Residual Stress Analysis of Cylindrical Solid Oxide Fuel Cells

Tohru KATO, Akihiko MOMMA, Susumu NAGATA and Yasuhiro KASUGA

Energy Fundamentals Division, Electrotechnical Laboratory, AIST, 1-1-4, Umezono, Tsukuba-shi, Ibaraki 305

円筒型固体電解質燃料電池の残留応力解析

嘉藤 徹・門馬昭彦・永田 進・春日康弘

電子技術総合研究所エネルギー基礎部, 305 茨城県つくば市梅園 1-1-4

The dependence of the residual stress in cylindrical solid oxide fuel cells (SOFCs) on the structures and the process temperatures was estimated using the analytical modeling of an axisymmetric structure. From the results of the analysis the following points were discovered. In the case of a 4-layered structure, which is supported by a porous insulation tube of calcia-stabilized zirconia (CSZ), the circumferential and axial stresses induced in the electrodes are so high that they can break the structure under the assumed realistic conditions. A method for reducing these stresses is discussed. On the other hand, in the case of a 3-layered structure which is supported by an inner electrode tube, tensile stresses in the electrodes can be reduced to several MPa if the total thickness of two electrodes is more than 60 times the thickness of the electrolyte. New material for the substrate tube is proposed on the basis of the obtained results.

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1. Introduction

The Solid oxide fuel cell (SOFC) is an all solid state fuel cell which is operated at approximately 1000°C. The cell consists of a dense oxide ion conducting electrolyte and two porous electrodes. Yttria-stabilized zirconia (YSZ) is most commonly used as the electrolyte in SOFCs. Ni-YSZ cermet and perovskite oxide like $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ are often selected as the anode and cathode, respectively, due to their electronic conductivity, catalytic performance and chemical stability.¹⁾ In addition to the general advantages of fuel cells,²⁾ like high energy conversion efficiency and low air pollutant emission rates, the SOFCs have other advantages,^{1),3)} such as the simple system concept without an external reformer, generation of high quality heat and high CO-resistance because of high temperature operations.

The degradation of the performance of SOFCs is frequently observed during long term operations. There may be several factors that can cause this degradation: thermal stress,^{4),5)} decrease of mechanical strength of the component material with the thermal cycle and the operation time, the sintering behavior of porous electrodes⁶⁾ and chemical reactions among component materials under operating condition.⁷⁾⁻¹²⁾ So far, several investigations have been carried out on chemical degradation. However, information regarding other factors has been extremely limited.

As all components of SOFC are solid, during the fabrication of SOFC or at the beginning of the operation, the thermal stress, which was caused by temperature distribution and the mismatches of coefficient of thermal expansion (CTE) between the component materials, can become a serious problem resulting in the degradation of SOFC. From this point of view, Kanamura et al. estimated the thermal stress under the operating conditions.^{4),5)} In general, however, SOFC is fabricated at temperatures higher than 1000°C by some manufacturing processes such as sintering or CVD/EVD¹³⁾⁻¹⁵⁾ and their operation temperature is approximately 1000°C. Hence, considering the thermal stress problem, the residual stress at room temperature can be fatal for the SOFC structure. Therefore, in this paper, dependence of the residual stress on material properties and dimensions of cell components is studied and a method for prevention is discussed for the cylindrical SOFCs. Cylindrical SOFCs can be divided into two types depending on the cell structure. One is a 4-layered structure composed of a CSZ substrate tube having a similar value for the CTE as the YSZ electrolyte, the other structure is a 3-layered structure supported by an electrode tube. The analysis is performed for both types.

2. Calculation of residual stress

For this analysis, the cell was treated as a long coaxial multilayer tube (Fig. 1) under uniform temperature conditions without any external force. It was assumed that each layer was isotropic and elastic. The components of stress on each layer satisfy the equations of equilibrium as follows.¹⁶⁾

$$\frac{\partial \sigma_{rr}}{\partial r} + \frac{\partial \sigma_{zr}}{\partial z} + \frac{\sigma_{rr} - \sigma_{\theta\theta}}{r} = 0 \quad (1)$$

$$\frac{\partial \sigma_{zr}}{\partial r} + \frac{\partial \sigma_{zz}}{\partial z} + \frac{\sigma_{zr}}{r} = 0 \quad (2)$$

The stress-displacement relationships are expressed with cylindrical coordinates as follows.

Fig. 1. The model of cylindrical SOFC.

$$\sigma_{rr} = \frac{E}{1-\nu} \left\{ \frac{1-\nu}{1-2\nu} \frac{\partial u_r}{\partial r} - \frac{\nu}{1-2\nu} \left(\frac{u_r}{r} + \frac{\partial u_z}{\partial z} \right) \right\} - \frac{\alpha E}{1-\nu} \Delta T \quad (3)$$

$$\sigma_{\theta\theta} = \frac{E}{1-\nu} \left\{ \frac{1-\nu}{1-2\nu} \frac{u_r}{r} - \frac{\nu}{1-2\nu} \left(\frac{\partial u_r}{\partial r} + \frac{\partial u_z}{\partial z} \right) \right\} - \frac{\alpha E}{1-\nu} \Delta T \quad (4)$$

$$\sigma_{zz} = \frac{E}{1-\nu} \left\{ \frac{1-\nu}{1-2\nu} \frac{\partial u_z}{\partial z} - \frac{\nu}{1-2\nu} \left(\frac{\partial u_r}{\partial r} + \frac{u_r}{r} \right) \right\} - \frac{\alpha E}{1-\nu} \Delta T \quad (5)$$

$$\sigma_{rz} = \frac{E}{2(1-\nu)} \left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r} \right) \quad (6)$$

Where, σ , u , E , α and ν denote stress tensor, displacement vector, Young's modulus, CTE and Poisson's ratio, respectively. ΔT denotes the temperature difference of each layer between the assumed temperature for calculating stress and the fabrication temperature. The shear stresses $\sigma_{\theta z}$ and $\sigma_{\theta r}$ are zero because of their symmetry about the z -axis. Assuming that the tube is long enough, it is considered that all layers can elongate or shrink uniformly along the z -axis as the temperature changes. Therefore, axial shear stress σ_{rz} is supposed to be approximately zero.

It was assumed that each layer would be fabricated in order starting from the inside on the substrate tube at the fabrication temperature T_i and the thickness d_i (the subscript i denotes order of layer from the inside) and its thermal stress would be zero when it is deposited. The following boundary conditions were adopted.

(1) Radial stresses σ_{rr} at the inner and the outer surface are zero.

(2) σ_{rr} is balanced and radial displacement u_r is continuous at the interface between layers.

(3) Integration of axial stress σ_{zz} on the parallel r - θ plane cross section is zero.

The equations of boundary conditions for each layer are as follows. According to continuity of displacement,

$$u_{r,i,1}(r_{1,2}, T) = u_{r,i,2}(r_{1,2}, T) \quad (i \geq 2) \quad (7)$$

$$u_{z,i,1}(r_{1,2}, T) = u_{z,i,2}(r_{1,2}, T) \quad (i \geq 2) \quad (8)$$

When i -th layer ($i \geq 3$) is fabricated, the displacement of i -th layer is zero, while the displacement of $(i-1)$ -th layer arises from a temperature difference between T_i and T_{i-1} . This displacement is equivalent to the displacement of $(i-1)$ -th layer in $(i-1)$ -layered structure at temperature T_i because of the assumption mentioned above.

$$\begin{aligned} u_{r,i,i}(r_{i-1,i}, T) \\ = u_{r,i,i-1}(r_{i-1,i}, T) - u_{r,i,i-1}(r_{i-1,i}, T_i) \\ = u_{r,i,i-1}(r_{i-1,i}, T) - u_{r,i-1,i-1}(r_{i-1,i}, T_i) \end{aligned} \quad (i \geq 3) \quad (9)$$

$$\begin{aligned} u_{z,i,i}(r_{i-1,i}, T) \\ = u_{z,i,i-1}(r_{i-1,i}, T) - u_{z,i,i-1}(r_{i-1,i}, T_i) \\ = u_{z,i,i-1}(r_{i-1,i}, T) - u_{z,i-1,i-1}(r_{i-1,i}, T_i) \end{aligned} \quad (i \geq 3) \quad (10)$$

According to the boundary conditions for σ_{rr} ,

$$\sigma_{r,i,1}(r_{0,1}, T) = 0 \quad (i \geq 2) \quad (11)$$

$$\sigma_{r,i,i}(r_{i,i+1}, T) = 0 \quad (i \geq 2) \quad (12)$$

$$\sigma_{r,i,k}(r_{k,k+1}, T) = \sigma_{r,i,k+1}(r_{k,k+1}, T) \quad (i \geq 2, i-1 \geq k). \quad (13)$$

Considering that stresses in the direction of z -axis are balanced and σ_{rz} is zero,

Table 1. Material Properties of the Components of SOFC

Component material	Young's modulus E_0 / GPa	Poisson's ratio ν	CTE $10^6 \alpha$ / $1/^\circ\text{C}$	Porosity P / %	Young's modulus of porous material E / GPa
CSZ	208	0.3	9.1	32.6	99
Ni-YSZ					
(Ni:YSZ= 40:60 mass%)	207	0.3	12.1	30	106
YSZ	208	0.3	10.3	0	—
La _{0.85} Sr _{0.1} MnO ₃	154	0.3	12	30	79

$$\sum_{k=1}^i \int_{r_{k-1,k}}^{r_{k,k+1}} \sigma_{zz,i,k}(r, T) r dr = 0 \quad (14)$$

In these equations, $u_{r,i,j}$ represents u_r in j -th layer when i -th layer has been fabricated. $u_{z,i,j}$, $\sigma_{rr,i,j}$ and $\sigma_{zz,i,j}$ have similar meaning. $r_{i-1,i}$ denotes the location of interface between $(i-1)$ -th layer and i -th layer. In particular, $r_{i,i+1}$ in i -layered structure and $r_{0,1}$ denote the locations of the outer surface and the inner surface.

The properties of SOFC component materials are listed in Table 1. These were used to decide the parameter ranges for calculation. Young's moduli for the porous materials were estimated using the following empirical equation.¹⁷⁾

$$E = E_0(1 - 1.9P + 0.9P^2) \quad (15)$$

E_0 and P denote Young's modulus of the dense material and porosity of porous material, respectively. CTE of Ni-YSZ cermet α_{cer} was estimated using Turner's model.¹⁸⁾

$$\alpha_{\text{cer}} = \frac{\sum_i \alpha_i K_i F_i / \rho_i}{\sum_i K_i F_i / \rho_i} \quad (16)$$

Where K_i , F_i and ρ_i denote bulk modulus, weight fraction and density of component i , respectively.

For the actual fabrication of SOFC, the material properties and the thickness of the YSZ electrolyte should be selected in a very narrow range so as not to decrease cell performance. On the contrary, for the electrodes, the material properties and the thicknesses can be widely changed by controlling composition and porosity of the materials. Therefore, in the calculation, parameters on the properties of electrodes were widely changed. The inner diameter of the cell was fixed at 12.7 mm and the thickness of the electrolyte was 0.05 mm. The material properties of YSZ are shown in Table 1.

3. Results and discussion

3.1 4-layered structure

Figure 2 shows the residual stress distributions obtained for the 4-layered structure by employing the data given in Table 1. σ_{rr} is a small compressive stress over all regions. However, σ_{zz} and $\sigma_{\theta\theta}$ induced in the two electrodes are large tensile stresses. Particularly, those in the inner electrode are more than 200 MPa under the given conditions. These stresses are too large and result in the fracturing of the porous electrodes. The influence of material properties on stress distribution in the inner electrode is shown in Fig. 3. For simplifying the calculation, it was assumed that material properties of both electrodes were equivalent and CTE of substrate was equal to that of YSZ. The stress decreases with decreasing $E(\alpha - \alpha_3)$. To reduce the stress to MPa level, the difference between CTE of component

Fig. 2. Residual stress distribution for the 4-layered structure. Ni-YSZ was assumed as the inner electrode. $T_2=1300^\circ\text{C}$, $T_3=T_4=1100^\circ\text{C}$, $d_1=1.2$ mm, $d_2=1.4$ mm, $d_4=0.1$ mm.

Fig. 3. Dependence of the circumferential stress $\sigma_{\theta\theta}$ in the inner electrode on the material constants of electrodes. The gradation from white to black corresponds with the increase of $\sigma_{\theta\theta}$ and one line was drawn every 10 MPa. $T_2=T_3=T_4=1100^\circ\text{C}$, $\alpha=\alpha_2=\alpha_4$, $\alpha_1=\alpha_3=10.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, $E=E_2=E_4$, $E_1=99$ GPa, $E_3=208$ GPa, $d_1=1.2$ mm, $d_2=1.4$ mm, $d_4=0.1$ mm.

materials must be within the order of $10^{-7} \text{ }^\circ\text{C}^{-1}$ or Young's moduli of porous materials must be very small. Because a reduction of the difference between CTE of component materials could deteriorate the electrical performance of electrodes and the decrease in Young's moduli could lower

Fig. 4. Dependence of the circumferential stress $\sigma_{\theta\theta}$ in the inner electrode on the thickness of electrodes. The gradation from white to black corresponds with the increase of $\sigma_{\theta\theta}$ and one line was drawn every 20 MPa. $T_2=T_3=T_4=1100^\circ\text{C}$.

the strength of porous materials, these concepts must be applied carefully. Figure 4 shows the dependence of the stress distribution in the inner electrode on the electrode thickness. The tensile stress decreases with increasing the total thickness of electrodes, but, the decreasing rate is not large, because the substrate thickness is thicker than the total thickness of electrodes. Even if the total thickness of electrodes is equal to that of the substrate, the magnitude of stress in the inner electrode is more than 240 MPa. Therefore, this is not a promising method.

Figure 5 shows the stress dependence on the fabrication temperatures of electrodes. σ_{zz} and $\sigma_{\theta\theta}$ of the electrodes at room temperature decrease with reducing electrode fabrication temperatures. In order to reduce σ_{zz} and $\sigma_{\theta\theta}$ to MPa level, two electrodes must be fabricated at the temperature lower than 100°C . In this case, the tensile stress in every layer at the operating temperature can be decreased to the magnitude of several MPa too. However, σ_{rr} at the operating temperature is tensile in all regions and shows the maximum value at the interface between the substrate and the inner electrode. Then, if bonding strength in some interfaces is lower than σ_{rr} , the delamination will occur at the interface. Furthermore, it can be consider that the stress distribution profile is changed during the long term operation by the annealing effect and σ_{zz} and $\sigma_{\theta\theta}$ at room temperature increase to a harmful value. For SOFC fabricated by the plasma spraying method, degradation is sometimes observed during the cooling after the operation. The details of this phenomenon have not yet been determined. The statements given above can hypothetically explain the degradation if the temperatures of the porous electrode fabricated by plasma spraying are much lower than the operating temperature.

3.2 3-layered structure

Figure 6 shows the residual stress distribution in the 3-layered structure. In contrast to the 4-layered structure, σ_{zz} and $\sigma_{\theta\theta}$ in the two electrodes are in the magnitude of several MPa because the total thickness of the electrodes d_1+d_3 is much larger than the thickness of electrolyte d_2 . The dependence of $\sigma_{\theta\theta}$ in the inner electrode on both electrodes thicknesses is shown in Fig. 7. If d_1+d_3 are approximately 60 times thicker than d_2 , σ_{zz} and $\sigma_{\theta\theta}$ become less than 10 MPa. This gives a practical condition for cylindrical SOFCs. On the one hand, σ_{zz} and $\sigma_{\theta\theta}$ in the electrolyte show compressive stresses more than 600 MPa. But the com-

Fig. 5. The stress distribution of the 4-layered structure with the two electrodes deposited at low temperature. (a) Room temperature (30°C), (b) Operating temperature (1000°C). $T_2 = T_4 = 110^\circ\text{C}$, $T_3 = 1100^\circ\text{C}$, $d_2 = d_4 = 0.1$ mm, $d_1 = 2$ mm, $d_3 = 0.05$ mm, $\alpha_1 = 10.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$.

pressive strength of YSZ is more than several GPa, which is large enough in comparison with σ_{zz} and $\sigma_{\theta\theta}$. On the other hand, σ_r is tensile in all regions and shows the maximum value at the interface between the inner electrode and the electrolyte, as in the case shown in Fig. 5. The dependence of σ_r at the point on d_1 and d_3 is shown in Fig. 8. For the parameters in the lower right area, which are actual values for the cylindrical SOFC, σ_r is approximately 3 MPa and almost independent of d_1 and d_3 . Figure 9 shows the dependence of σ_r on T_3 . σ_r slightly decreases with increasing T_3 . Hence, if the delamination occurs at any interface, the bonding strength is required to overcome it.

Figure 10 shows the influence of the difference in CTE between the inner and the outer electrodes on the stress in

Fig. 6. Residual stress distribution for the 3-layered structure. $T_2 = T_3 = 1300^\circ\text{C}$, $d_1 = 2.6$ mm, $d_3 = 0.1$ mm.

Fig. 7. Dependence of the circumferential stress $\sigma_{\theta\theta}$ in the outer electrode on the thickness of electrodes. The gradation from white to black corresponds with the increase of $\sigma_{\theta\theta}$ and one line was drawn every 10 MPa.

the outer electrode. If the CTE of the thick inner electrode is slightly smaller than that of the outer electrode, higher tensile stress is induced in the outer electrode. So, the electrode in which CTE is larger than that of another electrode should be employed as the support tube.

As mentioned above, it is clear that the 3-layered struc-

Fig. 8. Dependence of the radial stress σ_r at the interface between the inner electrode and the electrolyte on the thickness of electrodes. The gradation from white to black corresponds with the increase of σ_r and one line was drawn every 0.5 MPa.

Fig. 9. Dependence of the radial stress σ_r at the interface between the inner electrode and the electrolyte on T_3 . $T_2=1100^\circ\text{C}$.

Fig. 10. Dependence of the circumferential stress σ_θ in the outer electrode on CTE of the inner electrode α_1 . $T_2=T_3=1300^\circ\text{C}$, $d_1=2.6\text{ mm}$, $d_3=0.1\text{ mm}$.

ture is superior to the 4-layered type only if each interface has a strength high enough to resist radial tensile stresses. But this type has a few demerits with respect to the limitation in the configuration of interconnection and the expense of the substrate electrode tube. Practically, the long and narrow interconnection along the z -axis which has been adopted by Westinghouse Electric Corporation is only a

reasonable form for this type.¹⁹⁾ As to the cost, both electrode materials are more expensive than CSZ. Because the thickness of the support tube is much thicker than that of the cell itself, applying the electrode to the support tube results in an increase in the cost of the cell.

If the support tube of the 4-layered cell is made from the insulator whose CTE is equal to that of the inner electrode material, then this cell has the same merits of mechanical properties as those of the 3-layered type. In addition, applying such a support tube to the cell construction will permit flexibility in selecting interconnection configurations.

A mixture of MgAl_2O_4 and MgO , which is a good insulator under the operating conditions, is one of the promising materials for the support tube, because its CTE is controlled to be within $9 \times 10^{-6} \sim 13 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ by changing its composition and its cost may be less than that of CSZ.

4. Conclusions

From the results of this analysis, the following points were clarified. For the 4-layered structure supported by CSZ, the σ_{zz} and $\sigma_{\theta\theta}$ in the electrodes are too large to prevent its deterioration. The 3-layered structure can overcome this demerit. If the total thickness of the two electrodes is more than 60 times the thickness of the electrolyte, these stresses due to the difference in CTE decrease to a magnitude of several MPa. In this case, σ_r is a small tensile stress. Finally, the residual stress of the 4-layered type is reduced using the support tube of which CTE is larger than those of electrodes.

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