MATHEMATICAL ANALYSIS OF STRESS DISTRIBUTION IN ACCEPTOR-DOPED LANTHANUM CHROMITES UNDER AN OXYGEN POTENTIAL GRADIENT

I. Yasuda and M. Hishinuma
Fundamental Technology Research Laboratory
Tokyo Gas Co., Ltd.
Shibaura, Minato-ku, Tokyo, 105 Japan

ABSTRACT

Acceptor-doped lanthanum chromites are promising candidates for interconnectors in solid oxide fuel cells. When placed under an oxygen potential gradient, stresses are generated in these materials due to the lattice expansion caused by the oxygen loss at the reducing side. A simple one-dimensional model has been developed to analyze mathematically the lattice-expansion-induced stress. Using the literature data of the lattice expansion and the oxygen potential profile, distributions of internal stresses are calculated for both steady and non-steady states, and fracture probabilities are estimated.

INTRODUCTION

Acceptor-doped lanthanum chromites are widely used as interconnectors in solid oxide fuel cells (SOFCs) because of their excellent properties such as high electrical conductivity and chemical stability under operating conditions of SOFC. These materials are known to possess oxygen-deficient type nonstoichiometry and release lattice oxygen under high-temperature reducing atmospheres like the fuel environment in SOFC (1-3). The formation of oxygen vacancies under reducing conditions is accompanied by reduction of Cr$^{4+}$ ions into larger Cr$^{3+}$ ions, generation of space in the crystal lattice, and a decrease of coulombic attraction between cations and oxide ions, which results in an expansion of the crystal lattice. When placed under an oxygen potential gradient, doped lanthanum chromites will show a relative expansion at the reducing side. This means that non-uniform expansion will cause internal stresses even though there is no significant temperature distribution within the material. The internal stresses thus generated will be called lattice-expansion-induced stresses (LEIS) in this paper. If the LEIS is too large, the interconnection material will be in a danger of self-destruction. Estimating the magnitude of LEIS is thus important in view of materials selection and stack design.

The maximum relative dimensional change due to a variation of the oxygen partial pressure from 0.21 bar to $10^{-15}$ bar at 1000°C was reported by Schafer et al. (4) to be as high as 0.3% for La$_{0.9}$Ca$_{0.1}$CrO$_{4.5}$. For Sr-doped materials, different thermal expansion characteristics in air and in reducing atmospheres were found by Sugiura et al (5). These expansion data for the two extreme conditions (the most oxidizing and reducing conditions) are insufficient.
to calculate an internal stress distribution; the expansion data as a function of oxygen partial pressure ($P_{O_2}$) are required. Up to now only Sriolomsak et al. (6) have given such data. In the present study, the distribution of LEIS in doped lanthanum chromites is calculated for a practical SOFC operating condition by using the reported expansion data as a function of $P_{O_2}$ (6) and the oxygen potential profile (7).

THEORETICAL TREATMENT

Analysis of The Steady State

The steady-state thermal stress, $\sigma$, in an infinitely wide, free plate subject to a temperature distribution, $T(z)$, which varies only in the direction of its thickness, $z$, can be expressed as (8)

$$\sigma_s = \sigma_y = -\frac{\alpha ET}{1-\nu} + \frac{1}{2t(1-\nu)} \int \alpha ET dz + \frac{3z}{2t^3(1-\nu)} \int \alpha ET dz$$ \[1\]

where $\alpha$ is the thermal expansion coefficient, $E$ is the Young’s modulus, $\nu$ is the Poisson’s ratio, and $t$ is the half-thickness of the plate. An orthogonal coordination system is used, where the origin is set at the center of the plate. The strain caused by the lattice expansion is defined as a relative dimensional change:

$$\varepsilon = \frac{l - l_0}{l_0}$$ \[2\]

where $l_0$ and $l$ represent the sample length at the higher and lower $P_{O_2}$, respectively. Assuming here that the lattice-expansion-induced strain can be treated the same way as the thermal strain, $\alpha T$, Eq. [1] can be rewritten as

$$\sigma_s = \sigma_y = \frac{E}{1-\nu} \left( -\varepsilon + \frac{1}{2t} \int \varepsilon dz + \frac{3z}{2t^3} \int \varepsilon dz \right)$$ \[3\]

With this equation it is possible to calculate a distribution of internal stresses if the strain, $\varepsilon$, is available as a function of the position, $z$. The literature data of the lattice expansion, however, are given as a function of $P_{O_2}$ and can not be used directly to perform the integration in the above equation. For this purpose, the literature data are converted into a function of position by using the oxygen potential profile (7) which relates the oxygen potential to the position. The maximum tensile stress thus calculated is corrected for the conditions of the 4-point bending test and for the size of the plate in consideration by the equation (9)
\[
\frac{\sigma_{eq}}{\sigma_{x,y}} = \left( \frac{8(m + 1)^3}{(m + 2)^3} \right)^{1/m} \left( \frac{V_{plate}}{V_{sample}} \right)^{1/m}
\]  

where \(V_{plate}\) and \(V_{sample}\) are respectively the volume of an interconnection plate and the sample used for the bending test. Using the corrected stress, \(\sigma_{eq}\), and experimentally determined Weibull coefficient, \(m\), the fracture probability and the warpage of an interconnection plate are evaluated. Although the present model is very simple—it is only one-dimensional and assumes an arbitrary contour—it, its results can be used for the estimation of LEIS. To support the soundness of the model and to examine the effect of the shape (edges and corners of a rectangular plate) and the fixation of the plate, three-dimensional FEM analyses have also been undertaken for a limited number of cases.

Analysis of Non-steady State

In a practical start-up of SOFC, the whole stack is assumed to be heated with flows of air over the cathode and reducing gases over the anode. Above a certain temperature, both surfaces of the interconnection plates start to respond to their respective oxygen potentials, and a distribution of oxygen vacancy concentration is set up in the plate. This process is extremely complicated to model, since the temperature changes with time, and correspondingly, the \(P_{O_2}\) of the reducing gases and the diffusion coefficient of oxygen vacancies, which determine the profiles of vacancy concentration and the oxygen potential, change with time. Further, at relatively low temperatures there is a pronounced effect of surface reaction. Instead of taking many time-dependent variables into account simultaneously, the situation has been simplified as illustrated in Figure 1. Here it is supposed that a reducing gas with \(P_{O_2}\) equal to \(10^{-18}\ atm\) is supplied to one side of the interconnection plate which has been pre-equilibrated in air at 1000°C.

When the \(P_{O_2}\) at one side is abruptly changed, a distribution of the oxygen vacancy concentration is set up in the interconnection plate, which is the driving force for the transport of oxygen vacancies. In the initial state, the vacancy concentration is constant in the whole plate. In the final state, a concentration profile, such that the flux of oxide ions becomes independent of the position, is established. An intermediate state going from the initial to the final state can be described by a chemical diffusion process in which materials are transported under a chemical potential gradient. In this case, the time dependence of the vacancy concentration, \(\delta\), at the position, \(x\), is given by using the Fick’s second law:

\[
\frac{\partial \delta}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{chem}} \frac{\partial \delta}{\partial x} \right)
\]

Combining the ambipolar diffusion theory (10) and the point defect model (1-3), the chemical diffusion coefficient, \(D_{\text{chem}}\), can be written (11):
where $D_v$ and $\alpha$ denote the vacancy diffusion coefficient and the concentration of acceptors, respectively. Solving Eq. [5] under the following initial and boundary conditions,

\[
\delta = \delta_0 \text{ at } 0 \leq x \leq L, \ t = 0 \quad [7a]
\]

\[
\delta = \delta_0 \text{ at } x = 0, \ t > 0 \quad [7b]
\]

\[
\delta = \delta_\alpha \text{ at } x = L, \ t > 0 \quad [7c]
\]

the vacancy concentration can be expressed as a function of time and position. In the next step, the oxygen potential profile is obtained by calculating the corresponding $P_{O2}$ from the vacancy concentration by using the reported equilibrium constant for the vacancy formation (2). Then, as has been already described, the literature data of lattice expansion (6) are converted into a function of position. Because the change of vacancy concentration profile is slow and hence the lattice-expansion-induced strain changes in a quasi-static manner, Eq. [3] can again be used to calculate a distribution of LEIS under a non-steady state.

RESULTS AND DISCUSSION

Steady State

Figure 2 shows an oxygen potential profile in an interconnection plate made of $La_{0.8}Sr_{0.2}CrO_3$ under an oxygen potential gradient from 0.21 atm to $10^{-18}$ atm and the converted data of lattice expansion. At just a short distance from the air-side surface, the oxygen potential sharply decreases, and the lattice-expansion-induced strain starts to be generated. The more the oxygen potential decreases, the more the lattice-expansion-induced strain increases and reaches its maximum value of about 0.3% at the fuel-side surface. Because the converted values of the reported lattice expansion data are scattered, the integration in Eq. [3] can not be performed with sufficient accuracy. For interpolation, the original literature data are approximated by a cubic function of oxygen partial pressure, converted into a function of position and then substituted for $\delta$ in Eq. [3] to obtain a LEIS profile. The results are shown in Figure 3, using a dotted line for the converted strain profile and a solid line for the distribution of the non-dimensional stress parameter. The positive and the negative signs of the normalized stress correspond to a tensile and compressive stress, respectively. As can be seen from the Figure, both surfaces are subject to a tensile stress with a magnitude being much higher at the air-side surface. Because ceramic materials are generally much weaker to tensile stresses than to compressive stresses, the probability of fracture due to the tensile stresses at both sides should be examined.

Table I lists the mechanical properties of the sintered $La_{0.8}Sr_{0.2}CrO_3$ samples which are measured by a 4-point bending test at room temperature. Using these values, the non-dimensional stress parameter in Figure 3 has been converted into a tensile stress, and the

\[
D_{chem} = D_v \left(1 + \frac{4\delta}{\alpha - 2\delta} \right) \quad [6]
\]
Table I Mechanical properties used in the calculation.

| Property                        | Value |
|---------------------------------|-------|
| Average bending strength [MPa]  | 101   |
| Young's modulus [GPa]           | 46.5  |
| Poisson's ratio                 | 0.3   |
| Weibull coefficient             | 10.5  |
| * assumed value                 |       |

Table II Fracture probability and warpage of an interconnection plate of 100x100x3 mm³ under a steady state.

|          | σ         | σeq       | Fracture probability | Warp [mm] |
|----------|-----------|-----------|----------------------|-----------|
| Fuel side| 1.43      | 9.5       | 21.6                 | 5.7x10⁻⁶  |
|          |           |           |                      | 3.3       |
| Air side | 2.68      | 17.8      | 40.3                 | 4.0x10⁻⁶  |

* tensile stress corrected for the condition of 4-point bending tests and for the size effect.

Weibull statistical analysis has been performed to evaluate the fracture probability for a plate of 100 mm x 100 mm x 3 mm. The results are given in Table II together with the calculated warpage. The estimated fracture probability is low enough to conclude that under a steady state the interconnection plate will not break due to the LEIS as long as it is free. The large warpage of more than 3 mm, however, will pose problems of increased contact resistance at the electrode/interconnector interface and of loss of mechanical integrity of a stack.

The three-dimensional FEM analyses for a free plate has given similar results to those obtained from the one-dimensional model, suggesting that the shape factor is not so important. When the plate is clamped and the displacement along the z-axis is not allowed, however, very high tensile stresses of over 80 MPa are found to be generated at the cathode-side surface, resulting in a dramatically increased fracture probability. Therefore, a stack design such that deformation of the interconnection plate can be absorbed is preferable.

Non-steady state

The time dependence of the oxygen vacancy concentration profile has been calculated using the parameters in Table I, and the results are shown in Figure 4. The concentration profile changes with time from a concave through an "inverse-S" shape with an inflection point, and then to a convex. The resulting drastic changes in the calculated profiles of oxygen potential and lattice-expansion-induced strain can be seen in Figures 5 and 6.

Using these strain profiles in Eq. [3], the time dependence of the LEIS profile can be calculated for the non-steady state. Figure 7 shows the results. The stress distributions 1 to 6 show compressive stresses at both sides and tensile stresses in between. For the stress distribu-
Table III List of parameters used in the calculation for a non-steady state.

| Parameter | Value     |
|-----------|-----------|
| $\delta_0$ (in mole fraction) | $3.85 \times 10^{-8}$ |
| $\delta_{\infty}$ (in mole fraction) | $9.38 \times 10^{-2}$ |
| $\alpha$ (in mole fraction) | 0.2 |
| $D_v$ [cm$^2$s$^{-1}$] | $7.80 \times 10^{-7}$ |
| $L$ [cm] | 0.3 |

For distributions 1 to 5, one can recognize a good correspondence between the position of the peak tensile stress and the strain front. The strain front is defined as the position, $x$, at which the strain starts to increase (see Fig. 6). The strain distribution 7 is close to the steady state distribution profile. The peak grows and shifts towards the air-side surface, reaching a maximum after about 500 sec., then declines, and finally disappears to give the steady-state LEIS profile which has already been shown in Figure 3. The peak tensile stress and the position where it is generated are plotted in Figure 8 as a function of time. It can be seen that the tensile stress generated under the non-steady state is much higher than that for the steady state which was given in Table II. The maximum tensile stress of about 45 MPa is induced at one millimeter inside from the fuel-side surface after approximately 500 sec. The fracture probability for this condition is estimated to be as high as 50%, which suggests that the plate will certainly break.

These results lead to the conclusion that the risk of fracture is higher when the interconnection plate is heated under an oxygen potential gradient than when heated in a homogeneous atmosphere. The LEIS arises inherently from the oxygen nonstoichiometry of doped lanthanum chromites. To lower the probability of fracture due to the LEIS and to decrease the warpage, materials showing a smaller degree of oxygen deficiency and a smaller lattice expansion should be selected.

CONCLUSIONS

A simple one-dimensional model has been developed to analyze mathematically the lattice-expansion-induced stress in doped lanthanum chromites under an oxygen potential gradient. Using the literature data of the lattice expansion and the previously reported oxygen potential profile, the distribution of the internal stress in a free plate was calculated for both steady and non-steady states. The following conclusions have been drawn:

1) A tensile stress is established on both sides of a free plate under a steady state. Although the estimated fracture probability is sufficiently low, a large warpage will pose problems.
2) When the plate is clamped, very high tensile stresses are generated at the cathode-side surface, resulting in a dramatically increased fracture probability. Deformation of the plate should be absorbed by a proper stack design.
3) Under a non-steady state in which reducing gases are suddenly supplied to one side, the tensile stress and the corresponding fracture probability are much higher than those calculated.
for the steady state.

4) Materials showing a small degree of oxygen deficiency and a small lattice expansion should be selected for use as interconnectors. The present model suggests a criterion for lowering the fracture probability.

REFERENCES

1. B. K. Flandermeyer, M. M. Nasrallah, A. K. Agarwal, and H. U. Anderson, J. Am. Ceram. Soc., 67, 195 (1984).
2. J. Mizusaki, S. Yamauchi, K. Fueki, and A. Ishikawa, Solid State Ionics, 12, 119 (1984).
3. I. Yasuda and T. Hikita, J. Electrochem. Soc., 140, 1699 (1993).
4. W. Schafer and R. Schmidberger, in High Tech Ceramics, P. Vincenzini, Editor, p. 1737, Elsevier Science Publishers, Amsterdam (1987).
5. N. Sugiura, S. Otoki, A. Kajimura, M. Suzuki, H. Onishi, H. Sasaki, and M. Ippomatsu, J. Ceram. Soc. Jpn, 101, 769 (1993).
6. S. Srilomsak, D. P. Scilling, and H. U. Anderson, in Proc. 1st Int. Symp. Solid Oxide Fuel Cells, ed. S. C. Singhal, PV 89-11, p. 129, The Electrochemical Society Proceedings Series, Pennington, NJ (1989).
7. I. Yasuda and T. Hikita, in Proc. 3rd Int. Symp. Solid Oxide Fuel Cells, eds. S. C. Singhal and H. Iwahara, PV 93-5, p. 354, The Electrochemical Society Proceedings Series, Pennington, NJ (1993).
8. T. R. Tauchert, in Thermal Stresses I, R. B. Hetnarski, Editor, p. 36, Elsevier Science Publishers, Amsterdam (1986).
9. "Seramikkusu no kikaiteki-seisihitsu (Mechanical Properties of Ceramics)", p. 22, The Ceramic Society of Japan (1977).
10. W. van Roosbroeck, Phys. Rev., 91, 282 (1953).
11. I. Yasuda and M. Hishinurna, accepted for publication in J. Solid State Chem.

Figure 1. Schematic illustration of oxygen vacancy concentration profile before and after changing the oxygen partial pressure at one side.
Figure 2. Distribution of oxygen potential and strain induced by lattice expansion in a plate of \( \text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3.8} \). The original expansion data are taken from Ref. 6.

Figure 3. Distribution of strain and stress caused by lattice expansion under a steady state.
Figure 4. Time dependence of oxygen vacancy concentration profile. Numbers on the lines represent time after introduction of fuel at one side (see the legend box).

Figure 5. Time dependence of oxygen potential profile.

Figure 6. Time dependence of strain induced by lattice expansion. Numbers on the lines refer to the legend in Fig. 5.
Figure 7. Time dependence of stress distribution after changing the oxygen partial pressure at one side.

Figure 8. Time dependence of maximum tensile stress and the location where it is generated.