SECA Core Program– Recent Development of Modeling Activities at PNNL

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SECA Core Technology Program Peer Review
Philadelphia, PA
September 12-14, 2006

R&D Objectives & Approach

- **Objective**: Develop integrated modeling tools to:
  - Evaluate the tightly coupled multi-physical phenomena in SOFCs
  - Aid SOFC manufacturers with materials development
  - Allow SOFC manufacturers to numerically test changes in stack design to meet DOE technical targets
- **Approach**: Finite element-based analysis tools:
  - Mentat-FC: Easy-to-use pre- and post-processor to construct a complete analytical model from generic geometry or templates
  - SOFC-MP: A multi-physics solver that quickly computes the coupled flow-thermal-electrochemical response for multi-cell SOFC stacks
  - Targeted evaluation tools for eminent engineering challenges:
    - Interface and coating durability
    - Reliable sealing
    - On-cell reformation for thermal management
    - Scale up
    - Time dependent material degradation

Technical Issues Addressed

- Provide a flexible, multi-physics SOFC stack design tool capable of importing SOFC manufacturer designs (planar & tubular) for electrochemical/thermal/structural analyses.
- Provide a coarse design methodology by which SOFC manufacturers can develop a stack design.
- Provide analysis tools for evaluating the effects of on-cell steam-methane reformation in stacks for optimal thermal management.
- Address the challenging reliability issues of glass-ceramic seals, interfaces, and scales due to steady operation and thermal cycling of stacks.
- Experimentally gather necessary physical and mechanical property data to support model development.

Accomplishments

- **Commercially Available SOFC Stack Design Tool**: PNNL and MSC-Software combined efforts to develop and release a user-friendly electrochemical-thermal-structural stack design software package. Design tool capability includes import of planar and non-planar SOFC stack designs
- **Tools and Methods for Optimization of Internal Reforming**: Methodology developed in which control of the reaction rate via custom anode and/or control of the percentage of reformation to occur on-cell is used to optimize the thermal management of a proposed stack design
- **Glass-Ceramic Sealant Damage Model**: Developed a viscoelastic continuum damage mechanics model based on experimental characterization of G18 glass-ceramic to evaluate sealants in SOFC stack models to prevent failure/delamination
- **Interconnect Creep and Degradation**: Developed a modeling methodology to predict interconnect integrity at different stages of oxide scale growth. Examined influence of interconnect creep on the possible stack geometry change and stress redistribution
- **Experiments Provide Critical Properties**: Testing has provided fundamental material properties enabling model development

Publications

- SECA Presentations
  - Khaleel MA, KP Recknagle, JS Vetrano, X Sun, BJ Koeppel, KI Johnson, V Korolev, BN Nguyen, AM Tartakovsky, and P Singh, "SECA Core Program-Recent Development of Modeling Activities at PNNL." SECA Core Technology Peer Review, Lakewood, CO, October 25-26, 2005.
- Topical Reports
  - Vetrano J.S., Y.-S. Chou, G.J. Grant, B.J. Koeppel, B.N. Nguyen and M.A. Khaleel, "Mechanical Testing of Glass Seals for Solid Oxide Fuel Cells." PNNL-15463.
  - Koeppel BJ, BN Nguyen, JS Vetrano, and MA Khaleel, "Experimental Characterization, Model Development, and Numerical Analysis of Glass-Ceramic Sealant Relaxation Under Thermal-Mechanical Loading." PNNL-15659.
  - Recknagle KP, ST Yokuda, DT Jarboe, MA Khaleel, "Analysis of Percent On-Cell Reformation of Methane in SOFC Stacks: Thermal, Electrical, and Stress Analysis." PNNL-15787.
  - Sun X, WN Liu, P Singh, and MA Khaleel, "Effects of Oxide Thickness on Scale and Interface Stresses under Isothermal Cooling and Micro-Indentation." PNNL-15794.
- Conference Papers & Presentations
  - Vetrano JS, Y-S Chou, BJ Koeppel, BN Nguyen and MA Khaleel, "Modeling and Measurement of Material Behavior in Solid Oxide Fuel Cells," Fuel Cell Seminar, November 15, 2005, Palm Springs, CA. PNNL-46383.
  - Khaleel MA, X Sun and A Tartakovsky, "Multi-Component-Based Reliability Design for SOFC- A Coarse Design Methodology," Fuel Cell Seminar, November 15, 2005, Palm Springs, CA. PNNL-SA- 47472.
  - Recknagle KP, KI Johnson, V Korolev, DT Jarboe, MA Khaleel, and P Singh, "Electrochemistry and On-Cell Reformation Modeling for Solid Oxide Fuel Cell Stacks," 30th International Conference & Exposition Advanced Ceramics, January 24, 2006, Cocoa Beach, FL.
  - Koeppel BJ, JS Vetrano, BN Nguyen, X Sun, and MA Khaleel, "Mechanical Property Characterizations and Performance Modeling of SOFC Seals," 30th International Conference & Exposition Advanced Ceramics, January 24, 2006, Cocoa Beach, FL.
  - Nguyen BN, BJ Koeppel, JS Vetrano, and MA Khaleel, "On the Nonlinear Behavior of a Glass-Ceramic Seal and Its Application in Planar SOFC Systems," 4th International Conference on Fuel Cell Science, Engineering, and Technology, June 19-21, 2006, Irvine, CA.
- Journal Articles
  - Nguyen BN, BJ Koeppel, S Ahzi, MA Khaleel, and P Singh. 2006. "Crack Growth in Solid Oxide Fuel Cell Materials: From Discrete to Continuum Damage Modeling." *J Am Ceram Soc* 89(4):1135-1368.

Teaming & Collaborations

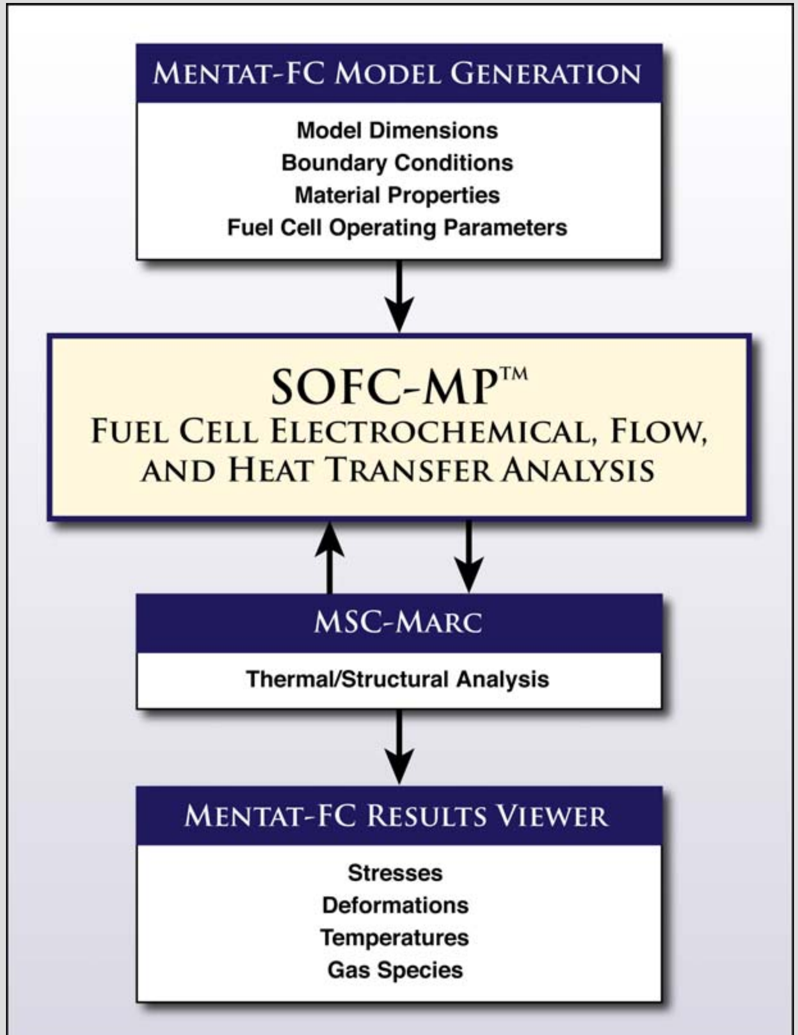
- Industry
  - Modeling and Software Training
    - GE
    - Delphi
    - Acumentrics
    - Siemens
    - FCE
- University & National Labs
  - Modeling
    - U of Illinois, Chicago
    - Georgia Tech
  - Materials
    - ORNL
    - Carnegie Mellon University
    - Penn State
  - Software Training
    - U of Connecticut

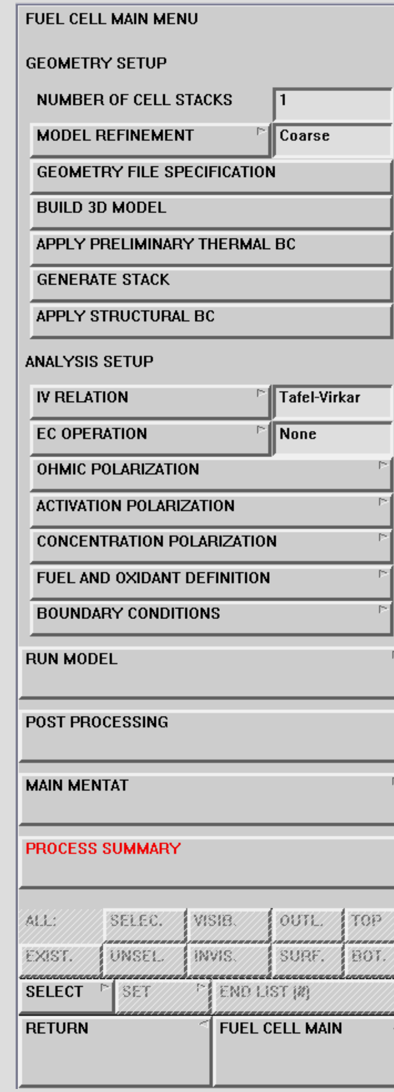
Results

SOFC Analysis Overview
SOFC-MP/Mentat-FC
On-Cell Reformation & Thermal Management
Seal Property & Time Dependent Behavior
Interconnect-Coating Interface & Interconnect Creep
Experimental Property Measurement

SOFC Analysis Overview

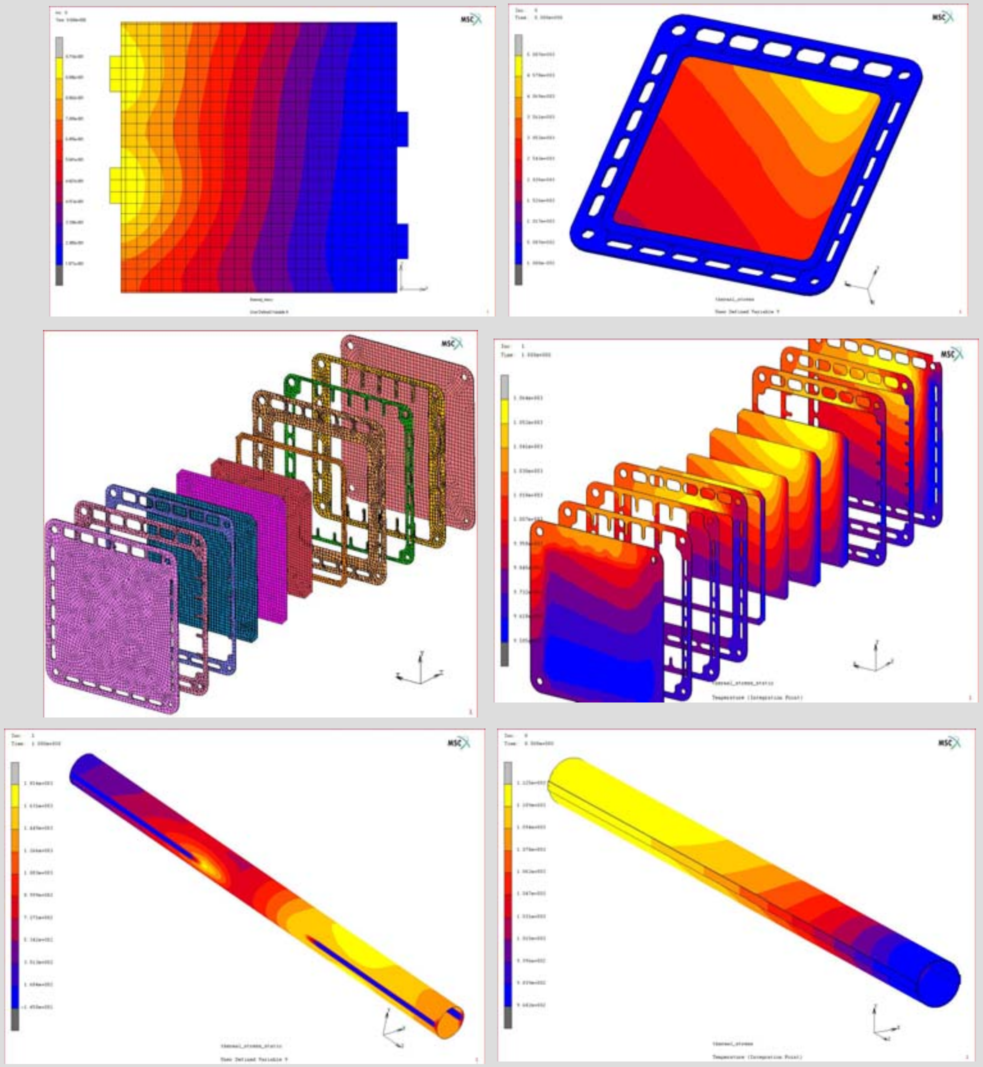
- Developed tools to build/analyze SOFC cells and stacks
  - **Mentat-FC**: GUI to build models from templates, CAD files, or FEA meshes
  - **SOFC-MP**: Coupled thermal, flow, and electrochemistry solver
  - **MSC.Marc**: Structural finite element analysis using SOFC-MP temperatures



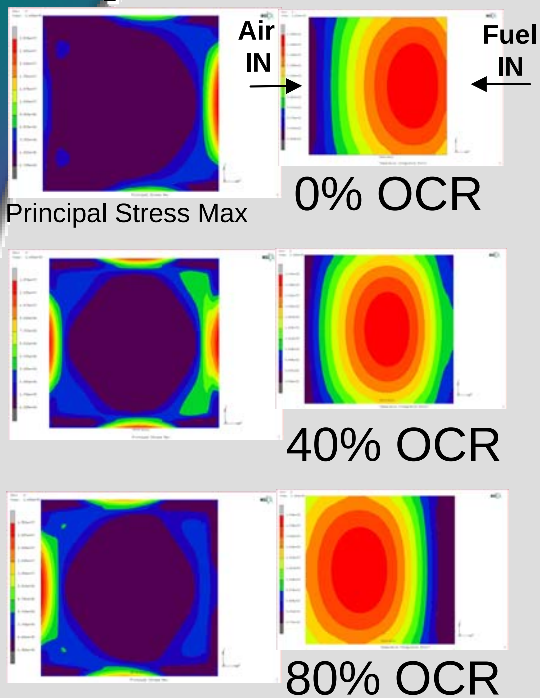


SOFC-MP/Mentat-FC

- Mentat-FC GUI
  - Guides user through entire analysis
  - Builds geometry from CAD files, FEA meshes, or templates (planar co-, counter-, cross-flow)
  - SOFC operating parameters (I-V, fuel/oxidant inputs, polarizations)
  - Exterior thermal boundary conditions
  - Material properties database
  - Has tubular capability
- SOFC-MP Solver
  - Finite element based
  - Generic fuel and oxidants (CEA)
  - Efficient reduced order dimensional analyses for electrochemistry and gas flows
  - Contact algorithms treat incompatible meshes
- Post-processing of electrical output, species, thermal distribution, deformations, and stresses



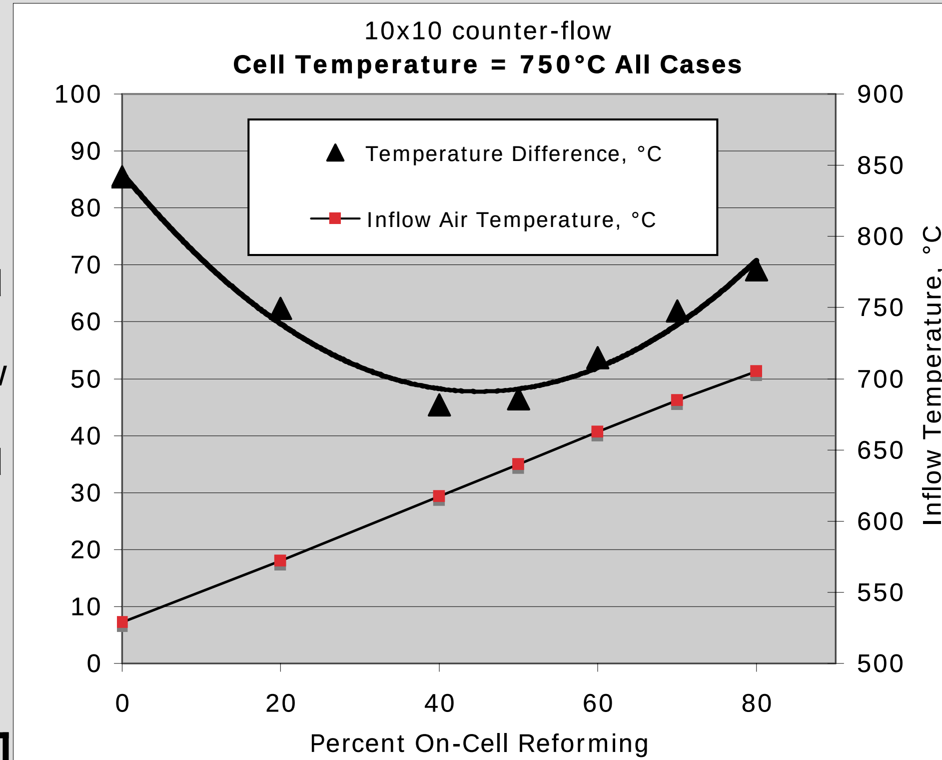
On-Cell Reforming & Thermal Management: Optimization of Percent On-Cell Reformation



At 0% OCR temperature reached maximum at air exit

40% OCR heat load was decreased with cooling at fuel inflow

80% OCR heat load was minimum but air temperature was high

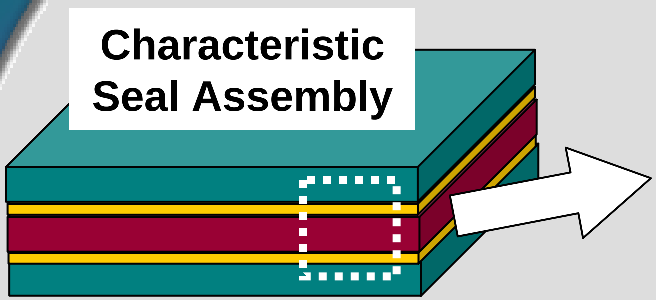


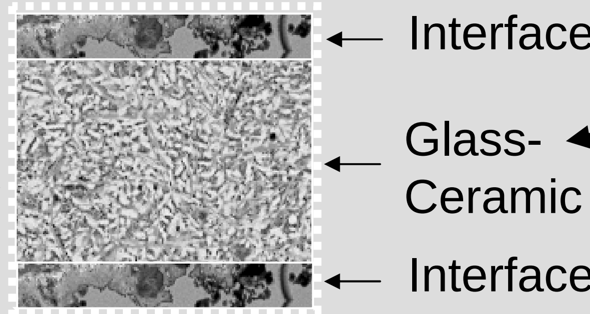
% OCR	ΔT	T_{max}	Anode $S1_{max}$	Seal $S1_{max}$
0	85	781	25.8	11.3
40	45	768	13.8	8.7
50	47	768	14.7	8.8
60	54	769	16.3	9.2
80	69	773	19.0	10.2

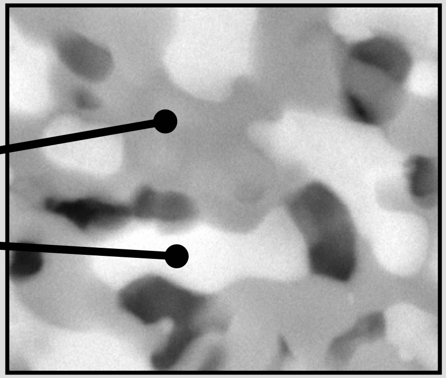
SUMMARY:

- To maintain 750°C, inflow temperature increased to offset decreased heat load due to reforming (all configurations and sizes)
- Seal stresses, anode stresses, and ΔT had minimums at 40-50% OCR for this configuration and cell size

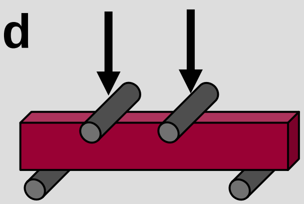
Seal Property & Time Dependent Behavior: Glass-Ceramic Seals

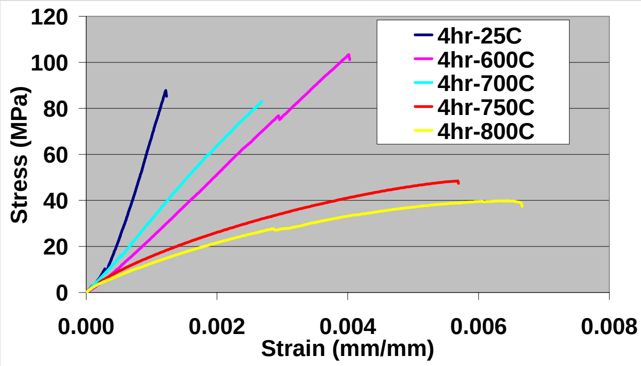


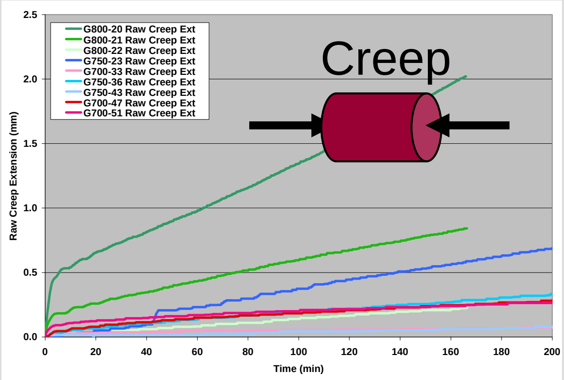




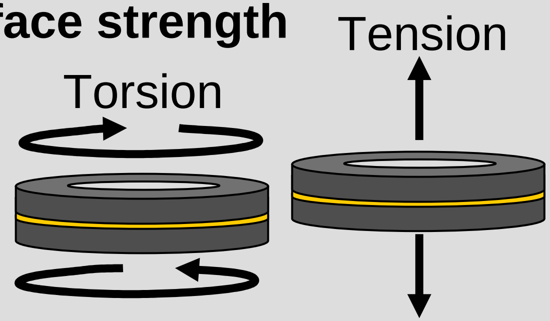
1. Test the glass-ceramic strength and creep behavior

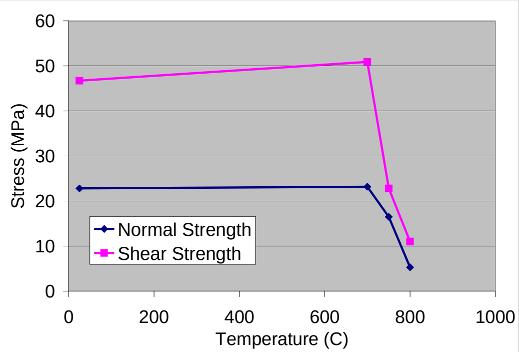






2. Test the weaker interface strength



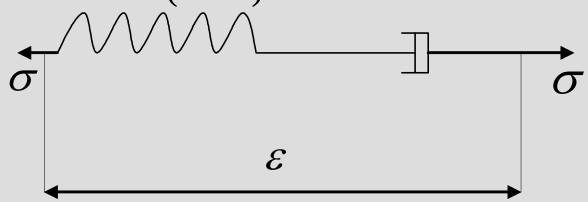


3. Obtain coefficient of thermal expansion (CTE) and elastic modulus

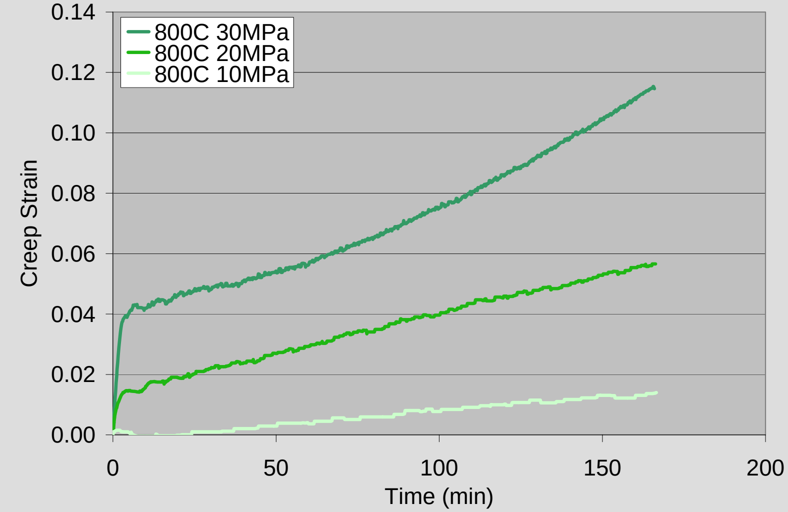
Seal Property & Time Dependent Behavior: Creep of Glass-Ceramics

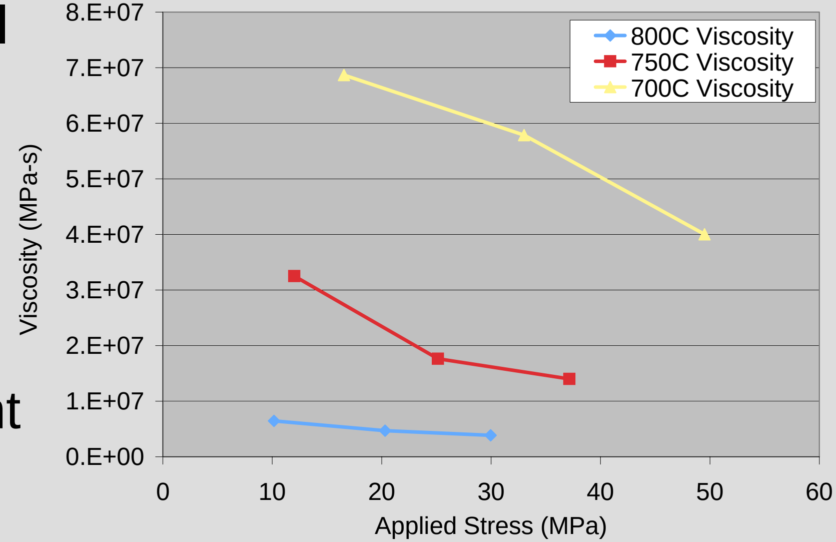
- Evaluated short-term creep behavior of G18
  - Glassy matrix above its Tg at cell operating temperatures
  - Creep rate increased with applied stress and temperature
- Estimated G18 viscosity
  - Assume Maxwell material model

$$E = E^{o}(1 - D)$$



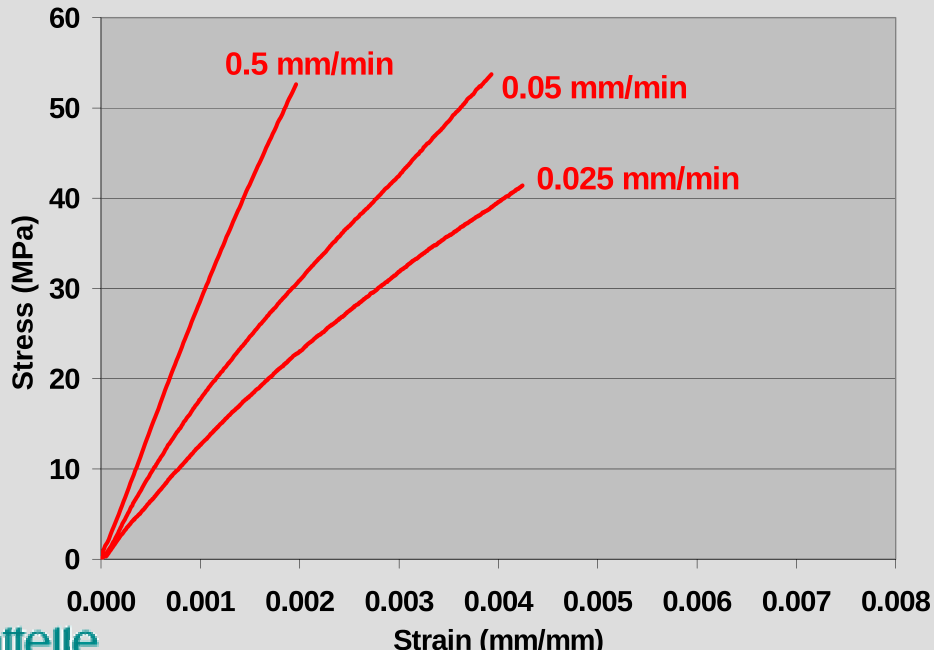
  - Derived viscosity is very high (5-65e[6] MPa-s) but still important for assessing steady state seal stresses in the stack



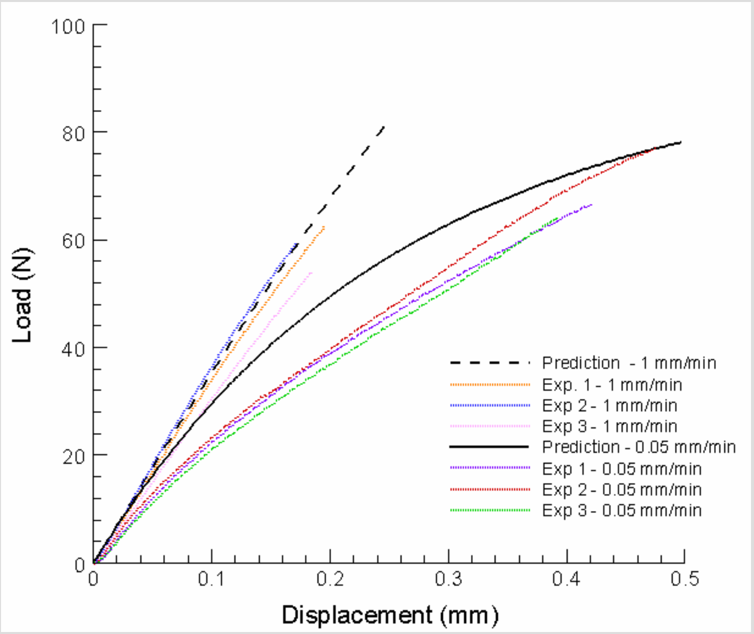


Seal Property & Time Dependent Behavior: Glass-Ceramic Constitutive Model

- Stress-strain response of G18 glass-ceramic shows strong rate dependence
  - Due to viscoelastic response of residual glass
  - Processing/microstructure variations noted

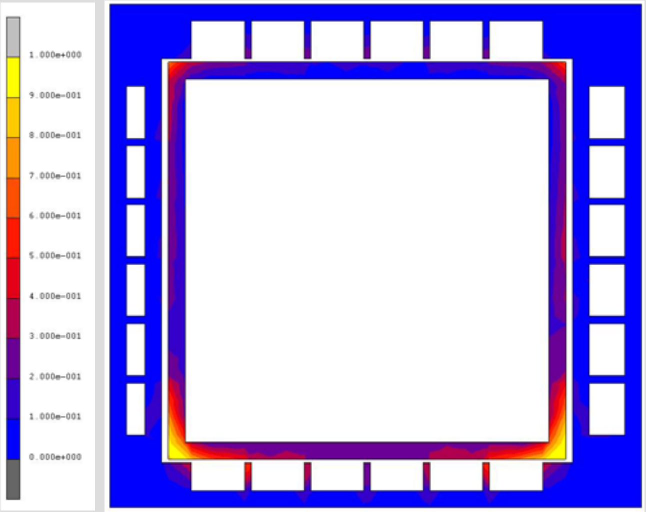


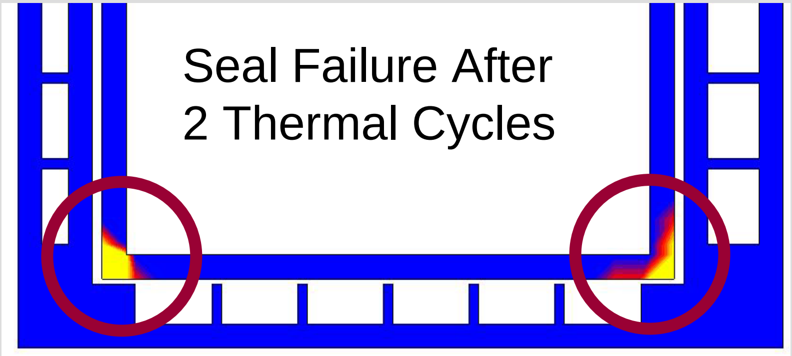
- Viscoelastic damage model predictions compare reasonably well to experimental data
  - Failure strain prediction good
  - Stress prediction possibly affected by heterogeneous structure



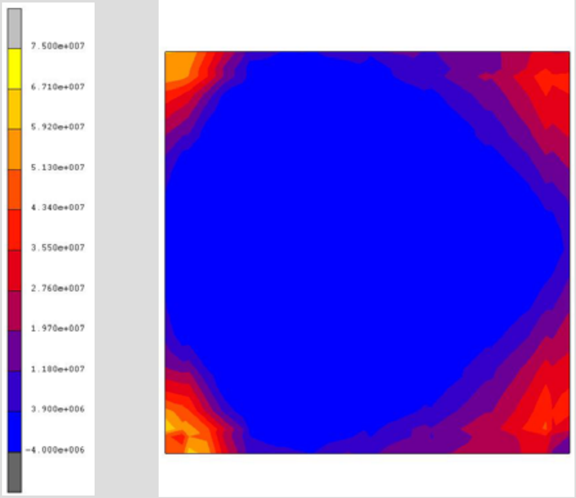
Seal Property & Time Dependent Behavior: Stack Modeling Results

Seal Damage Distribution





Anode Principal Stress Distribution

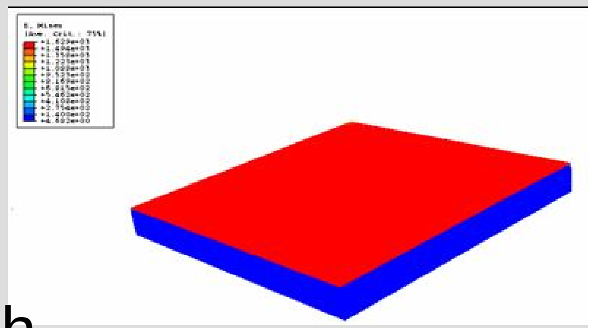


Temperature (C)	Elastic Model: Anode Maximum Principal Stress (MPa)	Viscoelastic Model: Anode Maximum Principal Stress (MPa)	Change
Cycle 1 Operation	38.4	36	6.3%
Cycle 1 Shut-Down	65.6	62.7	4.4%
Cycle 2 Operation	40.2	40	0.5%
Cycle 2 Shut-Down	74.4	67.4	9.4%

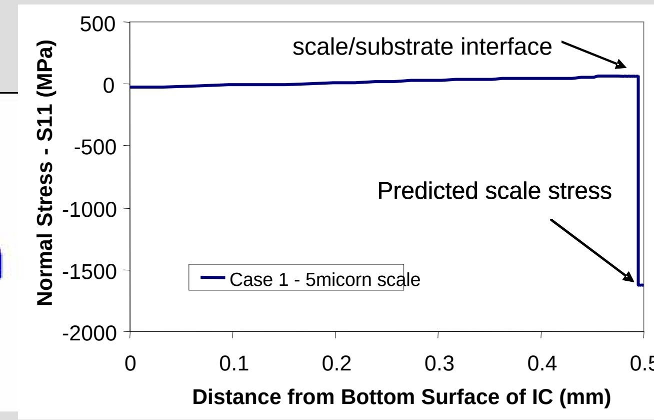
Interconnect Life Prediction

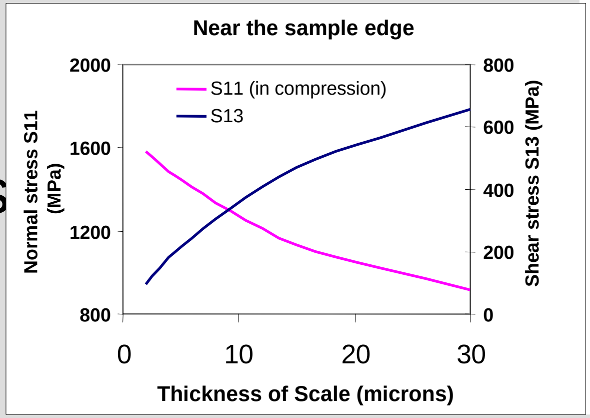
- Sources of interconnect stress studied:
  - Thermal stress
  - Growth stress
- Predicted interfacial stress compared with interface strength →scale delamination
- Predicted scale stress compared with critical buckling stress

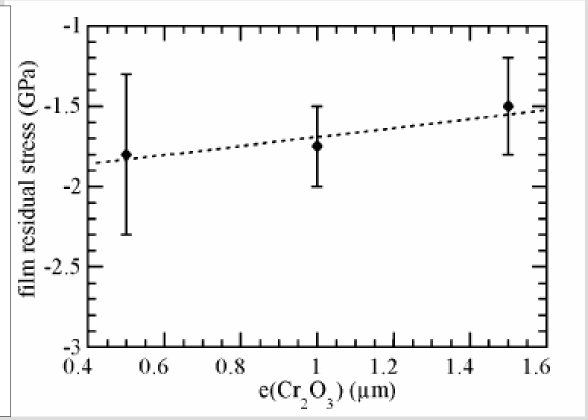
  → scale spallation



Predicted stress profile through the thickness of the IC/oxide



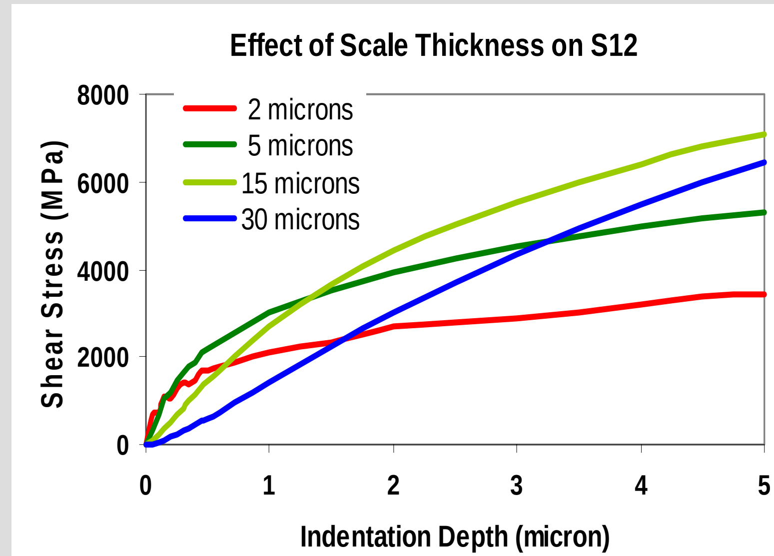


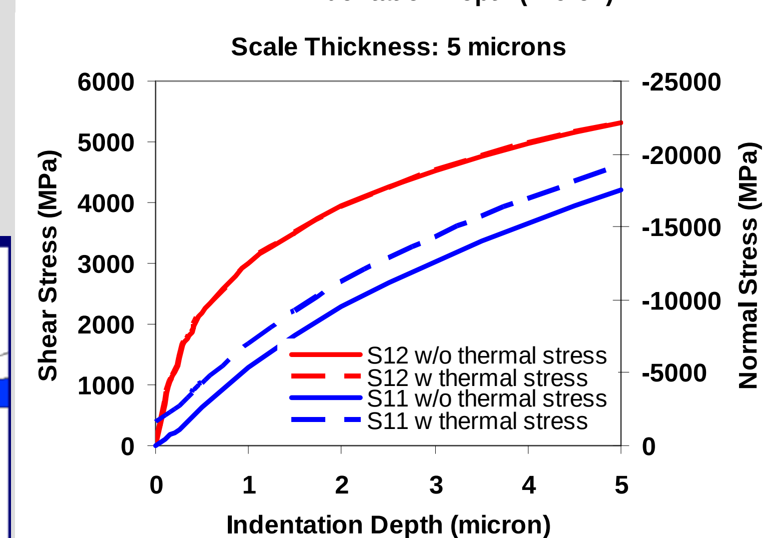


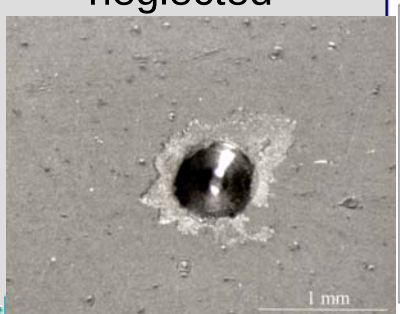
Residual stresses measurements in Cr2O3 films*

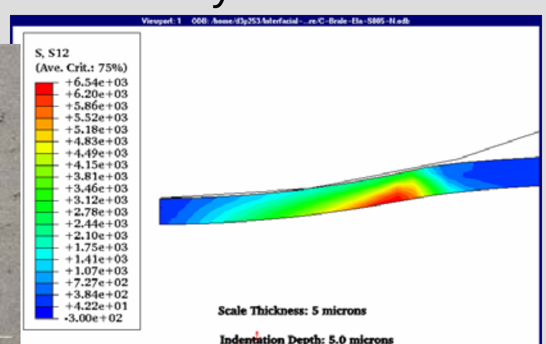
Interconnect Life Prediction

- Using indentation test to quantify strength of oxide/interconnect interface:
  - Effect of scale growth on interfacial shear stress
  - Effects of thermal stress on indentation stress
- Conclusions:
  - Shear stress on the interface caused by indenter contact is high enough to lead to delamination
  - Shear stress dominates the fracture mode of the interface
  - The thinner the thickness of oxide scale is, the bigger the interfacial shear stress is, at the small indentation depth
  - Effect of thermal stress on the interfacial shear stress may be neglected





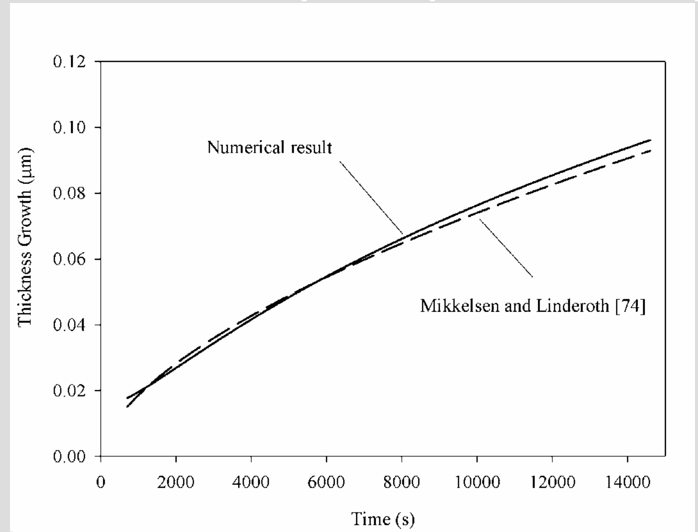




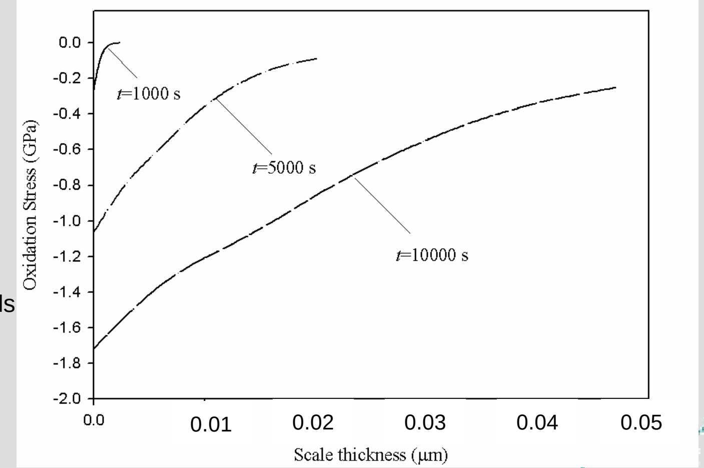
Interconnect Scale Growth Kinetics and Growth Stress Prediction

- Diffusion potential used to govern stress-diffusion interaction
- Predicting:
  - Oxidation kinetics
  - Diffusion and concentration evolution of species
  - Stress distribution in scale and substrate

Oxidation kinetics profile (22% Cr-Fe alloy)



Stress distribution and evolution



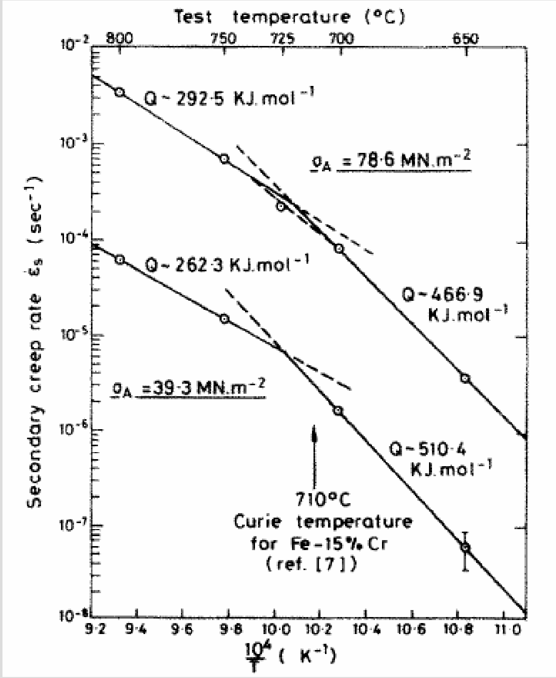
[74]. Mikkelsen, L. and S. Linderoth,. Materials Science & Engineering A (Structural Materials Properties, Microstructure and Processing), 2003. **A361**(1-2): p. 198-212

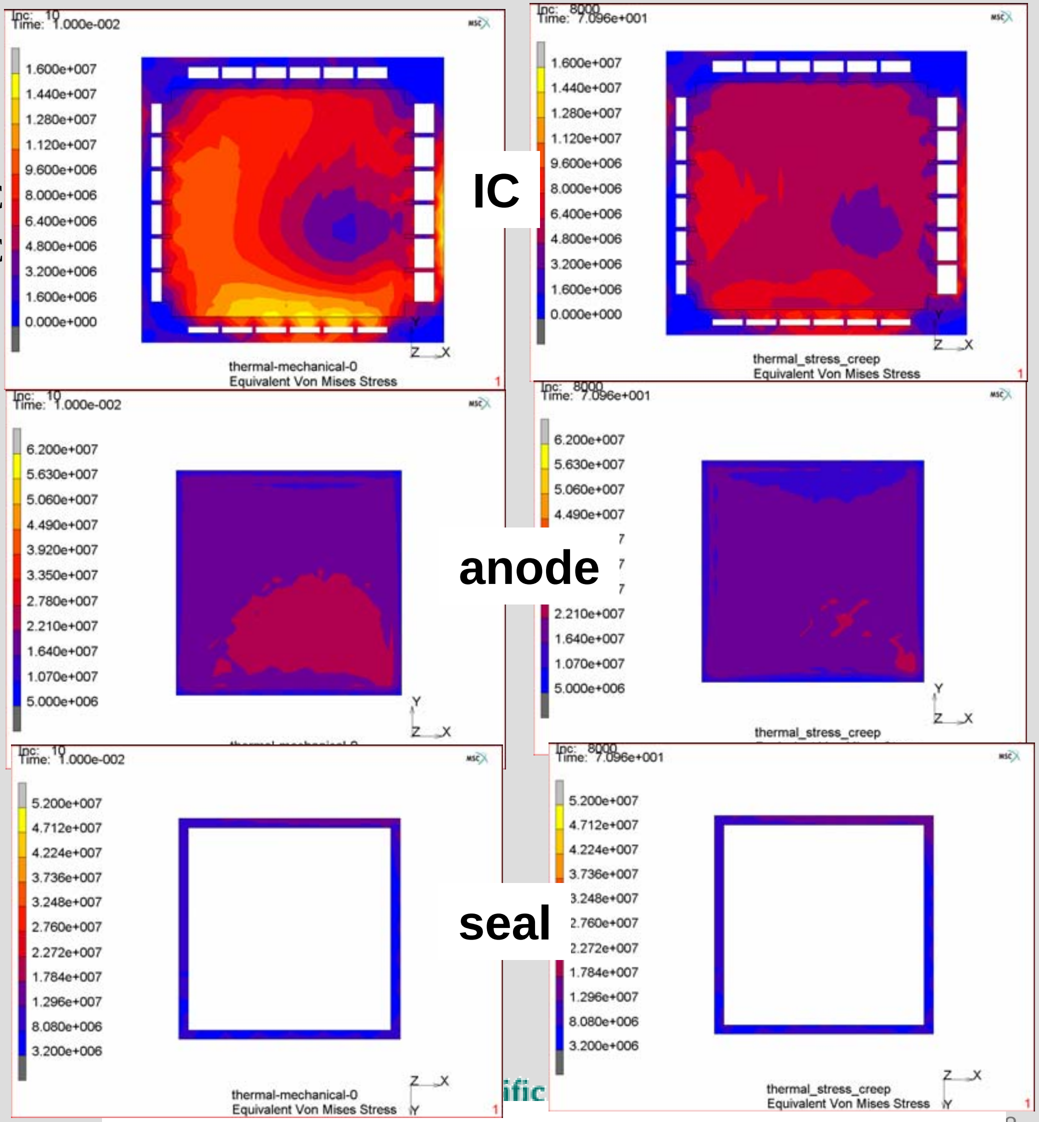
Interconnect Creep and Stress Re-distribution

- Creep law used for IC

$$\sigma < 100MPa \quad \dot{\varepsilon}_c = \begin{cases} 1.72\sigma^{5.5} e^{-277400/RT} & \text{for} \quad T \geq 725^{o}\text{C} \\ 1.65\times10^{11}\sigma^{5.8} e^{-488700/RT} & \text{for} \quad T \leq 710^{o}\text{C} \end{cases}$$

$$\sigma > 100MPa \quad \dot{\varepsilon}_c = \begin{cases} >10^{-3} & \text{for} \quad T \geq 725^{o}\text{C} \\ 28.2\times\sigma^{10.5} e^{-488700/RT} & \text{for} \quad T \leq 710^{o}\text{C} \end{cases}$$





Time = 0.01 h

Time = 70 h

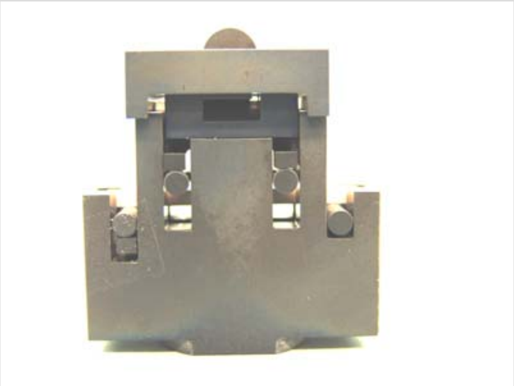
Battelle

Experimental Support of Modeling

Providing input data to the material models and validating the models through experimental testing. In addition, contributing to the materials database maintained by NETL.

Creep testing of G18 glass to measure long-term deformation behavior

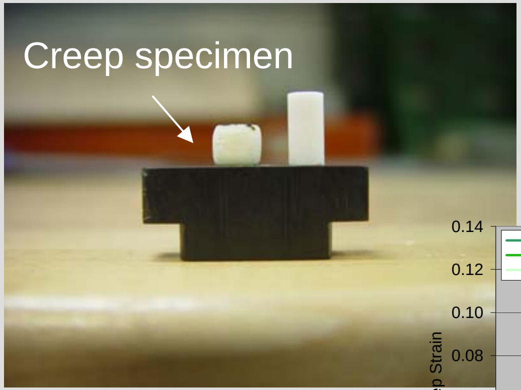
Torsion testing of thin glass-seal analogs to determine failure stress and fracture behavior



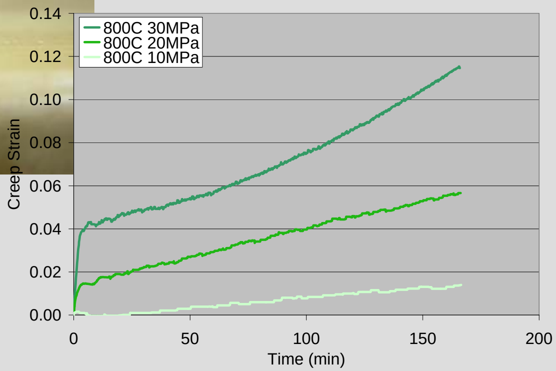
4-pt bend bar testing of G18 glass to capture constitutive and failure behavior of the material

Experimental Property Measurement

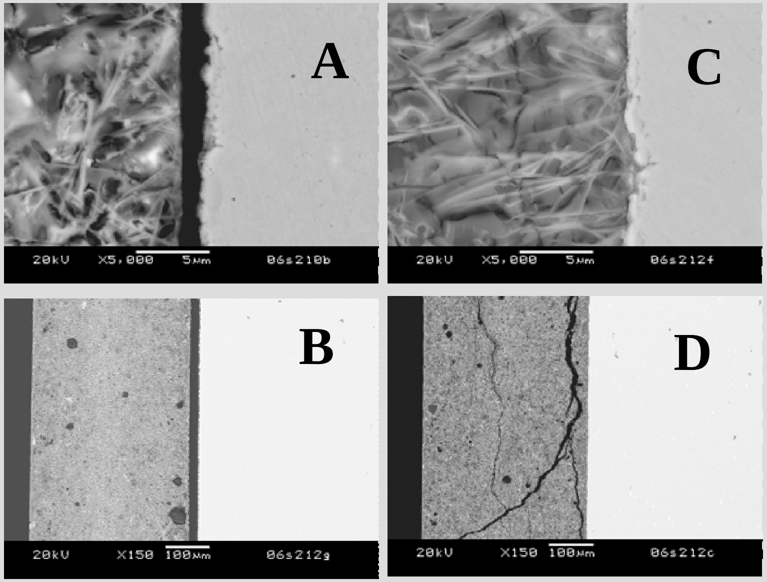
- Seal Property & Time – Dependent Behavior
  - Creep tests of the G-18 glass performed to support damage models in predicting the long-term stack performance
- Interfacial Degradation and Failure Mechanisms
  - Investigating failure locations and mechanisms to incorporate into seal and coating development models



Comparison of a non-tested creep sample and a sample tested at 800°C and loaded at 129lb. Forty-three percent strain observed.



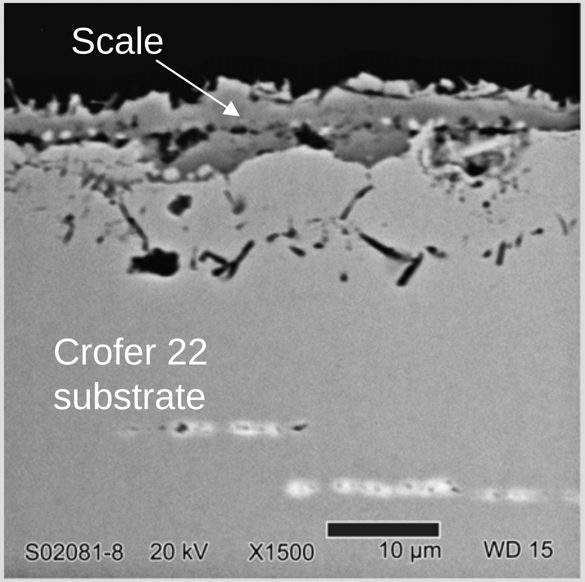
Creep strain results of samples tested at 800°C under three different loadings



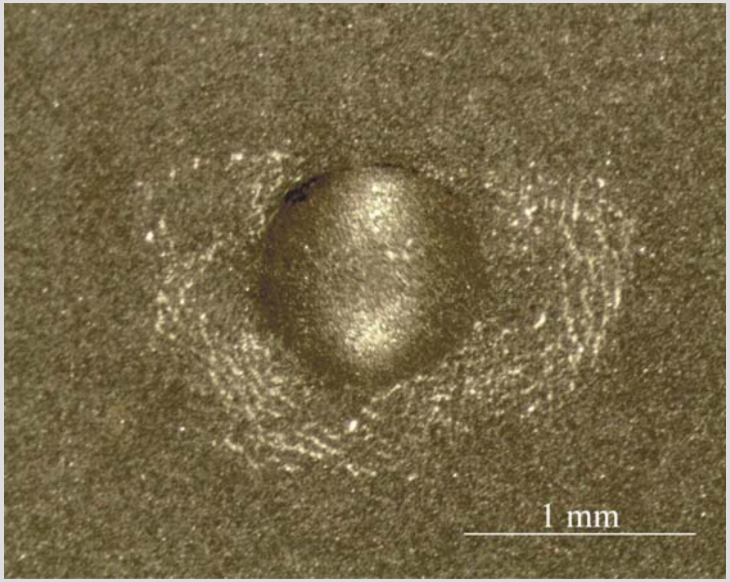
SEM cross-section of a torsion sample that failed at 800°C

Experimental Property Measurements

- Interconnect-Scale/Coating Interface Properties
  - Indentation tests performed to support interface models in establishing a stress-based criteria for interfacial strength and fracture toughness



SEM image of the cross-section of a crofer plate oxidized at 800^{o}C for 12hr



Top view of the indent test. Spallation of the oxide observed under 150kg load

Activities for the Next 6 Months

- Mentat-FC/SOFC-MP: Deploy at the 6 industry sites and provide training and support.
- Scale-up: Examine planar SOFC design limitations considering electrochemistry, flow, and structural
- Parametric studies on the effects of creep of various SOFC components on long-term behavior of multiple cell stacks
- Continue interconnect degradation and life prediction work
- Development of structure-property relationships for glass-ceramic sealants; improvement via microstructural design
- Effect of high pressure on electrochemistry and stack performance
- Measurement of Oxide-Crofer and Spinel-Crofer interfacial properties

Looking Forward- Phase II

- Design Limitations for Scale-up of SOFC Stacks
  - Virtual feasibility study on:
    - Stack EC performance and thermal management
    - Stack structural reliability
- Degradation modeling and life prediction
  - Creep considerations on the structural stability of stacks
  - Seal and seal interfaces
  - Interconnect scale and coatings
  - Cell and cell interfaces
  - Current collector interfaces
- System integration
  - Stack thermal management and cell thermal profiles
  - System integration, power electronics and control
- Validation