MODEL ANALYSIS FOR LATTICE EXPANSION AND INTERNAL STRESS IN LaCrO₃ UNDER AN OXYGEN POTENTIAL GRADIENT

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ABSTRACT

Doped lanthanum chromites show lattice expansion under high-temperature reducing atmospheres. We have proposed a numerical simulation model for analyzing the static and the transient expansion behavior of the doped lanthanum chromites under a stationary oxygen potential gradient or a stepwise change of oxygen potential in the atmosphere. A lanthanum chromite interconnector plate, $100 \times 100 \times 3 \text{ mm}^3$, was found to warp under a stable SOFC operating condition. The maximum displacement of the center part normal to the originally flat surface was calculated to be about 0.77 mm. A stepwise change of the atmospheric condition caused a transient oxygen potential gradient in a lanthanum chromite rod, $3 \times 3 \times 20 \text{ mm}^3$, resulting in a deformation of the sample. The calculated tensile stress coming from the transient deformation was as high as 50 MPa or more.

INTRODUCTION

In solid oxide fuel cells (SOFCs), interconnecting materials are required to be electrically conducting and chemically stable both in reducing and oxidizing atmospheres at high temperatures. Doped lanthanum chromites meet the requirements, and thus the LaCrO₃ system is a promising candidate for the interconnector. However, it has been reported that, in doped lanthanum chromites, the number of oxygen vacancies increases under high-temperature reducing atmospheres (1, 2), and as a result the expansion of the lattice occurs (3, 4). For the lanthanum chromites doped with alkaline-earth metals, the sample sizes measured in 4%H₂-N₂ were more than 0.1 % larger than those measured in air (5). Under SOFC operating conditions, the interconnectors are exposed to both oxidizing and reducing atmospheres, and thus the interconnectors would expand non-uniformly. The non-uniform expansion causes deformations of the interconnectors, resulting in a poor electrical contact between the interconnector and the electrodes, a failure of the gas seal, and generation of internal stresses. The internal stresses could (in the worst case) lead to formation of cracks or a self-destruction of the interconnectors. Consequently, elucidating the expansion behavior and estimating the magnitude of the internal stresses quantitatively are of high significance for the development of SOFCs with mechanical reliability.

Recently, Yasuda and Hishinuma investigated the lattice expansion behavior of the doped lanthanum chromites systematically, and reported the correlation between the...
mole fraction of oxygen vacancy $\delta$ in the sample and the relative expansion $\Delta L/L$ for various doped lanthanum chromites (5). In this study, on the basis of the reported $\delta$ dependence of $\Delta L/L$, a model has been developed to precisely describe the lattice expansion behavior of the doped lanthanum chromite, and the deformations of the lanthanum chromite interconnectors and the internal stresses have been calculated. The static and the transient stress calculations were carried out for a plate and a rod type sample, respectively. The purposes for the steady state calculation are estimating the magnitude of the deformations and the internal stresses of the interconnectors under practical SOFC operating conditions, and investigating the possibility to reduce the internal stresses by optimizing the shape of the interconnector. The non-steady state calculation was aimed at evaluating the risk for destruction of the interconnectors due to the transientsly generated internal stresses from the startup or shutdown processes.

**ANALYTICAL MODEL**

The stresses in the samples were calculated according to the following procedure. The flow chart for the procedure is shown in Fig. 1. In both the steady state and the non-steady state calculations, similar calculating methods were used.

1) Calculation of the oxygen vacancy concentration on the sample surface

On the basis of the point defect theory, the oxygen vacancy concentration (mole fraction) $\delta$ on the fuel side and the air side surfaces of the interconnector was calculated (6). In an equilibrium state, the formation of the oxygen vacancy can be described as follows using Kröger-Vink notation (7);

$$\frac{1}{2}O_2 + V_0^{\circ} + 2Cr^{\circ}_C = O_0^\circ + 2Cr^{\circ}_C$$

$$K_{ox} = \frac{[Cr^{\circ}_C]^2[O_0^\circ]}{[Cr^{\circ}_C][V_0^\circ]P_{O2}^{1/2}}$$

where $K_{ox}$ is the equilibrium constant. Imposing the following electroneutrality condition and the conservation law for the Cr sites,

$$[S_{Cr}^\circ] = [Cr^{\circ}_C] + 2[V_0^\circ]$$

$$[Cr^{\circ}_C] + [Cr^{\circ}_C] = 1$$

$\delta$ ([V$\circ$]) can be obtained to be a function of oxygen partial pressure $P_{O2}$.

2) Calculation of the oxygen vacancy distribution in the sample

Using the computational fluid dynamics tool "STAR-CD" (Computational Dynamics Ltd.), $\delta$ distributions in the samples were simulated. As the boundary conditions, the $\delta$ values at the surface calculated in the previous step were used. In this calculation, the dependence of the chemical diffusion coefficient $D_{chem}$ on the oxygen vacancy concentration $\delta$ was taken into account. On the basis of the point defect theory and the ambipolar diffusion theory (8), assuming the hopping conduction (9) of the oxygen vacancies inside the sample, and the conservation of the charge neutrality condition in...
the mixed conduction of the oxygen vacancies and the holes, $D_{chem}$ can be described as

$$D_{chem} = D_v \left(1 + \frac{4\delta}{p}\right)$$

the following formula (10):

where $D_v$ is the diffusion coefficient of the oxygen vacancy and $p$ is the concentration of hole.

3) Determination of the strain distribution in the sample

The strain distributions in the samples were determined from the $\delta$ distributions. The measured relationship between the relative expansion $\Delta L/L$ and the oxygen vacancy concentrations for LaCrO$_3$ under the uniform atmosphere with the various oxygen partial pressures (5) was employed for the determination of the strain distributions.

4) Conversion of the strain distribution to the temperature distribution

The determined strain distributions were converted to the equivalent temperature distributions in the samples. In order to convert the strain distributions to the temperature distributions, a strain value at an arbitrary point in the sample was divided by the thermal expansion coefficient (TEC).

5) Computation of the displacement and the internal stress

From the calculated temperature distributions, the deformation and the internal stresses of the sample were calculated using the finite element program "ABAQUS" (Hibbit, Karlsson and Sorensen, Inc.).

The composition of the sample used for the steady state calculation was La$_{0.8}$Sr$_{0.2}$Cr$_{0.9}$Ni$_{0.1}$O$_3$, and the typical sample shape was flat plate type, 100 $\times$ 100 $\times$ 3 mm$^3$. In the study for the effects of the sample shape on the non-uniform expansion, two-dimensional modeling was employed for simplicity. Plates with convex or concave shapes at the electrode sides were tested for the study of the shape effects. Additional simulations under a pressure of $4 \times 10^7$ Pa on the fuel side surface were performed to investigate the effect of external load. This situation corresponds to the cells located at the lowest part of a cell stack with an external load of 400 N on top. From the calculated outputs, the deformation of the sample, the flatness of the air side surface, and the maximum tensile stresses under the external load were evaluated.

For the non-steady state calculation, a calculation method almost the same as that for the steady state simulation was employed. As the first step, a transient oxygen vacancy distribution in the sample after a stepwise change of the atmospheric composition was calculated. Next, the calculation of the internal stress was carried out using the same procedure for the steady state calculation. The sample shape was a rod, 3 $\times$ 3 $\times$ 20 mm$^3$, and the simulations were performed with a three-dimensional model.

Table 1 shows the parameters used for the analysis, and the sample shapes used in the shape effect analysis are listed in Table 2.
RESULTS AND DISCUSSION

Static Calculation

The steady state simulation revealed that, without an external load, the flat interconnector plates warped toward the fuel side due to the non-uniform expansion. Figure 2 shows the contour plot for the displacement of the sample position along the y direction normal to the initially flat surface. In Fig. 2, to magnify the deformation, the deformed shape of the sample is illustrated at ×10 magnification. The center part of the plate shifted toward the fuel side by about 0.77 mm, indicating the presence of a gap of 0.77 mm between the interconnector and the cathode in the center part.

Under the external load on the fuel side surface, the magnitude of the warp decreased. Figure 3 exhibits the displacement of the sample position and the maximum tensile stress inside the sample under the external load condition. In this figure, the deformed shape is illustrated at ×10 magnification similarly to Fig. 2. It is found that the magnitude of the displacement in the center decreased to about 0.29 mm, whereas the maximum tensile stress of 28.2 MPa generated in the center of the air side surface.

Next, the effects of sample shape on the expansion behavior were studied. As mentioned before, the shape effects were analyzed with the two-dimensional model. Because of approximating the three-dimensional sample two-dimensionally, the obtained results are slightly different from those with the three-dimensional model (Figs. 3 and 4) as can be seen in Fig. 4. In the two-dimensional simulation, the finite planar sample was modeled as a plate with an infinite depth, and hence the magnitude of the displacement and the internal stress became smaller.

It was found from the simulated results for all the samples with various shapes that the non-uniform expansion always caused warps of the plates toward the fuel side. Figure 5 displays the principal stress in the sample under the external load condition for the geometry #2 with a convex surface at the fuel side. The maximum value of the displacement was 0.2 mm, slightly larger than that for the flat plate, while the maximum tensile stress was reduced to 10 MPa. All the calculation results are listed in Table 3. The $\Delta l$ is the displacement of the center part along the y direction relative to the corner point, from which the flatness on the air side surface can be evaluated. The sample geometries in the table correspond to those in Table 2. We can see the following characteristic features from Table 3.

(a) $\Delta l$ depends on the average thickness of the sample negatively; $\Delta l$ decreases with the average sample thickness.

(b) As for the shape effects, the magnitude of the warp for the sample with the convex surface (geometry #2, 3) is smaller than that for the sample with the concave surface (geometry #4, 5).

(c) Comparing the convex shape sample (geometry #2, 3), there is no remarkable difference in the magnitude of the warp between the samples with convex shape at the air side and at the fuel side.

(d) By employing the convex shape sample, the maximum tensile stress under the external load condition can be reduced to half of that in the flat plate sample.

In view of the contact between the cathode and the interconnector as well as the
magnitude of the maximum tensile stress under the external load, geometry #7 is the most favorable design. This particular geometry gives the smaller \( \Delta l \) of 0.03 mm and the reduced maximum tensile stress of 8 MPa, with which high mechanical reliability against self-destruction and a good contact between the cathode and the interconnector can be achieved simultaneously. Thus by optimizing the sample shape, it is possible to reduce both the magnitude of the warp and the internal stress caused by the non-uniform expansion.

**Transient Response**

Figure 6 displays the observed transient responses of the sample length after the stepwise change of the atmospheric conditions. The relaxation processes of the sample size were measured for LaCr\(_{0.85}\)Mg\(_{0.1}\)Co\(_{0.05}\)O\(_3\) (LCMC) after the stepwise change of the atmospheric gas composition. The gas composition was controlled by changing the mixing ratio of the supplied gases, and the sample length was measured with a dilatometer as a function of time. In the figure the upper plot is for the reduction case and the lower plot is for the oxidation case. In both cases, the relaxation time was several hours. The transient response was simulated with a three-dimensional model, and a comparison of the measured time change of the sample length with the calculated results is exhibited in Figure 7. In the figure, the vertical axis corresponds to the change of sample length normalized by that in the equilibrium state. The calculated transient response agreed satisfactorily with the measurements, and thus this model analysis technique is valid for simulating the transient expansion or contraction behavior of the LaCrO\(_3\) after the atmospheric changes. The transient response of the maximum tensile stress in the sample after the stepwise change of the atmospheric condition was also simulated, and the result is shown in Figure 8. The principal stress reached the peak value just after the atmospheric change, and then gradually decreased with time. The peak value of the principal stress was about 11 MPa, which will not directly lead to the destruction of the sample.

In a practical use of SOFCs, however, \( P_{o2} \) of the atmospheric gas may change over several orders of magnitude, and as a result large internal stresses could occur. We simulated the transient response of the internal stresses after drastic changes of \( P_{o2} \) in the atmosphere. The atmosphere was changed from air to the mixed gas of H\(_2\)/H\(_2\)O=80/20 or from H\(_2\)/H\(_2\)O=80/20 to air. When the atmospheric condition changes in the oxidizing direction, the sample is subjected to a thermal shock on the surface similar to an abrupt cooling which generates tensile stresses in a near-surface region. On the other hand, when the atmospheric condition changes in the reducing direction which is equivalent to an abrupt heating, the tensile stresses occur inside the sample. Figure 9 shows the transient change of the maximum tensile stress inside the sample after the stepwise change of the atmospheric condition between the mixed gas of H\(_2\)/H\(_2\)O =80/20 and air. The maximum tensile stresses showed the peak values just after the atmospheric change and after two hours for the oxidizing and reducing cases, respectively. The peak values of the maximum tensile stresses were as high as 50 MPa or more in both cases, which could cause destruction of the interconnectors in the actual operation of SOFCs. Because the sample geometry and the externally applied mechanical load will increase the magnitude of the internal stresses, SOFCs have to be operated so as the \( P_{o2} \) in both the cathode and anode environments may not change drastically.
CONCLUSIONS

We simulated the static and transient expansion behavior of doped lanthanum chromites using a computational calculating technique. For the calculation of the deformation and internal stresses in interconnector, $100 \times 100 \times 3 \text{ mm}^3$, under a practical operating condition, the two-dimensional steady-state model was employed. The simulation has shown that the plate will warp and a gap of 0.77 mm between the interconnector and the cathode will occur in the center part. By optimizing the sample shape, it is possible to reduce both the magnitudes of the warp and the internal stress.

A stepwise $P_{O_2}$ change of the atmospheric condition caused a transient oxygen potential gradient in a lanthanum chromite rod, $3 \times 3 \times 20 \text{ mm}^3$. The oxygen potential gradient thus induced can generate thermal-shock-like internal stresses in the sample. The maximum tensile stress of this type was calculated to be as high as 50 MPa or more. In the development of SOFCs with high mechanical reliability, the simulation technique used in this study is useful for the selection of the composition of the lanthanum chromite, geometry of the interconnector, and the evaluation of the SOFCs operating conditions.

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Table 1. Parameters used for the simulation.

| Sample composition     | Sample size | Temperature [°C] | $P_{O_2}$ [atm] | $D_v$ $^a$ [cm$^2$/s$^{-1}$] | Young's modulus [GPa] | Poisson's ratio $^c$ |
|------------------------|-------------|-----------------|-----------------|-----------------------------|-----------------------|-------------------|
| Static                 | La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Ni$_{0.2}$O$_3$ | $100 \times 100 \times 3 \text{ mm}^3$ | 1000 | air: 0.21 | 1.34$\times$10$^{-4}$ | 46.5 | 0.3 |
|                        |             |                 |                 | fuel: 4.53$\times$10$^{-14}$ |                       |                   |
| Transient              | La$_{0.5}$Mg$_{0.5}$Co$_{0.8}$O$_{2.75}$O$_3$ | $2 \times 2 \times 20 \text{ mm}^3$ | 1000 | 9.33$\times$10$^{-12}$ to 9.12$\times$10$^{-13}$ | 1.5$\times$10$^{-3}$ | 62.8 | 0.3 |
|                        |             |                 |                 | 3.09$\times$10$^{-14}$ to 3.02$\times$10$^{-14}$ |                       |                   |

$a$) Oxygen vacancy diffusion coefficient.

$b$) From 4-point bending tests at room temperature.

$c$) Assumed value.
Table 2. List of sample shape.

| sample geometry | surface shape | thickness (mm) | fuel side | air side | edge part | center part |
|-----------------|---------------|----------------|-----------|----------|-----------|-------------|
| # 1             | flat          | flat           | 3         | 3        |           |             |
| # 2             | convex        | flat           | 3         | 4        |           |             |
| # 3             | flat          | convex         | 3         | 4        |           |             |
| # 4             | concave       | flat           | 4         | 3        |           |             |
| # 5             | flat          | concave        | 4         | 3        |           |             |
| # 6             | convex        | flat           | 2         | 3        |           |             |
| # 7             | flat          | convex         | 3         | 3.5      |           |             |

calculate the δ value at the boundary using the point defect model (6)
calculate the δ distribution using the ambipolar diffusion theory (8)
convert the δ distribution to strain using δ vs. ΔL/L relation (5)
calculate the temperature profile using thermal expansion coefficient

Table 3. List of the simulated results.

| sample geometry | displacement (10^{-4}mm) | ΔL a) (10^{-4}mm) | ΔL (10^{-4}mm) | maximum tensile stress (MPa) |
|-----------------|--------------------------|-------------------|----------------|-----------------------------|
| # 1             | 4.17                     | 4.17              | 1.51           | 17.4                        |
| # 2             | 3.28                     | 3.28              | 2.03           | 10.3                        |
| # 3             | 3.29                     | -6.71             | -5.93          | 7.1                         |
| # 4             | 3.97                     | 3.97              | 1.58           | 17.4                        |
| # 5             | 3.97                     | 13.97             | 11.59          | 17.4                        |
| # 6             | 4.43                     | 4.43              | 1.39           | 17.5                        |
| # 7             | 3.67                     | -1.32             | -0.30          | 8.0                         |

calculate the displacement and the stress using general-purpose finite element program ABAQUS

Figure 1. The flow chart of the simulation procedure for the non-uniform expansion.

Figure 2. The displacement of the sample position along y direction. At the four corners on the air side the freedom along the y direction is prevented. The deformed shape is illustrated at × 10 magnification to magnify the deformation.
Figure 3. The displacement of the sample position along $y$ direction and the principal stress under the external load. At the four corners on the air side the freedom along the $y$ direction is prevented. The deformed shape is illustrated at $\times$ 10 magnification to magnify the deformation.

Figure 4. The displacement of the sample position along $y$ direction without load and the principal stress under the external load. At the four corners on the air side the freedom along the $y$ direction is prevented. The deformed shape is illustrated at $\times$ 10 magnification to magnify the deformation.
Figure 5. The principal stress under the external load for the sample with the convex surface on the air side. At the four corners on the air side the freedom along the $y$ direction is prevented. The deformed shape is illustrated at $\times 10$ magnification to magnify the deformation.

Figure 6. The observed transient change of the sample length after the stepwise change of the atmosphere (log$P_{O_2}$ (atm): -11.03 to -12.04 or -13.51 to -12.52).

Figure 7. Comparison of the transient response of the sample size between the experiments (traces) and the calculations (symbols). (a) log$P_{O_2}$ (atm): -11.03 to -12.04, (b) -13.51 to -12.5.
Figure 8. The transient change of the maximum tensile stress after the stepwise change of the atmosphere (logPo₂ (atm): -13.51 to -12.52).

Figure 9. The transient change of the maximum tensile stress after the stepwise change of the atmosphere (Air <=> H₂/H₂O=80/20).