with 42 ± 2% porosity to be 5.5 ± 5 GPa. There are no published data to date on the mechanical properties of thin porous LSCoO films. However, this work assumes that LSCoO has the same isotropic elastic modulus as LSM, due to the fact that both have very similar composition, are manufactured by the same method and their thicknesses are of the same order of magnitude. The porosity level of the LSCoO film of the samples was determined by direct observation of the film surface. Several digital images of the film were taken from randomly selected areas and analysed. The porosity was found to be approximately 40–45%. The Young’s modulus of the LSM and LSCoO is then assumed to be equal to that found by Adamson [16], namely 5.5 GPa. The thermo-elastic properties of the composite film were assumed to be linear volume averages of those of LSM and LSCoO. The Young’s modulus, the Poisson’s ratio and the thermal expansion coefficient of the materials used in this study are summarized in table 2.

### 3.1. Surface and channelling cracks

Two-dimensional finite element models of the multi-layered samples were developed to determine the surface crack driving force. A typical geometry and the mesh used in the models
are shown in figure 3. Due to symmetry, only one half of the cracked sample was modelled. Sensitivity studies revealed the effects of interaction between cracks to be negligible once \( L > 500 \mu m \). This is the case in our samples, where the average measured spacing between surface cracks is approximately 2 mm. The thickness of the YSZ substrate, \( h_{\text{YSZ}} \), was taken to be 2000 \( \mu m \) for efficiency of the model, since beyond this value the results are shown to be thickness independent.

Symmetric boundary conditions are prescribed on the plane \( x = 0 \) of the substrate and the film. The plane \( x = L \) has a symmetric boundary condition which stops at the distance \( a \) from the surface. The plane \( z = 0 \) is also constrained from bending as the substrate is much thicker than the films, thus resulting in no bending of the samples. Second-order isoparametric plane strain elements are used. The material variation within the film layers is achieved by defining the corresponding material properties at each integration point via a user-defined subroutine.

The model is loaded thermally by imposing a temperature decrease of 1080˚C, representing the cooling down from sintering to room temperature. The resulting energy release rates are given in terms of the \( J \)-integral evaluated from the contours surrounding the crack tip. Although this technique of calculating the energy release rate is only valid when the crack is located within an elastically homogeneous material [19], it has been applied to non-homogeneous materials such as functionally graded materials (FGMs) in the work of Gu et al [20]. It was found that by refining the mesh size (the smallest element size used in [20] was \( 10^{-5} \) times a characteristic length), the contour integral values around the crack tip converge. In this work, four contour integrals were used, and the mesh of the model was refined until the discrepancy of the \( J \)-integral evaluated from each contour was less than 5%.

The accuracy of the FE mesh was first checked by evaluating the energy release rate of a surface crack \( (G_{sc}) \) of a bimaterial system, and comparing the results with analytical solutions obtained following the work of Beuth [21]. A comparison between the normalized energy release rates as a function of the crack size calculated analytically and numerically for the LSCoO–YSZ system undergoing a temperature decrease of 1080˚C is given in figure 4. The case of film thicknesses of 40, 60 and 80 \( \mu m \) are shown. Note that the film thicknesses used here represent the total thickness of the film layers of samples 1 to 5. It can be seen from the figure that the energy release rates found analytically and numerically agree well in all cases.

Next, the energy release rates for the surface crack of depth \( a \) (\( 0 < a < h_{\text{film}} \)) in samples 1–5 are evaluated. Figure 5 shows \( G_{sc} \) values against the crack length for a surface crack in the samples. It can be seen from the figure that \( G_{sc} \) increases with the crack length when the crack is contained within the LSCoO layer, and decreases as the crack grows into either the composite or the LSM layer, i.e. \( a > 20 \mu m \) for samples 1 and 4, \( a > 40 \mu m \) in samples 2 and 3, and \( a > 60 \mu m \) in sample 5.
Figure 4. Normalized surface crack energy release rates against normalized crack lengths calculated analytically and numerically (FE) for a bimaterial (LSCoO–YSZ) system for various LSCoO layer thicknesses.

Figure 5. Energy release rates versus crack lengths calculated numerically (FE) for a surface crack in the multi-layered samples.

for samples 2 and 5 and $a > 60 \mu m$ for sample 3. In samples 4 and 5, $G_{sc}$ drops further once the crack grows into the LSM layer. As the stiffnesses of the film layers are equal, the lower $G_{sc}$ is a result of smaller thermal stresses experienced by the composite and the LSM layers. This implies that once the crack in the LSCoO layer initiates, it extends, normal to the film surface, releasing a higher amount of energy as it grows, until it reaches either the LSCoO–composite or the LSCoO–LSM interface. Whether or not the crack extends further depends on the composite or the LSM cohesive fracture toughness.
Fracture behaviour of multi-layered systems

Figure 6. Steady-state energy release rates versus crack lengths for a channelling crack in the multi-layered samples.

The energy release rates shown are obtained from the finite element models which assume a plane strain condition for the cracks. However, when the multi-layered systems cool down, contraction in the out of plane direction takes place and the materials are subjected to a weaker constraint than that of the plane strain models. This, as a result, alleviates the out of plane stresses. The energy release rates shown, therefore, represent the upper bound values for the surface cracks within the multi-layers.

Finite element modelling of a three-dimensional crack channelling across the film in a multi-layered system is highly complicated. Defining the shape of the crack front at each stage of crack growth such that the crack remains in a steady-state poses great difficulty. However, the energy release rate of a channelling crack \( G_{cc} \) of depth \( a \) can be thought of as the average energy release rate for a surface crack of depths 0 up to \( a \), i.e. [21]

\[
G_{cc} = \frac{1}{a} \int_0^a G_{sc}(a) \, da,
\]

where \( G_{sc}(a) \) is the energy release rate of a two-dimensional surface crack of depth \( a \). Therefore, the \( G_{cc} \) values for all the samples can be found by evaluating the areas under the \( G_{sc} \) curves in figure 5. They are shown in figure 6. It can be seen that the channelling crack energy release rates for all cases drop when the crack gets close to the substrate. This is in line with the behaviour of a channelling crack in a bimaterial system of a compliance film on a stiff substrate reported in Beuth [21].

By comparing the results shown in figures 5 and 6, one can see that both surface and channelling cracking can take place together within the multi-layers. A surface crack, once initiated, can grow towards the interface, then channel. This, however, requires a finite length nucleation site prior to propagation. Alternatively, an existing crack can grow initially as a thumbnail crack, in which case its driving force to grow in the thickness direction will decrease and the crack subsequently channels laterally across the surface. By considering that no crack channelling was seen in samples 1 and 4, the cohesive fracture toughness \( (G_c) \) of the LSM and LScO films, assuming they are equal, can be approximated to 42 J m\(^{-2}\). This value is relatively high but it was arrived at by assuming that the film contains the largest possible flaw.
and still survived the manufacture. This is a conservative assumption. Another factor that could contribute to the high $G_c$ value is our assumed Young’s modulus of 5.5 GPa. It was reported by Meixner and Cutler [13] that the moduli of such film materials are very sensitive to their compositional fractions which are not known in this work. In addition this work assumes that the fracture occurs at room temperature, which in fact could happen at a temperature between sintering and room temperature.

3.2. Interfacial cracks

The energy release rate of an interfacial crack observed in the multi-layered samples was evaluated using a finite element model similar to that of the surface crack. Examples of the geometry and the mesh used in the models are shown in figure 7. For a crack length longer than a few times the film thickness, a steady-state is reached and the energy release rate no longer depends on the crack length [22]. In this work it is therefore assumed that the crack length, $a$, is five times the total film thickness, $h_{\text{film}}$. The length $L$ is chosen to be 20 times $h_{\text{film}}$, in order to avoid any edge effects [23]. For substrate thickness independence, $h_{\text{YSZ}}$ is taken to be 10 times $h_{\text{film}}$. The planes $x = L$ and $z = 0$ are constrained to move in the $x$ and $z$ directions, respectively. The same element type as that chosen for the surface crack models is used. The model is loaded thermally and the resulting interfacial energy release rates ($G_i$) are obtained. The mode of crack extension or phase angle ($\psi$) is also calculated from stress intensity factors, $K_1$ and $K_2$, extracted from the models.

The accuracy of the FE models is first tested by comparing the analytical and numerical energy release rates and mode mixity for an interfacial crack in an LSCoO–YSZ bimaterial system. The analytical solutions for $G_i$ and $\psi$ were calculated following the work of Suo and Hutchinson [24]. The film thickness is taken to be $h_{\text{film}} = 40, 60, 80$ and $100 \mu\text{m}$. These values correspond to the total thickness of the film layers in the samples.

Figure 8 compares the analytical and numerical $G_i$ as a function of the film thickness. It can be seen that the $G_i$ values predicted numerically are in agreement with the analytical solutions. The analytical and numerical mode mixity were also determined. No significant differences were found for $\psi$ calculated analytically and the values extracted from the FE results. The $\psi$ values vary within the range of 46–50°.

Although the experiments showed that interfacial fracture only occurred between the LSM film and the substrate, e.g. in sample 6, the energy release rates and the mode mixity for cracks at all interfaces within the three- and four-layered samples were evaluated numerically. They are listed in table 3.

The energy release rate for a crack at all interfaces in samples 1 to 3 increases with increasing total film thickness. The crack at the LSM–YSZ interface in all samples is subjected
Figure 8. Analytical and numerical energy release rates as a function of the film thickness for an interfacial crack in an LSCoO–YSZ system.

Table 3. Energy release rates and mode mixity for a crack at interfaces in the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$h_{\text{film}}$ (µm)</th>
<th>$G_i$ (J m$^{-2}$) and ψ (in brackets) at interfaces between</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YSZ–LSM</td>
<td>LSM–LSCoO</td>
</tr>
<tr>
<td>1</td>
<td>40</td>
<td>7.8 (0°)</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>19.4 (5°)</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>25.9 (5°)</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>12.3 (0°)</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>24.7 (0°)</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>31.3 (6°)</td>
</tr>
</tbody>
</table>

to an almost pure mode 1 condition with little in-plane shearing, i.e. $\psi \leq 6^\circ$. By inserting an additional composite layer between the two film layers, the $G_i$ value for the film–substrate interface is reduced when compared with the system of the same film thickness but without the interlayer. This can be inferred by comparing the $G_i$ values at the LSM–YSZ interface between samples 2 and 4, and samples 3 and 5. The reduction can be as high as 35% in the case of samples 2 and 4, both having films 60 µm thick. Note that the use of an LSM layer also alleviates the film–substrate interfacial energy release rate, since $G_i$ would be as high as 39.7 J m$^{-2}$ if the 60 µm thick film was made up of LSCoO.

It is also interesting to compare the values of $G_i$ for cracks at other interfaces within the films. It is found that the presence of the composite interlayer helps alleviate the energy release rate at all interfaces within the films. This finding is in agreement with the work of Sorensen et al [22], where it was found that the energy release rate for an interfacial crack in a multi-layered system is reduced effectively by using interlayers with step-wise properties. Since only sample 6 shows film–substrate delamination, the interfacial fracture toughness, $G_{ic}$, can be approximated to 26 J m$^{-2}$. When interfacial cracking within the film is considered, one can compare the $G_i$ values with the film mode I fracture toughness of 42 J m$^{-2}$. Although the cracking is of mixed mode, using the mode I fracture toughness criterion is conservative.
As a result, no interfacial cracking within the films is expected. This is in agreement with experimental findings.

4. Conclusions

The fracture behaviour of an LSM and LSCoO-based multi-layered system typically used as a cathode–electrolyte system in SOFCs is investigated. The fracture modes observed experimentally during manufacture are surface and channelling cracks in the LSM and LSCoO films and interfacial cracks between the films and the substrate. They are caused by excessive residual stresses during cool down from sintering, arising from property mismatch between the layers. Energy release rates for surface and interfacial cracks are determined using finite element analysis, whereas the results for channelling cracks are numerically calculated from those of the surface crack. The LSM and the composite layer inserted between the LSCoO film and the substrate can effectively reduce the energy release rate for all the crack types due to the gradual transition of the property from the substrate to the LSCoO film.

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References

[18] ABAQUS 2001 HKS Inc., Providence, Rhode Island, USA