	たなか　じゅんや
氏　　　　　　名	田　中　順　也
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）機械機能創成専攻
学 位 論 文 題 目	Development of Numerical and Experimental Evaluation Methods of Cell Stress Evolution for Solid Oxide Fuel Cells in the Entire Process from Manufacturing to Power Generation (固体酸化物燃料電池の開発に向けた製造から発電までの全工程におけるセル発生応力の数値的および実験的評価法に関する研究)
論 文 審 査 委 員	主査　東北大学教授　橋田　俊之　東北大学教授　祖山　均 東北大学教授　川田　達也　東北大学准教授　佐藤　一永

論文内容要約

Solid oxide fuel cell (SOFC) is a power generation device that converts hydrogen or hydrocarbon fuel into electricity in a high-temperature environment, and attracting great attention as one of the leading technology to achieve a Carbon-Neutral society. On the other hand, SOFC cells have a potential risk of fracture, resulting in not only a significant degradation in performance but also safety risks such as hydrogen leakage or abnormal temperature rise due to direct combustion of hydrogen and air. Thus, establishing mechanical reliability of SOFCs is one of the top priorities for commercialization.

Several types of stresses are generated in the SOFC cells from manufacturing to operation, and all stresses may affect the cell failure. Specifically, the SOFC stack consists of cells, which are the power generation component, and other components such as frame, and start power generation through three main processes: sintering, stacking, and reduction process. Tensile or bending or compressive stresses are generated in the above all processes, causing a crack propagation or cell failure. Therefore, in order to discuss mechanical reliability, it is important to understand the stress evolution and its mechanism not only in a specific process but also in the entire process, however, not all processes have been sufficiently investigated in previous literatures. Especially, the mechanism of stress evolution in the reduction process has not been clarified, and few experimental verification methods has been proposed in the power generation process, thus further knowledge is needed.

The purpose of this study is to identify the stress evolution and its mechanism throughout the entire process, and to propose numerically and experimentally analysis methods for the stresses evolution in order to improve the mechanical reliability of SOFC.

In Chapter 1, the status of national and international energy and environmental issues and the usefulness of SOFC were first reviewed. Then, the structure of the SOFC and the functions of each component and technical issues were summarized. Finally, issues related to the mechanical reliability of SOFC and the outline of this thesis was described.

In Chapter 2, for the sintering process, cell stress evolution was analyzed using FEM analysis incorporating the temperature dependence of mechanical and thermal properties obtained from experiments and literatures. Then, in-situ measurements of residual stress changes in two layers of cells during heating were performed using X-ray diffractometry based on the cosα method for verification. The FEM analysis of half-cells with the sintering temperature as the stress-free state and the experimental results were in good agreement, including the temperature dependence. The analysis method and the cosα-based X-ray diffraction stress measurement are shown to be useful methods. For optimal design, a theoretical equation based on the bending due to thermal strain of a laminated flat plate in plane stress state was derived. The results of theoretical model developed in this study is in good agreement with that of the FEM analysis and the experiment, providing a useful framework for calculating the optimal cell structure at lower computational cost than the FEM analysis. The results of the optimal structure study showed that the thickness and linear expansion coefficient of the anode, Young's modulus and linear expansion coefficients of the electrolyte and intermediate layer have a significant effect on the cell safety ratio, and that other items besides mechanical reliability (e.g., power generation performance and limitations due to manufacturing process) can be given higher priority because the electrolyte and intermediate layer thickness do not affect the cell safety ratio as much as the above properties. Finally, the effect of cathode layer on the cell warp and stress evolution, which has not been almost reported in the previous literatures, was discussed in terms of a sintering condition. It was suggested that when the cathode layer is sintered at a relatively low temperature with a small holding time, the sintering of cathode material may be not advanced sufficiently, and cathode material may not be considered as a strength member. Based on the above, the desirable analysis conditions and model of a cell with cathode in the FEM analysis were proposed.

In Chapter 3, for the stacking process, the cell stress evolution during fastening in the stacking process was investigated using the stack structure with the current collector on the cathode side and ribbed frames on the anode side, which is one of the stack structures with better fuel supply, current collection characteristics, and manufacturability. The fastening load in stacking process caused the cell to bending deformation with the ribs as supports, and the maximum tensile stress was observed at the ribs for the cathode and the center position between the ribs for the anode. It was found that the amount of stress was higher on the cathode side than the anode side. The cell stress evolution increases as the rib pitch increases, and the cathode may break due to exceeding the allowable stress considering the residual stress in the sintering process. A proposed simply theoretical equation based on the bending of a flat plate due to uniformly distributed load under plane stress conditions showed a good trend with the FEM analysis, indicating that the theoretical equation is useful because the optimal stack structure can be derived in terms of mechanical reliability at a lower computational cost. Finally, a new current collector structure was proposed to reduce cell stress evolution.

In Chapter 4, for the reduction process, the deformation mechanism of anodes during reduction was clarified using experimentally monitor of anode deformation in-situ, a numerical construction method of three-dimensional structures, and a new evaluation method developed to quantitatively evaluate microstructures. The anode was generally considered to shrink during reduction because YSZ is dimensionally stable and NiO shrinks under reducing condition. However, it was clear that anodes showed expansion behavior depending on their compositions. It was quantitatively clarified that the expansion behavior during reduction was observed as a result of the release of residual compressive stress on the YSZ side induced before reduction (i.e., in the sintering process) by in-situ X-ray diffractometry based on the cosα method. For characterization of microstructure, a new evaluation index, "the path length of particles connection (PLPC)", was defined. The PLPC is a calculated minimum path length of a stroke from one face of the three-dimensional structure to another for any object, and can be used to quantitatively evaluate the particle connectivity and its contribution to the skeleton formation in accordance with the magnitude of the PLPC. A YSZ-Ni diagram was then proposed to systematically organize the relationship between composition and deformation behavior in terms of microstructure using PLPC index. The microstructure exerts significant effects on the deformation, and the deformation mechanisms are classified into four categories based on the PLPC results. The characteristic deformation behavior is discussed for each category. Finally, the effect of anode deformation behavior during reduction on cell stress evolution was examined and discussed using FEM analysis incorporating the above anode deformation and creep behavior.

In Chapter 5, for the operation process, numerical and experimental investigations of the cell stress evolution due to heat generation during power generation were carried out. A single-cell stack was fabricated, and several thermocouples were placed on the cathode side of the frame in contact with the cell to measure in-situ the temperature change of the cell during power generation. A CAE analysis combining thermo-fluid and electrochemical analysis was also performed using a stack model with the same geometry as the stack used in the experiment, showing that a good agreement between the analytical and experimental results for electrical (i.e., I-V characteristics) and thermal (i.e., temperature) characteristics. That is, the FEM analytical model was verified by the experiment. A cell stress analysis during power generation was performed by FEM analysis incorporating the stack temperature distribution observed from the CAE analysis and boundary conditions of the actual stack. Then, a deformation measurement method that can monitor the cell deformation during power generation in-situ was developed for experimentally verification of the analysis results. The maximum error of the developed measurement method was approximately 0.3 μm, which was sufficiently high accuracy for measuring cell deformation. The deformation of cells during power generation was measured using the above developed method and compared with the results of FEM analysis, which showed a generally good trend. The effect of current density on cell deformation was also investigated. Finally, the cell stress evolution during power generation was discussed using the calibrated analytical model.

Finally, in Chapter 6, the results, findings, and usefulness obtained in Chapters 2-5 were described as a summary.

The results of this research make it possible to examine the cell stress evolution in the entire processes from manufacturing to operation, and to determine the safety factor (or failure rate) of the cell in each process by comparing it to the strength. The results of this research may contribute to future discussions on inspection methods of cell failure in each process and may be applied not only to SOFC but also to SOEC or other cell configurations. In addition, the results of the sintering process in Chapter 2 can be applied to other research fields (e.g., all-solid-state batteries), thus this study is considered to be useful.