Summary Report

SECA Core Technology Program Seal Workshop

Workshop held at Hyatt Regency, San Antonio
August 10, 2007

Workshop organized by:

Dr. Ayyakkannu Manivannan,
National Energy technology Laboratory
Morgantown, WV

Dr. Prabhakar Singh
Pacific Northwest National Laboratory
Richland, WA

WELCOME

to the

SOFC Seal: Technology, Challenges and Future Direction

Brazos Boardroom

Hyatt Regency San Antonio

August 10, 2007

NETL

SECA

Pacific
Northwest
National
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Executive Summary

SECA Core Technology Program (SECA CTP) led workshop on the topical area titled "SOFC seal: Technology, Challenges and Future Directions" was held on August 10, 2007 at Hyatt Regency, San Antonio, TX. The workshop was attended by scientists and engineers presently involved in the development, engineering, fabrication, and testing of advanced solid oxide fuel cell seals. Attendees represented industries, national laboratories and academia.

The objective of the workshop was to present and disseminate technical information related to the recent development and findings in the areas of advanced seal materials chemistry, chemical interactions, long-term stability and reliability along with applications of predictive mathematical models utilizing SECA derived computational tools and methodologies. It was also the objective of the workshop to provide a forum for technical discussions on topics related to advanced sealing concepts and materials along with identification of technical priorities and developmental needs.

Overview technical presentation described the SOFC seal technology status currently being pursued under the SECA program. Literature related to global research and development work towards the development and testing of advanced seal technology was also reviewed and presented. Participants from fuel cell manufacturing industries presented their experience related to seal fabrication, electrical testing in short and tall stacks, long term endurance and post test characterization results. Seal specifications and requirements for SECA derived fuel cell stacks were presented. Selected highlights of the workshop include detailed presentations and discussions on seal materials, materials stability, seal-test conditions, design and engineering requirements and development needs.

(a) Seal materials: Technical discussions mostly concentrated on applications of refractory glass-ceramic and visco-elastic (self healing) glasses currently being developed under SECA-CTP. Advantages of higher temperature sealing process on the development and maintenance of adequate contacts in active and seal area were examined. Materials chemistry, experimental test results under SOFC exposure conditions, synthesis and seal fabrication processes were discussed in detail and the possible impact of long term exposure of such materials on interactions with adjoining cell components, and exposure environment in the 650-850C temperature range were discussed.

(b) Materials stability: Role of bulk, interfacial and surface stability of glass-ceramic and self healing glasses were examined and discussed to explore their long term role on chemical interactions, cell electrode poisoning and mechanical changes. Time dependent structural and chemical changes in the bulk glass, interactions with surface oxides resulting in dissolution and surface reaction product formation, along with evaporation of glass constituents and reaction products were discussed. Thermodynamic models for oxide dissolution, surface interaction and vapor species formation were presented.

(c) *Seal test conditions:* To meet the SECA coal based SOFC systems life and performance targets, SOFC seals must show chemical, structural and mechanical stability under nominal and transients conditions of cell and stack operations for up to 40,000 hours. Some of the typical requirements identified for stack design consideration, stack fabrication and cost effectiveness are-

- ➢ Temperature range: 650-850^{0}C
- ➢ Up to 85% fuel and 25% oxidant utilizations and 50% steam in anode environment
- ➢ Applied load of less than 35 kPa on seal area
- ➢ Electrical isolation (>500Ω.cm^2) between cells and stack at nominal stack operating condition (0.7 V @ 500-700 mA/cm^2)
- ➢ Tolerance to both anode and cathode electrode poisoning in order to meet 0.1%/1000hr performance degradation
- ➢ Seal application temperature not to exceed 1000-1050C
- ➢ Thermal cyclic stability demonstrated per systems requirement
- ➢ Use of low cost materials synthesis and application processes that meet SECA cost target

(d) *Seal design and engineering requirements:* Role of SECA developed computational tools for the development and optimization of engineering design and long term reliability of seals were presented. Need for materials properties data, time dependent properties changes, interface strength and measurement techniques were identified as key areas for further work.

R&D needs: Development of structurally and chemically compatible seals for SECA coal based SOFC power generation systems has been identified as one of the key R&D areas for further research and development. Both refractory glass-ceramic and self healing seals will be further studied for compositional, morphological, structural and interfacial stability to develop the desired composition, engineering design and fabrication/ application procedures. Of interest will be evaluation of the role of alkalis and boria base gaseous species on interactions with perovskite cathode and conventional anode materials. Advanced materials synthesis, high temperature materials properties measurement, bulk and surface characterization, electrode poisoning and over potential measurement techniques will be identified, developed and utilized for understanding the long term stability and reliability of developed seal materials and configurations. Selected R&D areas that need careful attention are -

- Bulk, interface and surface stability
- Seal constituent interactions with electrodes
- Time dependent materials properties
- Seal designs that incorporate visco-elastic glasses
- Fabrication processes

Agenda

SOFC Seal: Technology, Challenges and Future Direction
Friday August 10 2007

8.00 AM	---	Introduction, A. Manivannan (NETL)	
8.01 AM	---	Stevenson, J / Singh, P (Specific requirements) (PNNL)	
8.15 AM	---	Khaleel, M (PNNL)	
8.30 AM		Lara-Curzio, E (ORNL)	
8.45 AM		Singh, R (Univ. Cincinnati)	
9.15 AM	---	Loehman, R (SNL)	
9.45 AM	---	Brow, R (Univ. of Missouri)	
10.15 AM	---	Break	
10.30 AM	---	Chou, M / Stevenson, J (PNNL)	
11.00 AM	---	Open - Industry input (15 min. each)	
		Speakers:	
		Karl Haltiner	(Delphi)
		Tony Wood	(VPS/FCE)
		S. Elangovan	(Ceramatec)
		Nguyen Minh	(Consultant)
		Steve Shaffer	(Delphi)
		Peng Huang	(FCE)
		Joel Doyon	(FCE)
		Eric Tang	(VPS)
		Casey Brown	(VPS)
		Chuck Sishtla	(GTI)
		John Yamanis	(UTRC)
12.00 PM	----	Break for Lunch	
1:00 PM	__	Discussion / Wrap-up	
3.00PM	----	Adjourn	

The speakers are requested to make a 15 minutes presentation starting with the conclusion slide. A 15 minute discussion time will be available for each speaker following their talk. The speakers should specifically discuss their results, approach, related issues & future directions to solve them.

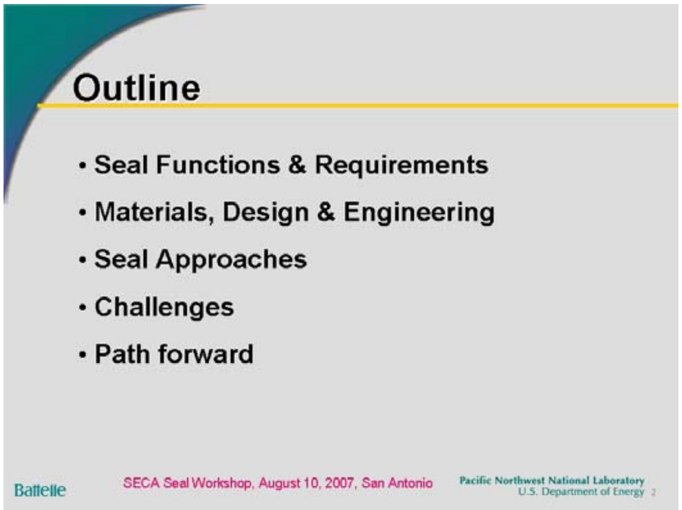
SOME OF THE TECHNICAL ISSUES / CHALLENGES TO ADDRESS:
(1) ROLE OF EVAPORATION & VAPORIZATION
(2) INTERFACE REACTIONS
(3) MANUFACTURABILTY / DESIGN APPROACHES
(4) FAILURE ANALYSIS
(5) MECHANICAL STABILITY, LONG TERM STRUCTURAL PREDICTIONS

Technical Presentations

SOFC Seals: Overview

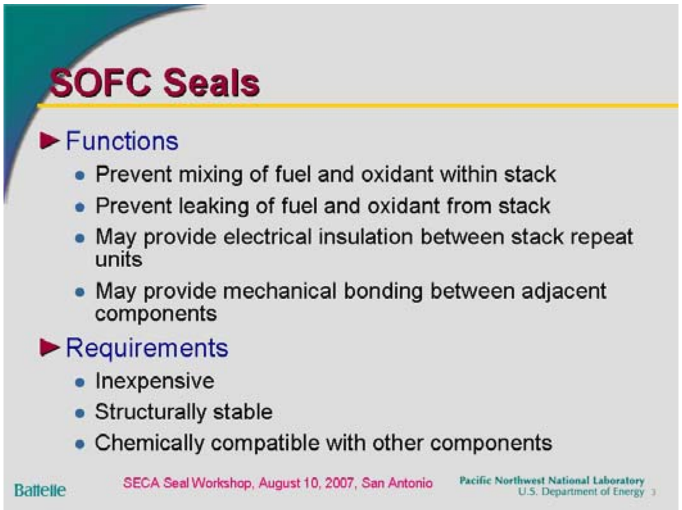
Jeff Stevenson & Prabhakar Singh
Pacific Northwest National Laboratory
Richland, WA

SECA Core Technology Program – SOFC Seal Meeting
August 10, 2007, San Antonio, TX



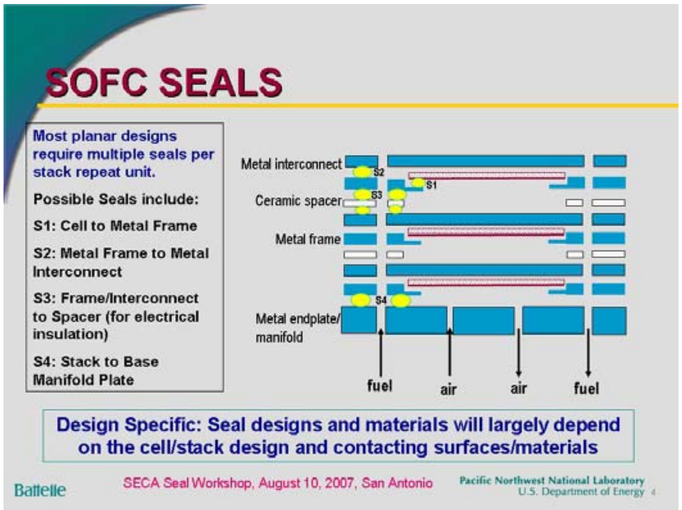
Outline

- Seal Functions & Requirements
- Materials, Design & Engineering
- Seal Approaches
- Challenges
- Path forward



SOFC Seals

- Functions
  - Prevent mixing of fuel and oxidant within stack
  - Prevent leaking of fuel and oxidant from stack
  - May provide electrical insulation between stack repeat units
  - May provide mechanical bonding between adjacent components
- Requirements
  - Inexpensive
  - Structurally stable
  - Chemically compatible with other components



SOFC SEALS

Most planar designs require multiple seals per stack repeat unit.

Possible Seals include:

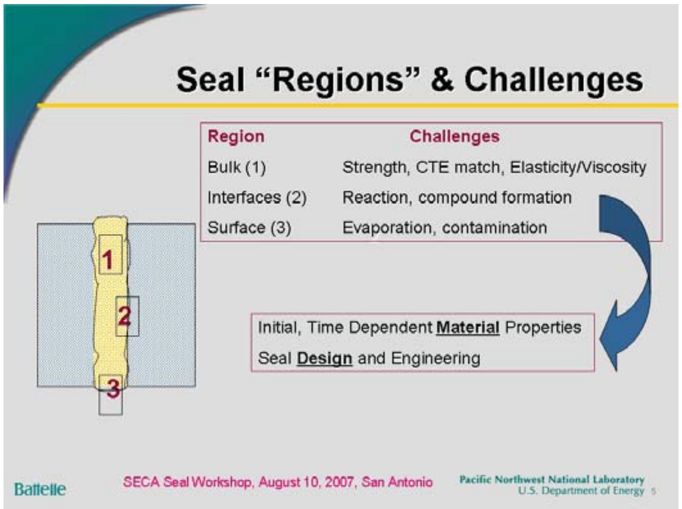
S1: Cell to Metal Frame

S2: Metal Frame to Metal Interconnect

S3: Frame/Interconnect to Spacer (for electrical insulation)

S4: Stack to Base Manifold Plate

Design Specific: Seal designs and materials will largely depend on the cell/stack design and contacting surfaces/materials

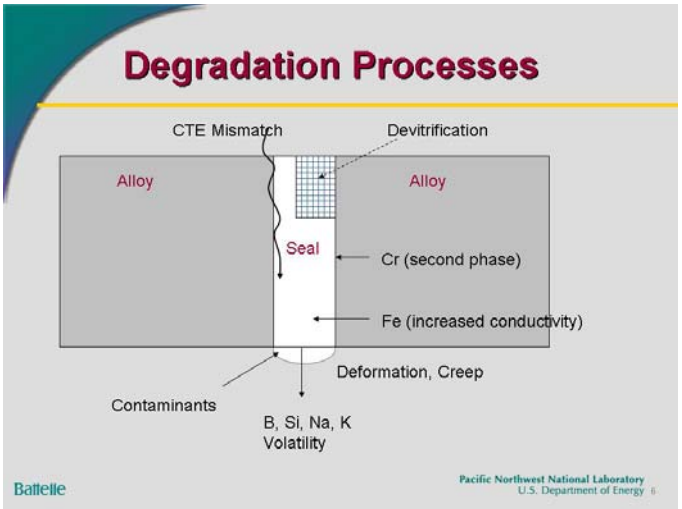


Seal "Regions" & Challenges

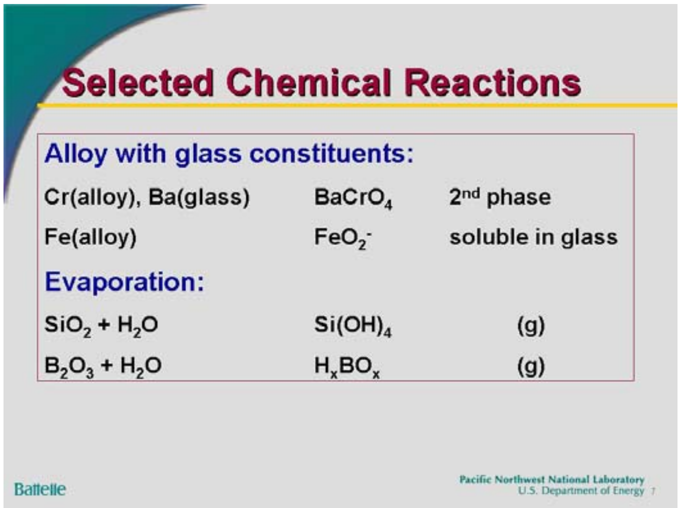
Region	Challenges
Bulk (1)	Strength, CTE match, Elasticity/Viscosity
Interfaces (2)	Reaction, compound formation
Surface (3)	Evaporation, contamination

Initial, Time Dependent **Material** Properties

Seal **Design** and Engineering



Degradation Processes



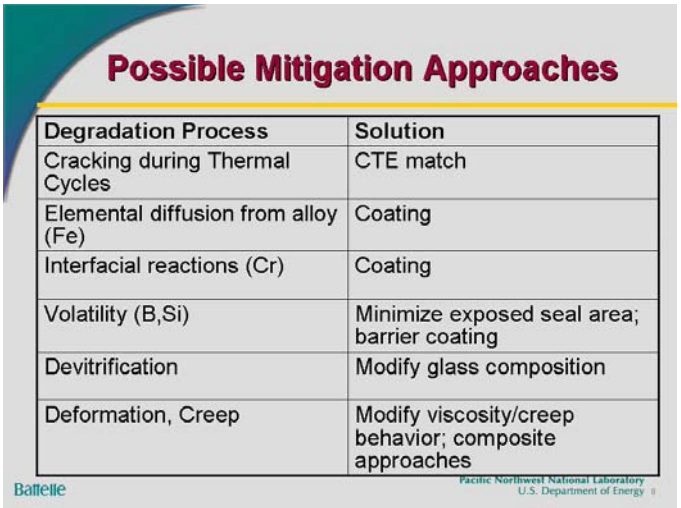
Selected Chemical Reactions

Alloy with glass constituents:

Cr(alloy), Ba(glass)	$BaCrO_4$	2nd phase
Fe(alloy)	FeO_2^-	soluble in glass

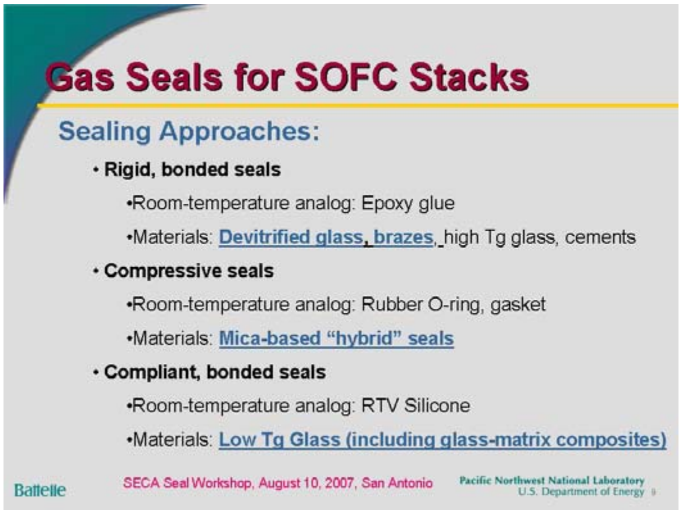
Evaporation:

$SiO_2 + H_2O$	$Si(OH)_4$	(g)
$B_2O_3 + H_2O$	H_xBO_x	(g)



Possible Mitigation Approaches

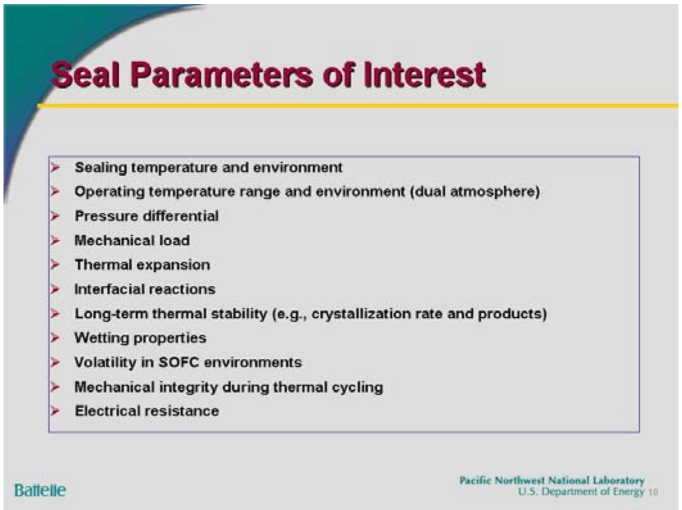
Degradation Process	Solution
Cracking during Thermal Cycles	CTE match
Elemental diffusion from alloy (Fe)	Coating
Interfacial reactions (Cr)	Coating
Volatility (B,Si)	Minimize exposed seal area; barrier coating
Devitrification	Modify glass composition
Deformation, Creep	Modify viscosity/creep behavior; composite approaches



Gas Seals for SOFC Stacks

Sealing Approaches:

- **Rigid, bonded seals**
  - Room-temperature analog: Epoxy glue
  - Materials: **Devitrified glass**, **brazes**, high Tg glass, cements
- **Compressive seals**
  - Room-temperature analog: Rubber O-ring, gasket
  - Materials: **Mica-based "hybrid" seals**
- **Compliant, bonded seals**
  - Room-temperature analog: RTV Silicone
  - Materials: **Low Tg Glass (including glass-matrix composites)**



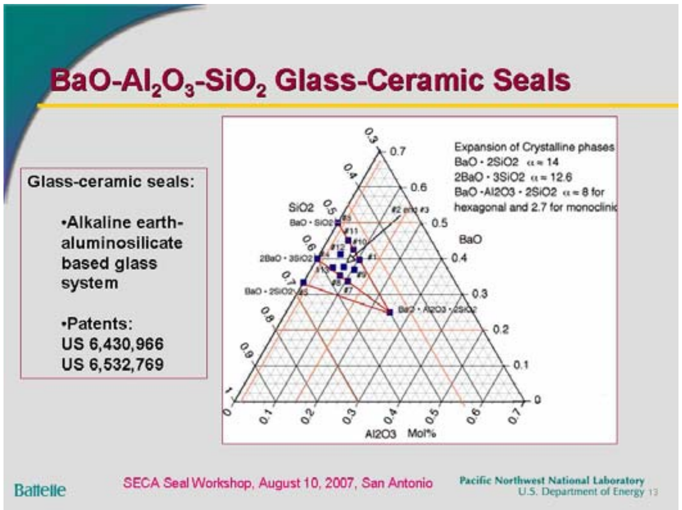
Seal Parameters of Interest

- Sealing temperature and environment
- Operating temperature range and environment (dual atmosphere)
- Pressure differential
- Mechanical load
- Thermal expansion
- Interfacial reactions
- Long-term thermal stability (e.g., crystallization rate and products)
- Wetting properties
- Volatility in SOFC environments
- Mechanical integrity during thermal cycling
- Electrical resistance

Seal Development – Methodology

For a given seal approach, need to:

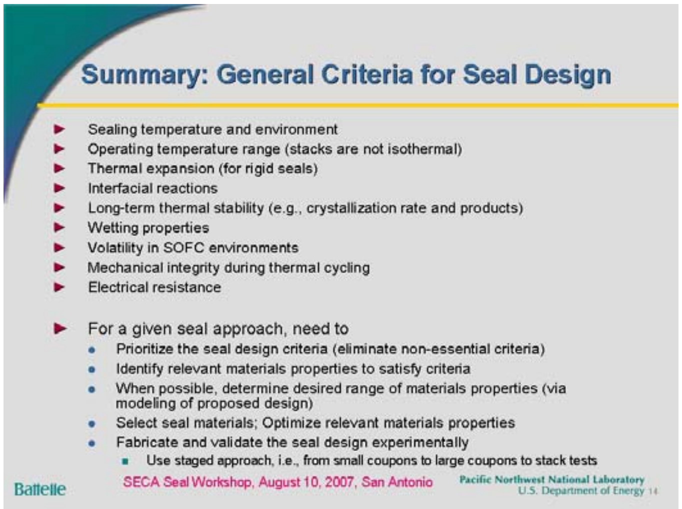
- Prioritize the seal design parameters (eliminate irrelevant or non-essential parameters)
- Identify relevant materials properties to satisfy criteria
- When possible, determine desired range of materials properties (via modeling of proposed design)
- Select seal materials; Optimize relevant materials properties
- Fabricate and validate the seal design experimentally
  - Use staged approach, i.e., from small coupons to large coupons to stack tests



BaO-Al_2O_3-SiO_2 Glass-Ceramic Seals

Glass-ceramic seals:

- **Alkaline earth-aluminosilicate based glass system**
- **Patents:**
  US 6,430,966
  US 6,532,769



Summary: General Criteria for Seal Design

- Sealing temperature and environment
- Operating temperature range (stacks are not isothermal)
- Thermal expansion (for rigid seals)
- Interfacial reactions
- Long-term thermal stability (e.g., crystallization rate and products)
- Wetting properties
- Volatility in SOFC environments
- Mechanical integrity during thermal cycling
- Electrical resistance

- For a given seal approach, need to
  - Prioritize the seal design criteria (eliminate non-essential criteria)
  - Identify relevant materials properties to satisfy criteria
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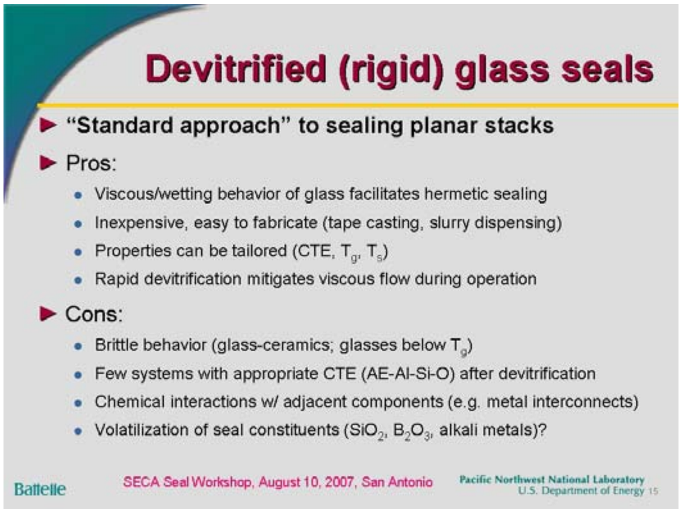
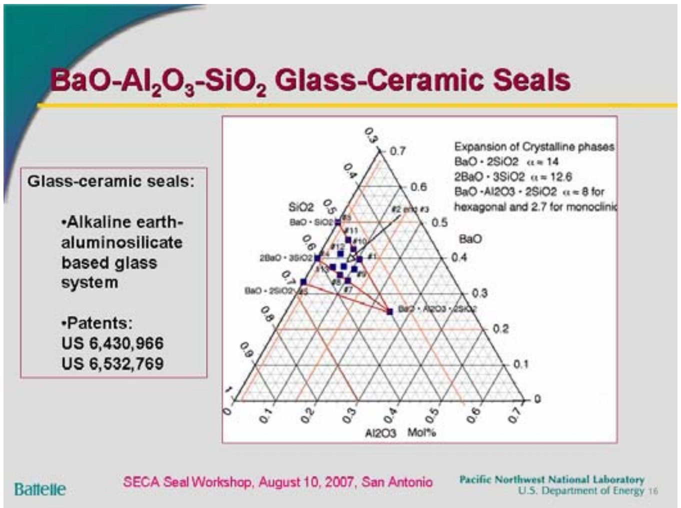


Devitrified (rigid) glass seals

- "Standard approach" to sealing planar stacks
- Pros:
  - Viscous/wetting behavior of glass facilitates hermetic sealing
  - Inexpensive, easy to fabricate (tape casting, slurry dispensing)
  - Properties can be tailored (CTE, T_g, T_s)
  - Rapid devitrification mitigates viscous flow during operation
- Cons:
  - Brittle behavior (glass-ceramics; glasses below T_g)
  - Few systems with appropriate CTE (AE-Al-Si-O) after devitrification
  - Chemical interactions w/ adjacent components (e.g. metal interconnects)
  - Volatilization of seal constituents (SiO_2, B_2O_3, alkali metals)?



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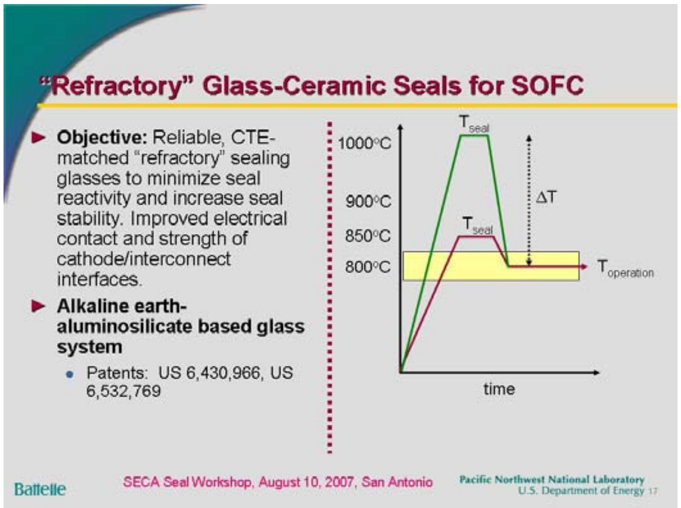
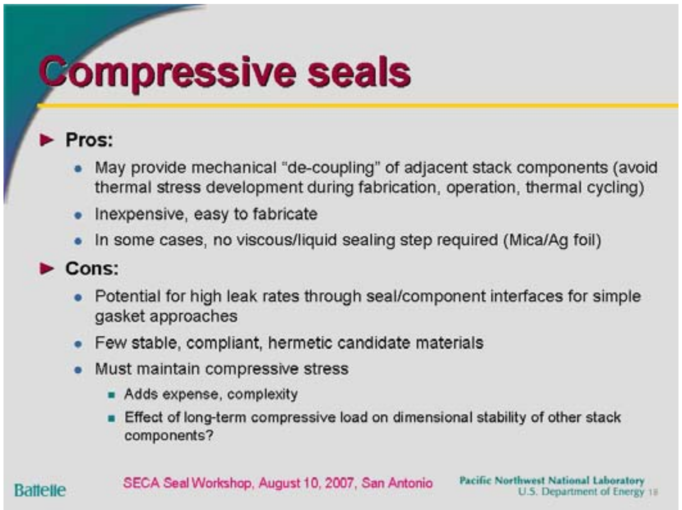


"Refractory" Glass-Ceramic Seals for SOFC

- **Objective:** Reliable, CTE-matched "refractory" sealing glasses to minimize seal reactivity and increase seal stability. Improved electrical contact and strength of cathode/interconnect interfaces.
- **Alkaline earth-aluminosilicate based glass system**
  - Patents: US 6,430,966, US 6,532,769



Compressive seals

- **Pros:**
  - May provide mechanical "de-coupling" of adjacent stack components (avoid thermal stress development during fabrication, operation, thermal cycling)
  - Inexpensive, easy to fabricate
  - In some cases, no viscous/liquid sealing step required (Mica/Ag foil)
- **Cons:**
  - Potential for high leak rates through seal/component interfaces for simple gasket approaches
  - Few stable, compliant, hermetic candidate materials
  - Must maintain compressive stress
    - Adds expense, complexity
    - Effect of long-term compressive load on dimensional stability of other stack components?

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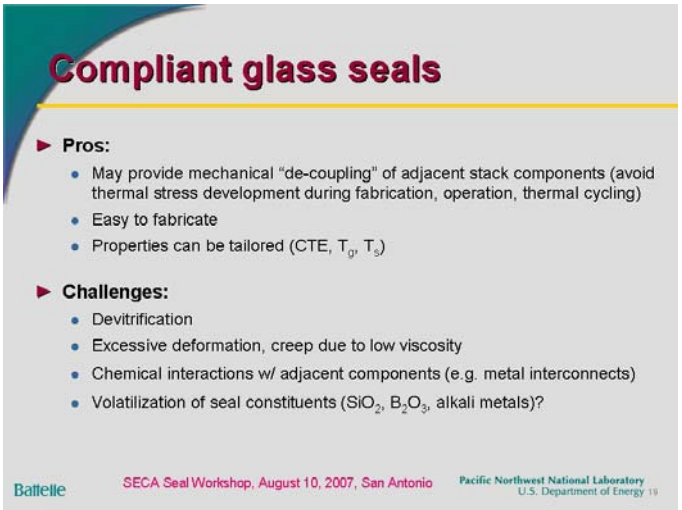

Compliant glass seals

- **Pros:**
  - May provide mechanical "de-coupling" of adjacent stack components (avoid thermal stress development during fabrication, operation, thermal cycling)
  - Easy to fabricate
  - Properties can be tailored (CTE, T_g, T_s)
- **Challenges:**
  - Devitrification
  - Excessive deformation, creep due to low viscosity
  - Chemical interactions w/ adjacent components (e.g. metal interconnects)
  - Volatilization of seal constituents (SiO_2, B_2O_3, alkali metals)?

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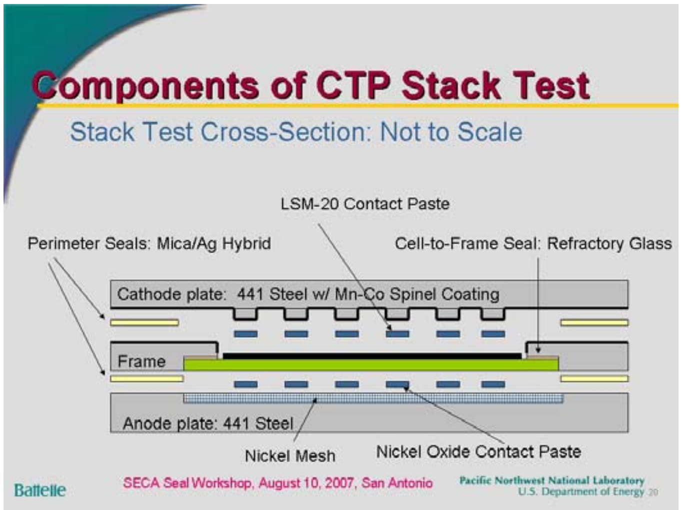

Components of CTP Stack Test

Stack Test Cross-Section: Not to Scale

LSM-20 Contact Paste

Perimeter Seals: Mica/Ag Hybrid

Cell-to-Frame Seal: Refractory Glass

Cathode plate: 441 Steel w/ Mn-Co Spinel Coating

Frame

Anode plate: 441 Steel

Nickel Mesh

Nickel Oxide Contact Paste

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MECHANICAL PROPERTY CHARACTERIZATIONS AND PERFORMANCE MODELING OF SOFC SEALS

Pacific Northwest National Laboratory

PNNL, Richland, WA

Structural Modeling and Sealing Objectives

- Develop reliable SOFC seals
  - Develop constitutive and damage models for glass-ceramic sealants and interfaces
  - Utilize experimental data for material model inputs
  - Evaluate reliability of glass-ceramic seals in the stack during thermal-cyclic operations
  - Identify the effects of the heterogeneous microstructures on the macroscopic response
  - Determine optimum material structure, properties, and seal dimensions

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Structural Modeling and Sealing Past and Present

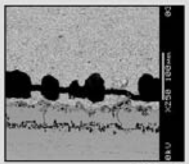
- Past
  - Developed constitutive models
    - Interface/bulk damage model
    - Viscoelastic damage model
  - Damage/thermal cycling report
  - Stress relaxation report
  - Compliant seal development
- Present
  - Evaluate stress relaxation benefits of glass-ceramic seals in stacks
  - Identify constituent data for G18 homogenization efforts

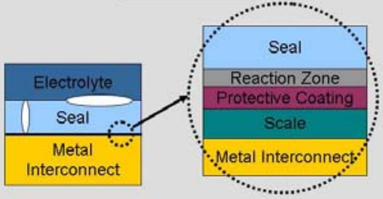
Structural Modeling and Sealing Outline

- Glass-ceramic issues
- Review of experimental data used in the models
- Viscoelastic damage model formulation
- Damage model results
- Stack model description
- Stack model results
- Future Work

Introduction: Glass-Ceramic Seals

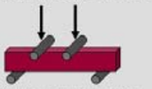
- Cracks problematic for structural integrity and leak
- Reactions can make the interfaces weak
- Reactions create enriched or depleted regions
- Seal fractures
  - Through glass layer
  - Between glass layer and scale
  - Between scale and metal interconnect
- Need predictive modeling tools
  - Stack-level approach

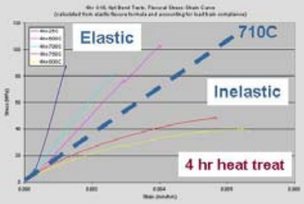


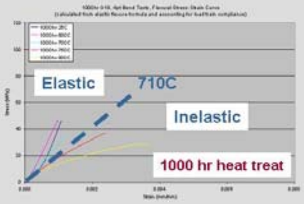


G18 Material Properties: Stress-Strain

- 4-point bend flexure tests performed at 25, 600, 700, 750, and 800°C
- Heat treatments of 4 and 1000 hr
- Elastic up to 700°C and inelastic above 750°C

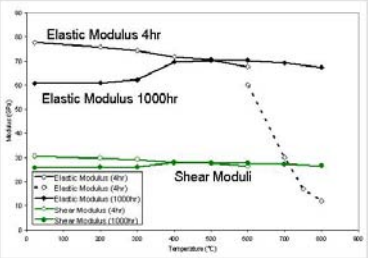






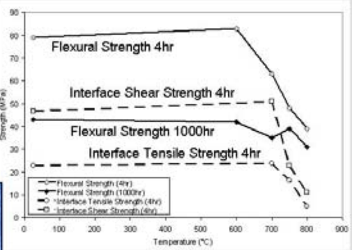
G18 Material Properties: Elastic Constants

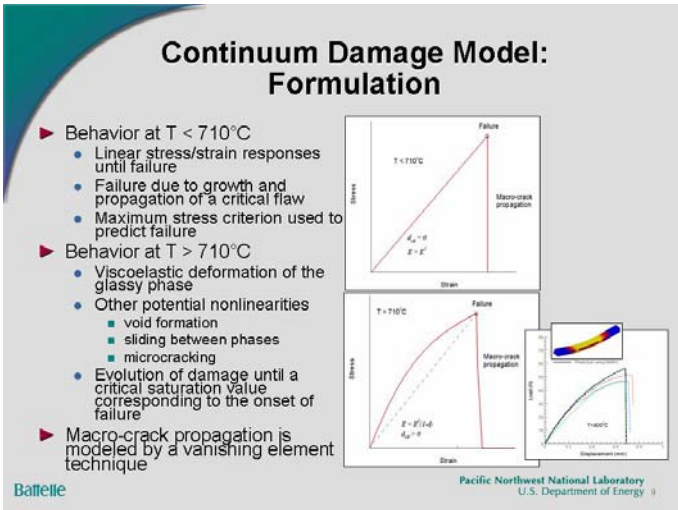
- Pulse-echo ultrasonic measurement for room temperature
- Dynamic resonance method for elevated temperature measurements
- Flexure tests used for temperatures greater than 600°C
- Glass-ceramic modulus drops considerably above 600°C for 4hr heat treatment



G18 Material Properties: Strength

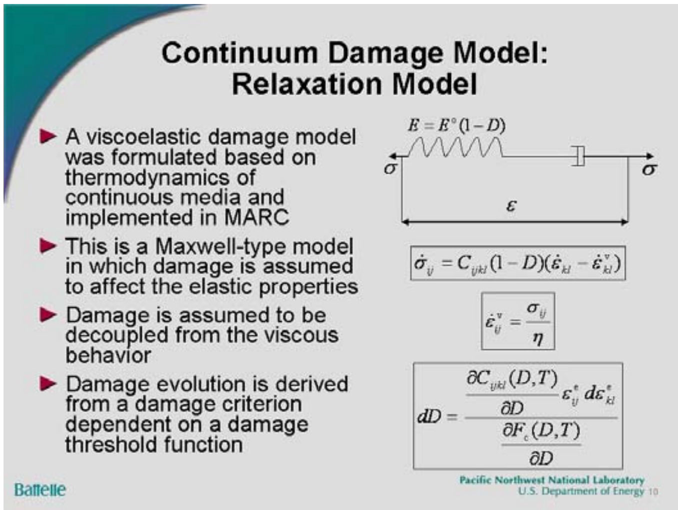
- G18 strength obtained from flexure tests
- Interface strengths obtained with tension and torsion tests
  - Crofer 22 APU assemblies
- Interface strength lower than glass-ceramic strength
- Interface shear strength greater than normal strength





Continuum Damage Model: Formulation

- Behavior at T < 710°C
  - Linear stress/strain responses until failure
  - Failure due to growth and propagation of a critical flaw
  - Maximum stress criterion used to predict failure
- Behavior at T > 710°C
  - Viscoelastic deformation of the glassy phase
  - Other potential nonlinearities
    - void formation
    - sliding between phases
    - microcracking
  - Evolution of damage until a critical saturation value corresponding to the onset of failure
- Macro-crack propagation is modeled by a vanishing element technique



Continuum Damage Model: Relaxation Model

- A viscoelastic damage model was formulated based on thermodynamics of continuous media and implemented in MARC
- This is a Maxwell-type model in which damage is assumed to affect the elastic properties
- Damage is assumed to be decoupled from the viscous behavior
- Damage evolution is derived from a damage criterion dependent on a damage threshold function

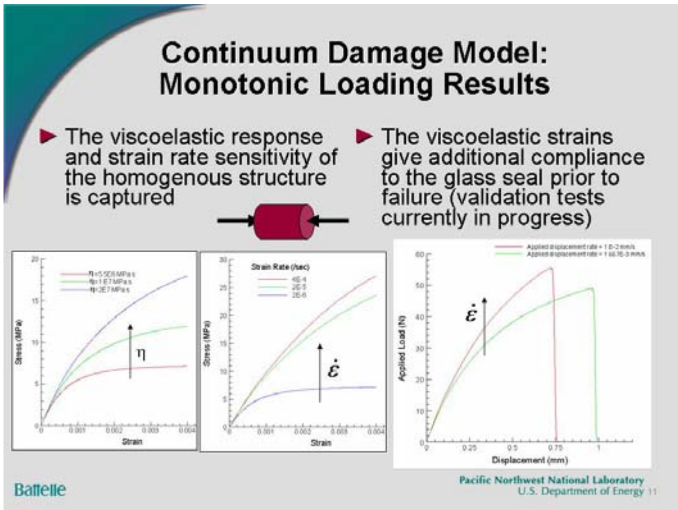
$E = E^{\circ}(1-D)$

σ σ ε

$$\dot{\sigma}_{ij} = C_{ijkl}(1-D)(\dot{\varepsilon}_{kl} - \dot{\varepsilon}^{v}_{kl})$$

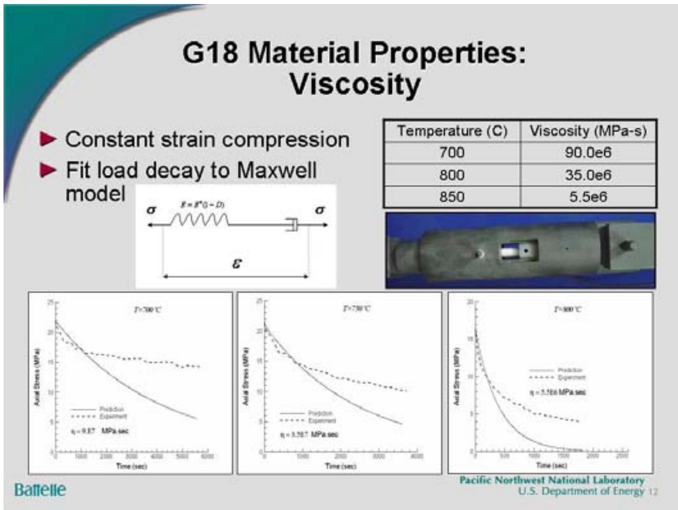
$$\dot{\varepsilon}^{v}_{ij} = \frac{\sigma_{ij}}{\eta}$$

$$dD = \frac{\dfrac{\partial C_{ijkl}(D,T)}{\partial D}\varepsilon^{e}_{ij}\, d\varepsilon^{e}_{kl}}{\dfrac{\partial F_{c}(D,T)}{\partial D}}$$



Continuum Damage Model: Monotonic Loading Results

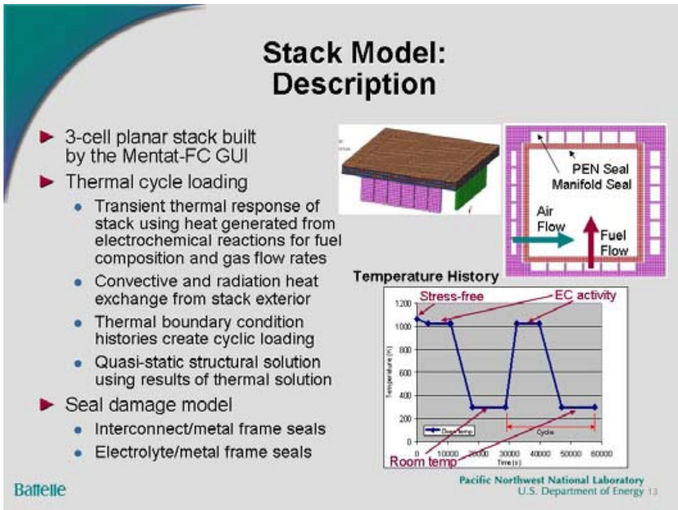
- The viscoelastic response and strain rate sensitivity of the homogenous structure is captured
- The viscoelastic strains give additional compliance to the glass seal prior to failure (validation tests currently in progress)



G18 Material Properties: Viscosity

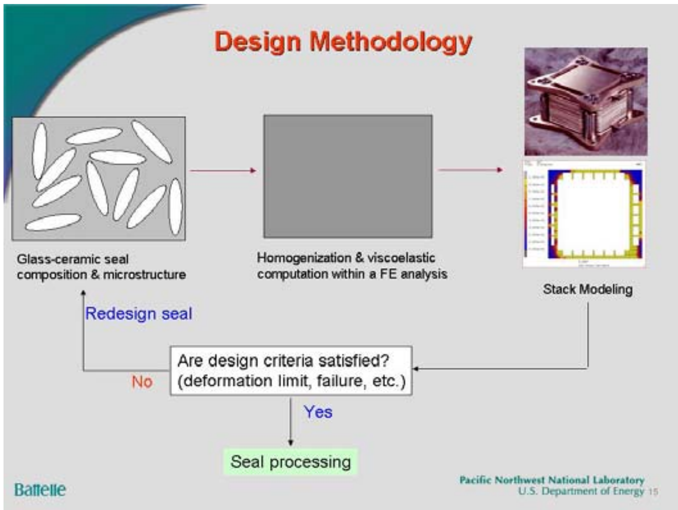
- Constant strain compression
- Fit load decay to Maxwell model

Temperature (C)	Viscosity (MPa-s)
700	90.0e6
800	35.0e6
850	5.5e6



Stack Model: Description

- 3-cell planar stack built by the Mentat-FC GUI
- Thermal cycle loading
  - Transient thermal response of stack using heat generated from electrochemical reactions for fuel composition and gas flow rates
  - Convective and radiation heat exchange from stack exterior
  - Thermal boundary condition histories create cyclic loading
  - Quasi-static structural solution using results of thermal solution
- Seal damage model
  - Interconnect/metal frame seals
  - Electrolyte/metal frame seals



Design Methodology

Glass-ceramic seal composition & microstructure

Homogenization & viscoelastic computation within a FE analysis

Stack Modeling

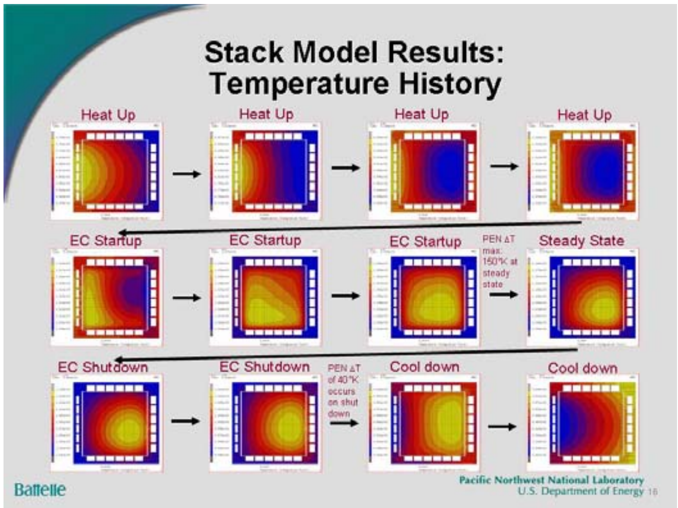
Are design criteria satisfied? (deformation limit, failure, etc.)

No

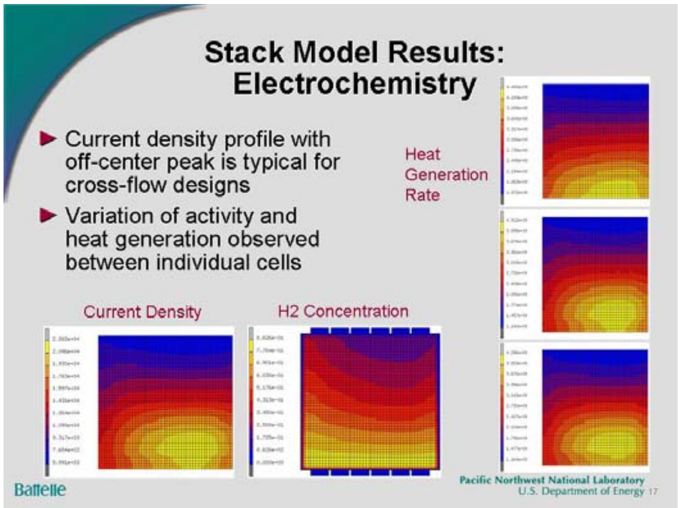
Redesign seal

Yes

Seal processing

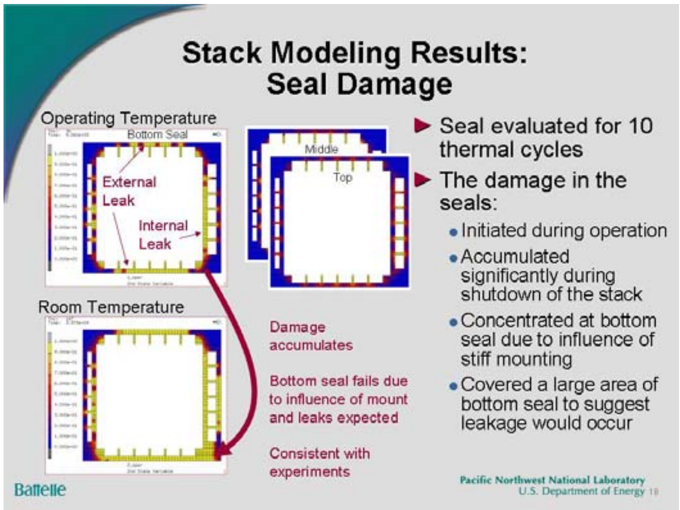


Stack Model Results: Temperature History



Stack Model Results: Electrochemistry

- Current density profile with off-center peak is typical for cross-flow designs
- Variation of activity and heat generation observed between individual cells



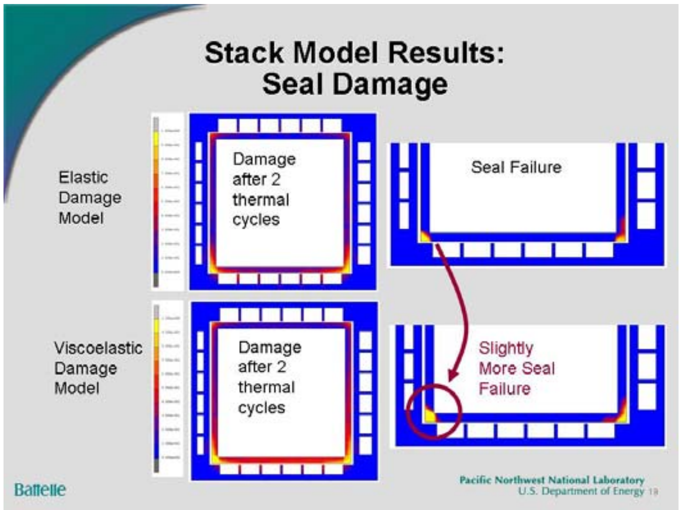
Stack Modeling Results: Seal Damage

Damage accumulates

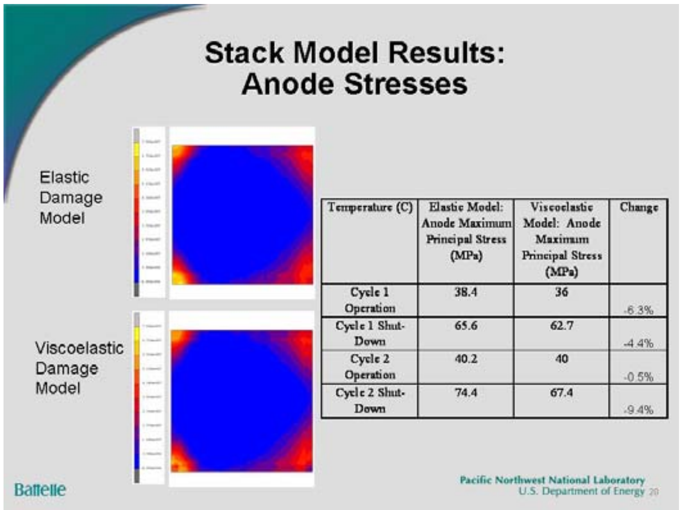
Bottom seal fails due to influence of mount and leaks expected

Consistent with experiments

- Seal evaluated for 10 thermal cycles
- The damage in the seals:
  - Initiated during operation
  - Accumulated significantly during shutdown of the stack
  - Concentrated at bottom seal due to influence of stiff mounting
  - Covered a large area of bottom seal to suggest leakage would occur

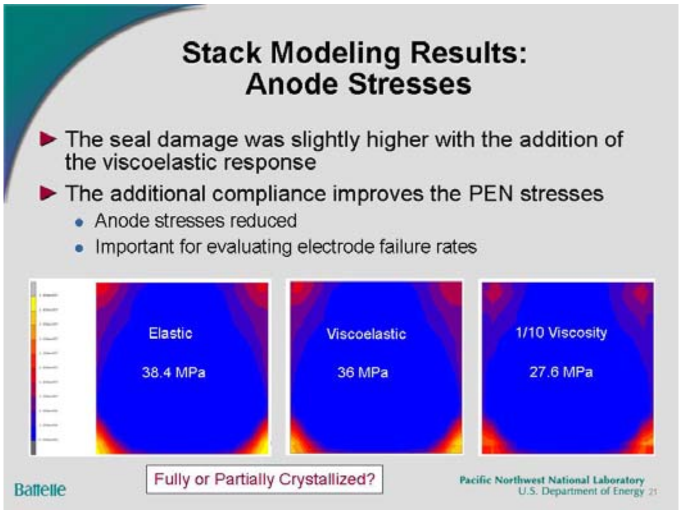


Stack Model Results: Seal Damage



Stack Model Results: Anode Stresses

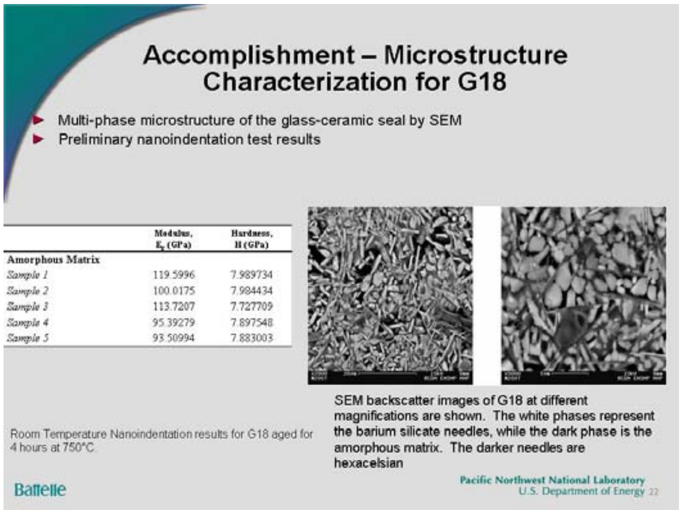
Temperature (C)	Elastic Model: Anode Maximum Principal Stress (MPa)	Viscoelastic Model: Anode Maximum Principal Stress (MPa)	Change
Cycle 1 Operation	38.4	36	-6.3%
Cycle 1 Shut-Down	65.6	62.7	-4.4%
Cycle 2 Operation	40.2	40	-0.5%
Cycle 2 Shut-Down	74.4	67.4	-9.4%



Stack Modeling Results: Anode Stresses

- The seal damage was slightly higher with the addition of the viscoelastic response
- The additional compliance improves the PEN stresses
  - Anode stresses reduced
  - Important for evaluating electrode failure rates

Fully or Partially Crystallized?



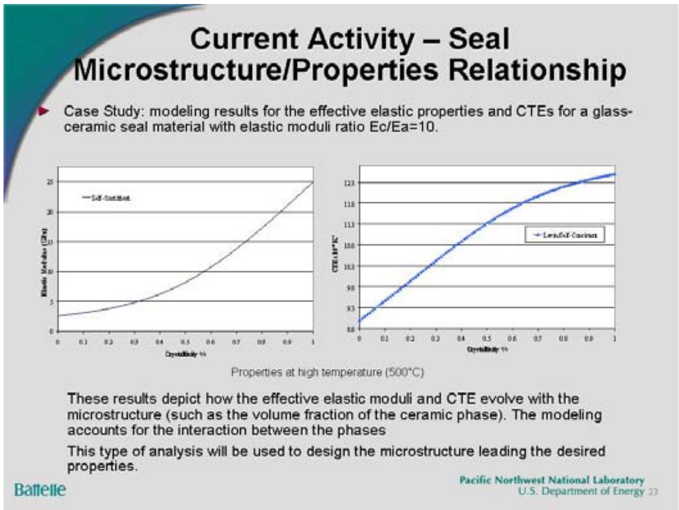
Accomplishment – Microstructure Characterization for G18

- Multi-phase microstructure of the glass-ceramic seal by SEM
- Preliminary nanoindentation test results

	Modulus, E_r (GPa)	Hardness, H (GPa)
Amorphous Matrix		
Sample 1	119.5996	7.989734
Sample 2	100.0175	7.984434
Sample 3	113.7207	7.727709
Sample 4	95.39279	7.897548
Sample 5	93.50994	7.883003

Room Temperature Nanoindentation results for G18 aged for 4 hours at 750°C

SEM backscatter images of G18 at different magnifications are shown. The white phases represent the barium silicate needles, while the dark phase is the amorphous matrix. The darker needles are hexacelsian



Current Activity – Seal Microstructure/Properties Relationship

- Case Study: modeling results for the effective elastic properties and CTEs for a glass-ceramic seal material with elastic moduli ratio Ec/Ea=10.

Properties at high temperature (500°C)

These results depict how the effective elastic moduli and CTE evolve with the microstructure (such as the volume fraction of the ceramic phase). The modeling accounts for the interaction between the phases

This type of analysis will be used to design the microstructure leading the desired properties.

Summary

- Developed procedure to evaluate damage of glass-ceramic seals in SOFC stacks
  - Experiments to identify material behavior
  - Constitutive and damage mechanics model
- Evaluation of thermal cyclic loading
  - Damage initiates in first loading cycle
  - Stiff mount increases damage in nearest cell of the multi-cell stack
- Viscoelastic response must be considered to capture high temperature stress-relaxation of glass-ceramic seals
  - Slightly more damage and seal failure predicted
  - Additional compliance is beneficial for relaxation of PEN stresses

The High Temperature Materials Laboratory is a DOE User Facility located at Oak Ridge National Laboratory

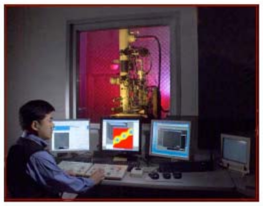
www.html.ornl.gov

The HTML User Program is funded by DOE's Office of FreedomCAR and Vehicle Technologies

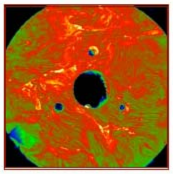
HTML Capabilities are Available to Users for Hands-On Materials Characterization Research

Materials Analysis;

Thermography and Thermophysical Properties:



Mechanical Characterization and Analysis:



HTML Capabilities are Available to Users for Hands-On Materials Characterization Research

Diffraction:

Residual Stresses

Friction and Wear

There are Numerous Ways to Work with the HTML

- HTML User Program
  - short-term materials characterization
  - non-proprietary or proprietary
- CRADAs
- Work for Others (WFO)
- Collaborative research

HTML Well Equipped for Microstructural and Microcompositional Characterization

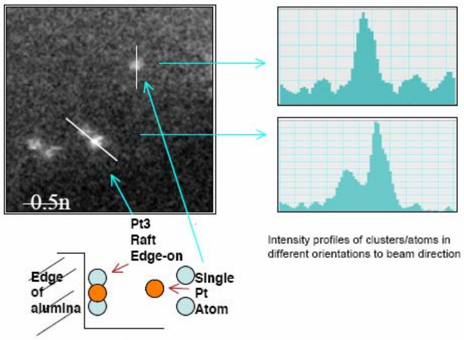
- Hitachi HF-2000 FEG-AEM w/EDS
- Hitachi S-4700 FEG-SEM w/EDS, Kikuchi backscatter detector
- Hitachi FB-2000 FIB Micro-mill
- Hitachi HD-2000 Dedicated STEM
- JEOL 8200 Electron Microprobe
- PHI 680 Scanning Auger Nanoprobe

ACEM

ACEM:

- is first probe corrected STEM/TEM in US
- has sub-Å resolution for structure and chemical analysis
- has resolved single Pt atoms on alumina substrates
- totally automated for remote operation
- user friendly
- special facility- low EM fields, mechanical vibrations.

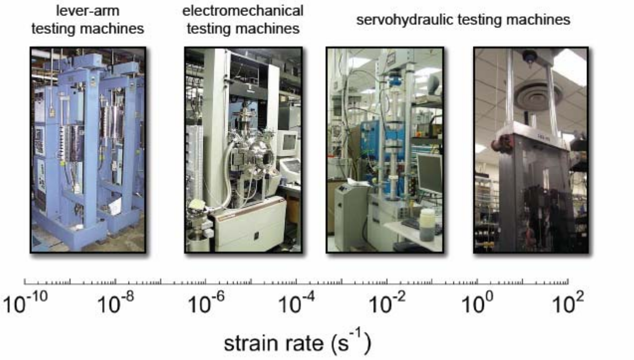
Images of Catalytic Materials Demonstrate ACEM's Capabilities



Intensity profiles of clusters/atoms in different orientations to beam direction

Electron beam direction

Evaluation of materials and structures over a wide range of time scales

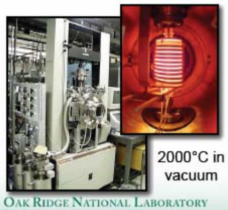


Effect of Temperature and Environment on Mechanical Behavior


microturbine


2000°C+ in vacuum


2000°C+ in inert gases

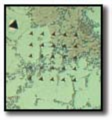

2000°C in vacuum


infrared heating


resistance heating


RF heating

Wide Array of Capabilities for Mechanical Testing & Analysis


Nanoindentation


DMA


RUS

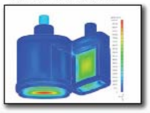

Spiral Notch

Fuel Cladding Ductility


Uniaxial and Biaxial Flexure


Double Torsion


very large collection of creep frames


Stress Analysis


structural and multiaxial testing

Thermal Transport Properties

- **Laser Flash Thermal Diffusivity**
  - Cryogenic to 2500°C
- **Xenon Flash Thermal Diffusivity System**
  - Fast room temperature measurements
- **Hot Disk Thermal Constants Analyzer**
  - Portable
  - RT to 650°C
- **ULVAC Thermal Diffusivity of thin Films**

Thermal Analysis

- **Simultaneous Thermal Analysis**
  - Small specimens up to 1500 °C
- **Dual Push-Rod Dilatometer**
  - Up to 1600 °C
- **Concurrent Thermal Analysis**
  - Large specimens up to 1700 °C
- **High Temperature DSC**
  - Up to 1650 °C
- **Vertical Dilatometer**
  - Up to 2400 °C
- **ULVAC ZEM-2 for High Temperature Seebeck Coefficient and Electrical Resistivity Measurements**
  - -80°C to 1000°C

IR Imaging and Sensing

- **Phoenix MWIR Camera** (1.5 – 5.0 μm)
- **Phoenix NIR Camera** (0.9 to 1.7 μm)
- **Radiance-HS IR Camera** (3 – 5.0 μm)
- **Fiber Optic Coupled 2-Color IR Detector**
  - Up to 100,000 measurements per second
  - 3-5 μm and 8-12 μm
- **Omega IR Camera** (7.5 – 13.5 μm)
- **Alpha IR Camera** (7.5 – 13.5 μm)
- **Hyperspectral Lens** (3 – 5.0 μm) NEW
- **Microscope Lens** (3 – 5.0 μm)
- **InGaAs Spectrometer** (0.9 – 2.5 μm)
- **SM-240 Spectrometer** (200 – 1050 nm)
- **ThermoSonix NDE System** NEW

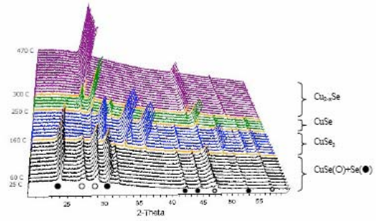
Diffraction User Center Has X-Ray, Synchrotron, and Neutron Capability

Several laboratory systems up to 18KV with furnaces, atmosphere control, position-sensitive detectors

NSLS at Brookhaven National Laboratory, beamline X-14A, with furnace, atmosphere control

Beamline HB-2 at the High Flux Isotope Reactor at ORNL, with furnace and Atmosphere control

Our Unique Capabilities Enable Quantitative Analysis Under Simulated Process Conditions



This project utilized the high-speed data collection on the Scintag PADX and PANalytical X'Pert Pro diffractometers. The different detector and furnace options on these instruments were complementary and enabled a range of kinetic data to be collected.

This plot shows the evolution of a glass/Cu/Se bilayer film on heating in air to 470°C. At around 160°C the $CuSe_2$ phase forms, but at higher temperatures volatization of selenium produces Cu-rich phases.

X-ray Stress Mapping of Cast Engine Blocks Demonstrates Mapping

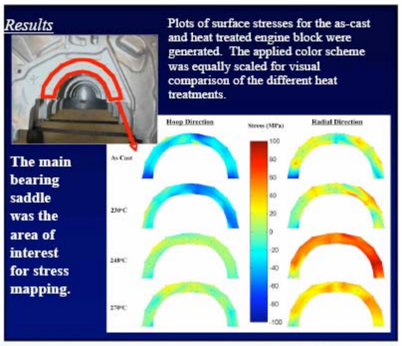
- Two engine blocks in as-cast condition
- Three blocks were heat treated: 230, 248 and 270°C for 4 hours

Material Properties

- Die cast SAE 383.0 (UNS A03830) alloy aluminum
- Young's Modulus = 70 GPa
- Poisson's Ratio = 0.33

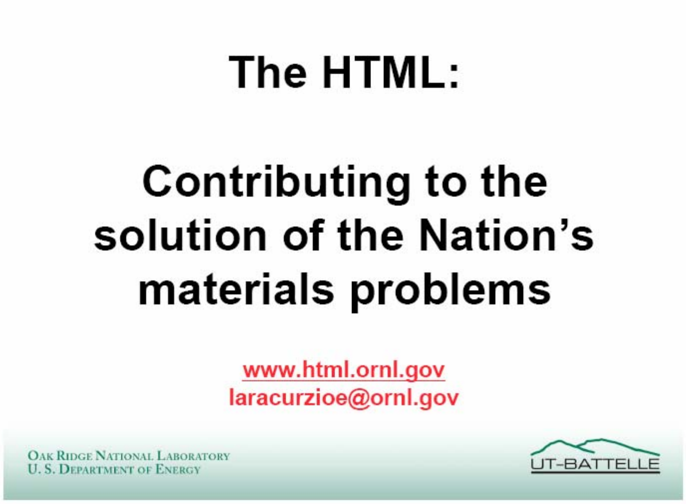
TEC Mapping

- 33 locations in bearing saddle
- Hoop and radial stresses measured


Results

Plots of surface stresses for the as-cast and heat treated engine block were generated. The applied color scheme was equally scaled for visual comparison of the different heat treatments.

The main bearing saddle was the area of interest for stress mapping.



The HTML:

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OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

INNOVATIVE SEALS FOR SOLID OXIDE FUEL CELLS (SOFC):*VISCO-ELASTIC SEALS*

Raj N. Singh

Department of Chemical and Materials Engineering
University of Cincinnati, Cincinnati
OH 45221-0012

Supported by DOE-SECA Program (Drs. Mani Mannvanan and Travis Shultz, Project Managers) and University of Cincinnati

SECA Workshop, San Antonio, August 7-9, 2007

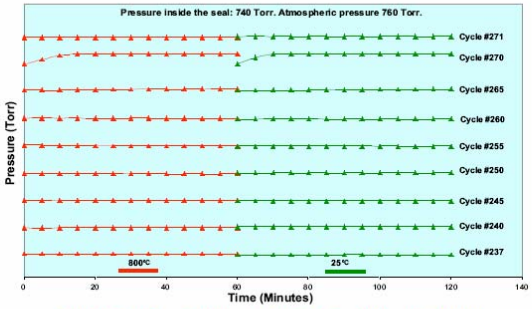
INTRODUCTION

- **Requirements of Seals for SOFC**
  - ✦ Electrochemical-insulating to avoid shorting
  - ✦ Lowest possible thermomechanical stresses upon processing, during heatup, cooldown, and in steady state/transient operations
  - ✦ Long life (40,000h) under electrochemical and oxidizing/reducing environments at high temperatures ~600-850°C
  - ✦ Low cost
- **Type of Seals**
  - ✦ Ceramic-Ceramic (Electrolyte-Ceramic Insulator)
  - ✦ Ceramic-Metal
  - ✦ Metal-Metal
  - ✦ Rigid and/or Compliant
  - ✦ Chemical/Mechanical/Liquid

PROGRAM OBJECTIVES AND ACCOMPLISHMENTS

- **Phase-I**
  - ✦ Select self-healing glasses for functionality as seals for SOFCs
  - ✦ Demonstrate functionality of the self-healing seals by leak tests
  - ✦ Measure stability of the self-healing glass in SOFC environments
  - ✦ Develop approaches to toughening self-healing glasses as seals for SOFs
  - ✦ Survey commercial glasses suitable for making seals for SOFCs
- **Accomplishments**
  - ✦ Developed glasses displaying self-healing ability
  - ✦ Demonstrated ability of self-healing glasses in sealing components through leak tests over a range of temperatures between 25-800°C
  - ✦ Achieved 300 thermal cycles between 25-800°C without leak of seals and accumulated 3000 hours of hermetic seal performance at 800°C
  - ✦ These results provide great promise towards meeting SECA goals of seals for SOFC.

DEMONSTRATION OF SELF-HEALING ABILITY AND SEAL DURABILITY BETWEEN 25-800°C IN DUAL ATMOSPHERE

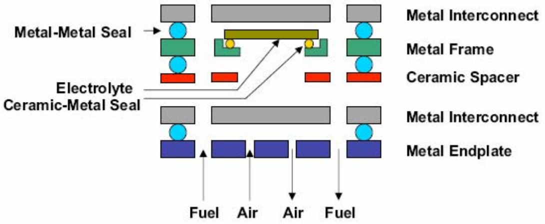


- **Self-healing in 271 cycle of leak in 270 cycle/2900 h**

PROGRAM OBJECTIVES AND ACCOMPLISHMENTS

- **Phase-II**
  - ✦ Develop self healing sealing glasses and demonstrate long-term stability
  - ✦ Demonstrate toughening of glasses by fiber/filler reinforcement
  - ✦ Demonstrate seal durability of self-healing and reinforced-glasses
  - ✦ Demonstrate and transition sealing technology to SECA team
- **Accomplishments**
  - ✦ Determined stability of the sealing glasses and glasses with fillers
  - ✦ Demonstrated ability of reinforced self-healing glasses in sealing components through leak tests at temperatures between 25-800°C
  - ✦ Achieved >1500 hours of hermetic seal performance
  - ✦ Measured DC electrical resistance/resistivity of sealing glass over 25-800°C
  - ✦ These results provide great promise towards meeting SECA goals of seals for SOFC.

SEALS FOR PLANAR SOFC



- **Metal-Ceramic and Metal-Metal Seals Must Work at 650-850°C in Corrosive Environments of Fuel and Air**

POSSIBLE APPROACHES TO SEALS FOR SOFC

- **Rigid Seals**
  - ✦ Glass-Metal, Ceramic Polymer-Ceramic/Metal, Brazes: require stable glasses, brazes, preceramic polymers
  - ✦ Low leak rates but susceptible to failures due to stresses
  - ✦ Feedback to materials and seal concept modifications to reduce stress buildup and avoid failure
- **Compliant Seals**
  - ✦ Bellows, Viscous Glass, Wet-Seals (MCFC): require flexible seal designs, stable glasses with appropriate viscosity over a range of temperature, wet-sealing materials and their containment
  - ✦ Moderate leak rate, some concepts may require pressure
- **Our Approaches for Seals**
  - ✦ Self-Healing Glass Seals
  - ✦ Reinforced-Glass Seals
  - ✦ Layered Composite Seals

A SELF-HEALING SEALING CONCEPT FOR SOFC

- **Rationale:** A glass of appropriate characteristics can self-heal the cracks created upon thermal cycling and/or stresses created during SOFC operation. In addition, thermomechnical incompatibilities between ceramic and metallic materials requiring seals/joining can be alleviated using a self-healing glass seal.
- **Advantages:** Materials with dramatically different expansions can potentially be used for seals because this approach can alleviate/minimize thermomechanical stresses and chemical reactions. The leaks developed upon SOFC operation and thermal cycling can be repaired in situ by the self-healing concept.
- **Challenges:** Develop appropriate glasses which satisfy thermomechanical and thermochemical compatibilities, remain stable for long-time, and maintain self-healing capability.
- **Approach:** Thermophysical and thermochemical property measurements and optimization,self-healing ability, and leak testing to demonstrate self-healing seals.

OBJECTIVES

- Demonstrate Stability of the Self-Healing Glasses under SOFC Environment
- Fabricate Glasses with Fillers and Fibers and Demonstrate Stability and Sealing Behaviors
- Describe Performance of Reinforced Glass Seals and Electrical Properties of Glasses

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EXPERIMENTAL

- Materials
  - ✦ Electrolyte YSZ (Tape Casting and Sintering)
  - ✦ Metal (Crofer22 APU)
  - ✦ Sealant-Silicate Glass
- Fabricate Seals Displaying Self-Healing Behavior
  - ✦ Self-healing Behavior in situ
- Durability of the Self-Healing Glass and Performance of Seals
  - ✦ Testing at RT and High Temperatures
  - ✦ Effect of Pressure Drop Across The Seal
  - ✦ Effect of Thermal Cycling Between 25-800°C
  - ✦ Effect of Test Atmosphere Typical of SOFC
  - ✦ Effect of Time at 800°C on Seal Durability

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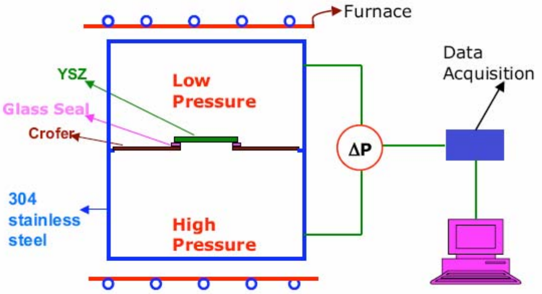
A SEAL PERFORMANCE TEST SYSTEM



- Continuous monitoring of leak test conditions

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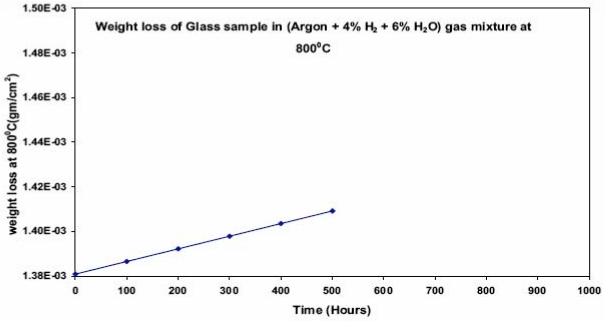
STABILITY OF THE GLASS IN MOIST FUEL ENVIRONMENT AT 800°C



- Calculated insignificant weight loss of 0.53% in 40,000 hours

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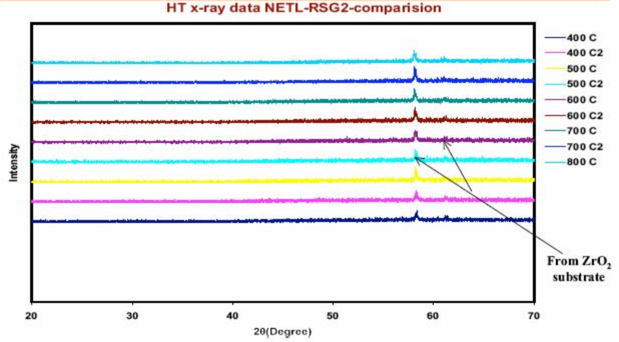
STABILITY OF THE GLASS TO 800°C IN AIR In Situ X-Ray Diffraction at NETL (Dr. C. Johnson)



- Stability against crystallization between 25-800°C

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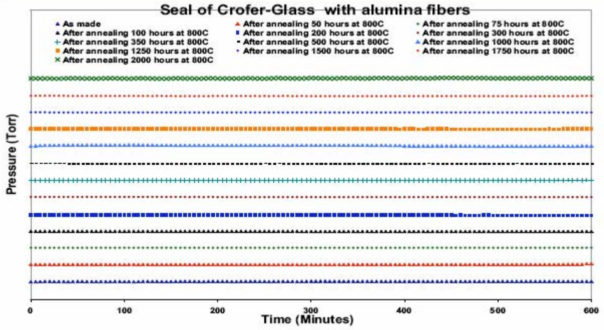
PERFORMANCE OF THE GLASS COMPOSITE SEAL AT 800°C



- Hermetic seal performance after 1750 hours

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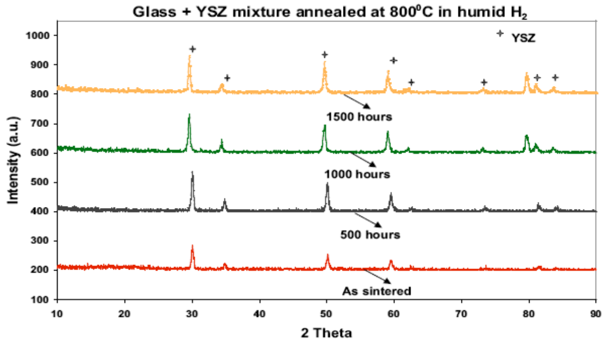
STABILITY OF THE GLASS+5%YSZ AT 800°C IN HUMID FUEL ENVIRONMENT



- Stability against crystallization to 1500 hours

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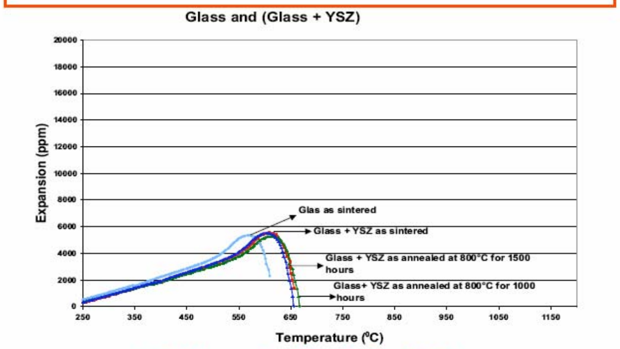
STABILITY OF THE GLASS+5%YSZ AT 800°C IN HUMID FUEL ENVIRONMENT



- Stable expansion behavior for 1500 hours

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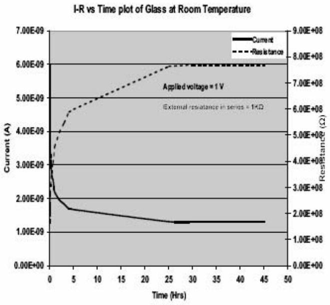
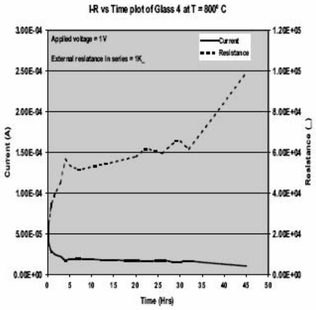
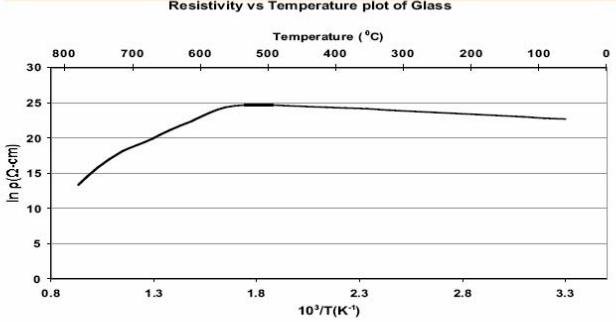
DC RESISTANCE MEASUREMENTS OF GLASS BETWEEN 25-800°C


I-R vs Time plot of Glass at Room Temperature


I-R vs Time plot of Glass 4 at T = 800° C

- High DC Resistance to 800°C

DC RESISTIVITY OF GLASS BETWEEN 25-800°C


Resistivity vs Temperature plot of Glass

- High DC Resistivity to 800°C

SUMMARY

- **A self-healing sealing concept is further developed for SOFC to satisfy significant thermochemical and thermomechanical incompatibilities among materials requiring hermetic seals.**
- **Stability of the self-healing and reinforced glasses were measured by x-situ experiments at 800°C for times >1500 hours and demonstrated stability.**
- **Performance of the self-healing seals with fibers for ~1750 hours was demonstrated via leak tests as a function of temperature.**
- **Long term stability and leak test results demonstrated promise of the self-healing seals for potential applications in SOFC.**

PROGRAM OBJECTIVES-Phase II

- ✦ Develop additional sealing glasses and demonstrate long-term stability
- ✦ Demonstrate toughening of glasses by fiber reinforcement
- ✦ Demonstrate seal durability of self-healing and reinforced-glasses in SOFC tests
- ✦ Demonstrate and transition sealing technology to SECA team

ACKNOWLEDGMENTS

- **SECA Core Technology for Program Support**
  Mani Mannvanan and Travis Shultz for Program Management and Guidance on the Project
  Wayne Surdoval, Don Collins, and Lane Wilson for Discussions on Seals
  Chris Johnson of NETL for help with in situ x-ray diffraction at high temperature.
- **S. Parihar, S. Singh, and S. Chavan for help with experiments**
- **PNNL, Ceramatec, and University of Utah for Electrolyte Samples**
  Matt Chou, Jeff Stevenson, P. Singh, S. Elangovan and Anil Virkar
- **GE Power Systems, FuelCell Energy, and Delphi for Guidance and Industry Perspective**
  N. Minh, Pinakin Patel, and Diane England

Glass Composite Seals for Solid Oxide Fuel Cells

Ronald Loehman and Erica Corral

Sandia National Laboratories
Albuquerque, NM USA

SECA Annual Review, San Antonio, Texas August 7-9, 2007

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---

Contributors

Marlene Chavez	Sandia National Laboratories
Tony Ohlhausen	Sandia National Laboratories
Scarlett Widgeon	University of New Mexico
Patrick Sims	University of New Mexico
Bryan Gauntt	New Mexico Tech
Luke Boyer	McGill University

Special thanks for advice and support to A. Mannivan, Wayne Surdoval, Travis Schultz, and Lane Wilson

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Summary and Conclusions

- Glass composites are a versatile technique for sealing SOFCs
- The method has been demonstrated for a range of glass and filler compositions
- Glass and filler compositions can be optimized independently
- Our borate and borosilicate sealing glasses exhibit long-term stability at 750°C
- They make strong, leak tight seals to ferritic stainless steel alloys and other SOFC materials

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Outline

- Introduction to composite seals
- Measurement and control of seal properties
  - Glass composite viscosity and flow
  - Seal material stability
  - Seal strengths
- Conclusions

The SECA goal of 40,000 hr stack lifetimes places extreme demands on SOFC materials

SOFC seals are subject to severe materials constraints

Function	Property
HT stability	decomposition, vaporization
chemically stable	interfacial reactions
mechanically stable	adhesion at temperature
insensitive to thermal cycling	thermal shock resistance
stress tolerant	accommodates CTE mismatch
no gas leaks	hermeticity

Composite seals are attractive because chemical and mechanical properties can be optimized independently

Initial pellet shape

Glass 14A - YSZ powder mixtures heated on Ebrite stainless steel for 10 min at 850°C Percentages indicate the volume of YSZ powder in composite

The Concept

- A deformable seal based on glass flow above its T_g
- Wetting and reaction controlled by glass chemistry
- Control viscosity and CTE with powder additive
- Slight flow to relieve stress, heal cracks
- Composite is rigid enough to remain in joint

We have evaluated a variety of glass and filler compositions for SOFC seals

Glass family: Mg-Ca-Ba-La-Al-Si-B-O

Glass Properties: T_g from 510 to 735°C

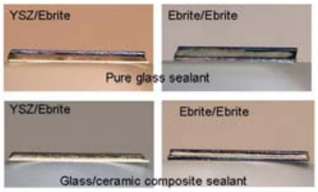
CTEs from 7 to 11.5 x 10^{-6}/°C

η from 45 to 600 MPa•s

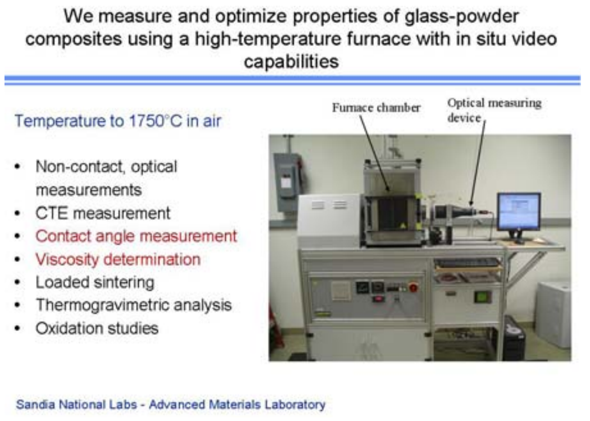
Additives: YSZ, Al_2O_3, Ni, Cr, Ag

We have sealed different SOFC materials with our glass composites

Anode/Glass-Ag/410 ss



410/Glass-Ag/410 ss



We measure and optimize properties of glass-powder composites using a high-temperature furnace with in situ video capabilities

Temperature to 1750°C in air

- Non-contact, optical measurements
- CTE measurement
- Contact angle measurement
- Viscosity determination
- Loaded sintering
- Thermogravimetric analysis
- Oxidation studies

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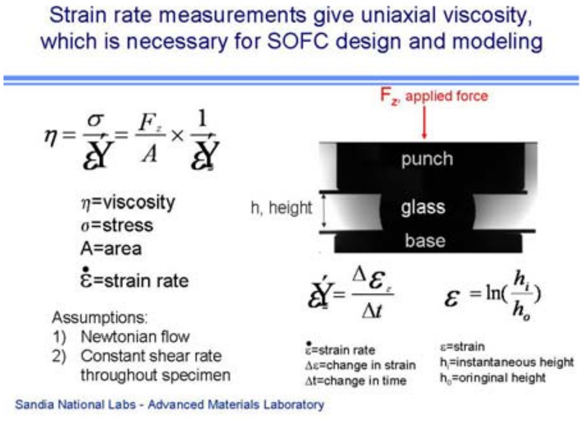

Strain rate measurements give uniaxial viscosity, which is necessary for SOFC design and modeling

$$\eta = \frac{\sigma}{\dot{\varepsilon}} = \frac{F_z}{A} \times \frac{1}{\dot{\varepsilon}}$$

η=viscosity
σ=stress
A=area
$\dot{\varepsilon}$=strain rate

Assumptions:
1) Newtonian flow
2) Constant shear rate throughout specimen

$$\dot{\varepsilon} = \frac{\Delta \varepsilon_z}{\Delta t} \qquad \varepsilon = \ln\left(\frac{h_i}{h_o}\right)$$

$\dot{\varepsilon}$=strain rate
$\Delta\varepsilon$=change in strain
Δt=change in time

ε=strain
h_i=instantaneous height
h_o=oringinal height

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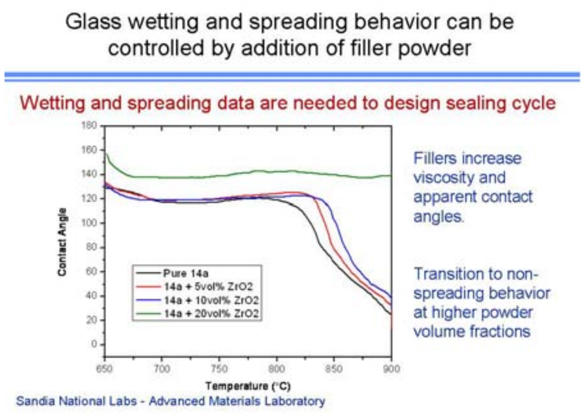

Glass wetting and spreading behavior can be controlled by addition of filler powder

Wetting and spreading data are needed to design sealing cycle

Fillers increase viscosity and apparent contact angles.

Transition to non-spreading behavior at higher powder volume fractions

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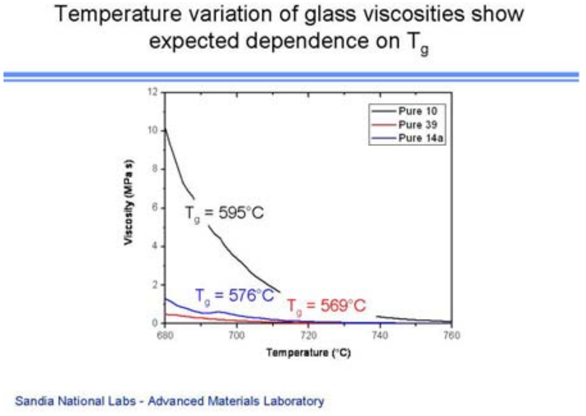

Temperature variation of glass viscosities show expected dependence on T_g

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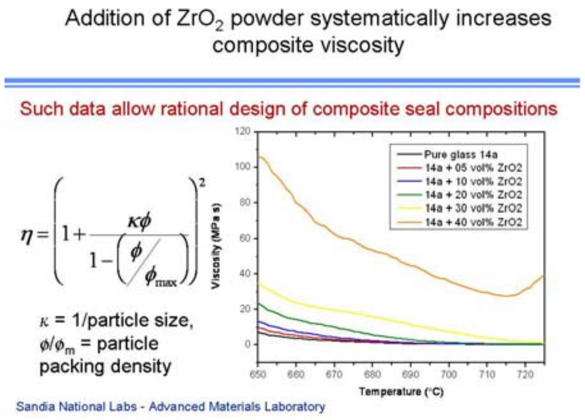

Addition of ZrO_2 powder systematically increases composite viscosity

Such data allow rational design of composite seal compositions

$$\eta = \left(1 + \frac{\kappa\phi}{1 - \left(\frac{\phi}{\phi_{max}}\right)}\right)^2$$

κ = 1/particle size,
ϕ/ϕ_m = particle packing density

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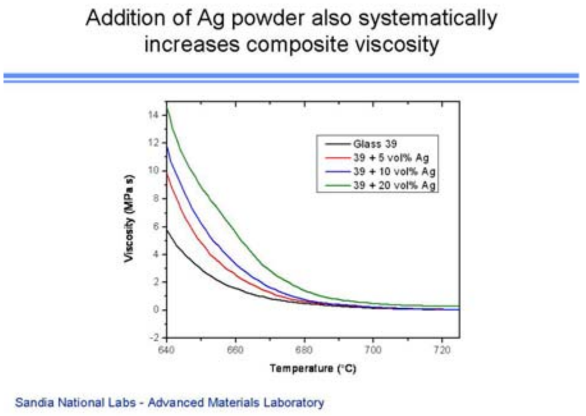

Addition of Ag powder also systematically increases composite viscosity

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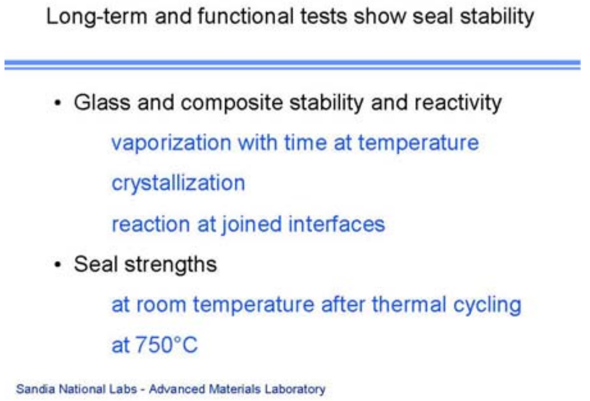

Long-term and functional tests show seal stability

- Glass and composite stability and reactivity
  - vaporization with time at temperature
  - crystallization
  - reaction at joined interfaces
- Seal strengths
  - at room temperature after thermal cycling
  - at 750°C

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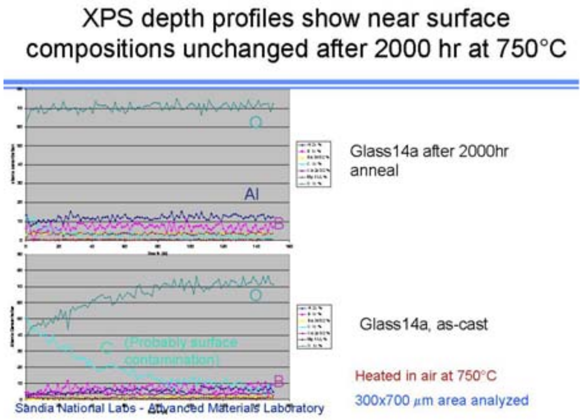

XPS depth profiles show near surface compositions unchanged after 2000 hr at 750°C

Glass14a after 2000hr anneal

Glass14a, as-cast

Heated in air at 750°C

300x700 μm area analyzed

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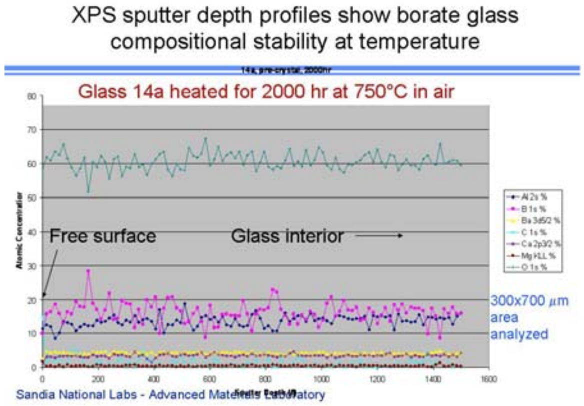

XPS sputter depth profiles show borate glass compositional stability at temperature

Glass 14a heated for 2000 hr at 750°C in air

300x700 μm area analyzed

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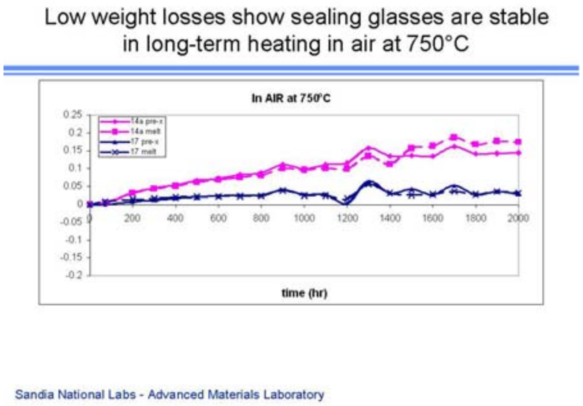

Low weight losses show sealing glasses are stable in long-term heating in air at 750°C

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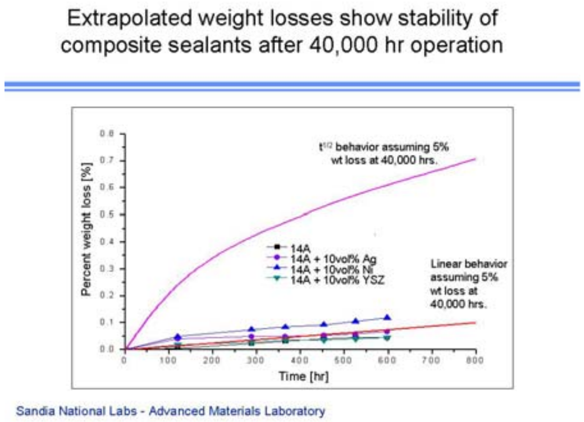

Extrapolated weight losses show stability of composite sealants after 40,000 hr operation

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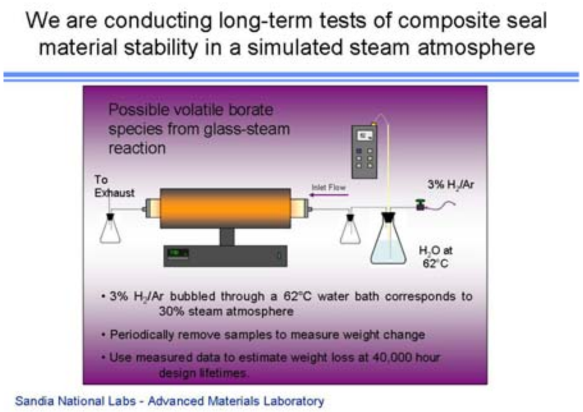

We are conducting long-term tests of composite seal material stability in a simulated steam atmosphere

Possible volatile borate species from glass-steam reaction

- 3% H_2/Ar bubbled through a 62°C water bath corresponds to 30% steam atmosphere
- Periodically remove samples to measure weight change
- Use measured data to estimate weight loss at 40,000 hour design lifetimes.

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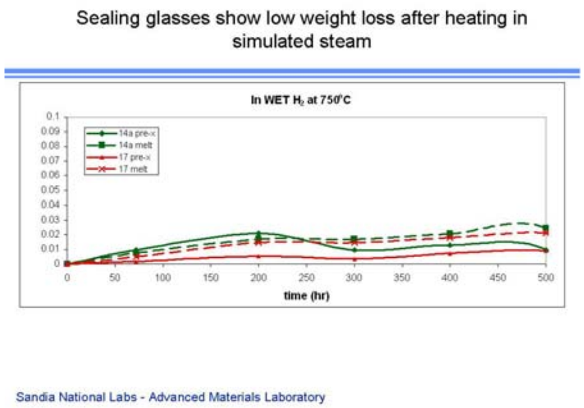

Sealing glasses show low weight loss after heating in simulated steam

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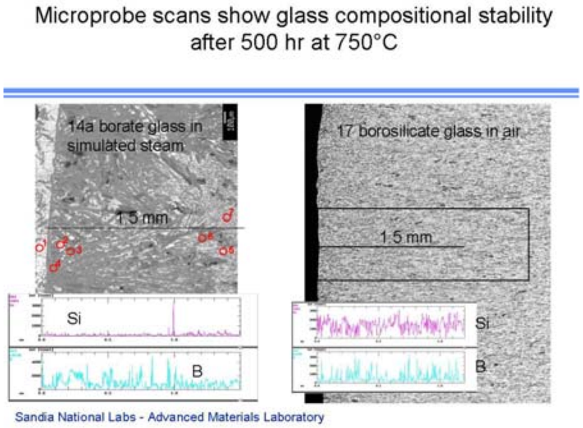

Microprobe scans show glass compositional stability after 500 hr at 750°C

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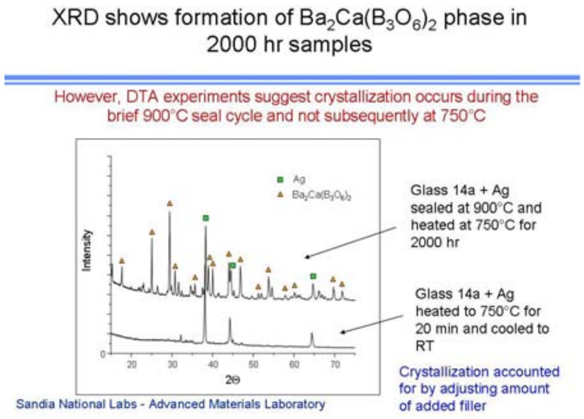

XRD shows formation of $Ba_2Ca(B_3O_6)_2$ phase in 2000 hr samples

However, DTA experiments suggest crystallization occurs during the brief 900°C seal cycle and not subsequently at 750°C

Glass 14a + Ag sealed at 900°C and heated at 750°C for 2000 hr

Glass 14a + Ag heated to 750°C for 20 min and cooled to RT

Crystallization accounted for by adjusting amount of added filler

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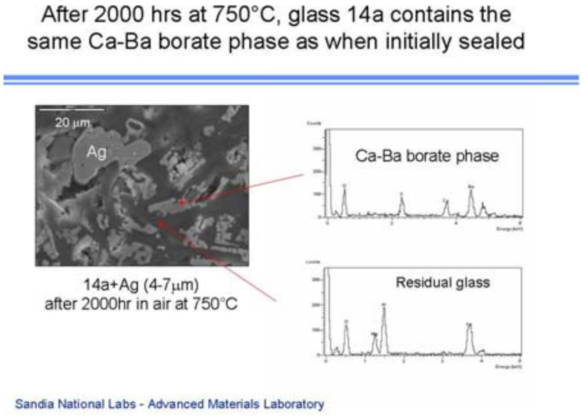

After 2000 hrs at 750°C, glass 14a contains the same Ca-Ba borate phase as when initially sealed

14a+Ag (4-7μm) after 2000hr in air at 750°C

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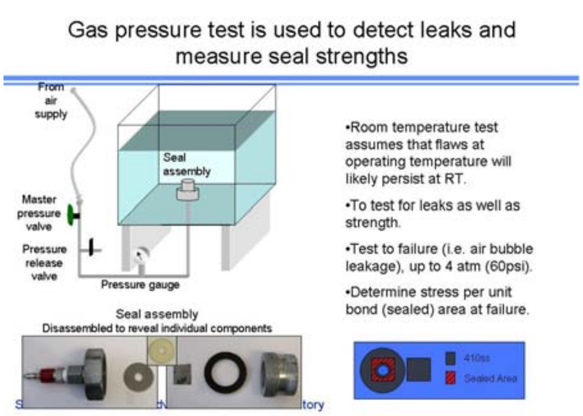

Gas pressure test is used to detect leaks and measure seal strengths

- Room temperature test assumes that flaws at operating temperature will likely persist at RT.
- To test for leaks as well as strength.
- Test to failure (i.e. air bubble leakage), up to 4 atm (60psi).
- Determine stress per unit bond (sealed) area at failure.

Seal assembly
Disassembled to reveal individual components

Glass-Ag composite seals are strong after repeated thermal cycles

SS410 - SS410 seals taken to 750°C and tested at room temperature

No. of samples	Bond thickness	Avg Pressure kPa (psi)	No. heat cycles ea.	Avg Strength# N/mm^2 (psi)
2*	0.22 mm	>413.7 (60)	10	0.084 (12.2)
5*	0.22	>413.7 (60)	9	0.126 (18.3)
1*	0.22	>413.7 (60)	3	0.129 (18.8)
1*	0.53	>413.7 (60)	3	0.126 (18.8)
1*	1.02	>413.7 (60)	3	0.124 (18.0)
3	0.46	39.3 (5.7)	1	0.010 (1.5)
3	0.22	34.9 (5.1)	1	0.0088 (1.3)

* Metal etched before sealing # failure stress/bond area

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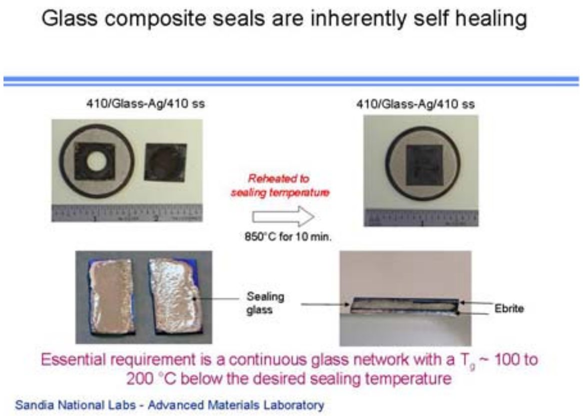

Glass composite seals are inherently self healing

Essential requirement is a continuous glass network with a T_g ~ 100 to 200 °C below the desired sealing temperature

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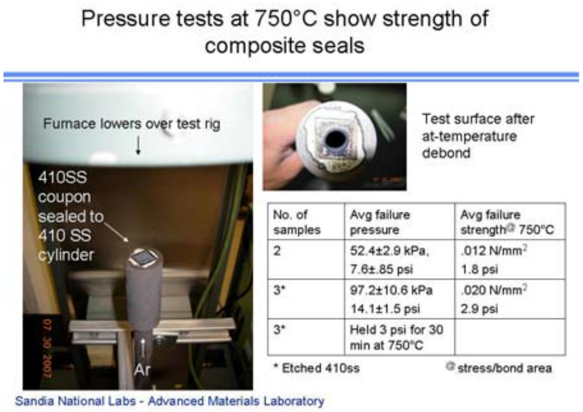

Pressure tests at 750°C show strength of composite seals

Test surface after at-temperature debond

No. of samples	Avg failure pressure	Avg failure strength@ 750°C
2	52.4±2.9 kPa, 7.6±.85 psi	.012 N/mm^2 1.8 psi
3*	97.2±10.6 kPa 14.1±1.5 psi	.020 N/mm^2 2.9 psi
3*	Held 3 psi for 30 min at 750°C	

* Etched 410ss @ stress/bond area

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Summary and Conclusions

- Glass composites are a versatile technique for sealing SOFCs
- The method has been demonstrated for a range of glass and filler compositions
- Glass and filler compositions can be optimized independently
- Our borate and borosilicate sealing glasses exhibit long-term stability at 750°C
- They make strong, leak tight seals to ferritic stainless steel alloys

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Future Work

- make seals to 441 alloy
- continue evaluating long-term stability
- obtain more strength data, particularly at temperature
- evaluate seals using PNNL test bed

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Thermochemically stable sealing glasses for solid oxide fuel cells

Richard Brow, Signo T. Reis and Teng Zhang

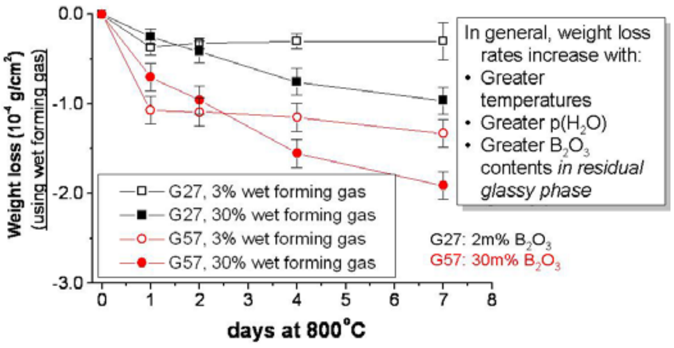
Materials Science & Engineering Department -
The Graduate Center for Materials Research
University of Missouri-Rolla
Rolla, MO 65409

U.S. Department of Energy's National Energy Technology
Laboratory (NETL) 8th Annual SECA Workshop
San Antonio, TX, August 7-9, 2007

Summary

- Borate species are most volatile at 800°C in dry oxidizing and wet reducing environments.
  - Silica-rich surfaces form, >50 nm
- Chromate formation at 800°C in air appears to be reduced by the presence of ZnO in the sealing glass.
  - $ZnCr_2O_4$ formation may compete with the chromate reaction
- Glass crystallization rates increase with decreased particle sizes
  - Competition with viscous sintering to create dense seals
- Seals made with thermo-mechanically stable glass-ceramics survive thermal cycles between 800°C and room temperature
  - Ceramic (YSZ or Ni-YSZ) fails after 30-60 cycles.

'Bulk' glasses lose weight in wet, reducing conditions



In general, weight loss rates increase with:
- Greater temperatures
- Greater $p(H_2O)$
- Greater B_2O_3 contents *in residual glassy phase*

Oxide volatilization was studied by thermochemical analyses

Thermochemical equilibrium models of oxide phase diagrams
- Consider transition free energies
- JANAF data sets for all oxide glass constituents
- Varied $p(O_2)$ or $p(H_2O)$
  - Model SOFC operational conditions
  - Construct volatility diagram under SOFC operational conditions

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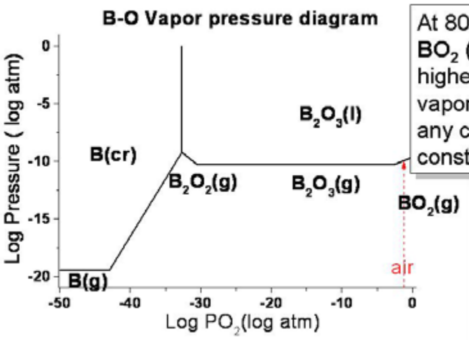
Oxide volatilization was studied by thermochemical analyses

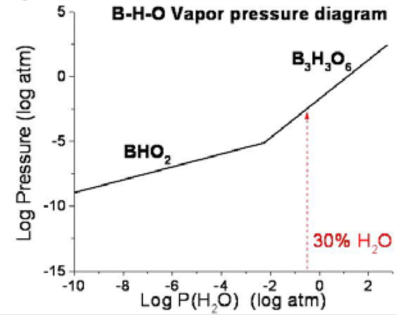


At 800°C in dry air, **BO_2 (g)** has the highest equilibrium vapor pressure for any common glass constituent

Vapor Species	log P, atm.
BO_2	-9.8
ZnO	-10.5
SiO_2	-19.1
SrO	-19.4

Oxide volatilization was studied by thermochemical analyses

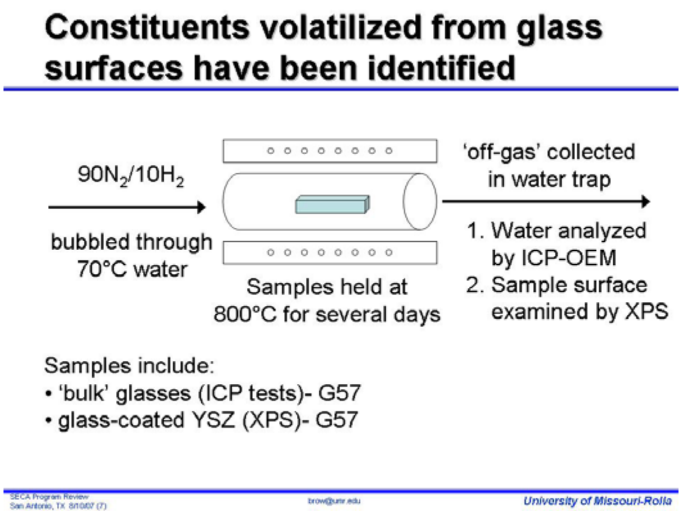
$P(O_2)$ fixed at 10^{-16} atm (forming gas)



800°C, wet reducing environments, **$B_3H_3O_6$ (g)** has the greatest equilibrium vapor pressure

Vapor Species	log P, atm.
$B_3H_3O_6$	-2.5
Zn (g)	-2.8
$Ba(OH)_2$	-5.9
Sr(OH)	-9.0
SiO	-17.6

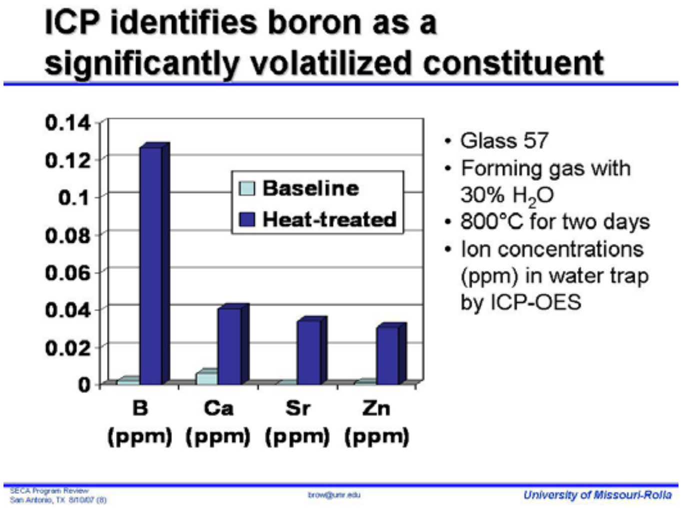
Note: B-, Zn-, Sr- and Ba-species vapor pressures are 10^6-10^{10} times greater under these conditions



Constituents volatilized from glass surfaces have been identified

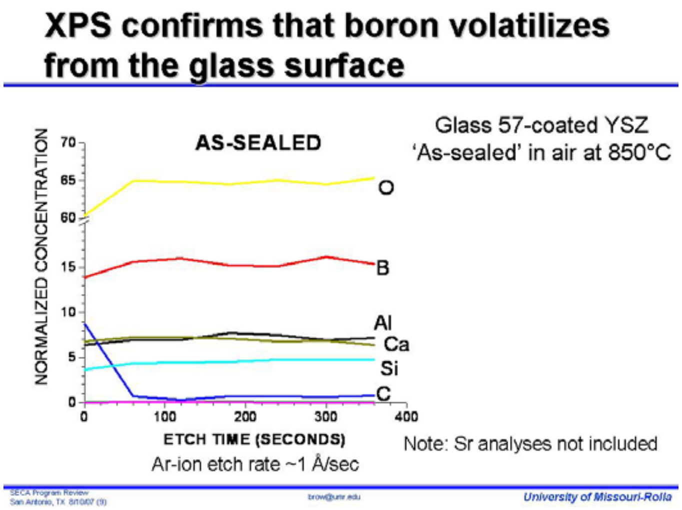
1. Water analyzed by ICP-OEM
2. Sample surface examined by XPS

Samples include:
- 'bulk' glasses (ICP tests)- G57
- glass-coated YSZ (XPS)- G57



ICP identifies boron as a significantly volatilized constituent

- Glass 57
- Forming gas with 30% H_2O
- 800°C for two days
- Ion concentrations (ppm) in water trap by ICP-OES

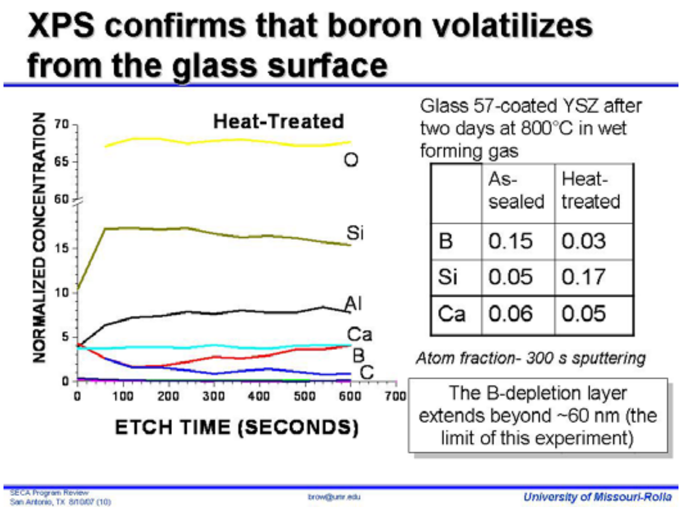


XPS confirms that boron volatilizes from the glass surface

Glass 57-coated YSZ
'As-sealed' in air at 850°C

Ar-ion etch rate ~1 Å/sec

Note: Sr analyses not included



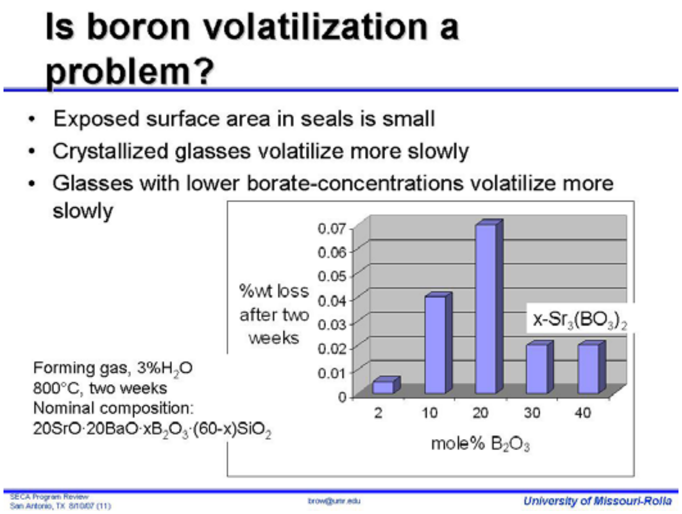
XPS confirms that boron volatilizes from the glass surface

Glass 57-coated YSZ after two days at 800°C in wet forming gas

	As-sealed	Heat-treated
B	0.15	0.03
Si	0.05	0.17
Ca	0.06	0.05

Atom fraction- 300 s sputtering

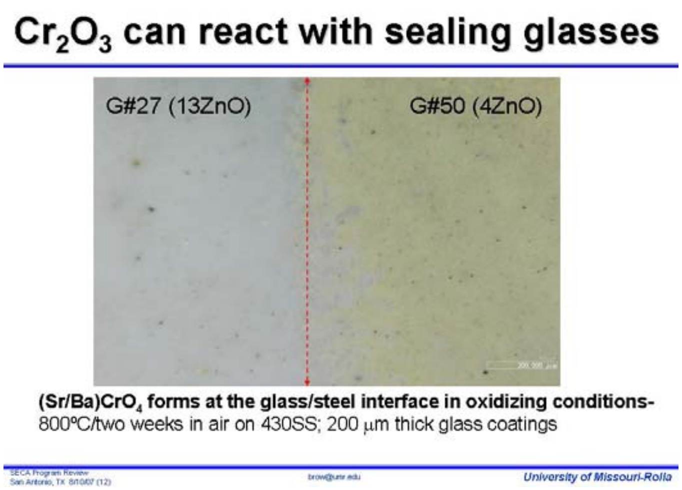
The B-depletion layer extends beyond ~60 nm (the limit of this experiment)



Is boron volatilization a problem?

- Exposed surface area in seals is small
- Crystallized glasses volatilize more slowly
- Glasses with lower borate-concentrations volatilize more slowly

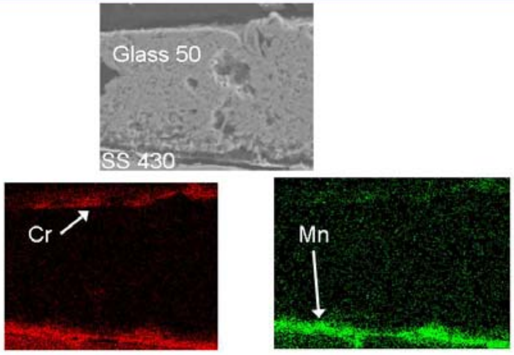
Forming gas, 3%H_2O
800°C, two weeks
Nominal composition:
$20SrO{\cdot}20BaO{\cdot}xB_2O_3{\cdot}(60-x)SiO_2$



Cr_2O_3 can react with sealing glasses

$(Sr/Ba)CrO_4$ forms at the glass/steel interface in oxidizing conditions-
800ºC/two weeks in air on 430SS; 200 μm thick glass coatings

EDS maps show Cr-enriched surfaces

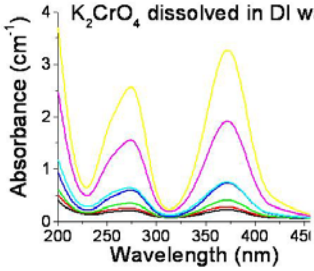


Glass50/430SS, 800°C for 2 months in air

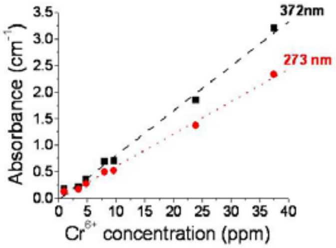
Cr_2O_3-glass reaction kinetics are under investigation

- Cr_2O_3 (10 wt%)-glass (90 wt%) powders were mixed, then reacted in air for various times and temperatures
- Reacted samples dissolved in DI water
- Cr-concentrations in solution determined by ICP-OEM, Cr^{6+} determined by optical spectrometry

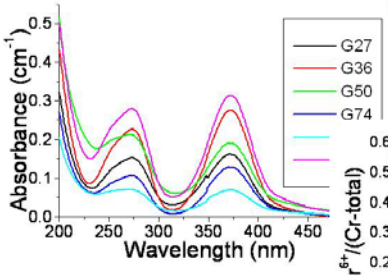
Cr^{6+} concentrations in solution are determined by UV/VIS spectrometry



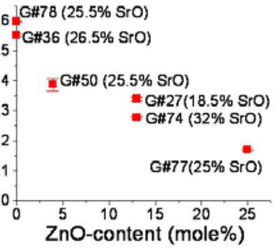
Cr concentration measured by ICP-OEM.



The chromate reaction rate appears to depend on glass composition



- Glass/Cr_2O_3 reaction couples
  - 820°C/24 hours in air
  - 10 mg sample dissolved in 100 ml DI water



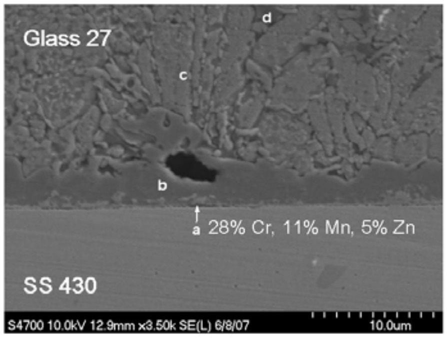
Increasing the ZnO-content *appears* to reduce the chromate formation rate.

Reaction free energies provide useful information

Reaction 1: $RO + Cr_2O_3 \rightarrow RCr_2O_4$
Reaction 2: $RO + 1/2Cr_2O_3 + 3/2O_2 \rightarrow RCrO_4$
Free energies per mole reactant at 800°C

	Reaction 1	Reaction 2
MgO	-27.2 kJ/mole	30.5 kJ/mole
SrO	n/a	-156.0 kJ/mole
BaO	n/a	-218.2 kJ/mole
ZnO	-58.2 kJ/mole	109.3 kJ/mole

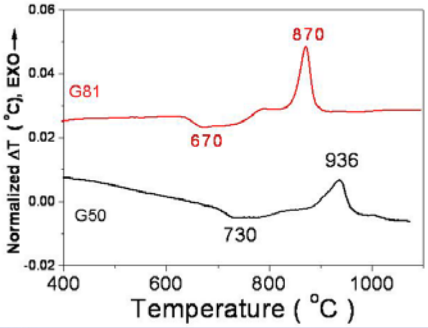
Cr/Mn-rich phases form at glass/metal interfaces



G27/430SS at 800°C for 2 months in air

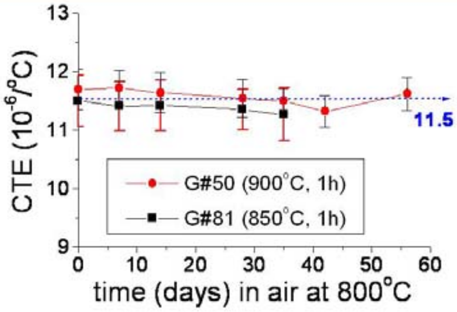
We continue to evaluate new sealing compositions

What effect does Mn^{2+} have on glass properties? (Similar ion properties to Zn^{2+}, possibly beneficial interfacial reactions.)

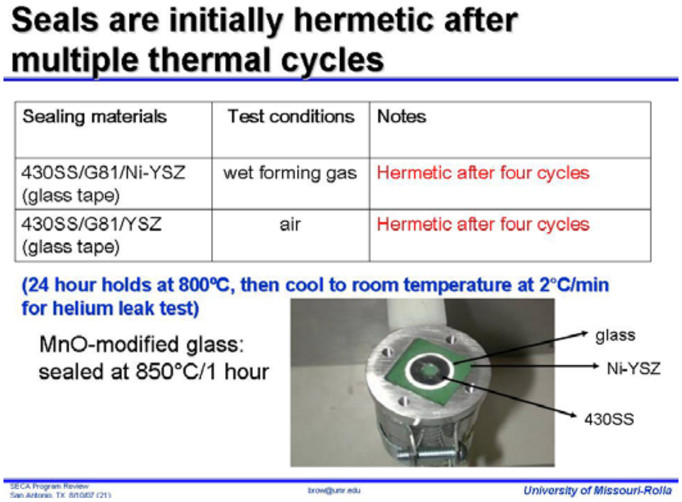


Removing TiO_2 and adding MnO and B_2O_3 to G50 reduces T_g.

New sealing compositions are thermally stable



Electrical properties are presently being evaluated

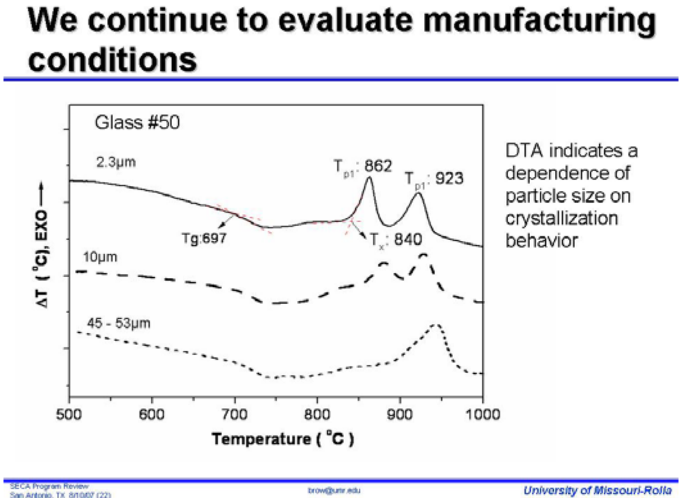


Seals are initially hermetic after multiple thermal cycles

Sealing materials	Test conditions	Notes
430SS/G81/Ni-YSZ (glass tape)	wet forming gas	Hermetic after four cycles
430SS/G81/YSZ (glass tape)	air	Hermetic after four cycles

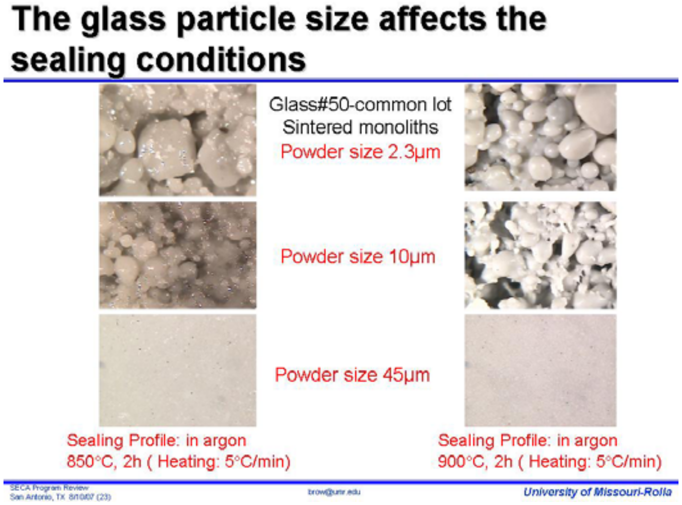
(24 hour holds at 800°C, then cool to room temperature at 2°C/min for helium leak test)

MnO-modified glass:
sealed at 850°C/1 hour



We continue to evaluate manufacturing conditions

DTA indicates a dependence of particle size on crystallization behavior



The glass particle size affects the sealing conditions

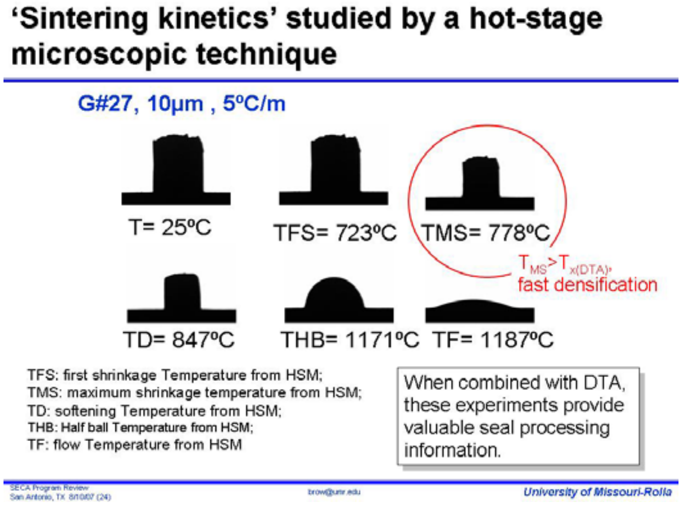
Glass#50-common lot
Sintered monoliths
Powder size 2.3μm

Powder size 10μm

Powder size 45μm

Sealing Profile: in argon
850°C, 2h (Heating: 5°C/min)

Sealing Profile: in argon
900°C, 2h (Heating: 5°C/min)

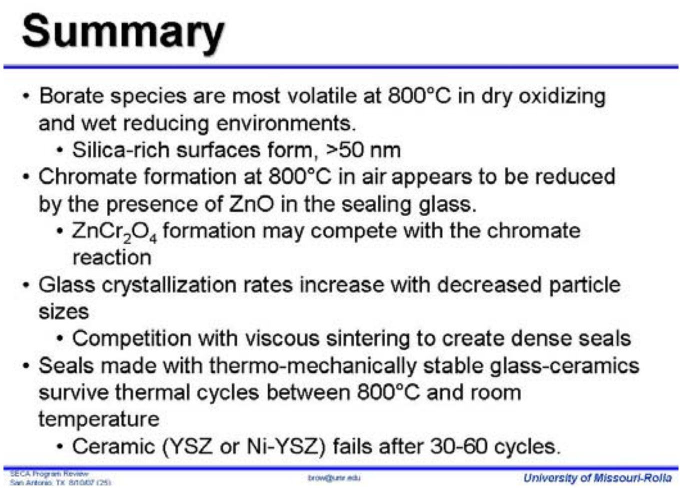


'Sintering kinetics' studied by a hot-stage microscopic technique

G#27, 10μm , 5°C/m

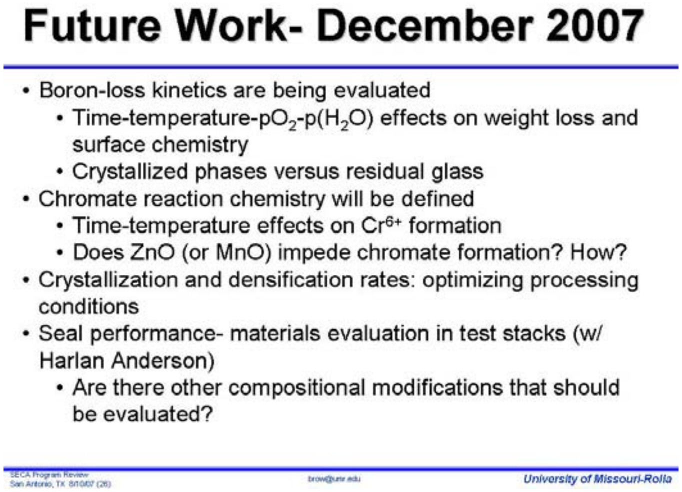
TFS: first shrinkage Temperature from HSM;
TMS: maximum shrinkage temperature from HSM;
TD: softening Temperature from HSM;
THB: Half ball Temperature from HSM;
TF: flow Temperature from HSM

When combined with DTA, these experiments provide valuable seal processing information.



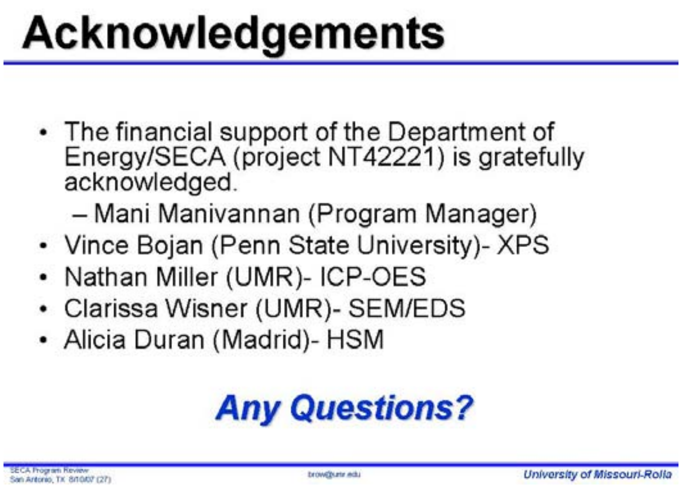
Summary

- Borate species are most volatile at 800°C in dry oxidizing and wet reducing environments.
  - Silica-rich surfaces form, >50 nm
- Chromate formation at 800°C in air appears to be reduced by the presence of ZnO in the sealing glass.
  - $ZnCr_2O_4$ formation may compete with the chromate reaction
- Glass crystallization rates increase with decreased particle sizes
  - Competition with viscous sintering to create dense seals
- Seals made with thermo-mechanically stable glass-ceramics survive thermal cycles between 800°C and room temperature
  - Ceramic (YSZ or Ni-YSZ) fails after 30-60 cycles.



Future Work- December 2007

- Boron-loss kinetics are being evaluated
  - Time-temperature-pO_2-$p(H_2O)$ effects on weight loss and surface chemistry
  - Crystallized phases versus residual glass
- Chromate reaction chemistry will be defined
  - Time-temperature effects on Cr^{6+} formation
  - Does ZnO (or MnO) impede chromate formation? How?
- Crystallization and densification rates: optimizing processing conditions
- Seal performance- materials evaluation in test stacks (w/ Harlan Anderson)
  - Are there other compositional modifications that should be evaluated?



Acknowledgements

- The financial support of the Department of Energy/SECA (project NT42221) is gratefully acknowledged.
  - Mani Manivannan (Program Manager)
- Vince Bojan (Penn State University)- XPS
- Nathan Miller (UMR)- ICP-OES
- Clarissa Wisner (UMR)- SEM/EDS
- Alicia Duran (Madrid)- HSM

Any Questions?

High Temperature Glass Seal

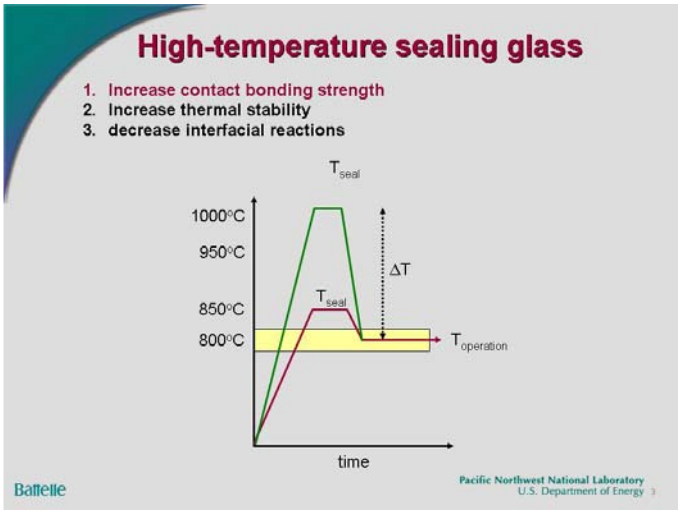
Y-S Chou, J.W. Stevenson, X. Li, G. Yang, and P. Singh
K2-44, Materials Division
Pacific Northwest National Laboratory

Funded under the SECA Core Technology Program
through US Department of Energy's
National Energy Technology Laboratory

August 7-9, 2007, San Antonio, Texas

FY07 Accomplishment

- Completed seal strength evaluation of high-temperature glass. Evaluated pre-oxidation, aging, coating, and environmental effects on strength.
- Without coating, strength would degrade if a thick Cr_2O_3 oxide layer present or aged in air. No strength reduction if aged in reducing gas. Cause for strength degradation was $SrCrO_4$ formation.
- Alumina coating is effective in blocking Cr; however, the deposition process needs to be optimized to minimize overdose.
- Spinel coating showed best results with minimum strength reduction even aging in air.
- Tested conventional and high-temperature sealing glasses in SOFC environment and 0.7 V DC loading. Conventional glass showed severe Fe diffusion and rapid increase in conductivity (830°C/~80hr), while high-temperature glass showed excellent electrical stability over ~1200hr at 850°C.



High-temperature sealing glass

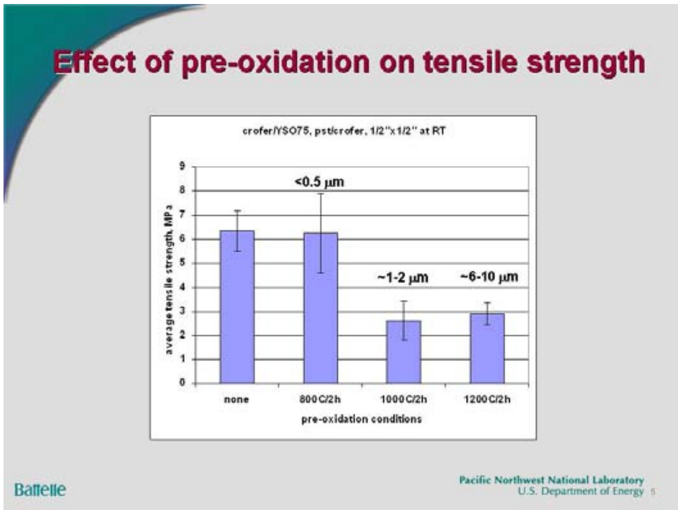
1. Increase contact bonding strength
2. Increase thermal stability
3. decrease interfacial reactions

Mechanical strength evaluation

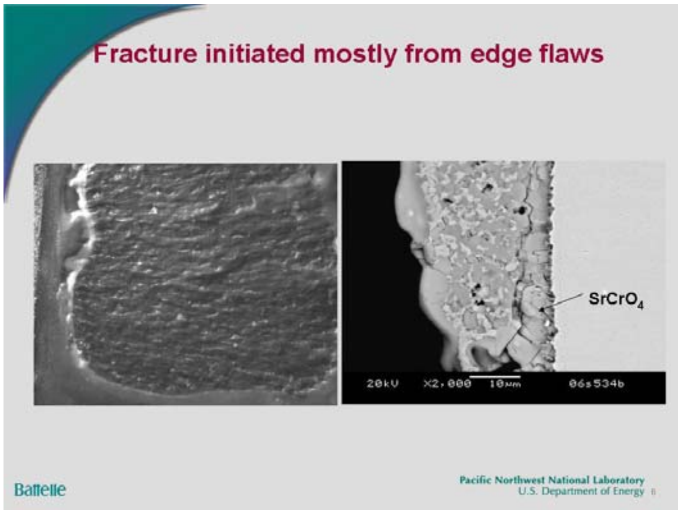
1. Effect of pre-oxidation: Cr_2O_3 layer thickness
2. Effect of different protective coating: Al_2O_3, $(Mn,Co)_3O_4$
3. Effect of environment: oxidizing, reducing
4. Accelerated condition:

◆ 850°C/500h in air

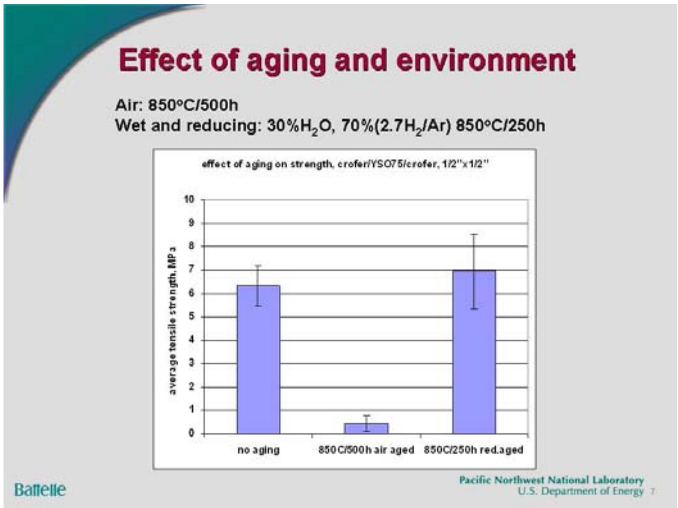
◆ 850°C/250h in 30%H_2O, 70%(2.7%H_2/Ar)



Effect of pre-oxidation on tensile strength

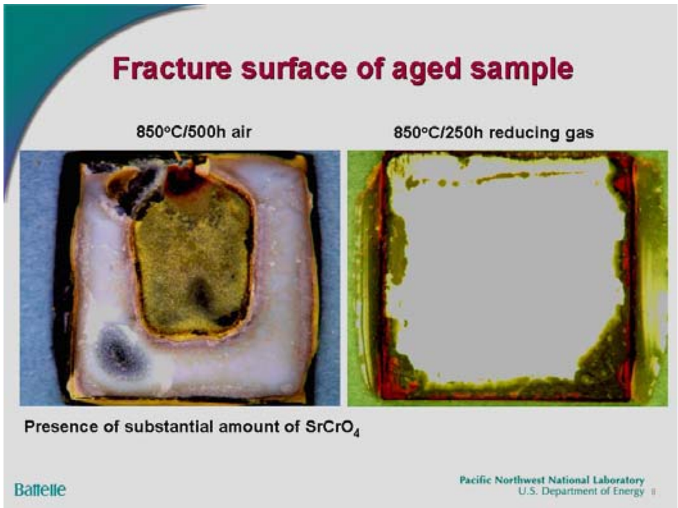


Fracture initiated mostly from edge flaws



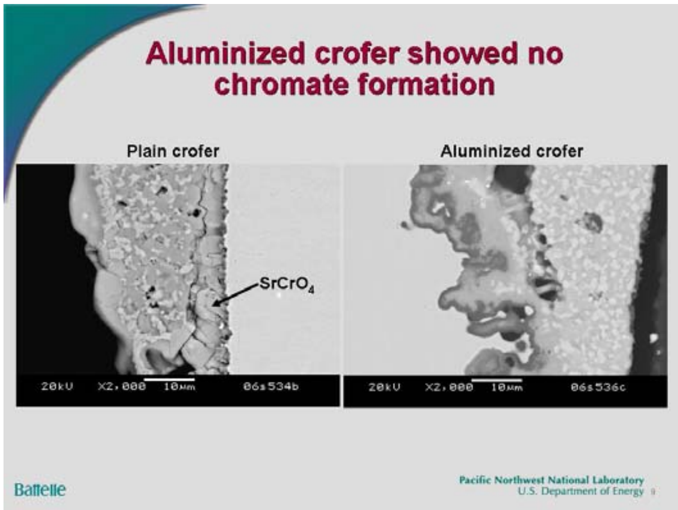
Effect of aging and environment

Air: 850°C/500h
Wet and reducing: 30%H_2O, 70%(2.7H_2/Ar) 850°C/250h

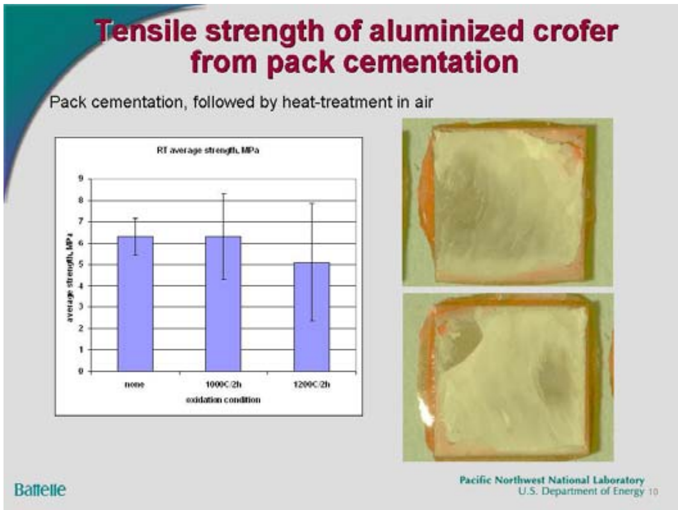


Fracture surface of aged sample

Presence of substantial amount of $SrCrO_4$

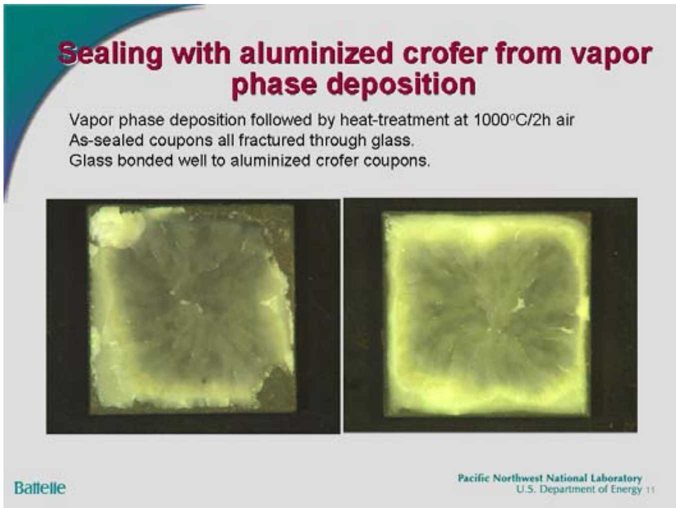


Aluminized crofer showed no chromate formation



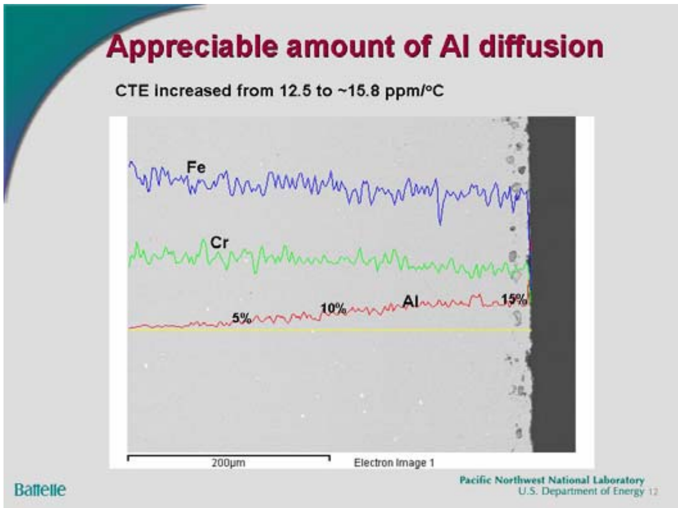
Tensile strength of aluminized crofer from pack cementation

Pack cementation, followed by heat-treatment in air



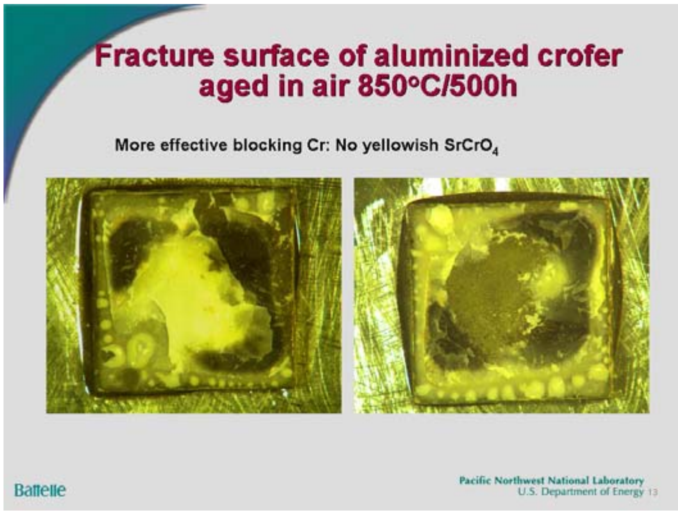
Sealing with aluminized crofer from vapor phase deposition

Vapor phase deposition followed by heat-treatment at 1000°C/2h air
As-sealed coupons all fractured through glass.
Glass bonded well to aluminized crofer coupons.



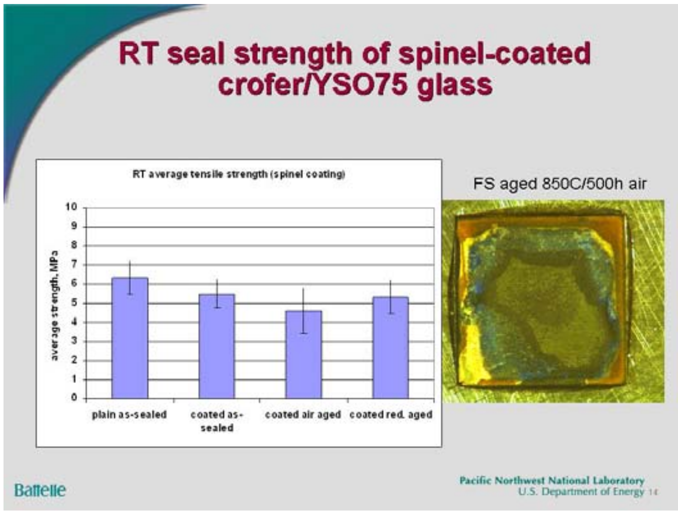
Appreciable amount of Al diffusion

CTE increased from 12.5 to ~15.8 ppm/°C



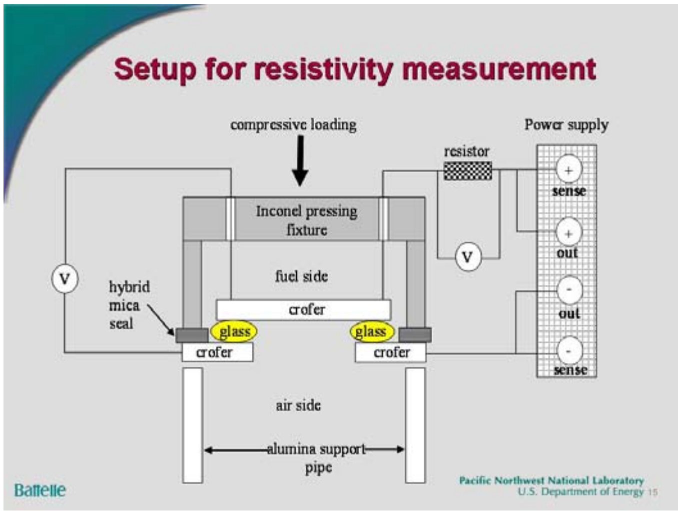
Fracture surface of aluminized crofer aged in air 850°C/500h

More effective blocking Cr: No yellowish $SrCrO_4$

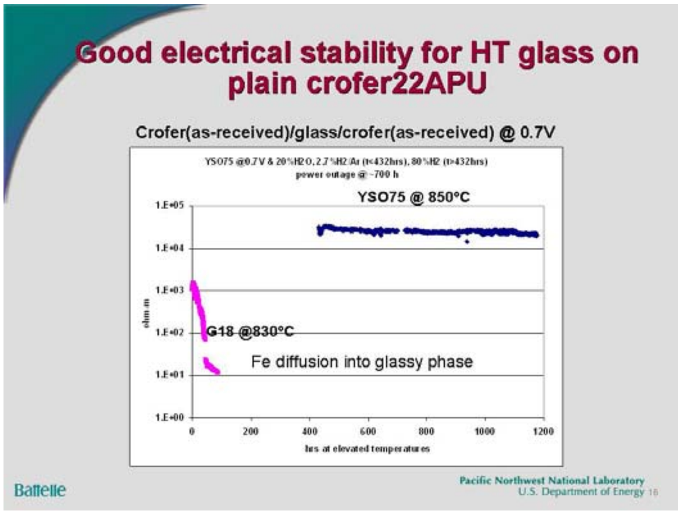


RT seal strength of spinel-coated crofer/YSO75 glass

FS aged 850C/500h air

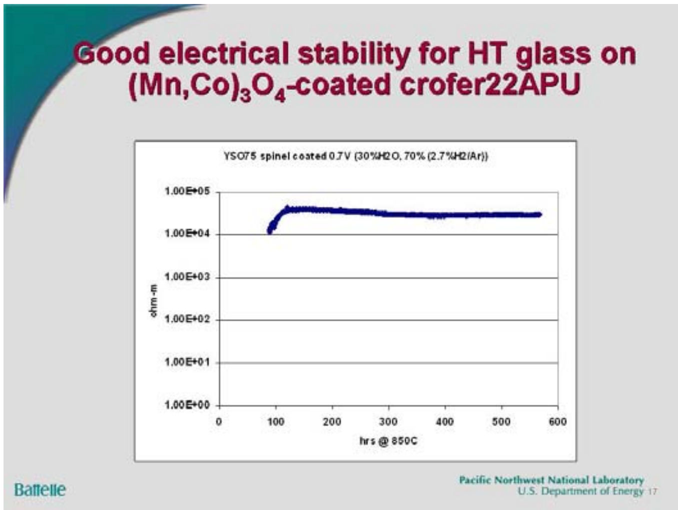


Setup for resistivity measurement

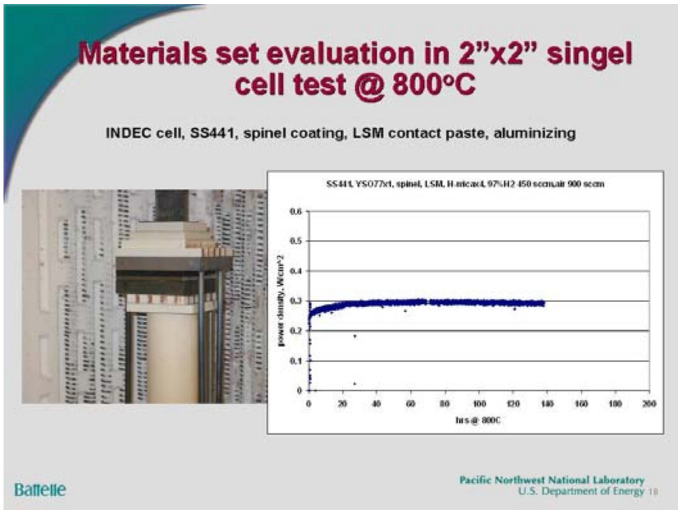


Good electrical stability for HT glass on plain crofer22APU

Crofer(as-received)/glass/crofer(as-received) @ 0.7V

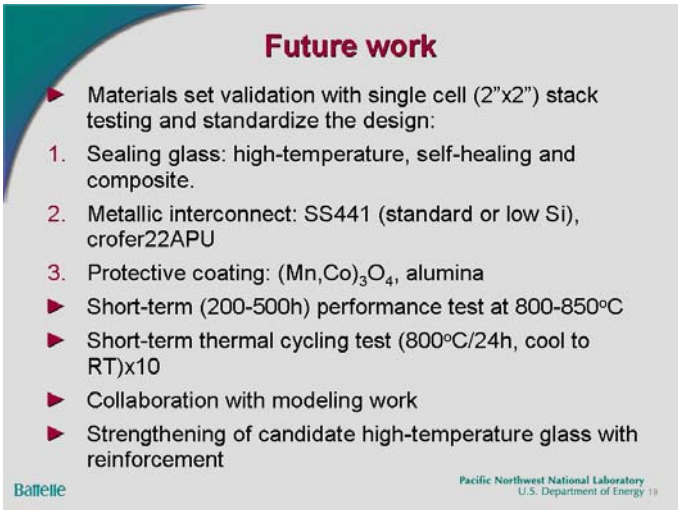


Good electrical stability for HT glass on $(Mn,Co)_3O_4$-coated crofer22APU



Materials set evaluation in 2”x2” singel cell test @ 800°C

INDEC cell, SS441, spinel coating, LSM contact paste, aluminizing



Future work

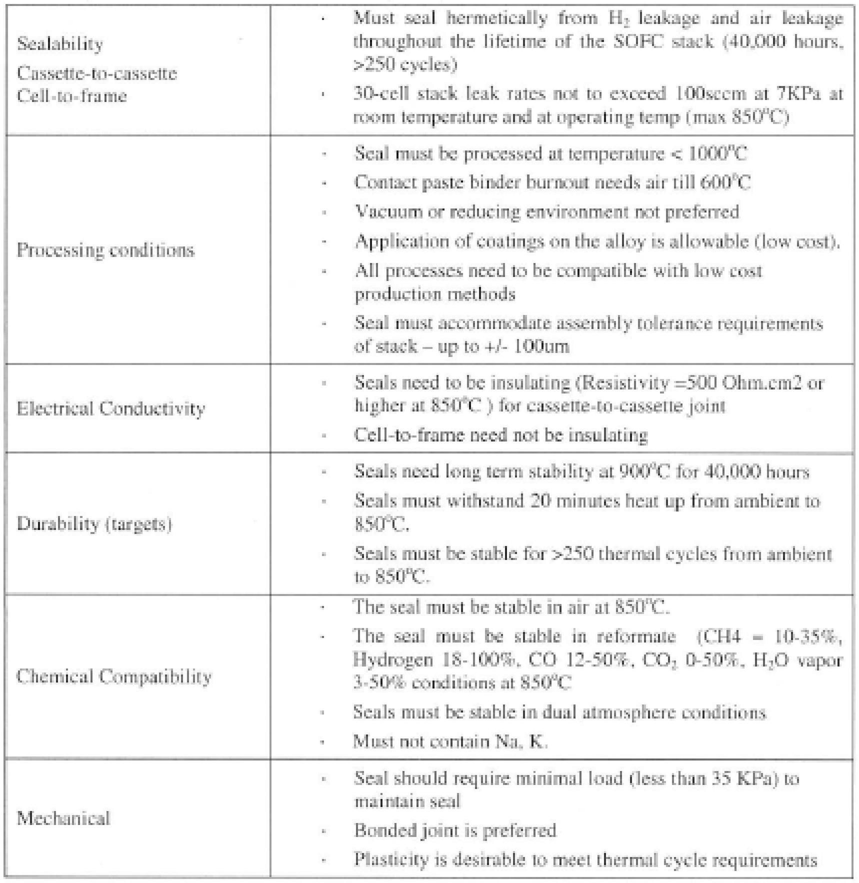
- Materials set validation with single cell (2”x2”) stack testing and standardize the design:

1. Sealing glass: high-temperature, self-healing and composite.
2. Metallic interconnect: SS441 (standard or low Si), crofer22APU
3. Protective coating: $(Mn,Co)_3O_4$, alumina

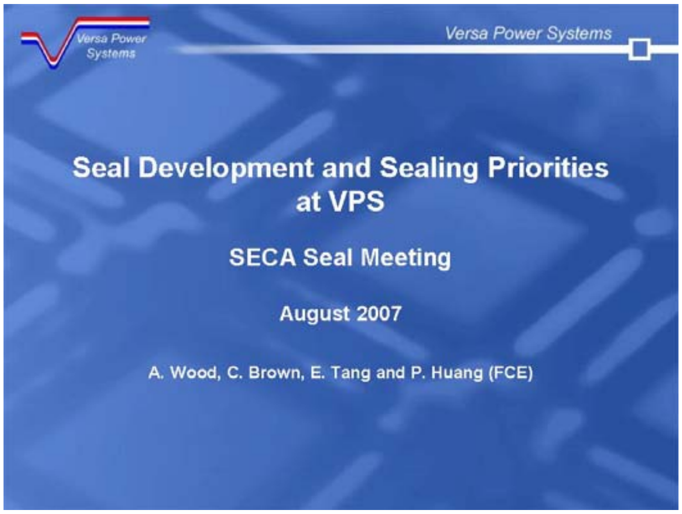
- Short-term (200-500h) performance test at 800-850°C
- Short-term thermal cycling test (800°C/24h, cool to RT)x10
- Collaboration with modeling work
- Strengthening of candidate high-temperature glass with reinforcement

INDUSTRY INPUT

Seal Requirements for a solid oxide fuel cell (SOFC) stack.



Sealability Cassette-to-cassette Cell-to-frame	· Must seal hermetically from H_2 leakage and air leakage throughout the lifetime of the SOFC stack (40,000 hours, >250 cycles) · 30-cell stack leak rates not to exceed 100sccm at 7KPa at room temperature and at operating temp (max 850°C)
Processing conditions	· Seal must be processed at temperature < 1000°C · Contact paste binder burnout needs air till 600°C · Vacuum or reducing environment not preferred · Application of coatings on the alloy is allowable (low cost). · All processes need to be compatible with low cost production methods · Seal must accommodate assembly tolerance requirements of stack – up to +/- 100um
Electrical Conductivity	· Seals need to be insulating (Resistivity =500 Ohm.cm2 or higher at 850°C) for cassette-to-cassette joint · Cell-to-frame need not be insulating
Durability (targets)	· Seals need long term stability at 900°C for 40,000 hours · Seals must withstand 20 minutes heat up from ambient to 850°C. · Seals must be stable for >250 thermal cycles from ambient to 850°C.
Chemical Compatibility	· The seal must be stable in air at 850°C. · The seal must be stable in reformate (CH4 = 10-35%, Hydrogen 18-100%, CO 12-50%, CO_2 0-50%, H_2O vapor 3-50% conditions at 850°C · Seals must be stable in dual atmosphere conditions · Must not contain Na, K.
Mechanical	· Seal should require minimal load (less than 35 KPa) to maintain seal · Bonded joint is preferred · Plasticity is desirable to meet thermal cycle requirements

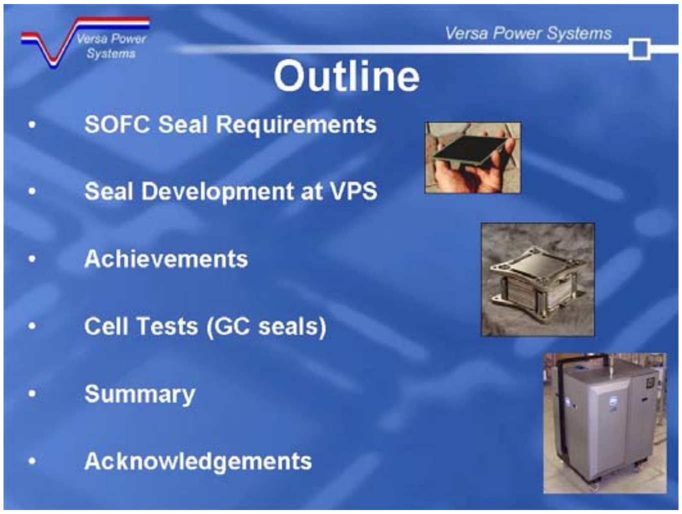


Seal Development and Sealing Priorities at VPS

SECA Seal Meeting

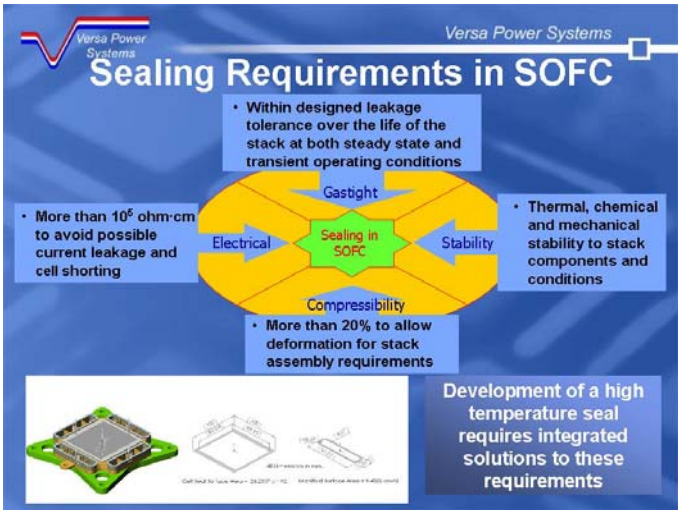
August 2007

A. Wood, C. Brown, E. Tang and P. Huang (FCE)



Outline

- SOFC Seal Requirements
- Seal Development at VPS
- Achievements
- Cell Tests (GC seals)
- Summary
- Acknowledgements

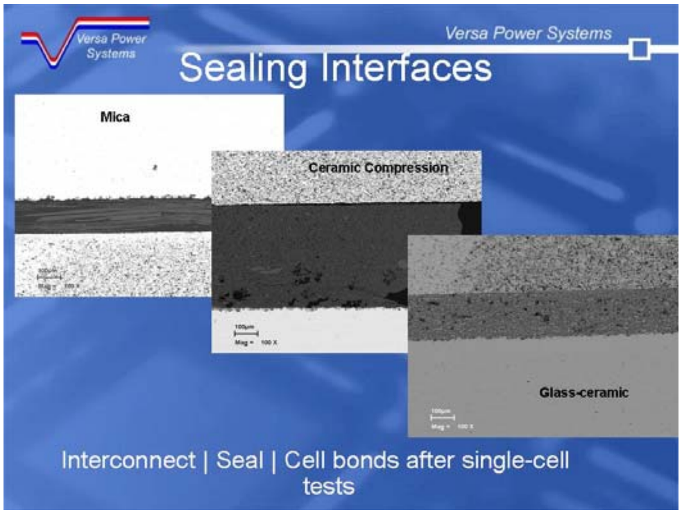


Sealing Requirements in SOFC

- Within designed leakage tolerance over the life of the stack at both steady state and transient operating conditions
- More than 10^5 ohm·cm to avoid possible current leakage and cell shorting
- Thermal, chemical and mechanical stability to stack components and conditions
- More than 20% to allow deformation for stack assembly requirements

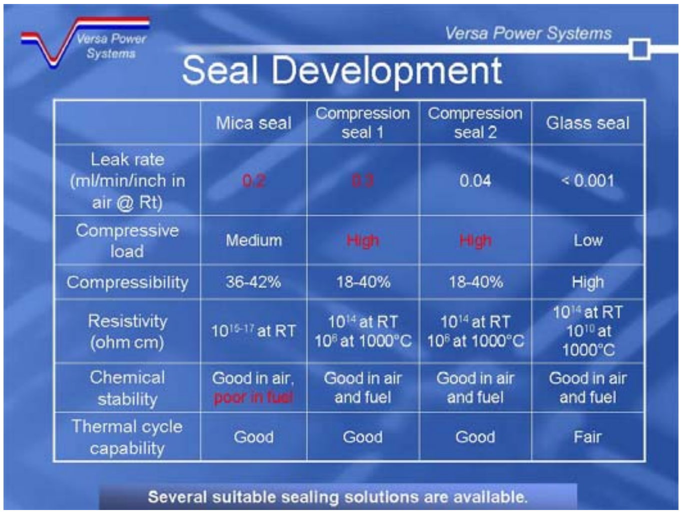
Development of a high temperature seal requires integrated solutions to these requirements

SOFC Seal Major Developments



Sealing Interfaces

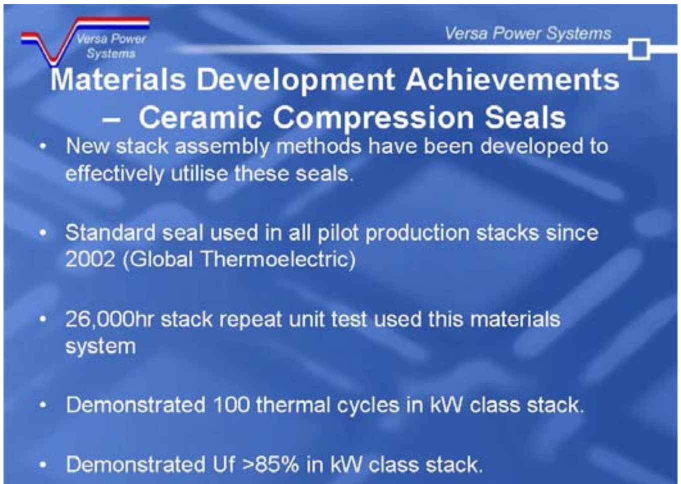
Interconnect | Seal | Cell bonds after single-cell tests



Seal Development

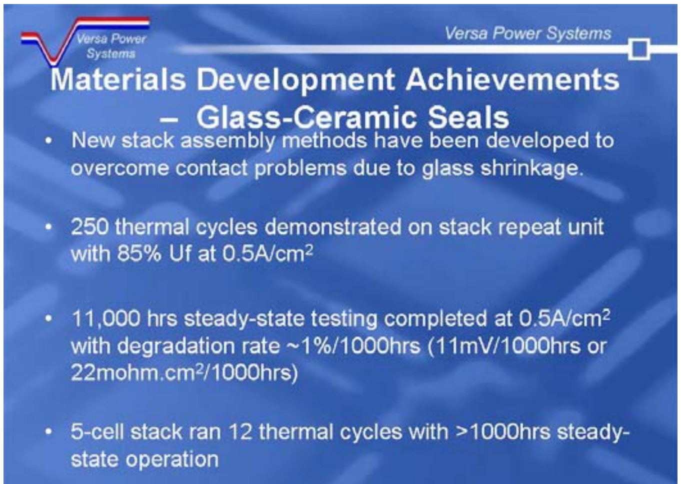
	Mica seal	Compression seal 1	Compression seal 2	Glass seal
Leak rate (ml/min/inch in air @ Rt)	0.2	0.3	0.04	< 0.001
Compressive load	Medium	High	High	Low
Compressibility	36-42%	18-40%	18-40%	High
Resistivity (ohm cm)	10^{15-17} at RT	10^{14} at RT 10^{6} at 1000°C	10^{14} at RT 10^{6} at 1000°C	10^{14} at RT 10^{10} at 1000°C
Chemical stability	Good in air, poor in fuel	Good in air and fuel	Good in air and fuel	Good in air and fuel
Thermal cycle capability	Good	Good	Good	Fair

Several suitable sealing solutions are available.



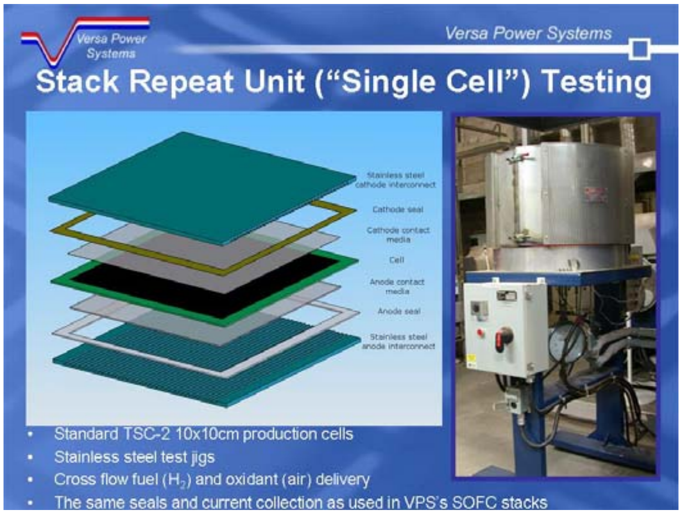
Materials Development Achievements – Ceramic Compression Seals

- New stack assembly methods have been developed to effectively utilise these seals.
- Standard seal used in all pilot production stacks since 2002 (Global Thermoelectric)
- 26,000hr stack repeat unit test used this materials system
- Demonstrated 100 thermal cycles in kW class stack.
- Demonstrated Uf >85% in kW class stack.



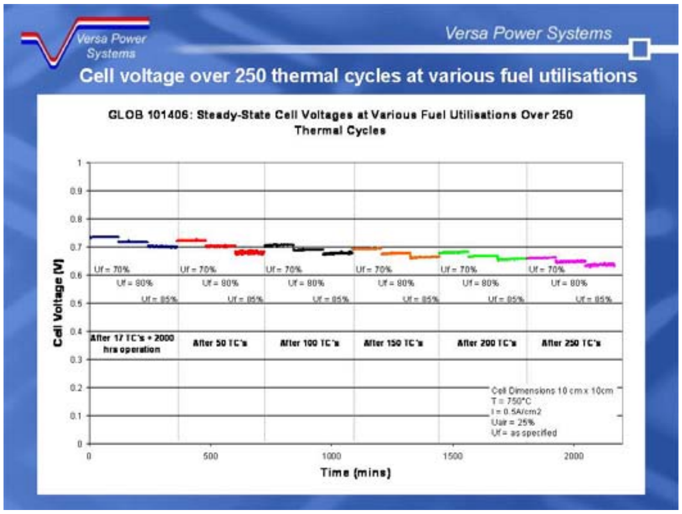
Materials Development Achievements – Glass-Ceramic Seals

- New stack assembly methods have been developed to overcome contact problems due to glass shrinkage.
- 250 thermal cycles demonstrated on stack repeat unit with 85% Uf at 0.5A/cm^2
- 11,000 hrs steady-state testing completed at 0.5A/cm^2 with degradation rate ~1%/1000hrs (11mV/1000hrs or 22mohm.cm^2/1000hrs)
- 5-cell stack ran 12 thermal cycles with >1000hrs steady-state operation



Stack Repeat Unit (“Single Cell”) Testing

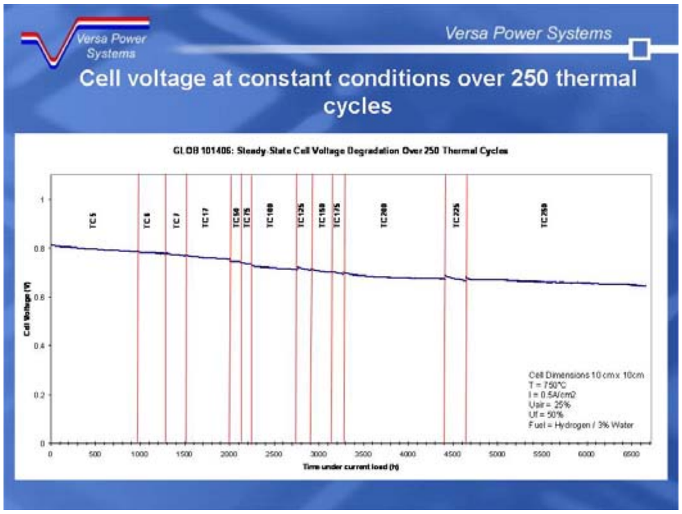
- Standard TSC-2 10x10cm production cells
- Stainless steel test jigs
- Cross flow fuel (H_2) and oxidant (air) delivery
- The same seals and current collection as used in VPS's SOFC stacks



Cell voltage over 250 thermal cycles at various fuel utilisations

GLOB 101406: Steady-State Cell Voltages at Various Fuel Utilisations Over 250 Thermal Cycles

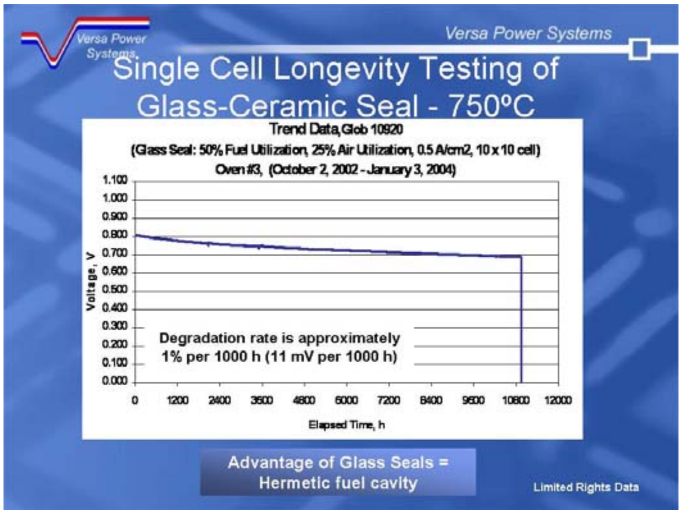
Cell Dimensions 10 cm x 10cm
T = 750°C
I = 0.5A/cm2
Uair = 25%
Uf = as specified



Cell voltage at constant conditions over 250 thermal cycles

GLOB 101406: Steady-State Cell Voltage Degradation Over 250 Thermal Cycles

Cell Dimensions 10 cm x 10cm
T = 750°C
I = 0.5A/cm2
Uair = 25%
Uf = 50%
Fuel = Hydrogen / 3% Water



Single Cell Longevity Testing of Glass-Ceramic Seal - 750°C

Trend Data, Glob 10920

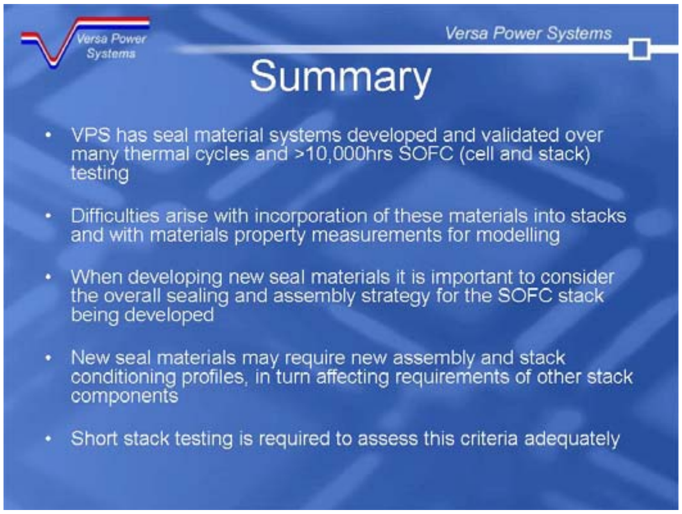
(Glass Seal: 50% Fuel Utilization, 25% Air Utilization, 0.5 A/cm2, 10 x 10 cell)

Oven #3, (October 2, 2002 - January 3, 2004)

Degradation rate is approximately 1% per 1000 h (11 mV per 1000 h)

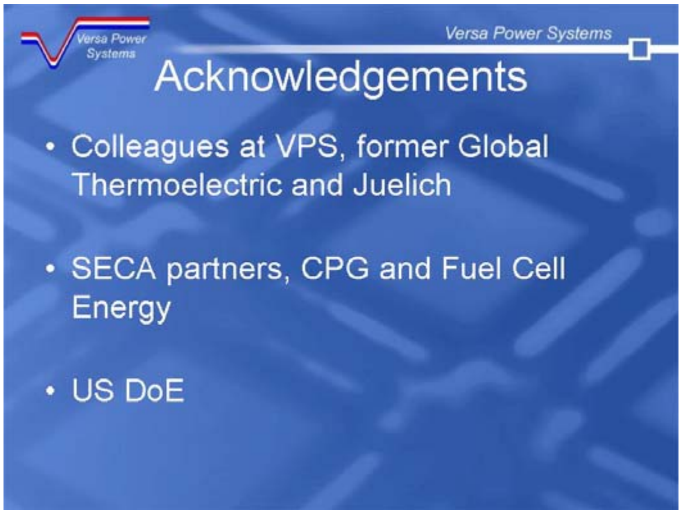
Advantage of Glass Seals = Hermetic fuel cavity

Limited Rights Data



Summary

- VPS has seal material systems developed and validated over many thermal cycles and >10,000hrs SOFC (cell and stack) testing
- Difficulties arise with incorporation of these materials into stacks and with materials property measurements for modelling
- When developing new seal materials it is important to consider the overall sealing and assembly strategy for the SOFC stack being developed
- New seal materials may require new assembly and stack conditioning profiles, in turn affecting requirements of other stack components
- Short stack testing is required to assess this criteria adequately



Acknowledgements

- Colleagues at VPS, former Global Thermoelectric and Juelich
- SECA partners, CPG and Fuel Cell Energy
- US DoE

Seal Workshop

San Antonio
10 August 2007

S. Elangovan
Ceramatec, Inc.

ceramatec
ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

High Temperature Seal

- Biggest challenge for planar SOFC
  - Remains as a key component for the success of planar SOFC for over 20 years

---

MCFC

- DOE, EPRI, GRI Workshop, Boston, 1988
  - Seal is a challenge
  - Internal vs External Manifold?
  - Pressurized Operation?
- 1995
  - 2 MW Santa Clara Demo FCE (ERC)
  - What can we learn from MCFC experience?

Requirements For Seal

- Determine 'allowable limits' rather than performance criteria
  - How good does it have to be?
  - How much leak can we tolerate?
  - How much differential pressure does it need to hold?
  - What seal geometry?

Seal Concept

- Have gone through a variety of design
  - Sliding Seal
  - Compressive Seal
  - Compliant Seal
  - Rigid Seal
- Mainly depends on stack design

Seal Material

- Depends on seal design and 'allowable limits'
  - Felt
  - Mica
  - Ceramic
  - Cement
  - Metal foil
  - Glass

Seal Material

- What not to use?
- What elements are incompatible with electrodes?
- Do we need to avoid Si at any cost?
- Do we need to avoid Ag?
  - Anecdotal or real problem?
  - Perhaps proprietary??
- What sealing temperature range and what atmosphere are acceptable?

Question

- Are we looking for a single material / design for all SOFC designs and applications?

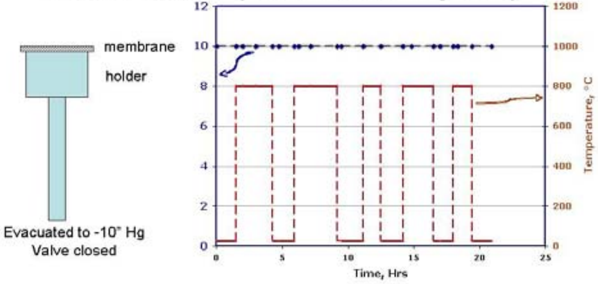
Hot Test Rig (Zirconia on SS Holder)

- As Fabricated

- After Five Thermal cycles to 800°C

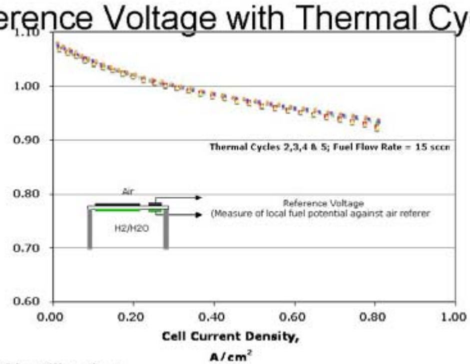
(Pressure test at RT and 800°C)

Seal Test (Thermal Cycle)

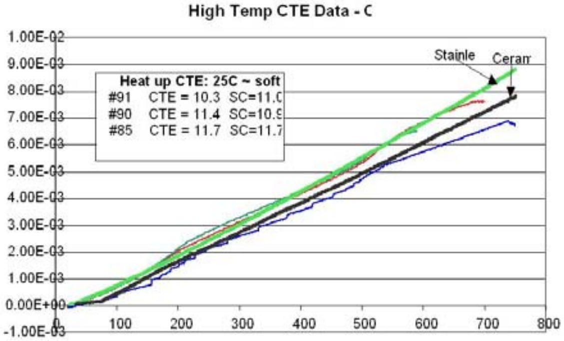


- Pressure decay test at pressure differential (~ 5 psi)
  - Monitored for 1 to 2 hours at RT and 800°C; five thermal cycles
  - Leaked at 7 psi at 850°C, but aging healed the seal

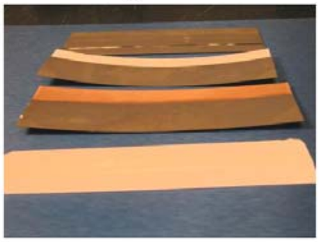
Zirconia Button Cell: Reference Voltage with Thermal Cycles



- > 70% utilization



Sealing of Materials Combinations



- SS - SS
- Zicronia - SS
- Gallate - SS
- Zirconia - Zirconia

- Flat specimens when components have matching CTE (SS-SS & Zirconia-Zirconia)
- How to handle CTE mismatch? graded seal?

Need Consensus on Specification

- Materials Space
- Seal Requirements & wiggle room
- Test Protocol
- Independent Evaluation

SOFC Seals

Nguyen Minh

Observations/Results - General

- No "universal" seals – Very much dependent on cell/stack configuration
- "Short-term" stability
- Failures – very much cell/stack design dependent and seal design dependent
- Stack failures – cell cracks due to leakages developed during operation
- Post-test analysis (leakage location, interactions/migration)

Background/Experience on Seals for SOFCs

- Materials
  - Cements, glasses, glass ceramics, composites, brazes
- Designs/methods
  - Various method and designs (gap filling, clamping, gasket, etc.)
- Stack sizes
  - 1 to 60 cell, 1"x1" to 14" diam.

Recommendations

- Minimize "foreign" materials/species in seals
- Develop designs for lower-temperature seals
- Develop methods of applications/procedures with improved reproducibility/quality control
- Demonstrate long-term stability (+10K hrs)
- Improve materials/designs that allow/tolerate changes and variations in stack component dimensions.

List of Participants:

Name	Affiliation
1. Casey Brown	VPS
2. Richard Brow,	Univ. of Missouri
3. Matt Chou	PNNL
4. Erica Corral	SNL
5. Joel Doyon	FCE
6. S. Elangovan	Ceramatec
7. Randy Gemmen	NETL
8. Karl Haltiner	Delphi
9. Peng Huang	FCE
10. Moe Khaleel	PNNL
11. Edgar Lara-Curzio	ORNL
12. Ron Loehman	SNL
13. A. Manivannan	NETL
14. Nguyen Minh	Consultant
15. Heather Quedenfeld	NETL
16. Steve Shaffer	Delphi
17. Reis Signo	Univ. of Missouri
18. Chuck Sishtla	GTI
19. Prabhakar Singh	PNNL
20. Raj Singh	Univ. Cincinnati
21. Jeff Stevenson	PNNL
22. Wayne Surdoval	NETL
23. Xin Sun	PNNL
24. Eric Tang	VPS
25. Briggs White	NETL
26. Lane Wilson	NETL
27. Tony Wood	VPS / FCE
28. John Yamanis	UTRC

Contacts:

Dr. Ayyakkannu Manivannan,
National Energy technology Laboratory
Morgantown, WV
Email: Ayyakkannu.Manivannan@NETL.DOE.GOV
Phone : (304) 285 2078

Dr. Prabhakar Singh
Pacific Northwest National Laboratory
Richland, WA
Email: prabhakar.singh@pnl.gov
Phone: (509) 375 5945