X-RAY STRESS MEASUREMENTS FOR ANODE-SUPPORTED PLANAR SOFC

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ABSTRACT
Residual thermal stresses in the electrolyte of the anode-supported planar SOFCs were measured using the X-ray diffraction method. The cell tested was fabricated by co-sintering bilayer of 8YSZ electrolyte on NiO/YSZ substrate at 1500 °C. The thicknesses of the electrolyte and the anode were about 20 μm and 2 mm, respectively. To estimate the residual stress precisely, the synchrotron radiation was used as an excellent X-ray source. The wavelength of the radiation beam used for the stress measurements was λ=0.154 nm, and 2θ=125° and 145° were selected for the constant Bragg angle. The estimated residual stress in the electrolyte was a compressive stress of about 650 to 720 MPa at room temperature.

INTRODUCTION
Anode-supported solid oxide fuel cells (SOFCs) are suited for operation at lower temperatures because of the substantially lower ohmic resistance of the electrolyte. By lowering the operating temperature of the SOFCs to around 700°C, conventional metal alloys can be used for interconnectors or auxiliary components with which high mechanical reliability of a cell-stack and lower manufacturing costs can be achieved. Thus anode-supported SOFCs are receiving much interest (1-5). The anode-supported cells are generally fabricated by co-firing the electrolyte/anode bilayer at 1400 ~ 1500°C (1-5). Ni/YSZ and YSZ are used as the anode substrate and the electrolyte, respectively. The thermal expansion coefficients of Ni/YSZ and YSZ do not match well, and thus the mismatch induces a large residual stress in the cell at room temperature. The thermal stress may cause micro-cracks and delamination of the electrolyte at the interface under a thermal cycle.

We have been studying the cell performance and the thermal stresses in the cell using computer simulation for the self-supporting type planar SOFCs (6-8). Recently we have also performed numerical analysis of cell performance (9) and thermal stresses in the cell for the anode-supported cell. However, it is complicated to precisely calculate the thermal stress in the cell under cell operating condition because the residual stresses in the cell are not known. Hence estimating the residual stress in the electrolyte of the anode-supported cell at room temperature is important to calculate the thermal stresses in the anode-supported cell under operation.

In this paper, we report the evaluation of the residual stress in the electrolyte of the anode-supported cell at room temperature. The X-ray diffraction method was used to measure the thermal residual stress in the electrolyte of the anode-supported cell. The synchrotron radiation (SR) was used as an X-ray source, which enables the estimation of the residual stresses in the electrolyte with a high accuracy. We also carried out a model calculation for the residual stresses in the electrolyte of the anode-supported cell, and the calculated stresses were close to those experimentally measured.
EXPERIMENTAL

We measured the X-ray diffraction pattern for the electrolyte of the anode-supported cell and estimated the residual stress by the sin^2\psi method (10-14). When a certain material is sustaining stresses, the interplanar spacing \( d \) between the specified diffracting planes in the crystallite in a microscopic grain can be expressed as

\[
d = \frac{1 + \nu}{E} \sigma \sin^2 \psi + \left\{ \frac{1 - \nu}{E} (\sigma_1 + \sigma_2) \right\} d_0
\]

where \( d_0 \) is the interplanar spacing in a stress-free condition, \( \psi \) is the inclination angle of the specified diffracting plane in the crystallite from the normal to the specimen surface, \( \nu \) is the Poisson's ratio, \( E \) is the Young's modulus, \( \sigma \) is the stress in the grain, and \( \sigma_1 \) and \( \sigma_2 \) are the principal stresses (10-13). Thus \( \sigma \) can be estimated from the slope of the \( d \)-sin^2\psi plot, which leads to the expression;

\[
\sigma = E \left( 1 + \frac{1}{\nu} \right) \frac{\partial d}{\partial \sin^2 \psi}
\]

In this measurement we employed the iso-inclination method and the fixed \( \psi_0 \) method. The configuration for the diffraction measurements and the stress analyses is indicated in Fig. 1. In Fig. 1, \( \varphi \) is the angle between the normal to the specimen surface and the incident beam, \( \eta \) is the angle between the incident beam and the normal to the specified diffracting plane in a crystallite, and \( \theta \) is the scattering angle of the specified diffracting plane in the crystallite. \( \psi, \psi_0, \varphi, \) and \( \eta \) are related to each other as follows.

In the fixed \( \psi_0 \) method, 2\( \theta \) scan is carried out with fixing \( \psi_0 \).

\[
\psi \geq \psi_0;
\]

\[
\psi_+ = \psi_0 + \eta = \frac{\pi}{2} - \theta + \psi_0
\]

\[
\psi < \psi_0;
\]

\[
\psi_- = \psi_0 - \eta = \psi_0 - \frac{\pi}{2} + \theta
\]

The synchrotron radiation was used as an X-ray source. The synchrotron radiation has a ultra-bright light and a highly directional, collimated beam. Besides, wide spectrum of wavelengths, stretching from infrared to X-rays is available. Using the synchrotron radiation as the beam source in the residual stress measurements has the following advantages (14);

1. The beam with an arbitrary wavelength is available and thus the residual stress measurement for an arbitrary diffracting plane with high accuracy is possible.
2. The beam is the monochromatic light and thus it is not necessary to consider the effect of \( K_{\alpha_1, \alpha_2} \) doublet.

For the measurements, we selected a wavelength of \( \lambda = 0.154 \) nm, which corresponds to the Cu \( K_\alpha \) line, to enable comparison of the results with those measured using a commercial X-ray diffraction apparatus. The beam size at the focal point was adjusted to be 1 mm(H) \( \times \) 1 mm(V). As for the diffraction angle, we selected around 125° and 145° in 2\( \theta \).

The anode-supported cell used for the stress measurement was fabricated by co-firing the electrolyte/anode bilayer at 1500°C (15). The 8YSZ electrolyte was first screen
printed on the green NiO/YSZ anode. To avoid cracks and micro pores in the electrolyte, the particle sizes of the raw powders for NiO/YSZ substrate and YSZ electrolyte were carefully selected. After co-firing, the specimen size was 40 mm × 40 mm × 2 mm, and the thickness of the electrolyte was about 20 μm. As compared with the substrate thickness, the electrolyte is thin enough to assume that the direction of the main stress in the electrolyte will be parallel to the film surface. To investigate the stress distribution in the electrolyte plane, two 10 mm × 10 mm pieces were cut from a center and corner part of the specimen.

The model calculation for the thermal stress in the electrolyte was carried out using the finite element program “ABAQUS” (Hibbit, Karlsson and Sorensen, Inc.). We modeled the geometry of the specimen of the electrolyte/anode bilayer, and calculated the residual thermal stress assuming that both the electrolyte and the anode constrained each other below 1400°C, and no mechanical loads were put on the specimen. The mechanical properties used for the calculation are listed in Table 1.

Table 1 List of the mechanical parameters used for the stress simulation

|                | Young’s modulus [GPa] | Poisson’s ratio | Thermal expansion coefficient [K⁻¹] |
|----------------|------------------------|----------------|-----------------------------------|
| Electrolyte    | 200  a)                | 0.3  c)        | 10.56 × 10⁻⁶  d)                  |
| Anode          | 96  b)                 | 0.3  c)        | 12.22 × 10⁻⁶  d)                  |

a) Taken from ref. 16.
b) From 4-point bending tests at room temperature for NiO/YSZ substrate.
c) Assumed value.
d) Assumed from the temperature dependence of TEC below 1000°C (8).

RESULTS AND DISCUSSION

Figure 2 shows the result of θ-2θ scan for the electrolyte of the anode-supported cell. First the specimen was set so that the specimen surface was parallel to the incident beam, and the incident beam was spotted at the center part of the specimen. All the peaks in the diffraction pattern can be assigned to the cubic YSZ structure.

Figure 3 indicates the change of the diffraction pattern around 2θ = 125° with the change of ψ for the center part of the anode-supported cell. With increasing ψ the peak position shifted to the higher angle, indicating that the interplanar spacing d decreased. This suggests that the stress type is compressive. As one can see in Fig. 3, the diffraction pattern is not symmetric, which may come from a distribution of the stress along the depth from the surface. Accordingly, to determine the peak position, we employed the middle point method (12). Figure 4 displays a d-sin²ψ diagram thus determined for the electrolyte of the anode-supported cell. The filled circles and open squares are for positive and negative ψ, respectively, and the solid line is the linear least-squares fit. Although the data are slightly scattering, d decreases linearly with the increase of sin²ψ. The d-sin²ψ diagram determined from the measured diffraction pattern around 2θ = 145° for the electrolyte of the anode-supported cell is also shown in Fig. 5. d decreases linearly with the increase of sin²ψ similar to the case of 2θ = 125°.

In X-ray stress measurements, a stress in a sample is estimated using the diffraction from the specified diffraction plane of the crystallite, and thus the estimated residual stress may be different from the macroscopic stress in the sample measured by a mechanical method. Consequently elastic constant E and ν in Eq. 1 are not those determined by mechanical methods, and we must use X-ray elastic constant E and ν determined by the X-ray diffraction method. However, in this study, it was difficult to determine E and ν in Eq. 1 by the X-ray diffraction method and thus we have assumed 200 GPa and 0.3 as E and ν in Eq. 1 (17), respectively, for the calculation of the residual stress in the electrolyte. From the slope of the d-sin²ψ plots in Fig. 4 and Fig. 5, the residual stresses
in the electrolyte were estimated to be compressive stresses of 660 MPa and 640 MPa, respectively. These values are very close to each other, which shows that the present measurement is reliable and the stress estimation does not depend on the selection of the diffracting plane.

Figure 6 shows the $d$-$\sin^2 \psi$ diagram measured using the diffraction peak around $2\theta$ =125° for the corner part of the anode-supported cell. The slope of $d$-$\sin^2 \psi$ plot in Fig. 6 is steeper than that in Fig. 4, which gives a slightly larger residual stress of 720 MPa.

To check the validity of the stress values determined from the X-ray measurements, a numerical simulation for the residual stresses in the electrolyte at room temperature was also performed using the finite element method. The sample geometry used for the simulation is the same as that for the x-ray stress measurements. Figure 7 shows the simulated stress distribution in the electrolyte for the anode-supported cell. Over the plane the stresses are almost homogeneous values of 650 MPa to 700 MPa. At the corner part the stress is slightly larger than that at the center part, which is qualitatively consistent with the result estimated from the X-ray stress measurements.

From the X-ray stress measurements and the stress simulation for the electrolyte of the anode-supported cell, it has been made clear that the residual stress in the electrolyte at room temperature is compressive stress of 640 ~ 720 MPa. The compressive strength of YSZ is more than 1 GPa (18) and thus these residual stresses are not so large as to induce a failure of the electrolyte. However, these large residual stresses may cause the delamination of the electrolyte at the electrolyte/anode interface under a thermal cycle. Consequently it is necessary to match the thermal expansion coefficients of the electrolyte and the anode to avoid damage to the cell under thermal cycles. For this reason certain metal-oxide composite materials are being considered as the candidates for the anode support (3).

CONCLUSION

The residual thermal stresses in the electrolyte of the anode-supported planar SOFCs were measured using the X-ray diffraction method. The use of synchrotron radiation as the beam source enabled us to carry out reliable estimation of the residual stresses. The residual stresses at the center and corner parts were found to be compressive stresses of about 650 and 720 MPa, respectively. We also carried out 3D model calculations for the residual stress in the electrolyte, which gave calculated stresses consistent with the measured values. Although the estimated residual stresses in the electrolyte are smaller than the compressive strength of YSZ, it is necessary to match the thermal expansion coefficients of the electrolyte and the anode to avoid damage to the cell under thermal cycles.

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Figure 1. Schematic diagram of the stress measurements using X-ray.
Figure 2. X-ray diffraction pattern for the electrolyte of the anode-supported cell.

Figure 3. Change of the diffraction peak around $2\theta = 125^\circ$ with the change of $\psi$. 
Figure 4. \( d - \sin^2 \psi \) diagram for the electrolyte of the center part of the anode-supported cell; filled circles and open squares are for the positive and negative \( \psi \), respectively, solid line is the linear least-squares fit. \( d \) was determined from the diffraction peak around \( 2\theta = 125^\circ \).

Figure 5. \( d - \sin^2 \psi \) diagram for the electrolyte of the center part of the anode-supported cell; filled circles and open squares are for the positive and negative \( \psi \), respectively, solid line is the linear least-squares fit. \( d \) was determined from the diffraction peak around \( 2\theta = 145^\circ \).
Figure 6. $d$-$\sin^2 \psi$ diagram for the electrolyte of the corner part of the anode-supported cell; filled circles and open squares are for the positive and negative $\psi$, respectively, solid line is the linear least-squares fit. $d$ was determined from the diffraction peak around $2\theta = 125^\circ$.

Figure 7. Simulated residual stress distribution in the electrolyte for the anode-supported cell at room temperature.