Durability and Reliability of Materials and Components for SOFC

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2020 SOFC Program Review
Outline

- Development of model to explain anomalous thermal dependence of residual stresses in SOFCs
- Microstructural characterization of multi-component silicate glasses
- Additive manufacturing of SOFC materials and structures
- Summary
Development of model to explain anomalous thermal dependence of residual stresses in SOFCs

• ORNL has measured the state of residual stresses in SOFC materials and components using various techniques, including X-ray diffraction, Raman spectroscopy, DIC.
• X-ray diffraction measurements of bilayers (NiO-YEZ/YSZ) have shown a non-linear temperature dependence of the residual stresses.
• A model that accounts for phase transitions of NiO at the Neel temperature and order-disorder transitions of YSZ has been developed to accurately explain the anomalous behavior.
Residual Stresses in SOFCs

![Diagram of YSZ layer on Porous NiO-YSZ substrate]

Non-linear dependence on temperature

Stress (MPa) vs. Temperature (°C)

- Sample 15-1
- Sample 15-2
- Sample 15-3
- Sample 15-4

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Lara-Curzio et al. (2020)
**Determination of Residual Stresses by X-Ray Diffraction**

\[ \epsilon_{\phi \psi} = \frac{1 + \nu}{E} \sigma_\phi \sin^2 \psi - \frac{\nu}{E} (\sigma_1 + \sigma_2) \]

\[ \epsilon_{\phi \psi} = \frac{d_{\phi \psi} - d_o}{d_o} \]

\( d_o \) is the stress-free lattice spacing and \( d_{\phi \psi} \) is the spacing between lattice planes measured in the direction defined by \( \phi \) and \( \psi \). Values of \( d_o \) are determined when \( \psi = 0 \).

The peak of interest was the (620) reflection of YSZ, which was found in the \( 2\theta = 141^\circ - 145^\circ \) range. The maximum value of \( \psi \) was \( 55^\circ \) and the sample was tilted in 7 equal steps of \( \sin^2 \psi \) (both positive and negative tilts). From the slope of a plot of \( \epsilon_{\phi \psi} \) vs. \( \sin^2 \psi \), we obtain the value of the equibiaxial residual stress on the surface of the specimen.
NiO-YSZ anodes are 3-phase composites

A micromechanics model has been developed to calculate the effective properties of a 3-phase composite (NiO, YSZ and porosity) as a function of temperature.

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Open symbols correspond to values of shear modulus, whereas closed symbols correspond to values of Young’s modulus.
Anomalous Young’s Modulus of NiO

Young’s modulus of NiO determined by impulse excitation as a function of temperature.

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Note the abrupt change at the Neél temperature.
Determination of Residual Stresses in Multilayers

\[ \sigma_s = \frac{E_s}{1 - \nu_s} (\varepsilon - \alpha_s \Delta T) \]

\[ \sigma_{YSZ} = \frac{E_{YSZ}}{1 - \nu_{YSZ}} (\varepsilon - \alpha_{YSZ} \Delta T) \]

\[ \varepsilon = \xi + \frac{z - t_b}{r} \quad (\text{for } t_s \leq z \leq t_{YSZ}) \]

Residual Stresses in SOFCs

- State of residual stresses in YSZ layer. The continuous curve corresponds to model predictions, which captures the effect of transitions in NiO and YSZ.

- Data points correspond to residual stress values determined by X-ray diffraction on the YSZ surface of NiO-YSZ/YSZ bilayers. Color distinguishes between values obtained from different test specimens originating from the same sample.
Microstructural characterization of multi-component silicate glasses

• ORNL is characterizing the evolution of the microstructure of multi-component silicate glasses for SOFC sealing applications.

• Two commercially-available glasses are being investigated: SCN and G6

• Glass samples were mounted on either YSZ or Al₂O₃ substrates, and exposed at 800°C to air or gas mixtures of H₂+H₂O+N₂ for up to 40,000 hours.

• A combination of techniques, that include Raman spectroscopy, X-ray diffraction, electron microprobe and scanning electron microscopy have been used.
Electron microprobe analysis of glasses

G6 glass on alumina after 10,000 hrs in H₂+H₂O+N₂.

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Electron microprobe analysis of glasses

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Electron microprobe analysis of glasses

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BSE images and EDS maps at SCN-\(\text{Al}_2\text{O}_3\) interface region

Structure and chemical changes at interfaces region by using SEM – three new phases formed at the SCN-\(\text{Al}_2\text{O}_3\) interface. Ba-Ca-O based (bulk in center), Ba-Si-O based (bright lath), and K-Al-Si-O based (dark lath). GB diffusion in substrate was apparent.

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Structure and chemical changes at interfaces region by using SEM – two new phases formed at the G6-Al2O3 interface: Al-Na-Si-O based (dark lath at interface) and Ba-Al-Si-O based (thin bright layer). Significant GB diffusion was noted.

Lara-Curzio et al. (2020)
Interphase thickness as a function of time

Results suggest diffusion controlled process

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Interphase thickness as a function of time
Region of Analysis

SCN-YSZ 25k Sub/Glass interface

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Substrate: Zr-Y-O with a half sphere void with Si-K
Interphase/layer: Ca-Ba-Si-O
Need high magnification to verify

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Phase transformation of YSZ at interfacial region – Raman analysis

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Raman spectroscopy was used to detect phase transformation of the G6 glass on an 8YSZ substrate after 40,000 hours in air.

The diffusion of yttria into the glass, results in a transformation of the substrate from cubic to tetragonal to monoclinic ZrO$_2$. 

Lara-Curzio et al. (2020)
Additional information about the characterization of these two multi-component silicate glasses can be obtained by contacting:

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Microstructural characterization of multi-component silicate glasses

- ORNL is compiling the results of this extensive study into a report and journal publications.
- Analysis of the results will provide information on the kinetics of crystallization of G6 and SCN glasses as a function of substrate (YSZ or Al$_3$O$_3$) and environment (air or H$_2$+H$_2$O+N$_2$)
• Additive manufacturing of SOFC materials and structures

• ORNL is developing slurries for the deposition of NiO-YSZ, YSZ and cathode materials.
• The focus has been on high-solid contents
• Rheology of slurries
Alternative Geometries

SOFCs don’t have to be planar or straight tubes

Lara-Curzio et al. (2020)
Rheology of 8YZ/NiO/Pore Former Showed Complex Flow Behavior – more refinement required
Zeta Potential

Materials’ surface charges are compatible over a wide pH range if aqueous solution chemistries are utilized.
Particle Size Distribution

- Nickel (II) Oxide: 15.16 microns
- Rice Starch: 1.234 microns, 8.83 microns
- 8YZ: 422 nm

Lara-Curzio et al. (2020)
• Additive manufacturing of SOFC materials and structures

• Activities are on hold because of COVID-19
• **Summary and Future Activities**

• A detailed analysis of the anomalous temperature-dependence of residual stresses in NiO-YSZ/YSZ bilayers has been completed. The analysis provides an explanation for the anomalous behavior based on transformations experienced by both NiO and YSZ as a function of temperature.

• A report documenting detailed characterization of multi-component silicate glasses as a function of time of exposure in SOFC-relevant environments is being completed.

• Work on the development of new design methodologies and fabrication techniques for SOFCs continues.