In-situ Measurement of Internal Stress in Solid Oxide Cell during Oxidation and Deoxidization of Anode in Heat Cycling

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Solid-oxide fuel cells are expected to be one of the most effective and clean energy sources because of their highest efficiency and simple systems. In order to guarantee their long durability, it is important to operate the cells at lower temperatures around 700 and 800 ℃ and to avoid the fracture or deformation of a unit cell consisting of three layered structures: anode, electrolyte and cathode. Thermal stresses due to the mismatch of thermal expansion are the main source for fracture and should be evaluated precisely.

In the present study, monochromatic X-rays with an energy level of 71.5 keV from a synchrotron source was used to measure the stress distribution in a unit cell during heat cycling to 700℃. The internal stresses in the electrolyte and the anode were determined by the constant-penetration depth method combined with the $\sin^2\psi$ method. Soller slits were placed in front of the receiving counter.

The electrolyte made of 10mol%Sc_2O_3 ZrO_2 (ScSZ) with a thickness of 20μm was stacked on the anode of a composite of NiO and 3mol% Y_2O_3 ZrO_2 (YSZ). The crystalline structure of YSZ was cubic and that of ScSZ was tetragonal. When the cell was deoxidized, Ni was produced from NiO in the anode. The diffractions of ZrO2 333, 511 and 115 were sued for stress measurement in ZrO2 phase in the electrolyte and the anode. During heat cycling, mixed gas of 5%H2-95%N2 was flown continuously in the furnace to simulate the deoxidization in actual SOFC cell.

First, the residual stress in three specimens with different degrees of oxidation after deoxidization was measured at room temperature by setting the penetration depth 20μm. Oxidation at 500 ℃ reduced the compressive residual stress from −500 to −285 MPa.

Figure 1 shows the diffraction profiles obtained at room temperature, 500 and 800℃, where the peak on the left is ZrO_2(333+511), and the one on the left NiO 420. The peak of NiO disappear in the profile at 800℃ by deoxidization.

Figure 2 shows the change of the stress in ZrO_2 at the penetration depth of 20μm obtained by in-situ measurement of an oxidized cell. The compressive residual stress reduces linearly with the temperature.

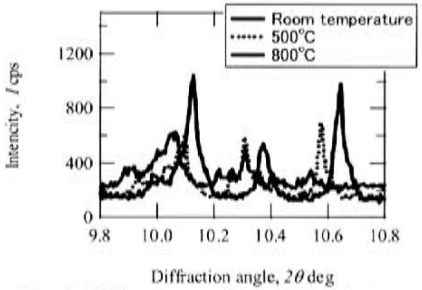

Fig. 1 Diffraction profiles obtained at room and high temperatures.

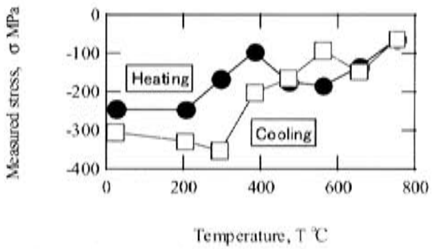

Fig.2 Change of stress in ZrO_2 electrolyte with temperature.

High-energy X-ray measurement of stresses of internal metallic connections in print-circuit boards during heat cycling

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High-density multi-layered structures with the internal metallic connections are required for print-circuit boards in order to miniaturize electronic devices. The durability of the print-circuit boards is heavily dependent on the resistance to thermal fatigue induced by the mismatch of the coefficient of thermal expansion during on-and-off switching. Especially, the thermal stress built up in the metallic connection is a key factor to guarantee the durability and should be controlled in the design process.

In the present study, monochromatic X-rays with an energy level of 72 keV from a synchrotron source was used to measure the stress of the internal metallic interconnects (Ag alloy) and the copper foils in the print-circuit boards. A cross section of an interconnection of one block is illustrated in Fig. 1, where the thickness of a Cu sheet is about 18μm and the size of a Ag alloy block of the interconnection is 50 μm in height and 100 μm in diameter. The mean value of the stress within several dozen blocks were measured by the $\sin^2\psi$ method during heat cycling between the room temperature and 120℃. A divergent slit had the dimensions of 0.3×5.0 mm for Ag alloy and 0.2×2.0mm for Cu films. Double slits with the height of 0.3mm and width 5.0mm for Ag alloy, 0.2×2.0mm for Cu films were placed in front of a receiving counter. The 243 diffraction of Ag alloy and the 423 diffraction of Cu were used for stress measurements. The oscillation within 30 deg around the ϕ axis was necessary to record X-ray profiles because of a large grain size compared with the irradiated area.

Figure 2 shows the 2θ-$\sin^2\psi$ diagram for 243 diffraction of Ag alloy. A good linearity is obtained. The stress value determined from the slope of the diagram is equal to ($\sigma_x - \sigma_z$) where σ_x is the in-plane stress and σ_z is the perpendicular stress. Table 1 summarizes the measured stress. The stress behavior and stress value during heat cycling have a similar results of the measurement of the stress within one block measured by BL46XU (2003B0548-NI-np-TU). The accuracy of the present measurement is fairly high.

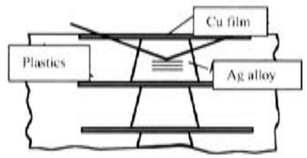

Fig. 1 Cross section of one block

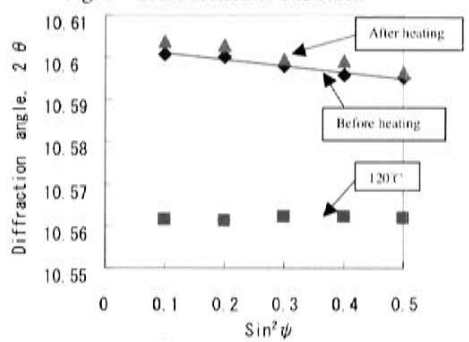

Fig. 2 2θ-$\sin^2\psi$ diagram of interconnection

Table 1 Measured stress ($\sigma_x - \sigma_z$)

Material	Stress (MPa)		
	Before heating	At 120℃	After heating
Ag alloy	50.1	-3.4	62.3