In situ investigation of curvature change induced by stress in multilayer structure during co-sintering for wavy type SOFC

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1. Introduction

2. Motivation / Research objectives

3. Viscosity/stress measurement

4. Curvature experiment / Results

5. Wavy type SOFCs

6. Conclusions
Introduction: Sintering process

Compact powders → Consolidated body

- 20°C
- 1000°C
- 1300°C
- 1200°C

(room temp.) → (high temp.)
Motivation: Develop co-sintering process for triple-layer

- **Conventional sintering**
  - Pros: fast, cheap, less energy consumption, etc.
  - Cons: warping, cracking

- **Co-sintering for triple-layer**
  - Anode
  - Electrolyte
  - Cathode
  - sintering
Research objectives

1. In situ investigation of curvature development during co-sintering

2. Understand stress & kinetics of bi- or triple-layer structure during co-sintering

3. Apply the understanding to fabricate wavy type SOFCs via co-sintering
1. Viscosity measurement

\[ \eta = \frac{\rho g L}{2 (\varepsilon_v - \varepsilon_f)} \]

2. Stress eq. proposed by Cai’s model

\[
\sigma_1 = \left[ \frac{m^4 + mn}{n^2 + 2mn (2m^2 + 3m + 2)} + m^4 \right] \sigma_1 \\
\overline{\sigma_1} = \left[ \frac{m^4 n^2 + 2mn (2m^2 + 3m + 2) + 1}{6 (m + 1)^2 mn} \right] \eta_1 k \\
\sigma_1^{Max} = \left[ \frac{m^2 n (4m + 3) + 1}{m^4 n^2 + 2mn (2m^2 + 3m + 2) + 1} \right] \sigma_1
\]

- \( m \) – thickness ratio
- \( \rho \) – density
- \( L \) – length of ceramic tape
- \( \sigma \) – sintering mismatch stress of upper layer
- \( \sigma_1 \) – viscous mismatch stress of upper layer
- \( n \) – viscosity ratio
- \( \eta \) – viscosity
- \( \varepsilon_v \) – strain rate during vertical sintering
- \( \varepsilon_f \) – strain rate during free sintering
- \( k \) – curvature rate
- \( \overline{\sigma_1} \) – stress at interface
- \( \sigma_1^{Max} \) – largest sintering mismatch stress at interface

Experimental conditions for co-sintering

1. Cell components (20μm thickness)
   
   Anode: Ni/CGO (Ni/Ce$_{0.8}$Gd$_{0.2}$O, 60wt%NiO-40wt%CGO)  
   Electrolyte : CGO (Ce$_{0.8}$Gd$_{0.2}$O, $d_{50}$: 0.1-0.4μm)  
   Cathode : LSCF (La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O, $d_{50}$: 0.7-1.1 μm)

2. Bi- or triple-layer by hot pressing method (50°C, 5MPa, 5 min)

3. Heat treatment:
   
   1°C/min to 750°C (de-binding process)  
   3°C/min to 1200°C (sintering process), holding for 10 min.
In situ monitoring of co-sintering behaviour

• Monitoring

• Bilayer curvature
  : Same thickness ratio (3:1), but different thicknesses

<table>
<thead>
<tr>
<th>No. layers for bilayer</th>
<th>Cathode</th>
<th>Electrolyte</th>
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Box furnace
Long-distance Microscope
Image processing
In situ monitoring of co-sintering behaviour

- Bilayer of anode/electrolyte
  (same thickness ratio, but different thicknesses)
In situ monitoring of co-sintering behaviour

- Bilayer of electrolyte/cathode
  (same thickness ratio, but different thicknesses)
In situ monitoring of co-sintering behaviour

- Curvature of triple-layer structure
1. Increase Ni/CGO layers in triple-layer structure
   (Ni/CGO-CGO-LSCF 15:1:1) → Anode supported wavy SOFCs

2. Pre-shaped wavy SOFCs:
   Al$_2$O$_3$ rods are used to guide the final wavy shape
Advantages of wavy type SOFCs

- Lower costs
  - Simpler manufacturing
  - Simple systems

- Better performance
  - Higher TPB

- More robust mechanical strength
In situ monitoring of co-sintering behaviour

- Curvature prediction & observation

![Curvature vs Temperature Graph]

- Normalised curvature
- Temp [°C]

- Ni/CGO-CGO (15:1)
- CGO-LSCF (1:1)
- Triple layer (15:1:1)
Co-sintering wavy SOFCs

- Anode supported wavy SOFCs (15:1:1)

(before sintering)

(after sintering)

(SEM image)
1. Properties like stress, viscosity, etc. are calculated by optical method

2. Understanding curvature changes during co-sintering process

3. Curvature prediction of a triple-layer cell is feasible, based on bilayer curvature observations

4. Energy and time efficient co-sintering process for wavy SOFCs has been developed
Thank you for your attention

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