Estimation of micro-size defects in electrolyte thin-film by X-ray stress measurement for anode-supported solid oxide fuel cells

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Abstract
For anode-supported solid oxide fuel cells (SOFCs), huge internal stress is generated in an electrolyte thin-film due to the difference of the coefficient of thermal expansion from an anode substrate. Micro-size defects are sometimes formed in the electrolyte thin-film during a manufacturing process, when the huge internal stress is released. The defects in the electrolyte thin-film cause cross leakage of fuel and air, which deteriorate the anode-supported SOFCs rapidly. The mechanical reliability of the electrolyte thin-film is important to prevent initial failure for cells and stacks. In the present work, the internal stress was evaluated by X-ray for planar anode-supported SOFCs with and without micro-size defects in an electrolyte thin-film. A compressive stress of 501-561 MPa was observed for yttria-stabilized zirconia (YSZ) electrolyte thin-film without micro-size defects on NiO-YSZ anode substrate sintered at 1350-1400 °C. However, the stress was 188 and 453 MPa for the electrolyte thin-films sintered at 1200 and 1300 °C, respectively, because of insufficient sintering. Many micro-size cracks and pores were observed in the electrolyte thin-films sintered at 1200 and 1300 °C. Furthermore, the internal stress decreased by 50-100 MPa due to stress relief for the electrolyte thin-film with micropores, which were made during the actual manufacturing process, in spite of the sintering temperature of 1350 °C. X-ray stress measurement has a potential to be applied as a non-destructive test method for anode-supported SOFCs.

Key words : Solid oxide fuel cell (SOFC), X-ray stress measurement, Micro-size defect, Electrolyte thin-film, Yttria-stabilized zirconia (YSZ)

1. Introduction

In Japan, solid oxide fuel cells (SOFCs) were commercialized as residential combined heat and power (CHP) systems in 2009 (Suzuki et al., 2009). The New Energy and Industrial Technology Development Organization (NEDO) project achieved the degradation rate of -0.1 %/kh on accelerated evaluation, which corresponded to less than 10 % performance degradation for 90000 h (10 years) by improving the chemical stability at interface between electrolyte and electrode, and decreasing the impurity effect such as chromium and sulfur poisoning (Yokokawa, 2015). Recently, much research has focused on decreasing the operating temperature of SOFCs from high temperatures of 800-1000 °C to intermediate temperatures (IT) range of 500-700 °C to improve durability, reduce costs, and increase start-up speed. Two major approaches have been proposed to decrease the operating temperature: One is to use new materials that have high ionic conductivity at low temperature, such as LaGaO_3 (Ishihara et al., 1994) and CeO_2 (Steele, 2000), and the other one is to thin down the electrolyte made of a conventional material such as yttria-stabilized zirconia (YSZ). Although good performance was achieved via the former approach at low temperature, the...
mechanical strength of LaGaO$_3$ and CeO$_2$ was lower than that of YSZ (Drennan et al., 1997, Seike et al., 1997). The latter approach has been developed as anode-supported cells, which are generally made by coating a YSZ electrolyte thin-film on a Ni-YSZ anode substrate, and sintering together at the same time at high temperatures above 1300 °C.

However, the coefficients of thermal expansion (CTE) are different between YSZ (10 × 10$^{-6}$ K$^{-1}$) (Montross et al., 2002) and Ni-YSZ (12 × 10$^{-6}$ K$^{-1}$) (Mori et al., 1998). Yakabe et al. (2004) detected the compressive internal stress as approximately 650 MPa from the YSZ electrolyte thin-film in an anode-supported cell, which is caused by the mismatch of CTEs between dense YSZ and porous Ni-YSZ, by X-ray stress measurement at room temperature. Furthermore, the internal stress is variable during thermal and reduction-oxidation (redox) cycles. During the manufacturing process, the anode substrate is in oxidized state (NiO-YSZ). The internal stress is almost zero at the sintering temperature, and is stored during the cooling process. When the anode substrate is reduced (Ni-YSZ) by a supply of hydrogen fuel, the internal stress of the electrolyte thin-film decreases due to the decrease in the CTE of anode substrate (Sumi et al., 2006). In an emergency shutdown situation, the anode substrate has a risk of re-oxidation by air. Tanaka et al. (2008) detected the tensile internal stress from the electrolyte thin-film during re-oxidation cycle by in-situ X-ray stress measurement at SPring-8 BL02B1, which was caused by an anomalous expansion of the NiO-YSZ anode substrate. The tensile internal stress sometimes produces microcracks in the electrolyte thin-film during the re-oxidation cycle (Hatae et al., 2009a, 2009b, 2010).

X-ray stress measurement is one of the most effective methods to detect defects nondestructively in the electrolyte thin-film for anode-supported cells. In the present work, we try to estimate micro-size defects formed during the manufacturing process. Firstly, the co-sintering temperature of YSZ electrolyte thin-film and NiO-YSZ anode substrate is varied to change the degree of sintering of the electrolyte thin-film. If the sintering of YSZ electrolyte thin-film is insufficient, many micro-size defects (cracks and pores) are obviously remained into the thin-film. We confirm whether the difference in internal stress can be evaluated by X-ray stress measurement using Cu-K$_\alpha$ radiation at room temperature for the samples sintered at various temperatures. Next, the internal stress of the electrolyte thin-film with and without micropores, which are formed during the actual manufacturing process, is measured. For example, the amount of micro-size defects in the thin-film made by screen printing using a clogged mesh is expected to be less than that in the insufficient sintering thin-film. A possibility of X-ray stress measurement is investigated for a non-destructive test method of practical SOFCs.

2. Experimental procedure

A planar anode substrate was made from NiO (Sumitomo metal mining), (Y$_2$O$_3$)$_{0.08}$(ZrO$_2$)$_{0.92}$ (YSZ; Tosoh) and pore former (acrylic resin; Sekisui Plastic). The weight ratio of NiO:YSZ:pore former was 6:4:1. The pore former of acrylic resin with a grain size of approximately 5 μm was added before sintering to increase anode porosity. These powders were mixed using mortar manually for 30 min, and the mixture was uniaxially pressed into a disk with 30 mm in diameter under 30 MPa. The NiO-YSZ disk was sintered for 1 h in air at 1200 °C before coating the YSZ electrolyte thin-film. The heating and cooling rate was 5 °C/min during sintering.

A YSZ paste was prepared by mixing YSZ powder, α-terpineol (Kanto Chemical) and ethyl cellulose (45 cp; Kishida Chemical) using a planetary centrifugal mixer (Thinky ARE-310). The YSZ paste was screen-printed onto the NiO-YSZ anode substrate. Then, the YSZ electrolyte thin-film and anode substrate were co-sintered for 3 h in air. Firstly, the sintering temperature was varied at 1200 °C (Sample1200), 1300 °C (Sample1300), and 1400 °C (Sample1400) to change the amount of micro-size defects in the electrolyte thin-film. Next, the samples sintered at 1350 °C for 3 h in air without micropores (Sample1350A) and with micropores (Sample1350B, C), which were formed in the electrolyte thin-film by the use of a clogged screen mesh during the manufacturing process, were evaluated. After sintering, the diameter and thickness of the disk were 24 mm and 1.0 mm, respectively.

X-ray stress measurement was based on the standard method of JSMS-SD-10-05 (The Society of Materials Science, Japan, 2005). The planar internal stress $\sigma_x$ can be derived from the following equation:

$$\sigma_x = -\frac{E}{2(1+\nu)\tan\theta_0}\frac{\partial}{\partial \psi}\left(\frac{2\theta_0}{\sin^2\psi}\right)$$

where $\theta_0$ is the diffraction angle of the free strain state, $\theta_0$ is the direction angle of the measurement, $\psi$ is the angle...
between the normal of the sample and the normal of the diffracting plane, \( E \) and \( \nu \) are the X-ray elastic constants of Young's modulus and Poisson's ratio, respectively. The 511+333 diffraction of YSZ was measured by iso-inclination method with an X-ray diffractometer (Rigaku SmartLab) using Cu-K\( \alpha \) radiation at room temperature in air. The values of \( E \) and \( \nu \) for YSZ are referred to be 206 GPa and 0.30, respectively (Yakabe et al., 2004).

3. Results and discussion

3.1 Change in sintering temperature

Figure 1 shows the scanning electron microscopic images of the cross-section for samples sintered at 1200, 1300 and 1400 °C. The thickness of YSZ electrolyte thin-film was approximately 10 \( \mu \)m. For Sample1200, small raw grains were observed in the YSZ electrolyte thin-film due to insufficient sintering. It simulated the situation that many defects, such as microcracks and pores, were formed in the YSZ electrolyte thin-film. For Sample1300, some micropores existed in the YSZ electrolyte thin-film, although no through-crack was observed. On the other hand, no micropore was observed for Sample1400. The porosity in the NiO-YSZ anode substrate decreases with increasing the sintering temperature, which causes an increase in diffusion polarization resistance (Suzuki et al., 2009). Therefore, the sintering temperature of 1350-1400 °C is a desirable condition for anode-supported SOFCs in the present work.

Figure 2 shows the X-ray diffraction pattern of Sample1400 measured in air at room temperature. The crystal structure of \( \text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92} \) is reported to be metastable tetragonal \( (t''') \) (Yashima et al., 1994). The space group of the \( t''' \) structure was assigned to be \( P4_2/nmc \) by neutron diffraction. However, the \( t''' \) structure cannot distinguish cubic fluorite-type structure \( (Fm\bar{3}m) \) by X-ray Cu-K\( \alpha \) diffraction, because the axial ratio of \( c/a \) is almost equal to unity within experimental error. The lattice parameter of YSZ electrolyte thin-film for Sample1400 was \( a = 0.51466 \) nm, when the space group was assumed to be \( Fm\bar{3}m \). This value well agreed with the previous report (Yashima et al., 1994).

![Scanning electron microscopic images of cross-section for Sample1200, 1300 and 1400.](image1)

![X-ray diffraction pattern of Sample1400.](image2)
Fig. 3 511+333 X-ray diffraction of YSZ electrolyte thin-film for Sample1200, 1300 and 1400.

Fig. 4 $2\theta$-$\sin^2 \psi$ diagram for Sample1200, 1300 and 1400.

Table 1 Compressive internal stress in the YSZ electrolyte thin-film sintered at various temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress (MPa)</th>
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<tbody>
<tr>
<td>Sample1200</td>
<td>$188 \pm 8$</td>
</tr>
<tr>
<td>Sample1300</td>
<td>$453 \pm 5$</td>
</tr>
<tr>
<td>Sample1400</td>
<td>$561 \pm 9$</td>
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</tbody>
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In the present work, the 511+333 diffraction of YSZ was chosen for X-ray stress measurement in a \( \psi \) range as wide as possible by iso-inclination method.

Figure 3 shows the 511+333 X-ray diffraction of YSZ electrolyte thin-film for Sample1200, 1300 and 1400 with a change in \( \psi \). The shift of diffraction peaks was small for Sample1200, which indicated that the internal stress was small. On the other hand, the diffraction peaks were shifted to higher angle with increasing \( \psi \) for Sample1300 and 1400. The YSZ electrolyte thin-film had a compressive internal stress for Sample1300 and 1400. Figure 4 shows the \( 2\theta\sin^2 \psi \) diagram for Sample1200, 1300 and 1400. The diffraction angle was almost proportional to \( \sin^2 \psi \) for all samples. The slope of \( 2\theta\sin^2 \psi \) line for Sample1400 was steeper than those for Sample1200 and 1300. The internal stress derived from Eq. (1) was shown in Table 1. The error of the stress was less than 3 %, when each sample was measured 5 times with changing the sample position. The fitting deviations from the regression lines were within 4 % in the present work. The internal stress by finite element method (FEM) was calculated as 542 MPa (Sumi et al., 2006), which is almost the same as the stress for Sample1400. The experimental internal stress was measured only at the surface of YSZ electrolyte thin-film in the present work, because the penetration depth of Cu-K\( \alpha \) is several microns. The internal stress at the interface between electrolyte and anode substrate is generally more important. For anode-supported SOFCs, the internal stress at the surface was previously confirmed to be almost the same as that at the interface by synchrotron radiation (72 keV) (Sumi et al., 2006). The stresses for Sample1200 and 1300 were smaller by 66 % and 19 %, respectively, than that for Sample1400. For Sample1200 and 1300, thermal stress was not stored due to insufficient sintering, and/or the stress was released around microcracks and pores in YSZ electrolyte thin-film. The result, of course, is varied by the change in raw materials and sintering condition. In that case, X-ray stress measurement can also qualitatively estimate the degree of sintering of YSZ electrolyte thin-film for anode-supported SOFCs. However, Sample1200 and 1300 had too many micro-size defects to evaluate the size and distribution of the defects quantitatively. We discuss the relation between the internal stress and the micropore size/distribution in the next section.

### 3.2 Formation of micro-size defects during manufacturing process

Wet ceramic processes, such as dip coating and screen printing, are simple and low-cost manufacturing methods. However, micro-size defects are sometimes formed into YSZ electrolyte thin-film during the manufacturing process. For example, no defect was observed with an optical microscope in YSZ electrolyte thin-film made by screen printing for the Sample1350A as shown in Fig. 5. On the other hand, micropores were observed for Sample1350B and 1350C.

![Fig. 5 Optical microscopic images of YSZ electrolyte thin-film surface for Sample1350A, 1350B and 1350C.](image-url)
Fig. 6  Size and distribution of the micropores in the area of 0.28 mm$^2$ for Sample1350B and 1350C.

Fig. 7  511+333 X-ray diffraction of YSZ electrolyte thin-film for Sample1350A, 1350B and 1350C.

due to the use of a clogged screen mesh. The sintering temperature was the same as 1350 °C for all Samples. Figure 6 shows the size and distribution of the micropores in the area of 0.28 mm$^2$ for Sample1350B and 1350C. The average diameters of micropores were approximately 7 and 10 µm for Sample1350B and 1350C, respectively. While the size of all micropores was less than 15 µm for Sample1350B, the micropores with more than 15 µm in diameter were observed for Sample1350C. The percentages of the total micropore areas were 1.0 % and 3.4 % for Sample1350B and 1350C, respectively. If X-ray stress measurement can estimate the presence or absence of defects in YSZ electrolyte thin-film, it becomes one of the most effective methods for a non-destructive test of anode-supported SOFCs.

Figure 7 shows the 511+333 X-ray diffraction of YSZ electrolyte thin-film for Sample1350A, 1350B and 1350C with a change in $\psi$. The diffraction peaks were shifted to higher angle with increasing $\psi$ for all samples, indicating that the YSZ electrolyte thin-film had a compressive internal stress. Figure 8 shows the 2$\theta$-sin$^2$ $\psi$ diagram for
Sample1350A, 1350B and 1350C. The diffraction angle was almost proportional to $\sin^2 \psi$ for all samples. The diffraction angle for Sample1350A was slightly larger than those for Sample1300 and 400, which might be caused by the change in surface roughness. The slope of $2\theta-\sin^2 \psi$ line for Sample1350A was intermediate between Sample1300 and Sample1400. The internal stress derived from Eq. (1) was shown in Table 2. The stresses for Sample1350B and 1350C were 8.4% and 19% smaller, respectively, than that for Sample1350A in spite of the same sintering temperature. The error of the stress was less than 3%, when each sample was measured 5 times with changing the sample position. Therefore, the differences in the stress among Sample1350A, 1350B and 1350C were significant. The decrease in the internal stress was caused by stress relief around micropores in YSZ electrolyte thin-film for Sample1350B and 1350C. On the other hand, Sample1350A had a huge compressive internal stress of $501 \pm 14$ MPa. It means that the YSZ electrolyte thin-film is strengthened. It is generally no problem in SOFC operation, unless micro-size defects are formed by stress relief. X-ray stress measurement has a potential to be applied as a non-destructive test of YSZ electrolyte thin-film for anode-supported SOFCs.

### 4. Conclusion

In the present work, we tried to estimate micro-size defects, which were formed during the manufacturing process, by X-ray stress measurement for anode-supported SOFCs. The internal stress of the YSZ electrolyte thin-film for the sample sintered at 1400 °C was $561 \pm 9$ MPa, which is almost the same as the FEM calculated value. The sintering temperatures at 1200 °C and 1300 °C were insufficient, because many defects, such as microcracks and pores, were observed in the YSZ electrolyte thin-film. The compressive internal stress decreased with the decrease of the sintering temperature. X-ray stress measurement can evaluate the degree of sintering of YSZ electrolyte thin-film for anode-supported SOFCs. Furthermore, it was confirmed that the micropores, which were formed in the YSZ...
electrolyte thin-film during the actual manufacturing process, decreased the internal stress. The micropores in YSZ electrolyte thin-film caused stress relief around the micro-size defects, which can be estimated by X-ray stress measurement for anode-supported SOFCs.

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