Durability and Reliability of Materials and Components for Solid-Oxide Fuel Cells

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Outline

• Background
• Residual Stresses in SOFCs
  • Experimental Conditions
  • Results
  • Implications
• Interfacial Fracture Toughness
• Data Base
• Summary
Background

• Tools are being developed for predicting the durability and reliability of SOFC materials and components.
• The integration of mechanical property data with life prediction models requires the definition of a reference state of stress and understanding how stresses and strength evolve with time and operating conditions.
Background

\[
\text{Reliability} = \exp\left(-\frac{\sigma_1}{\sigma_{1o}}\right)^{m_1}
\]

\[
\text{Reliability} = \exp\left(-\frac{\sigma_2}{\sigma_{2o}}\right)^{m_2}
\]
Background

- Residual stresses
- Assembly stresses
- Conditioning stresses (e.g., $\text{H}_2$ reduction)
- Temperature gradients and gas pressure induce additional stresses
Background

- Tools are being developed for predicting the durability and reliability of SOFC materials and components.
- The integration of mechanical property data with life prediction models requires the definition of a reference state of stress and understanding how stresses and strength evolve with time and operating conditions.
- The objective of this project is to determine the state of residual stresses in a NiO-YSZ/YSZ bilayer before and after reduction in H₂.
NiO-YSZ/YSZ bilayer

50 mm X 50 mm X 510 µm

500 µm

10 µm

NiO-YSZ

YSZ
Curvature of NiO-YSZ/YSZ bilayer: optical profilometry

collaboration with John Lannutti
Ohio State University

250 µm

-589 µm
Residual Stresses in NiO-YSZ/YSZ bilayer

- 5 mm x 5 mm bi-layers of NiO-YSZ/YSZ
- 10 µm-thick YSZ layer
- scans between 139° and 142° 2θ
- 20°C, 400°C, 600°C, 800°C and 900°C
- Air

- 5 mm x 5 mm bi-layers of Ni-YSZ/YSZ (after reduction at 800°C using gas mixture of 4%H₂ and 96% Ar)
- 10 µm-thick YSZ layer
- scans between 139° and 142° 2θ
- 20°C, 400°C, 600°C, 800°C and 900°C
- Ar
Residual Stresses in NiO-YSZ/YSZ bilayer

Peak shift is converted into strain

- Strain/stress (applied or residual) changes the interplanar spacing Θ peak shift

**Bragg’s Law**

\[ \lambda = 2d \sin \theta \]

where

- \( \lambda \) = wavelength
- \( d \) = interplanar spacing
- \( 2\theta \) = diffraction peak position

- Strain, \( \varepsilon = (d_B - d_A)/d_A \)
Residual Stresses in NiO-YSZ/YSZ bilayer
Residual Stresses in NiO-YSZ/YSZ bilayer

- Sample tilting is required for accurate strain measurement with x-rays
- Peak position as a function of tilt angle, $\psi$
- Slope of $d$ (interplanar spacing) vs. $\sin^2\psi$ is used to calculate strain.
Residual Stresses in NiO-YSZ/YSZ and NiO-YSZ/YSZ bilayers

![Graph showing residual stresses](image)
Residual Stresses in NiO-YSZ/YSZ bilayer

\[ \sigma_x = \sigma_y \]

20°C
Residual Stresses in NiO-YSZ/YSZ bilayer

\[ \sigma_x = \sigma_y \]

400°C
Residual Stresses in NiO-YSZ/YSZ bilayer

\[ \sigma_x = \sigma_y \]

600°C
Residual Stresses in NiO-YSZ/YSZ bilayer

In-plane biaxial stress (MPa)

\[ \sigma_x = \sigma_y \]

800°C
Implications

\[
\text{Reliability} = \exp\left(-\frac{\sigma_1}{\sigma_{1o}}\right)^{m_1}
\]

\[
\text{Reliability} = \exp\left(-\frac{\sigma_2}{\sigma_{2o}}\right)^{m_2}
\]

\[
\text{Reliability} = \exp\left(-\frac{k_1 (\sigma_1 + \sigma_{1res})}{\sigma_{1o}}\right)^{m_1} \exp\left(-\frac{k_2 (\sigma_2 + \sigma_{2res})}{\sigma_{2o}}\right)^{m_2}
\]
Summary

- Large residual compressive stress in zirconia layer at room temperature.
- The magnitude of residual stresses decreases linearly with temperature.
- The magnitude of residual stresses in both zirconia and Ni-YSZ layers decreases after NiO-YSZ reduction in H₂.
- The zero-stress temperature was found to be lower than the sintering temperature.
- Model predictions are consistent with curvature measurements and X-ray diffraction determined values.
Fracture Toughness
Fracture Toughness

Double Torsion

Load, P  Precrack  Specimen
Notch

\[ K_I = PW_m \left( \frac{3(1+\nu)}{Wt^4\xi} \right)^{1/2}, \xi = 1 - 1.26(t/W) + 2.4(t/W)\exp[-\pi W/(2t)] \]

P - maximum load, \( \nu \) – Poisson’s ratio
Precracked @ 0.02 mm/min and tested @ 1 mm/min
Fracture Toughness can be expressed using the following relationship:

\[ K_{IC} = K_{IC0} + bK \]

Fracture Toughness increases due to the formation of Ni ligaments as a result of H\(_2\) reduction.
Interfacial Fracture Toughness
Interfacial Fracture Toughness

Notches machined with laser beam
Interfacial Fracture Toughness

Notches machined with laser beam
Interfacial Fracture Toughness

Notches machined with diamond blade
Interfacial Fracture Toughness

- Work in progress to optimize sample preparation.
- Tests will be carried out under a microscope or using a special test fixture inside an SEM.
- Collaboration with J. Qu et al. (Ga. Tech)
A study to determine the effect of porosity, temperature and test specimen thickness on the elastic properties, strength, fracture toughness and thermophysical properties of NiO-YSZ, Ni-YSZ and YSZ has been completed.
Data Base

![Graph showing data base with various porosity and material properties.](image-url)
Data Base

Solid State Energy Conversion Alliance (SECA)

Physical and Mechanical Properties of SOFC Materials & Structures

- Elastic Properties
- Monotonic Strength
- Fracture Toughness
- Residual Stresses
- Thermal Conductivity
- Thermal Cycling
- Thermal Shock
- Creep Deformation
- NiO Reduction
- Thermal Expansion

Links
Data Base

Samples were prepared from a powder mixture of 75% mol NIO (J.T. Baker, Phillipsburg, NJ) and 25% ZrO$_2$ stabilized with 8 mol% Y$_2$O$_3$ (TOSOH Corp., Grove City, OH). Different amounts of organic pore former (rice starch, ICN Biomedicals, Irvine, CA) were added to obtain samples with different levels of porosity. Green samples were prepared by tape casting 250-mm thick single layers. Two, four, or six green tapes were subsequently laminated to make samples of different thicknesses. Discs with nominal diameter of 25.4 mm were hot-isostatically pressed from the assembled green tapes and sintered at 1400°C in air for 2 hours. Young’s and shear moduli were determined according to ASTM C1239
Data Base

- Thermophysical and mechanical properties of SOFC materials.
- Data generated at ORNL
- Data reported in open literature
- To be distributed to SECA Industrial Teams
Summary

• A methodology has been developed to determine the magnitude of residual stresses in SOFC layered systems as a function of temperature by means of X-ray diffraction.

• Information necessary for determining zero-stress reference temperature, for verifying thermoelastic models and for predictions of reliability and durability.

• Work is in progress to determine the fracture toughness of relevant SOFC interfaces.

• A data base has been assembled containing physical and mechanical properties of SOFC materials.

• All elements are in place for predicting reliability of SOFC assemblies.
Elastic Modulus of GDC

In collaboration with Eric Wachsman
University of Florida