Development of a Compliant Seal for Planar SOFCs

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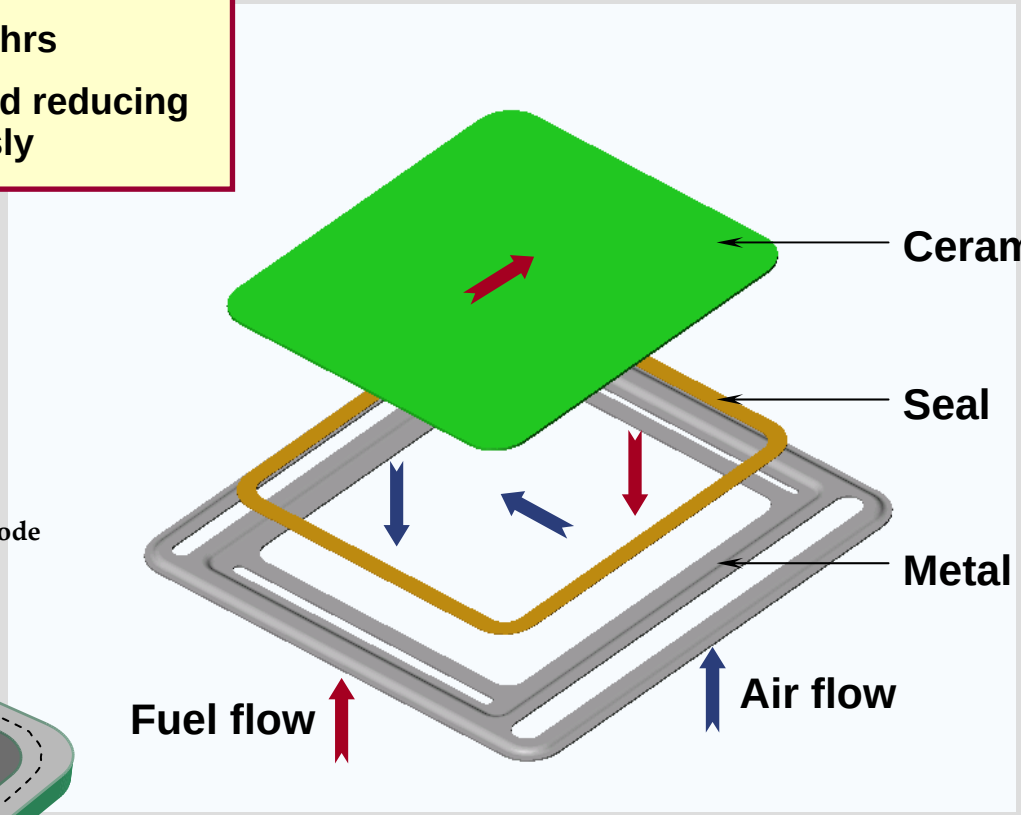
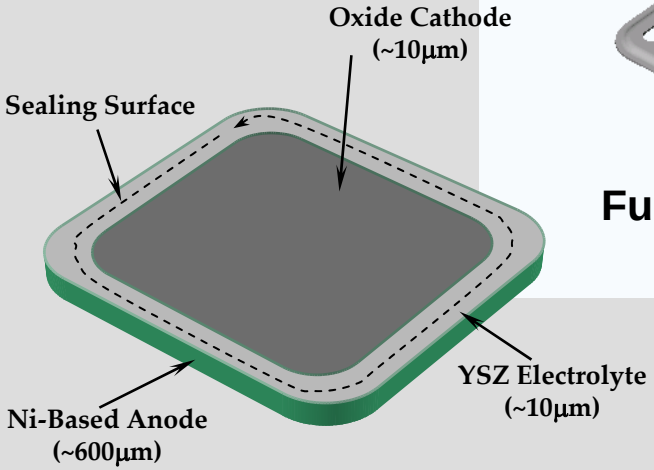
Support: DOE-FE SECA Program

SOFC Sealing

Typical Operating Conditions:

- T = 750°C
- $t_{(at\ 750^{o}C)}$ ~ 10000+ hrs
- Exposed to air and reducing gas simultaneously





Functional Requirements

General Performance

- Hermetic/marginal leak rate
- Resistant to chemical degradation at 650 – 800°C for tens of thousands of hours
  - Air/fuel environment
  - Interactions with substrates
- Resistant to degradation due to thermal cycling/thermal shock

- Electrical insulation
- Mechanical robustness

Designer's Concerns

- Manufacturability
  - Low cost
  - Facile application
  - Acceptable sealing environment/temperature
- Conformable to non-flat/roughened substrate surfaces

- Design flexibility: sealing to Ni-based alloys
- Ruggedness during transport/ operation/maintenance

Required

Desired

Primary Options

Rigid (glass)

- Merits
  - Good initial hermeticity
  - Good bulk stability in the dual atmosphere environment
- Disadvantages/Concerns
  - CTE matching required – limitation on interconnect
  - Concerns with long-term stability with metals (interfacial degradation)
  - Concerns with thermal cycling/shock performance

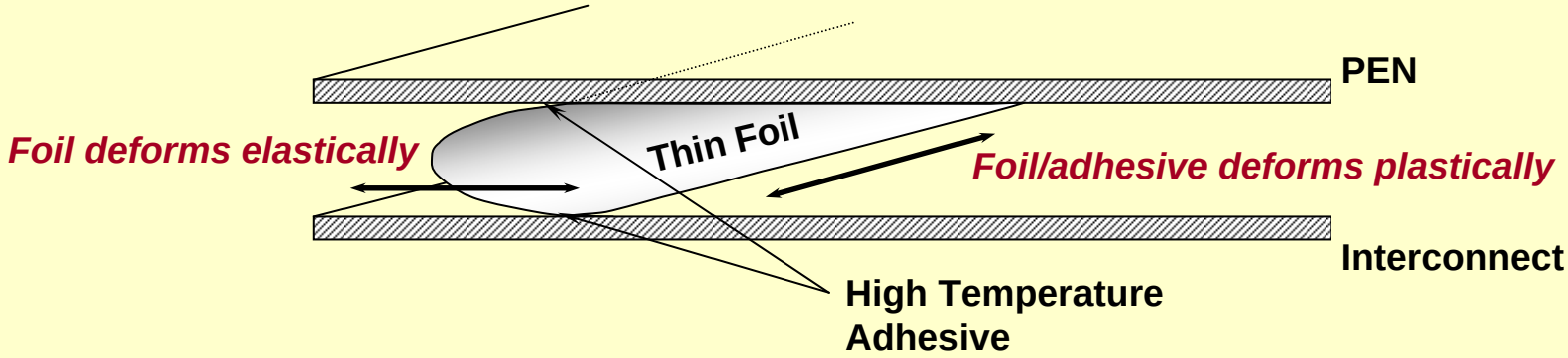
Compressive (mica-based)

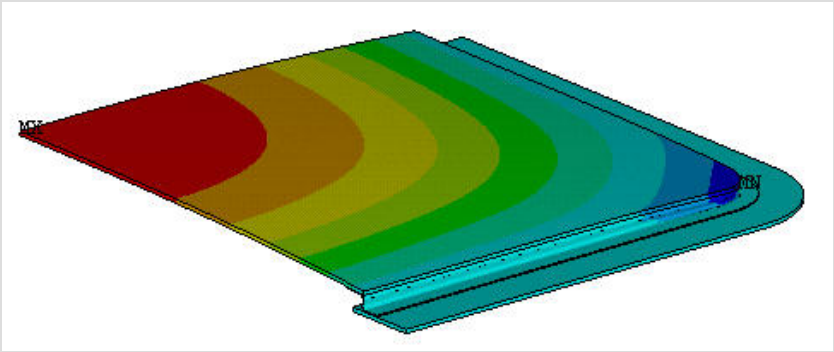
- Merits
  - CTE matching not required
  - Good bulk stability in the dual atmosphere environment
- Disadvantages/Concerns
  - Leaks (loss of efficiency, hot spots – potential for cell degradation)
  - Requires a load frame (adds expense and material/design complexity)

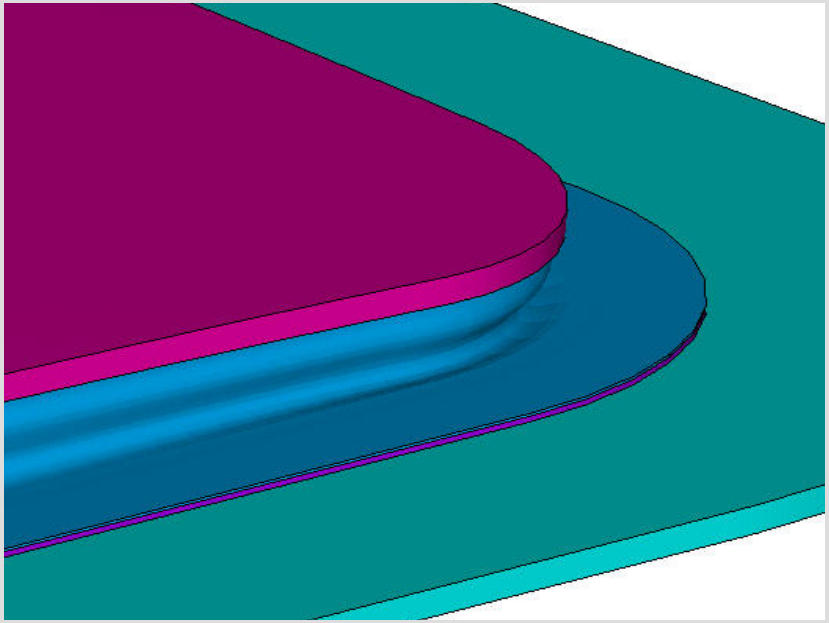
Alternative: Bonded compliant seal

Bonded Compliant Seal Concept

A hermetic elasto-plastic seal that allows independent motion between the two adjacent faying surfaces :



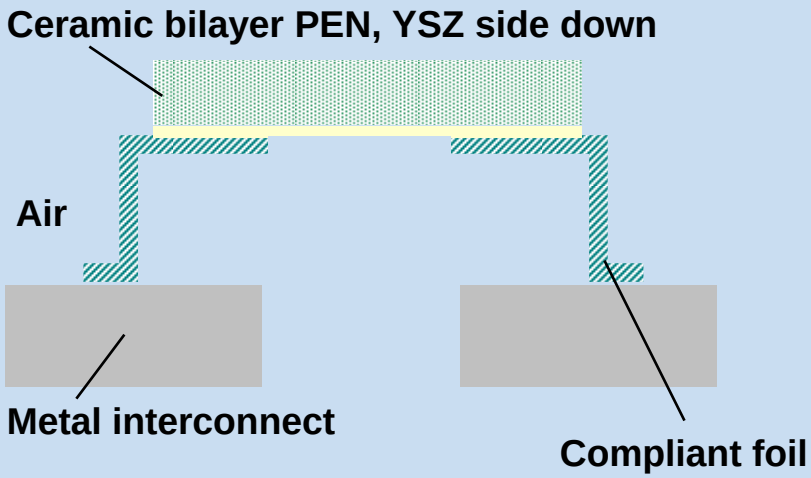




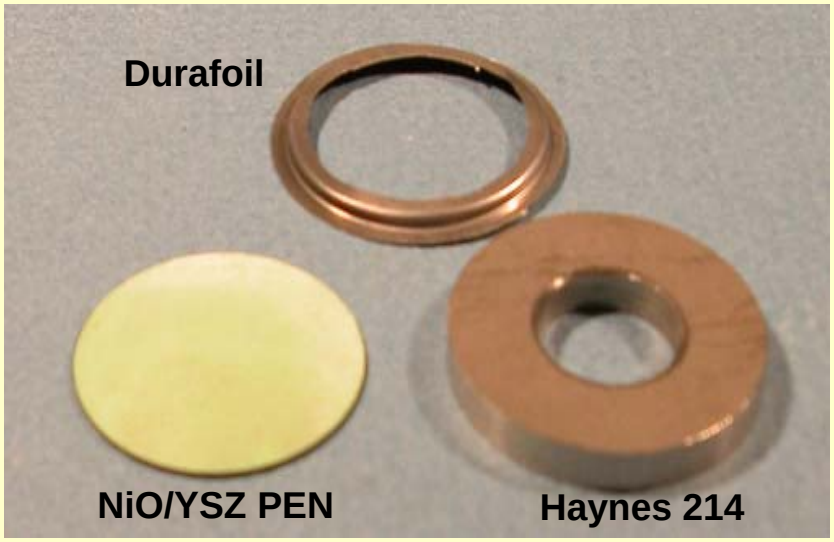
Thermal Cycle Test Specimens

A simple stamped foil geometry was chosen for initial feasibility study. The Durafoil was annealed at 700°C for 10hrs to improve its formability vis-à-vis the as-rolled condition, then stamped in a hand die to the final shape shown below in cross-section.

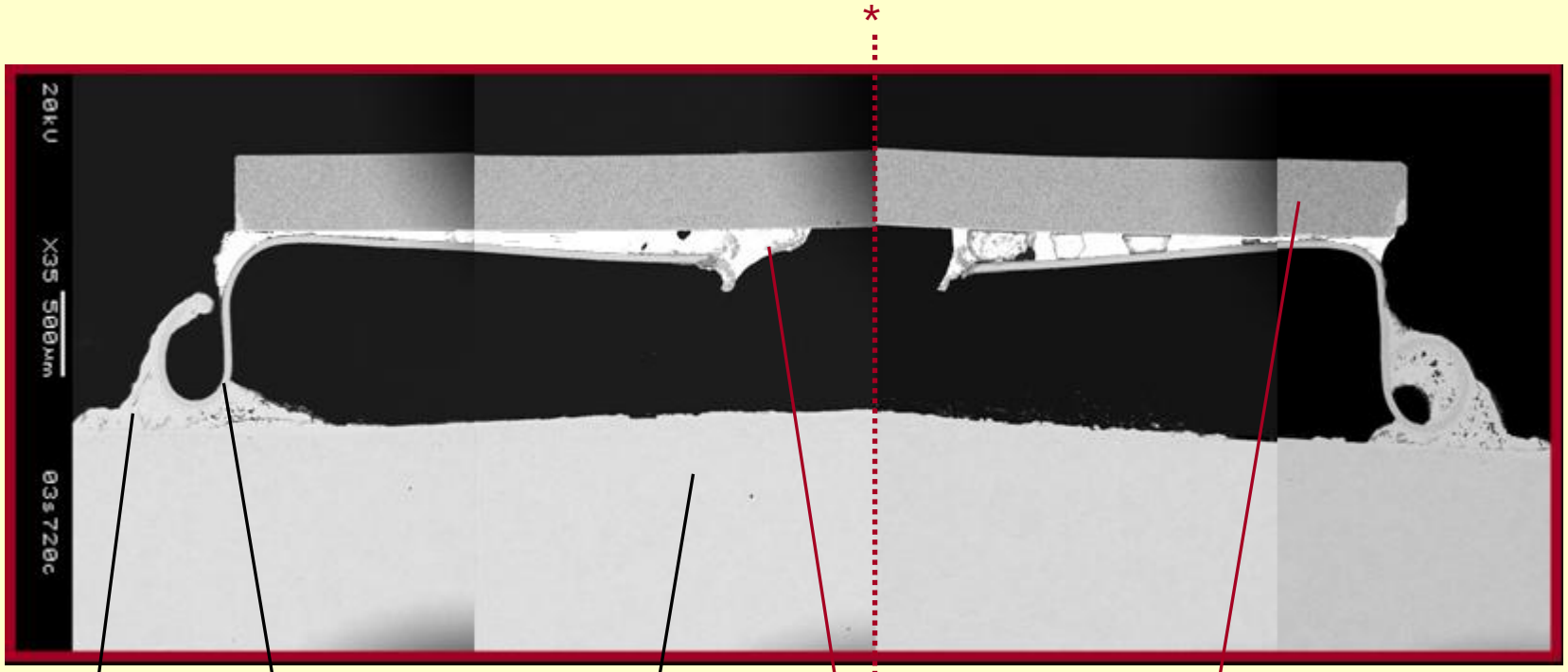
Cross-Sectional View of the Foil Seal



The PEN, compliant foil, and metal substrate parts for seal testing



Cross-Sectional Micrograph of the Compliant Foil Seal



BNi-2 Braze

2mil thick Durafoil

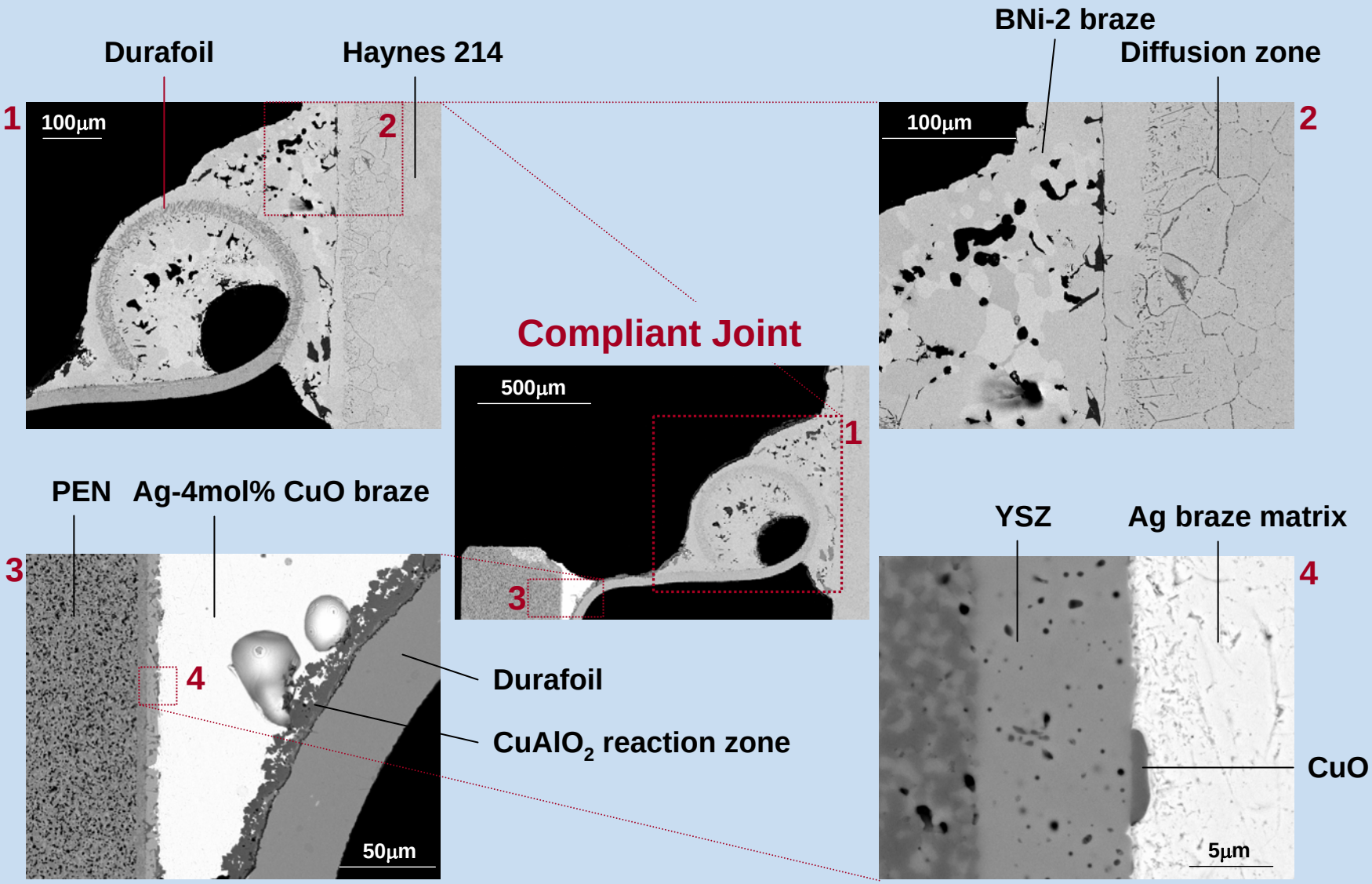
Haynes 214

Ag-4mol% CuO Air Braze

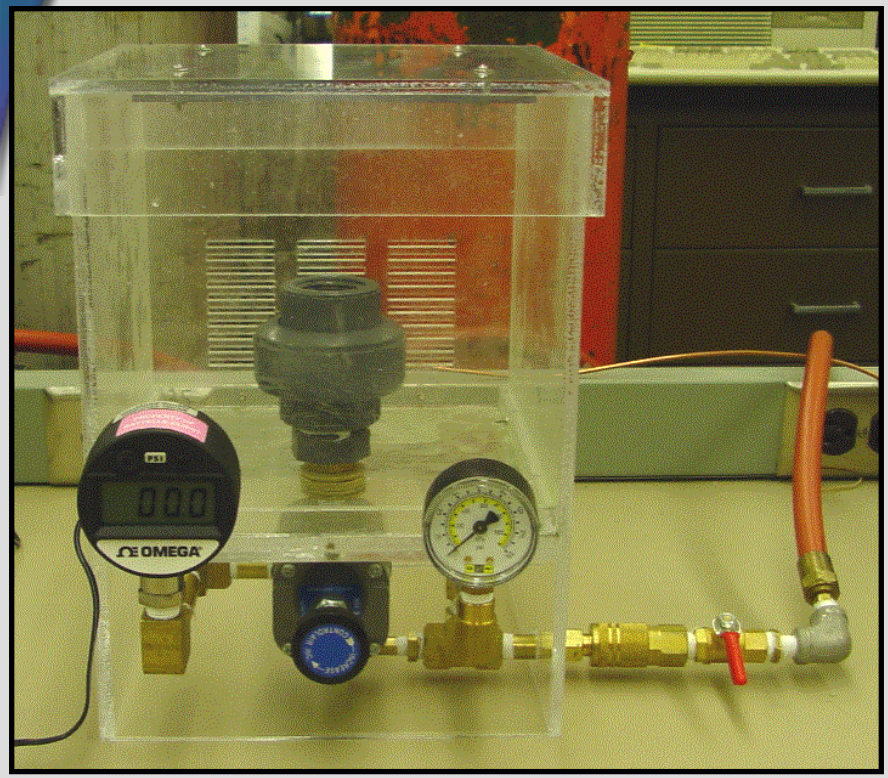
Ceramic PEN, YSZ Side Down

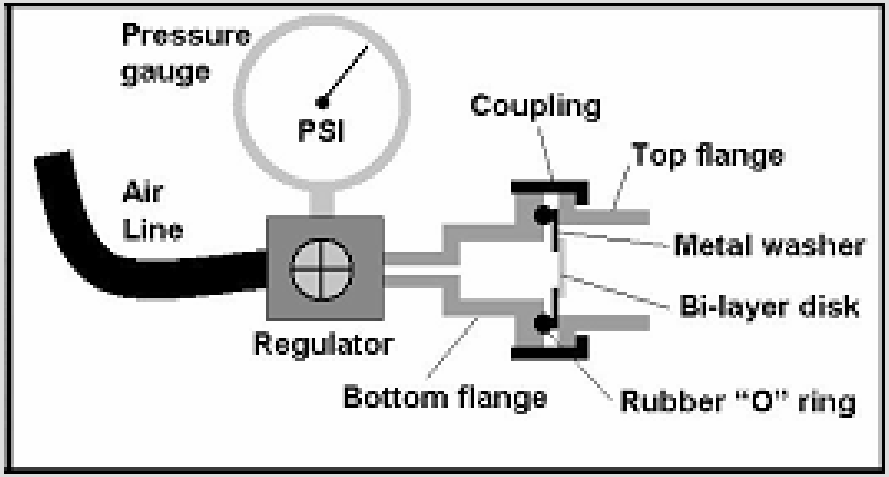
* Mid-section of the specimen not shown.

Cross-Sectional Micrographs (Interfaces)



Hermeticity/Seal Strength Testing





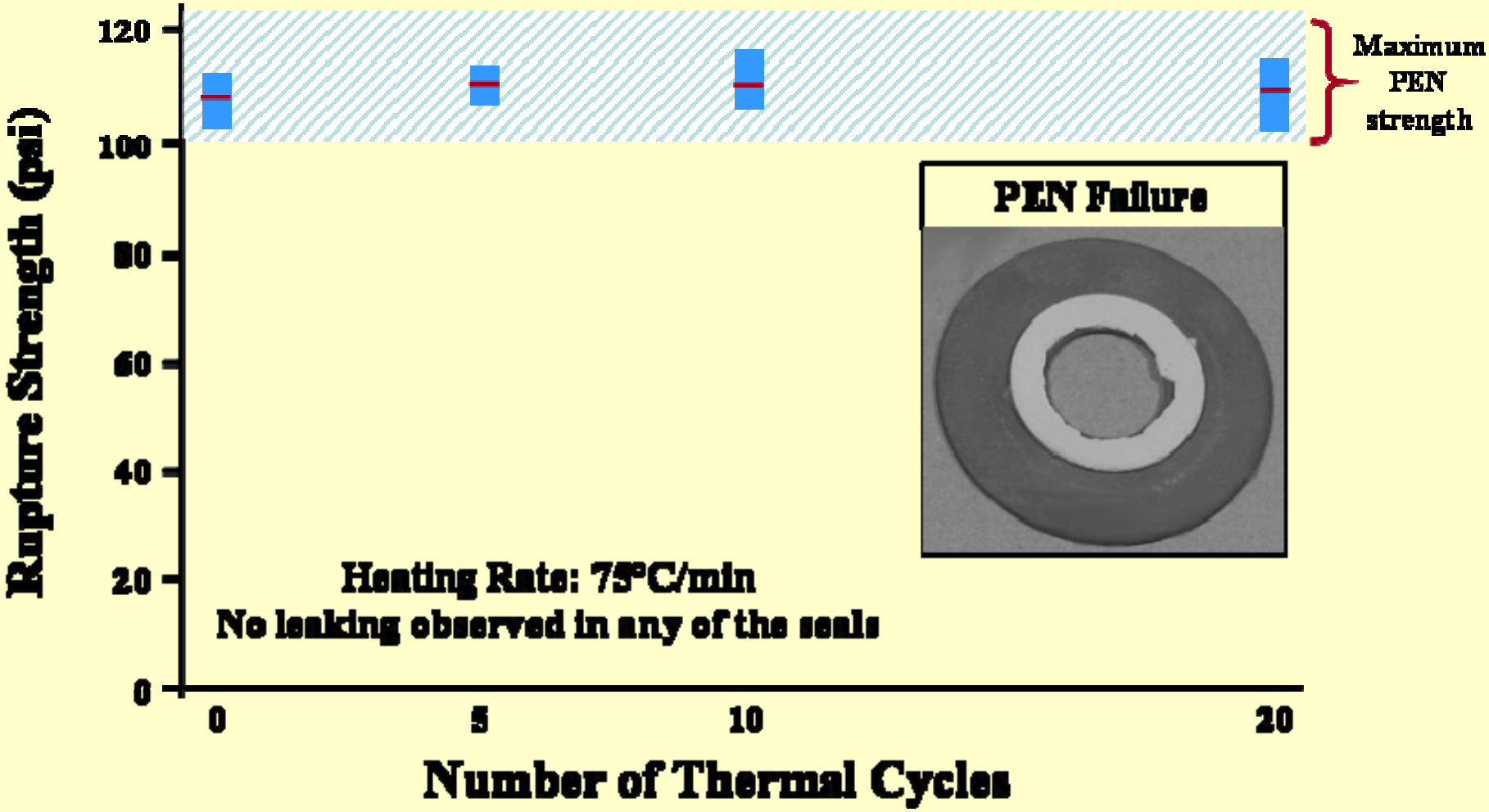
Seal tests using pressurized gas allow simultaneous hermeticity and strength evaluation

Used mainly for qualitative comparison

Limitations

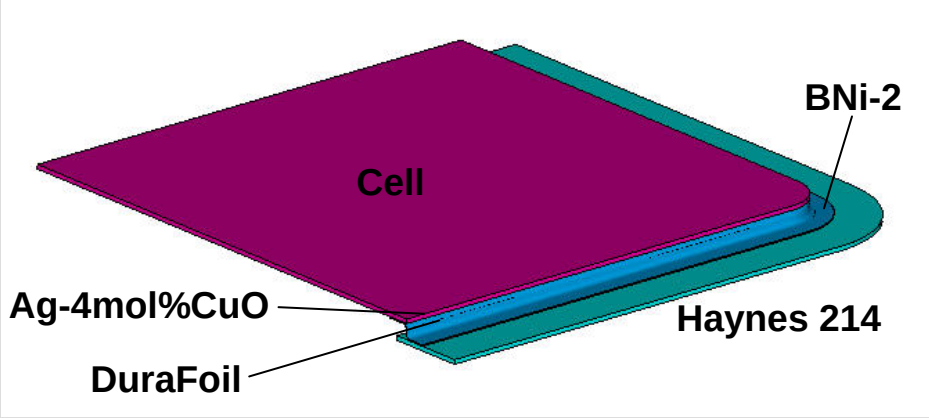
- **Room temperature**
- **150 psi regulator rating ∴test limits of ~130 psi gas pressure (~1.3 MPa tensile stress on seal)**
- **Bilayer strength**
- **≥ 5 specimens tested/condition**

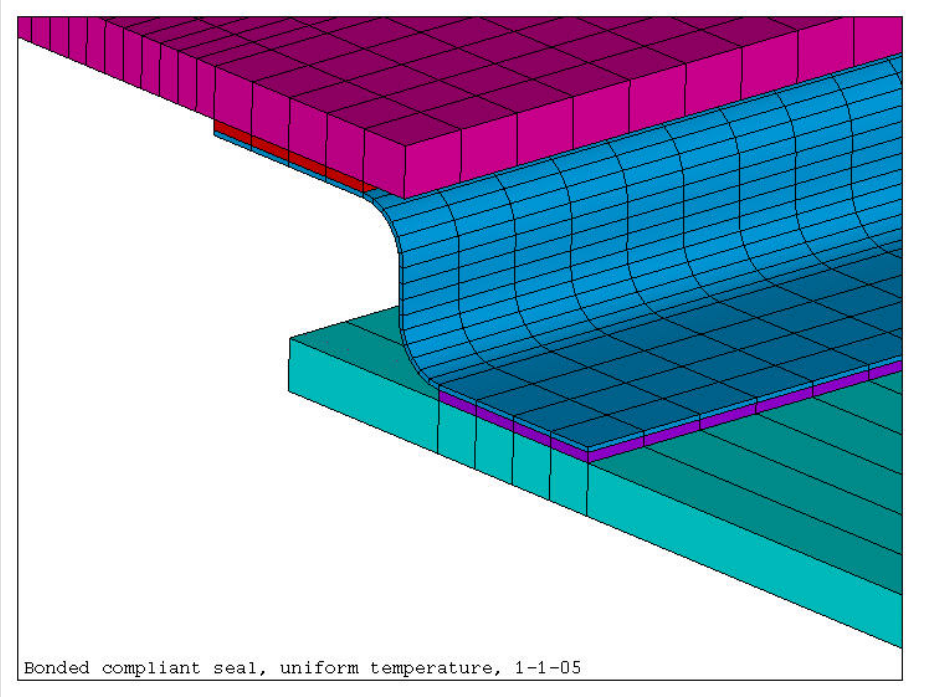
Hermeticity/Thermal Cycling Results



Scalability

- Geometry consists of five layers
  - Anode (600μm, Ni/8YSZ)
  - Braze layer (100μm, Ag-4CuO)
  - Foil seal (50μm, DuraFoil)
  - Braze layer (100μm, BNi-2)
  - Picture frame (500μm, Haynes 214)
- Modeled ¼ symmetry
- Mesh used 1 element through-thickness with enhanced strain formulation to capture bending effects

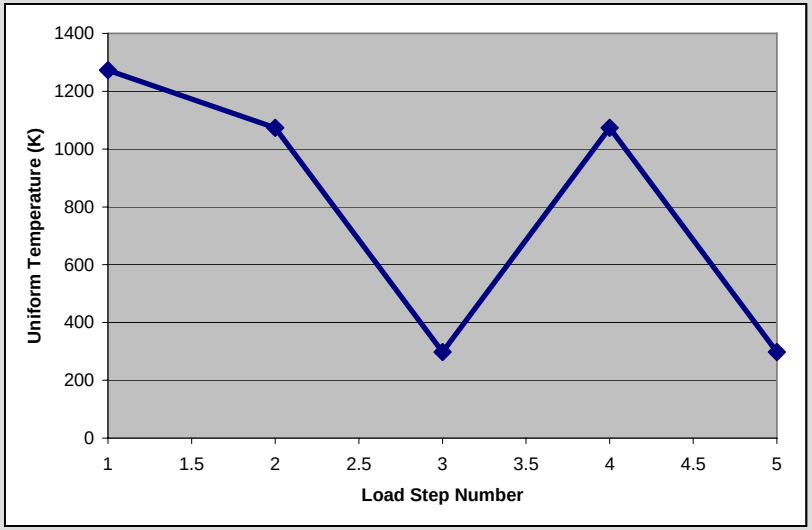


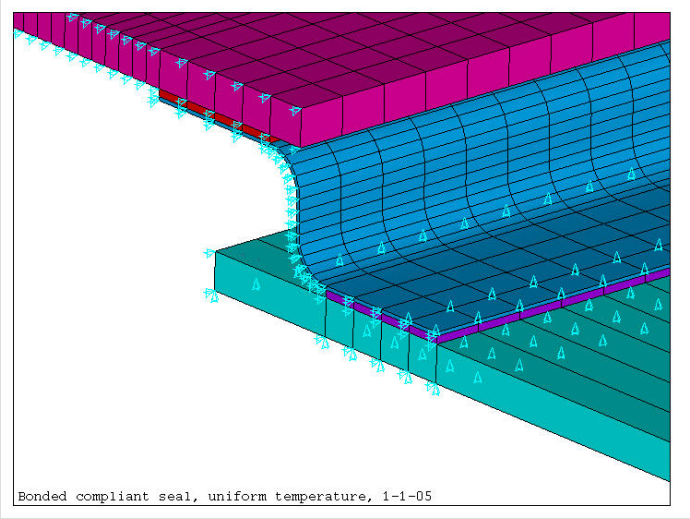


Scalability

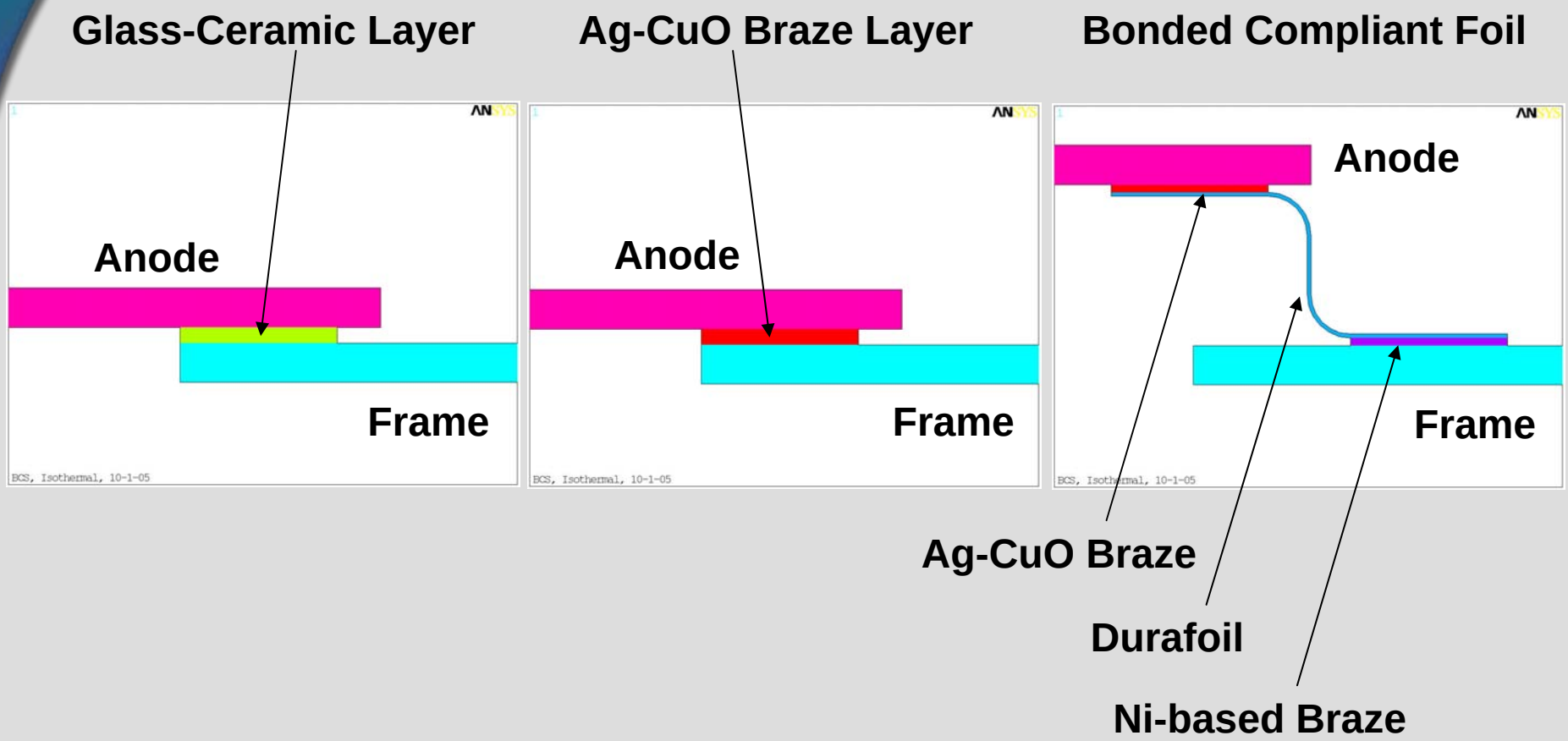
Loading & Boundary Conditions:

- **Uniform temperature loading applied to model**
  - Assumed stress free at the brazing temperature T=1273K (1000°C)
  - Operating temperature at T=1073K (800°C)
  - Room temperature at T=298K (25°C)
  - Repeat thermal cycle
- **Boundary conditions**
  - Bottom of picture frame constrained out-of-plane
  - Symmetry conditions applied

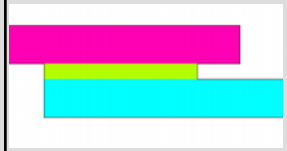
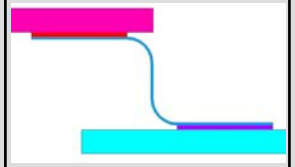




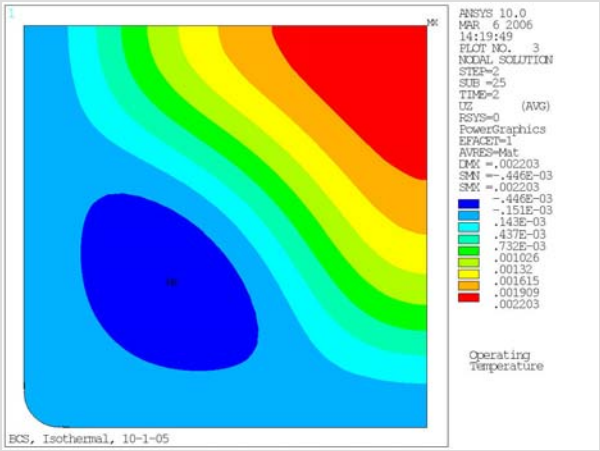
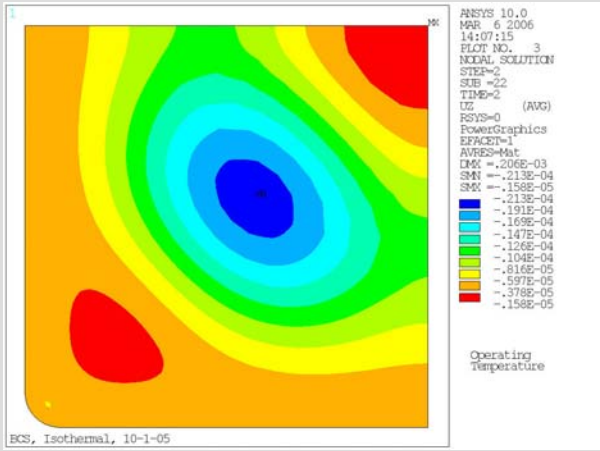
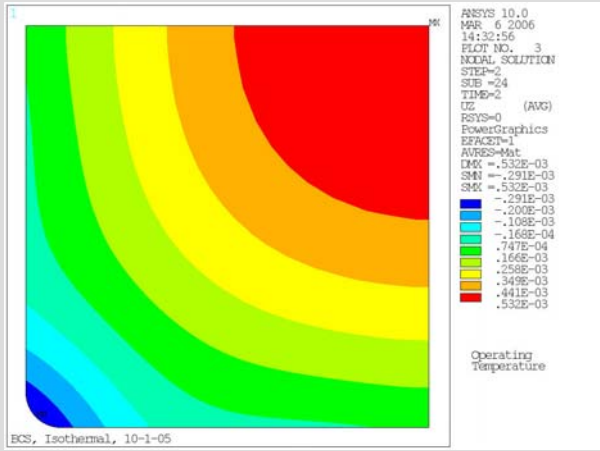
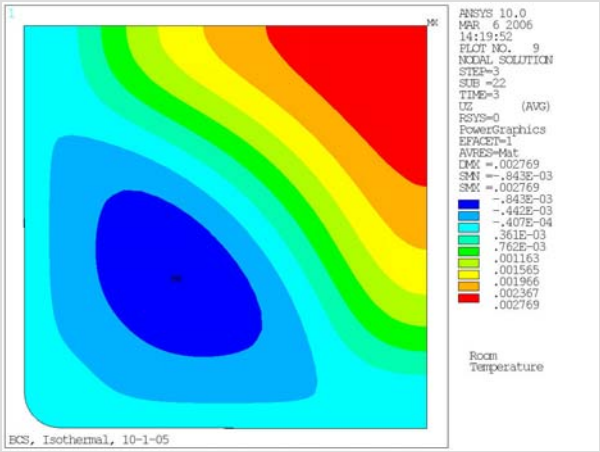
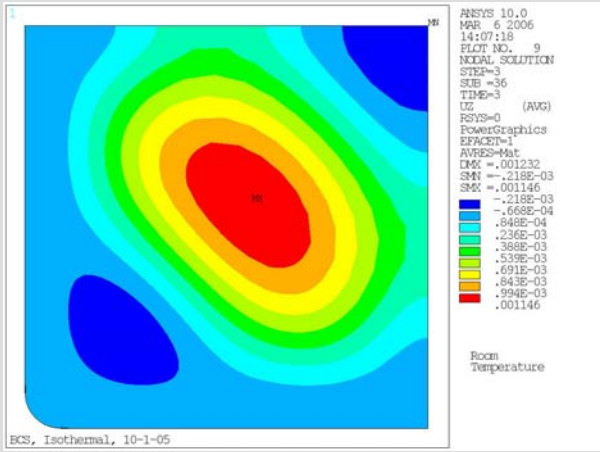
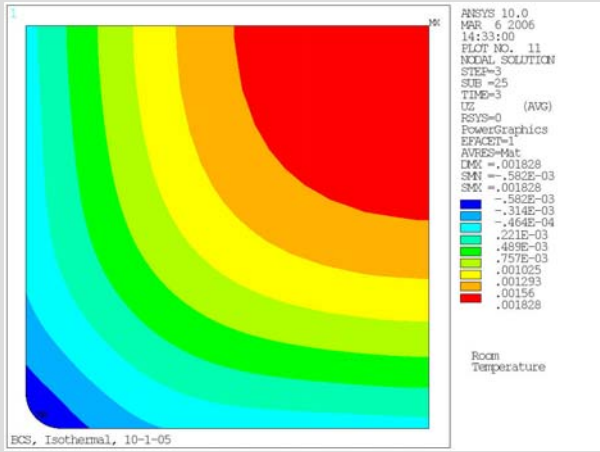
Seal Comparison



Benefit of Compliance

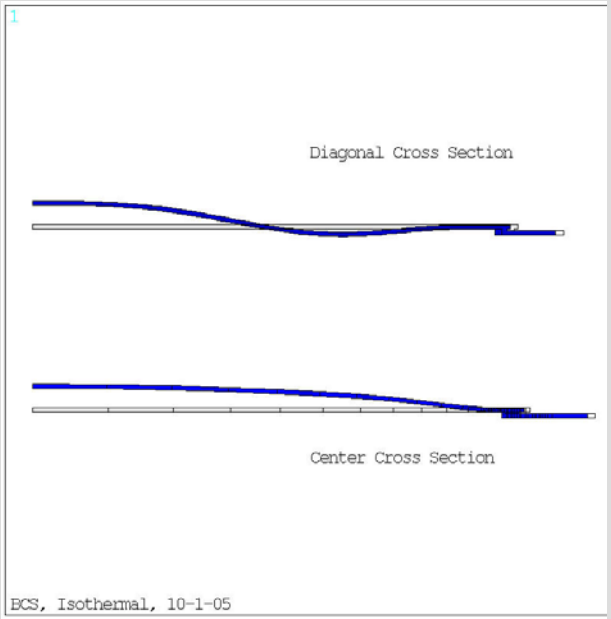
*Values at Operating/Room Temperatures	Seal Geometry	*Anode Maximum Principal Stress (MPa)	*Anode Deflection (mm)	*Seal Stresses (MPa)
Fully Crystallized Glass-Ceramic		354 / 1160	2.65 / 3.61	Glass 104 / 586
Ag-based Braze		19 / 459	0.02 / 1.36	Ag-Braze 22 / 362
Bonded Compliant Seal		24 / 90	0.82 / 2.41	Ag-Braze 3 / 333 Ni-Braze 160 / 238 Fecralloy Foil 92 / 453

Comparison of Anode Deflection

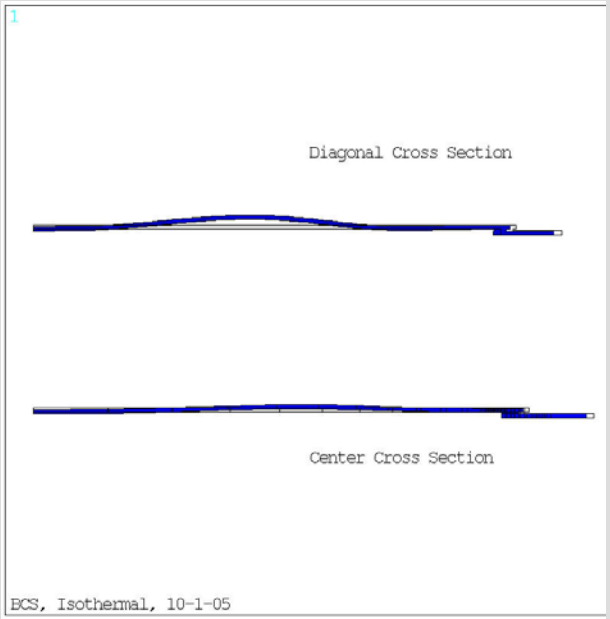
	Glass-Ceramic Layer	Ag Braze Layer	Bonded Compliant Foil
OT			
RT			

Comparison of RT Cell Deformation

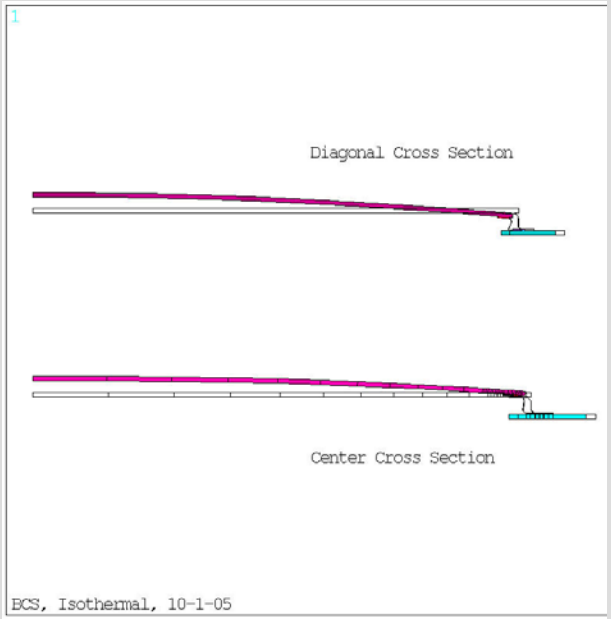
Glass-Ceramic Layer



Ag Braze Layer

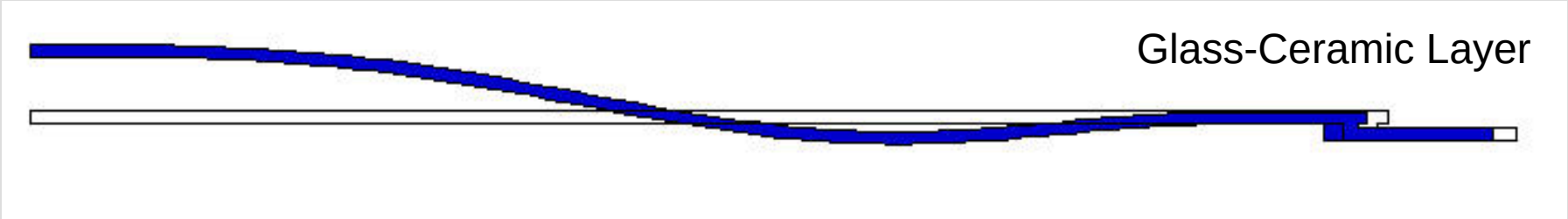


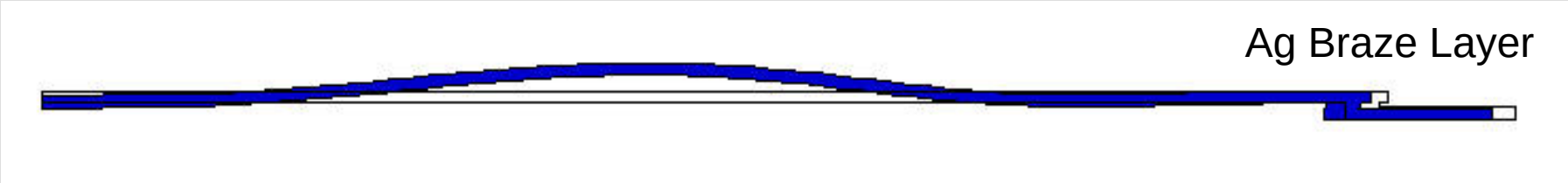
Bonded Compliant Foil



Comparison of RT Cell Deformation

Along the diagonal



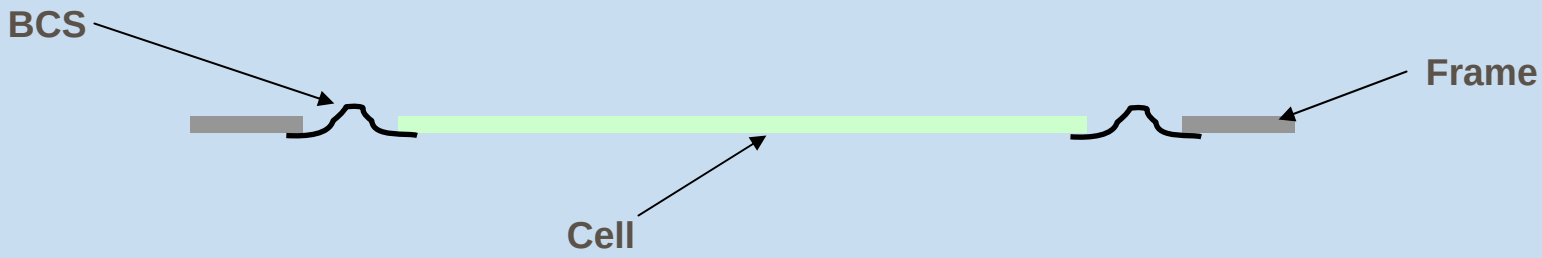


Conclusions

- **Developed a new sealing concept for SOFCs: the bonded compliant seal**
  - Employs a foil membrane that can undergo elasto-plastic deformation in response to thermally/mechanically induced differential strains in the adjacent ceramic PEN and interconnect materials
  - Shown to be hermetic upon sealing and after cycling up to 20x at 75°C/min
- **Finite element modeling indicates:**
  - Significantly reduces stresses/strains in the ceramic cell and metal frame relative to glass and braze sealing
  - The largest stresses are concentrated in the foil, away from the cell.
  - Stresses within the cell are less than 1/5th that required for fracture.
  - Stresses within the Haynes 214 are less than 1/100th that required for yielding.
  - Stresses within the foil are ~70% of the yield stress of the foil at room temperature.
  - Deflection of the seal causes cell bowing upon cooling due to contact with the frame. Some geometric re-design is needed.

Future Work

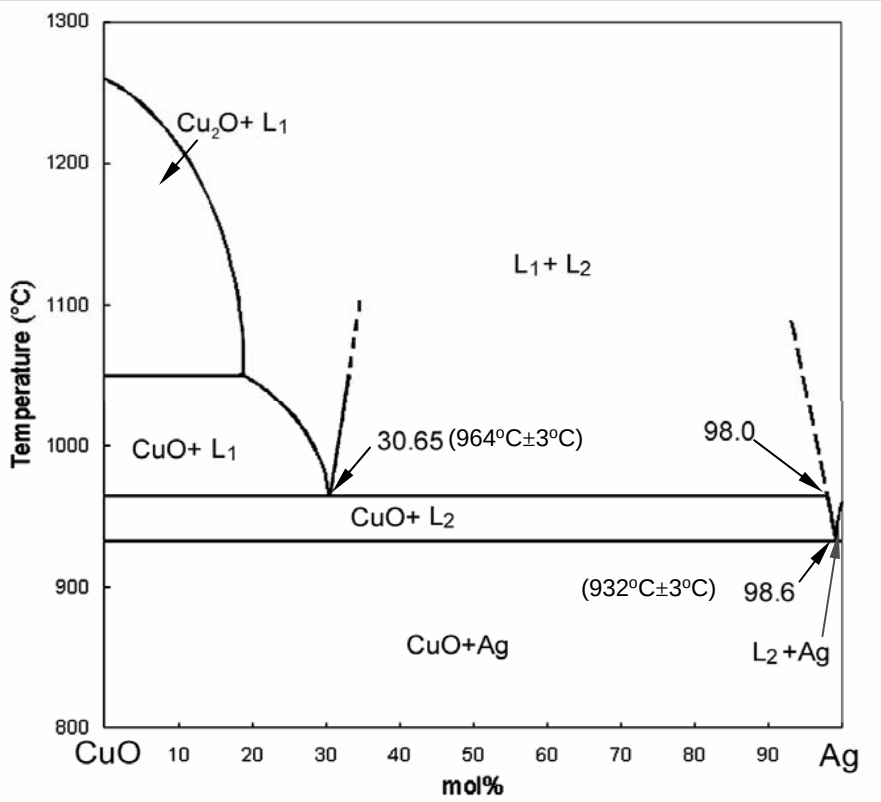
- (1) Conduct a sensitivity analysis to determine the effect of foil thickness and braze joining widths on the amount of out-of-plane deformation in the cell (and examine modifying the S-shaped cross-section to mitigate contact) and (2) begin examining an alternative design that may completely eliminate bowing and result in even lower component stresses:



- Begin developing a scaled-up version of the bonded compliant seal
- Continue work on an insulated version of this sealing concept

Development of "Adhesive" for Foil-to-YSZ Joining – Air Brazing

The CuO-Ag System



Shao et al, *J. Am. Ceram. Soc.* [1993] 2663

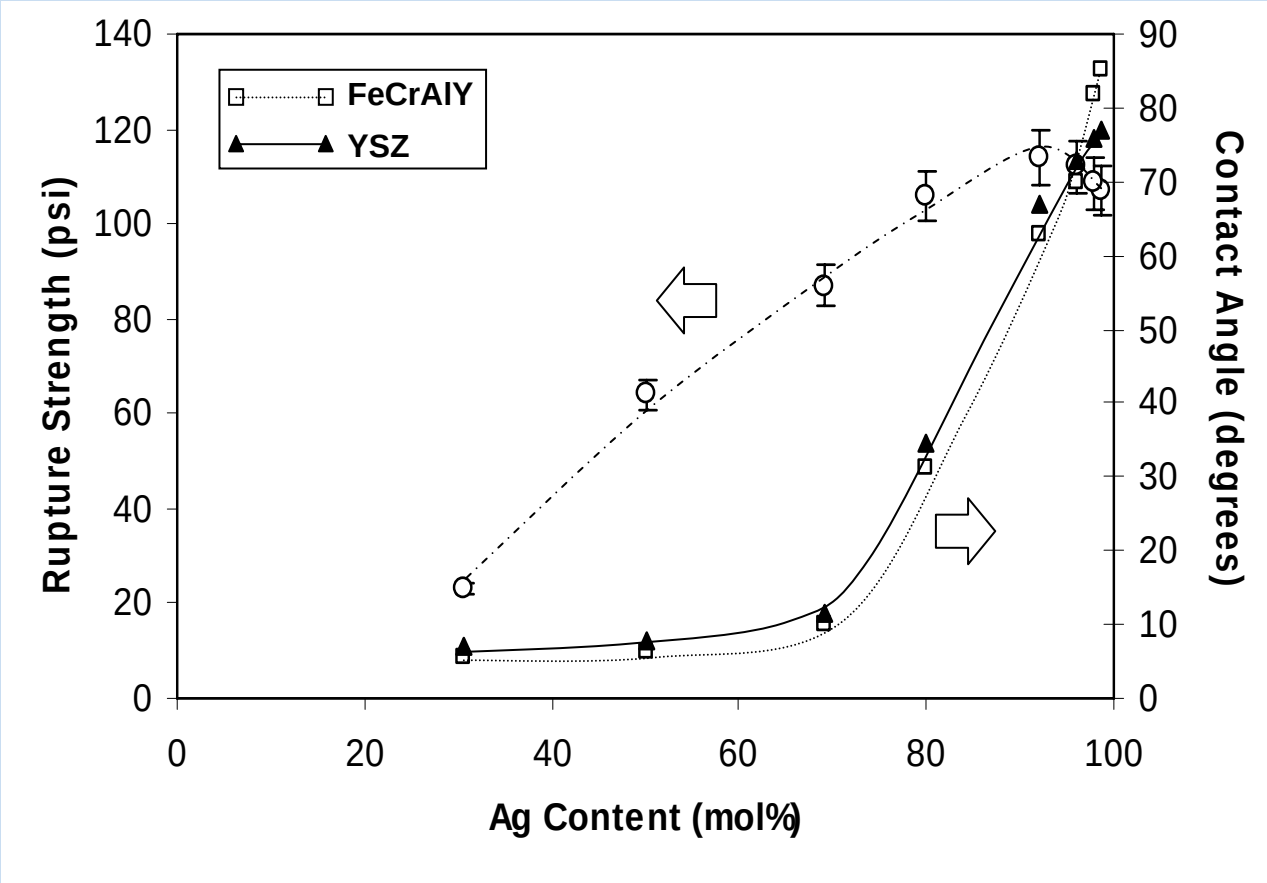
- The CuO-Ag system displays a monotectic point and a eutectic point)
- CuO known to react with Al_2O_3
  - Can form $CuAlO_2$ ~900 – 1000°C
  - CuO-Ag melts wet Al_2O_3 (Meier et al, *J. Mat. Sci.* [1995] 4781)
  - Cu-Ag melts wet YSZ (Hao et al, *J. Am. Cer. Soc.* [1995] 2157)
- Al_2O_3 scale forming steels - top candidates for balance of plant in electrochemical devices

Four Areas of Study:

- Determine the appropriate oxidation-resistant, low modulus alloy for use in the deformable foil
- Develop an appropriate “adhesive” to bond the seal to each faying surface
- Define the appropriate geometry of the seal to minimize the transfer of stresses from one component to the other
- Ensure that the seal is non-conductive (i.e. to eliminate shorting in the stack)

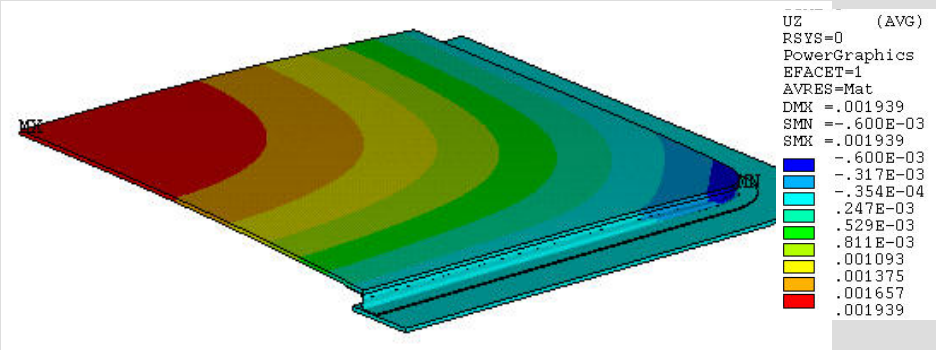
Compositional Dependence of Wetting and Joint Strength

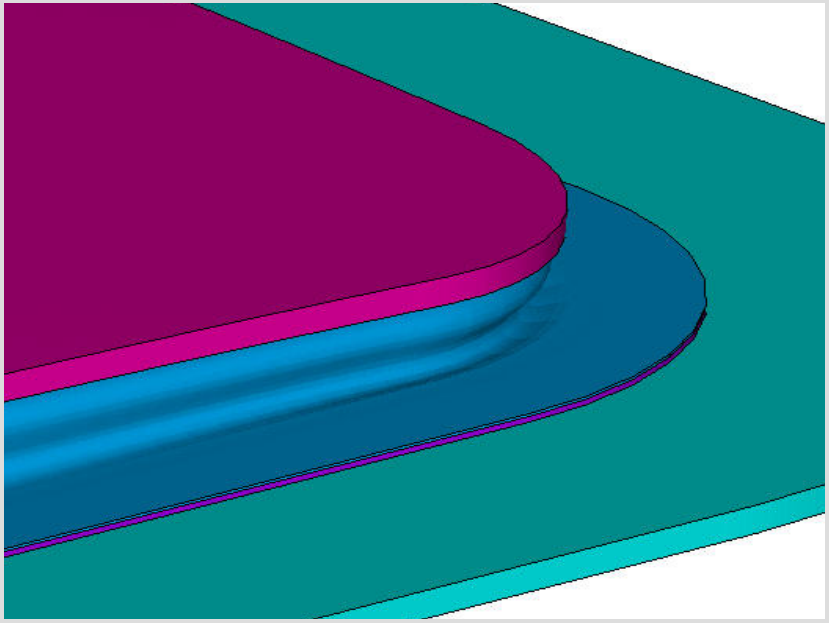
The CuO-Ag System



Scalability

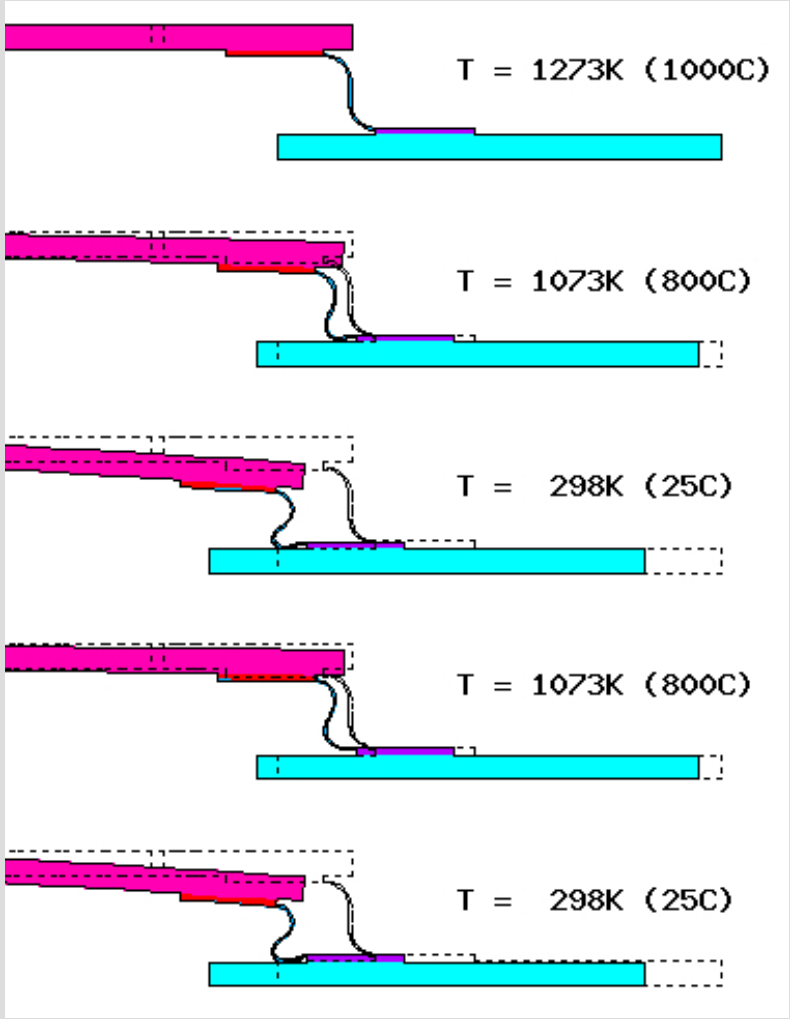
- With stress-free condition assumed at the sealing temperature, model contracts as cooled
- Mismatch CTE causes the anode to bow
- The anode bowing at the corner of the seal causes the seal to deform out of plane
- No lateral buckling observed in the foil seal





Scalability

- The as-fabricated and deformed cross-section of the seal is shown at the corner throughout the loading cycle
- At operating temperature, the anode causes the seal to bend down
- Further temperature drop causes the seal to contact the picture frame
  - Response can be corrected with braze layer length or modification of foil geometry



Identifying the Foil Material

Requirements:

- **Excellent oxidation resistance**
- **High elastic/plastic deformation at operating temperature**
- **Resistance to dual atmosphere degradation**
- **Good formability**
- **Low cost**
- **Chemical compatibility with "adhesive(s)"**

Examined several Cu-Al and stainless steels alloys

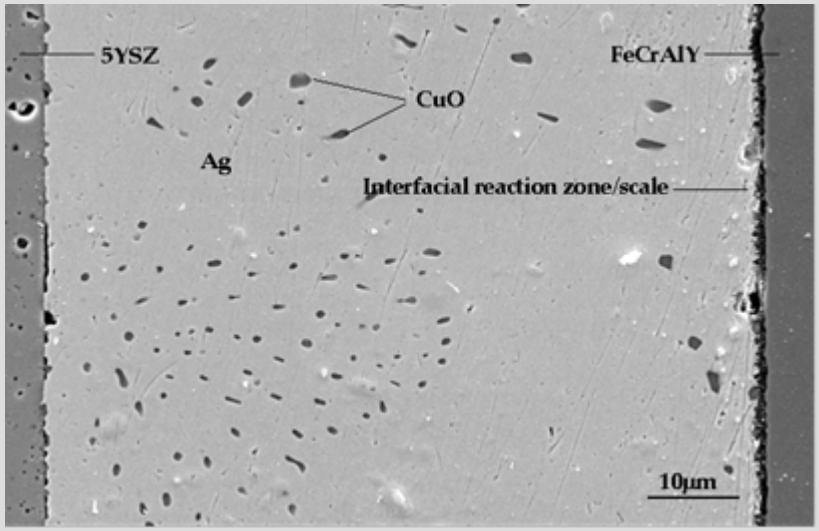
Alloy	Type	Al/Cr content	Oxidation Rate (750°C)
C61400	Aluminum bronze	7% Al	9.4×10^{-13} $g^2/cm^4 \cdot s$
642	Aluminum bronze	7% Al	4.5×10^{-13} $g^2/cm^4 \cdot s$
A-1	Aluminum bronze	4.5% Al	1.2×10^{-13} $g^2/cm^4 \cdot s$
Fecralloy	Stainless steel	23% Cr, 4.5% Al	0.035×10^{-13} $g^2/cm^4 \cdot s$
Durafoil	Stainless steel	21% Cr, 6.3% Al	0.012×10^{-13} $g^2/cm^4 \cdot s$
446	Stainless steel	25% Cr	0.489×10^{-13} $g^2/cm^4 \cdot s$

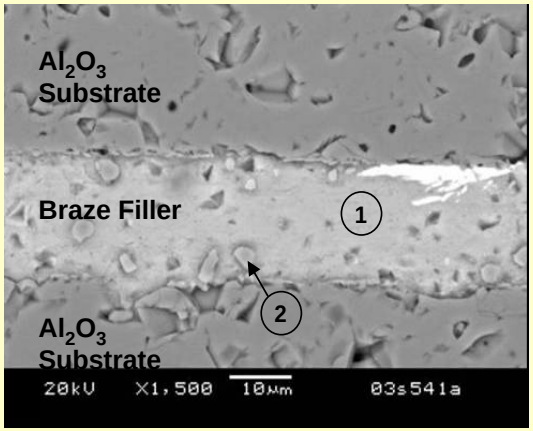
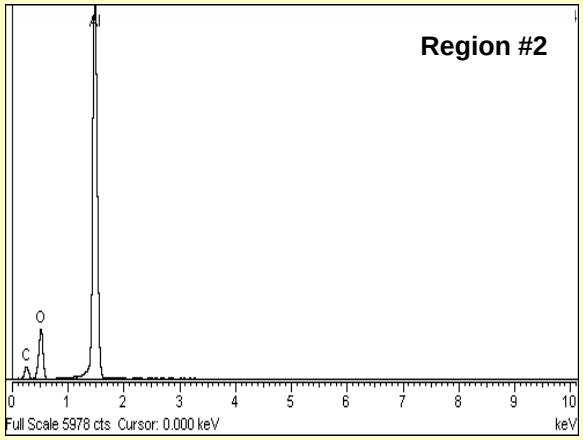
Selected for further development

“Adhesive” for Foil-to-YSZ Joining

CuO-Ag not only wets ceramics such as YSZ and Al_2O_3, but also the chromia and alumina scales on heat resistant metals. Thus it can form the basis for joining metal and ceramic components in a SOFC stack.

YSZ/FeCrAlY (Stainless Steel) Joint



Development of an alternative Al-based air braze

Al_2O_3/Al alloy/Al_2O_3 Joint