Compliant glass seal development

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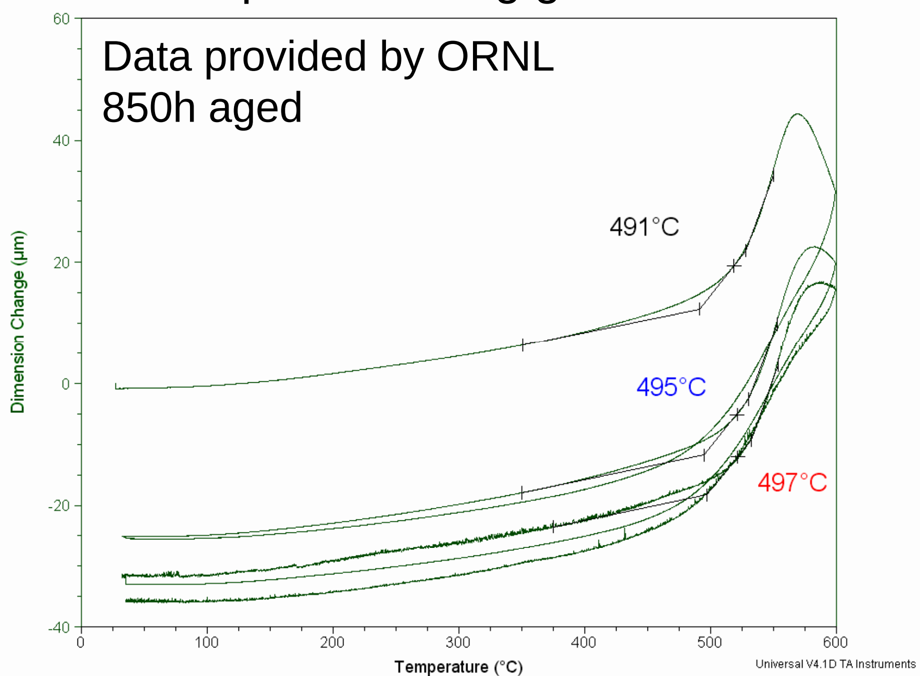
- Introduction and objectives
- Q1: Effect of differential pressure on thermal cycle stability
1. experimental
2. leak rates versus cycling (700-850^{o}C/1000h)
- Q2: thermal stability study in a duel environment
1. leak rates versus time (750-800^{o}C/1000h)
2. microstructure and interface characterization
- Q3: assess YSZ coating and other mat'l for spacer rings
- Summary
- Future work

Solid-State Energy Conversion Alliance Core Technology Programs Review, July 27-29, 2010, Pittsburgh, PA

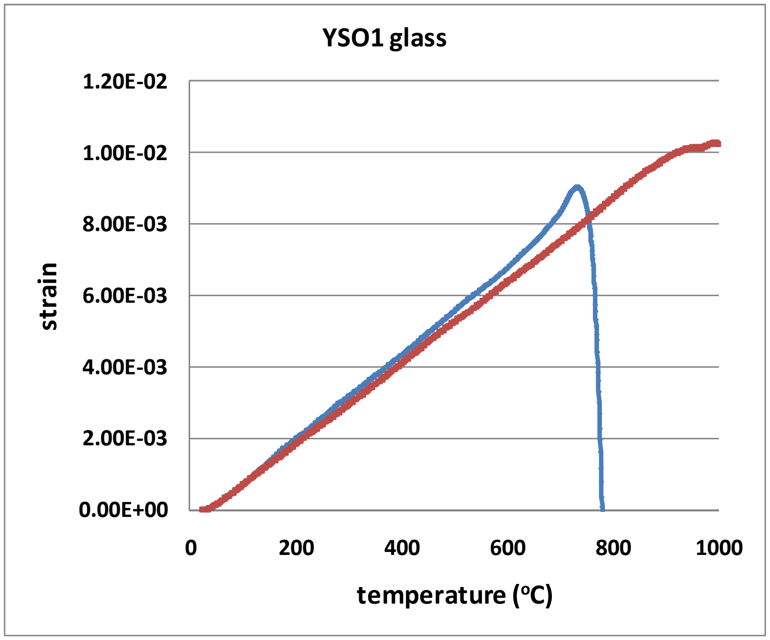
Compliant versus refractory sealing glass

$$\sigma = E\, \Delta\alpha\, \Delta T$$

Compliant sealing glass



Refractory sealing glass



<u>Advantage:</u>

Low stress or relaxation, healing?

Wetting,

<u>Disadvantage:</u>

metal-stable, narrow T window,

volatile, reactive/corrosive?

Objectives

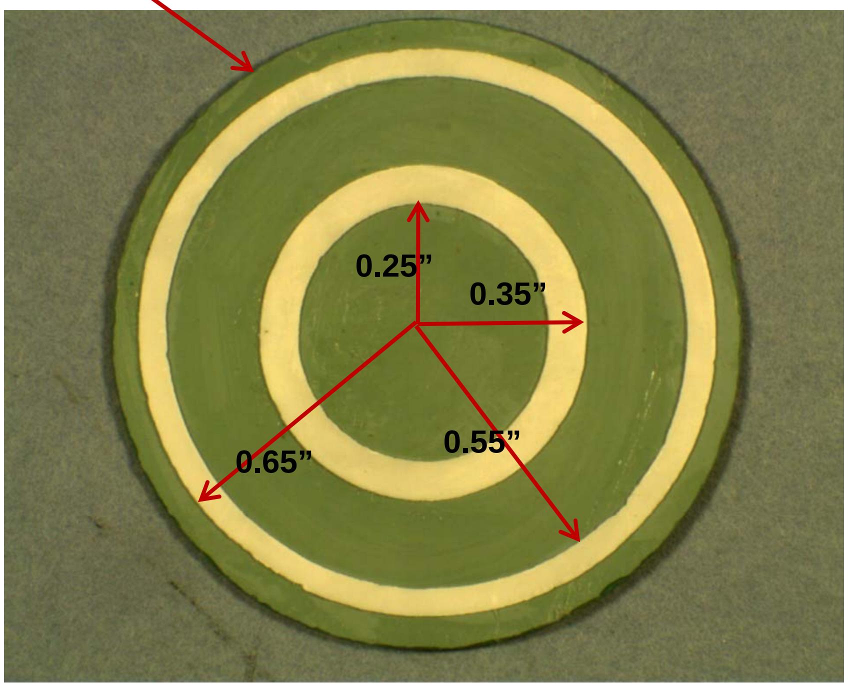
- To conduct a comprehensive study of a commercial compliant sealing glass in terms of *thermal, chemical*, physical, electrical, and mechanical stability in SOFC environments

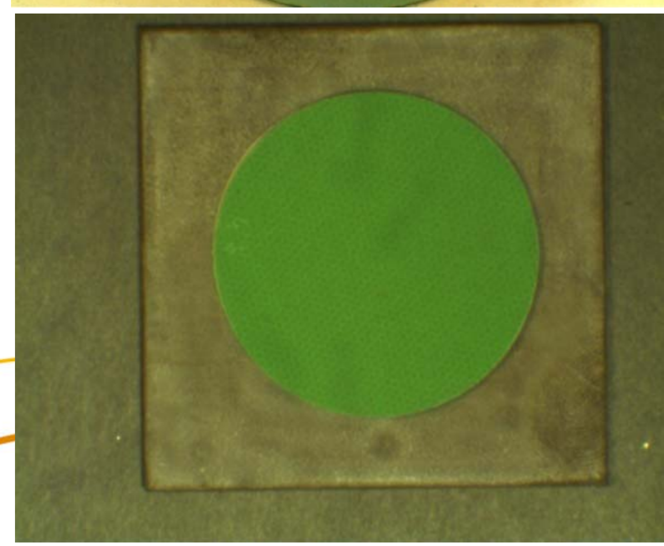
SCN-1 glass: Si, K, Na, Mg, Ba, Ca, Al

Experimental: sample preparation

1. Thickness of spacer rings ~220 μm
2. SCN-1 glass mixed with ESL450 binder to form paste

1.4” ϕ bilayer

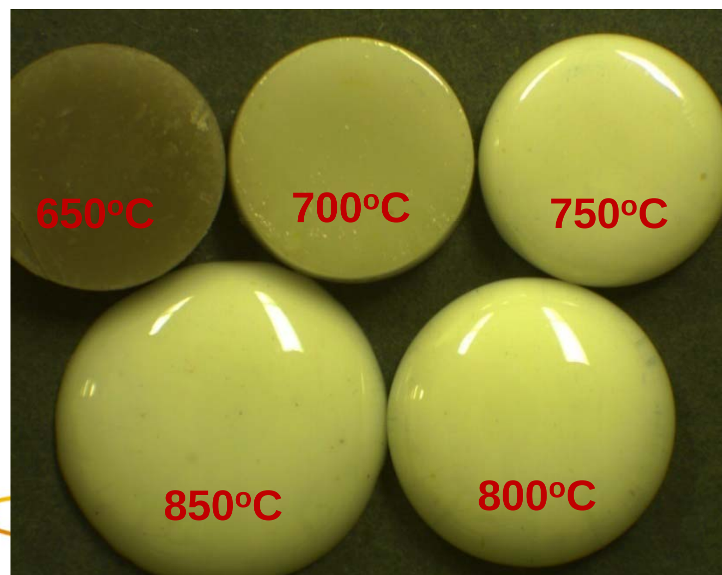




Sealing condition screening

- Sealing profile: RT to 550ºC/2h, T/2h, then cooled to RT with a contact load
- Leakage tested with ultra-pure helium @ 0.2 psi & iso-propanol

RT Hermeticity	700°C/2h	750°C/2h	800°C/2h	850°C/1h
Sample 1	No	No	Yes	Yes
Sample 2	No	No	Yes	Yes



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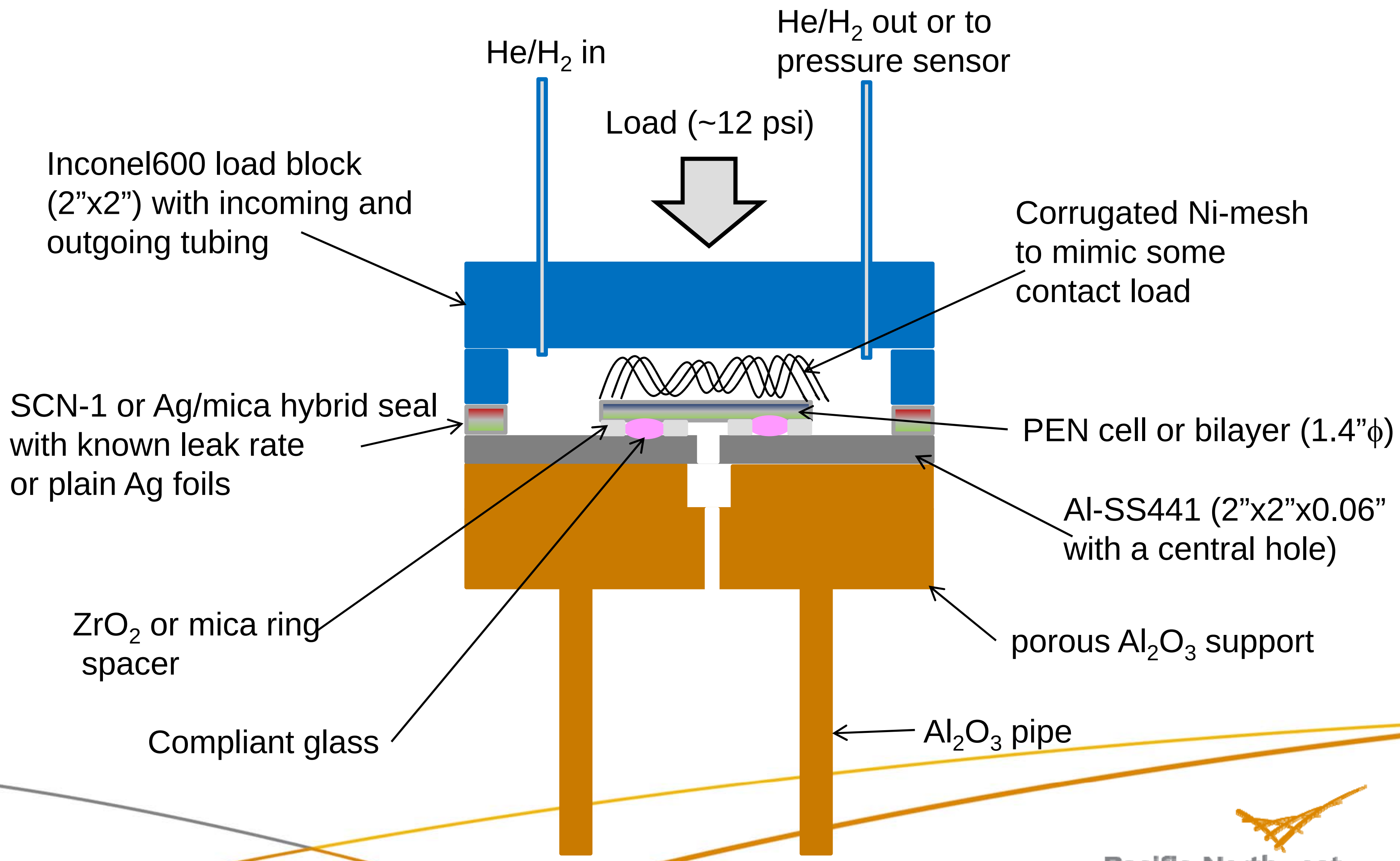
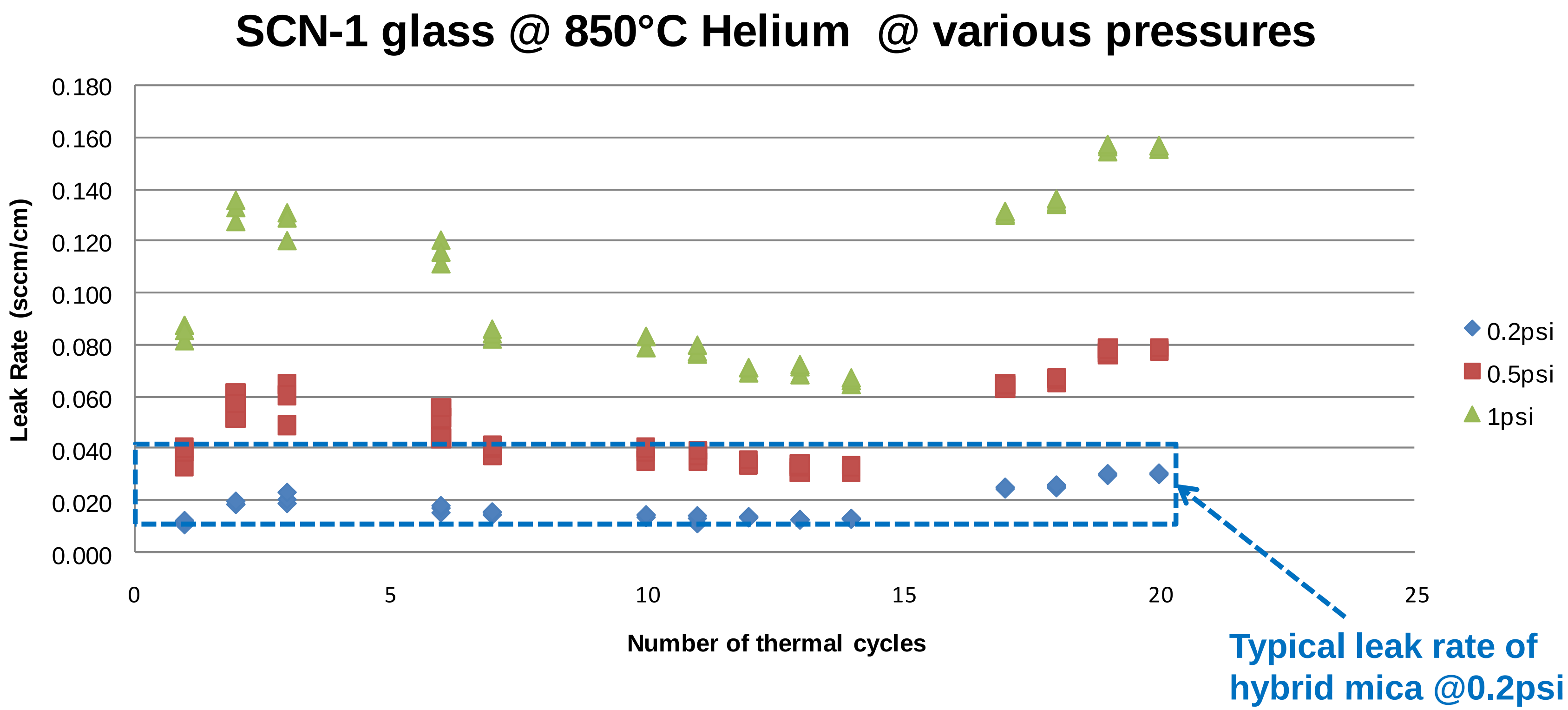
Experimental: high-temp leakage test

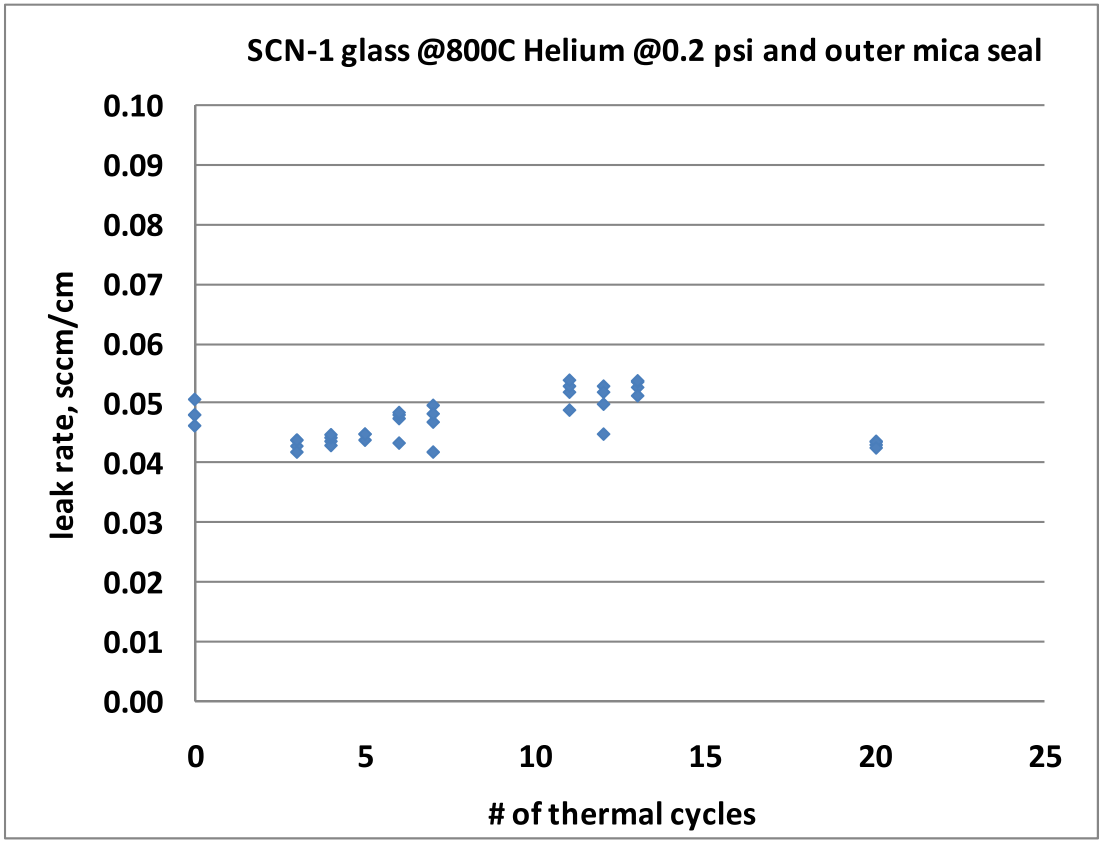


Thermal cycle stability at 850ºC in air



Aluminized AISI441 with YSZ spacer rings
Samples was tested with iso-propanol after cycling test and showed hermetic.

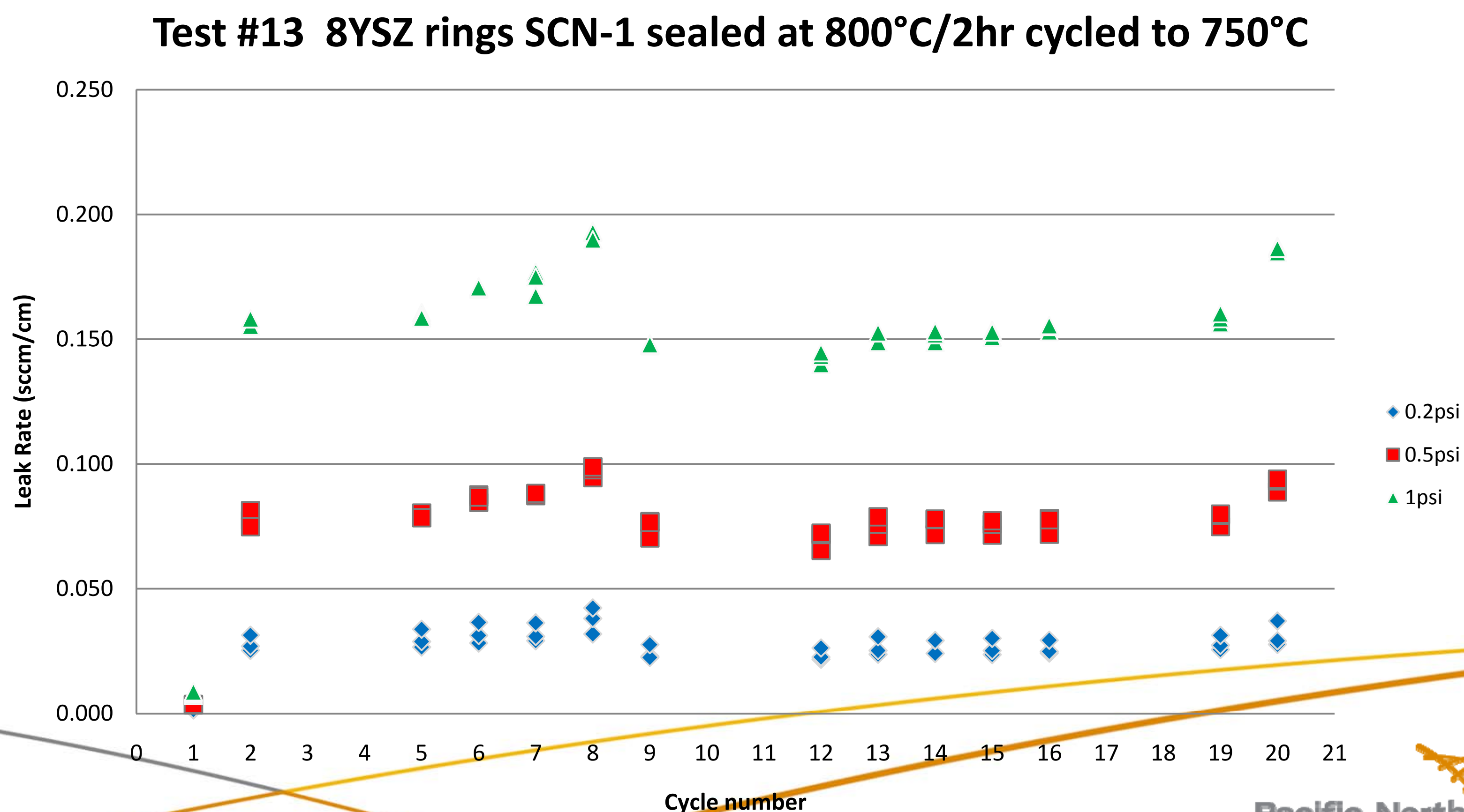
Thermal cycle stability at 800ºC in air



The measured leak rate is from mica seal not from (SCN-1) glass seal since the fracture of monolithic glass seal would contributed leakage an order of magnitude higher.

Thermal cycle stability at 750ºC in air

The leakage suggested the SCN-1 glass was hermetic that the measured leakage was from perimeter mica seals. Post-mortem leak test with iso-propanol also showed hermetic.



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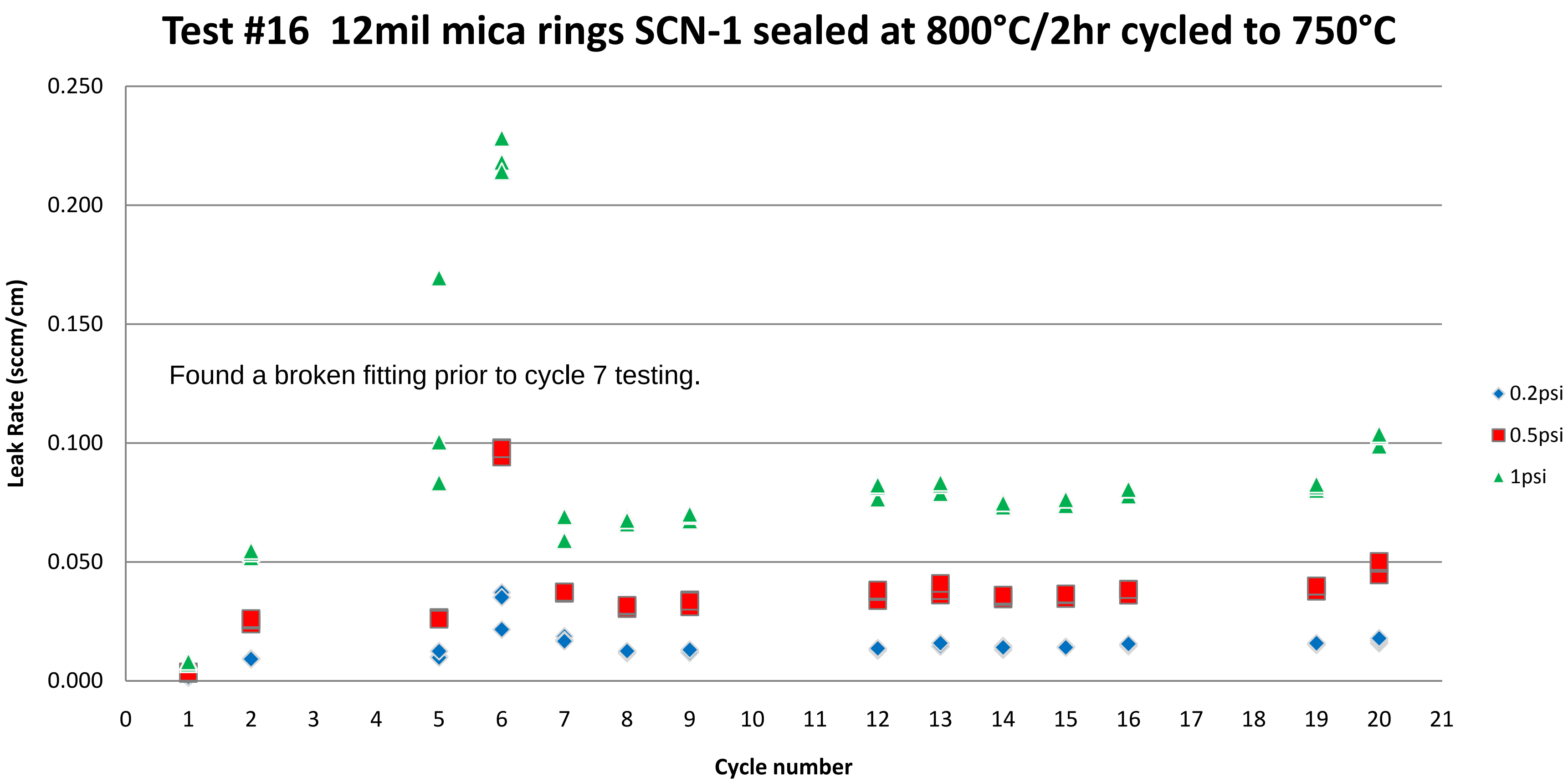
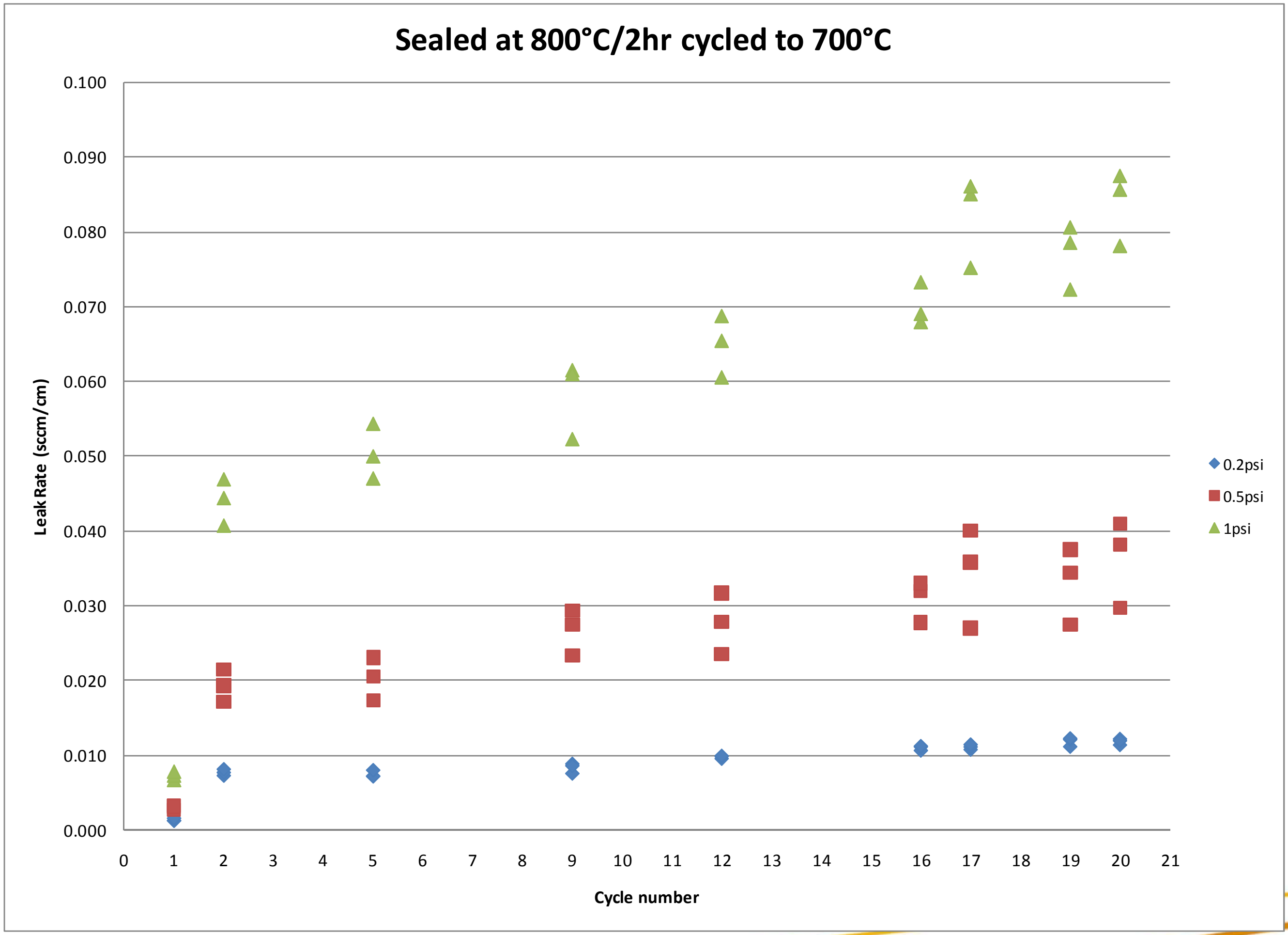
Thermal cycle stability at 750ºC in air



Mica as spacer rings

Samples was tested with iso-propanol after cycling test and showed hermetic.

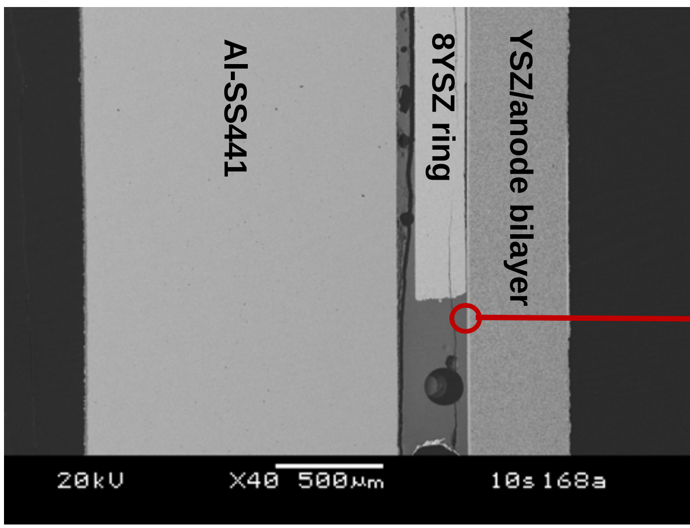
Leakage versus thermal cycling at 700ºC in air with aluminized SS441 and 8YSZ rings

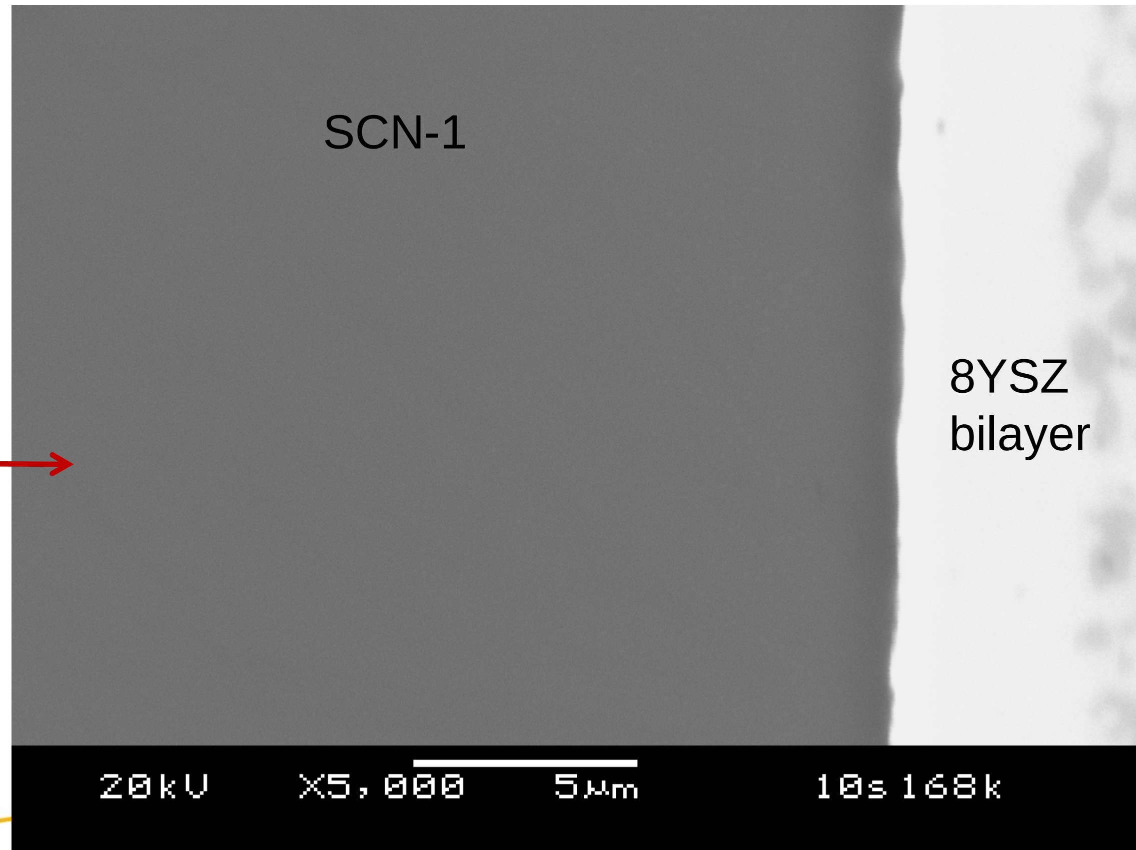


Samples was tested with iso-propanol after cycling test and showed hermetic.

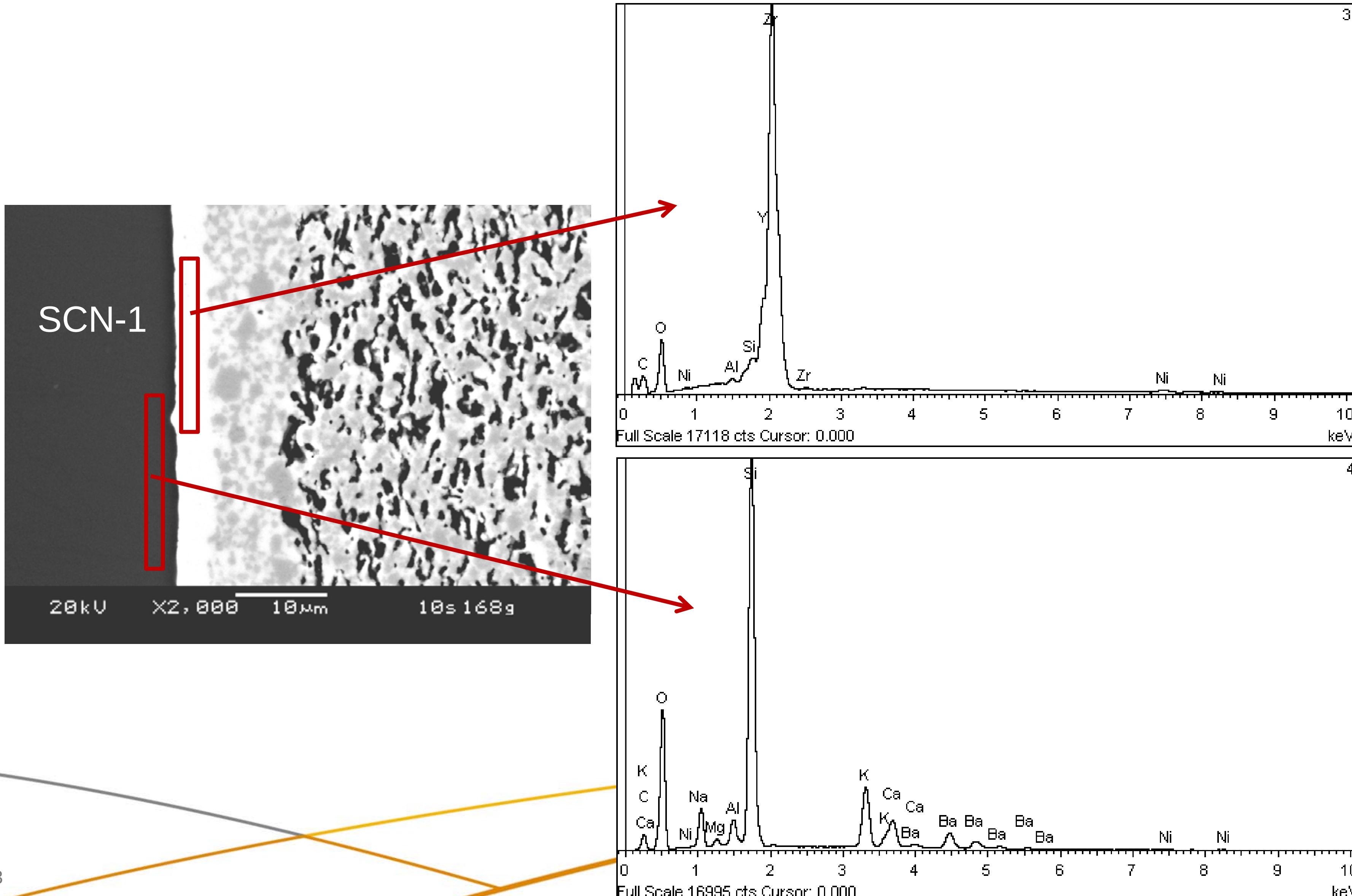
Characterization of 850ºC/20 cycled sample: SCN-1 glass/8YSZ bilayer interface

Exposed in air and 850ºC/3h per cycle
With aluminized SS441 plate, bilayer, and 8YSZ narrow rings (0.1”)

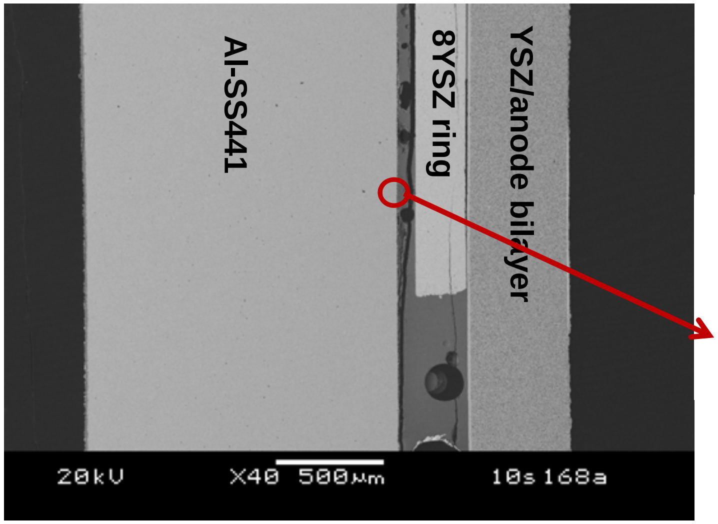


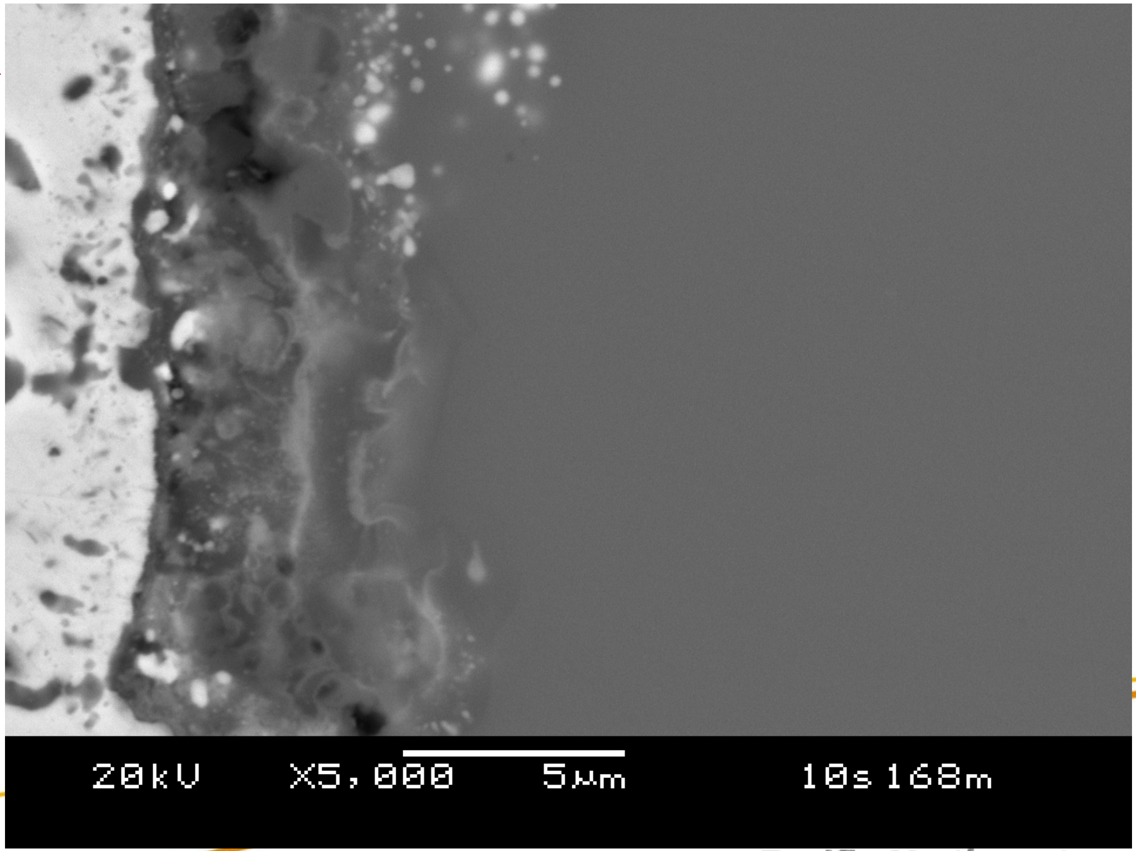


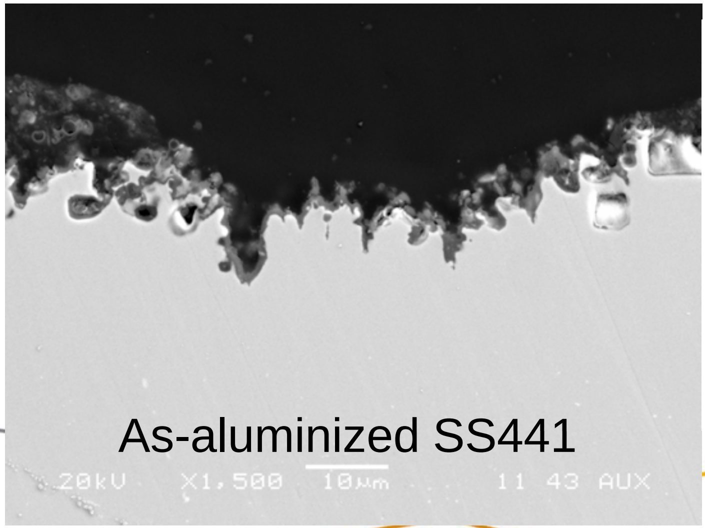
Characterization of 850ºC/20 cycled sample: SCN-1 glass/8YSZ bilayer interface



Characterization of 850ºC/20 cycled sample: SCN-1 glass/aluminized SS441 interface







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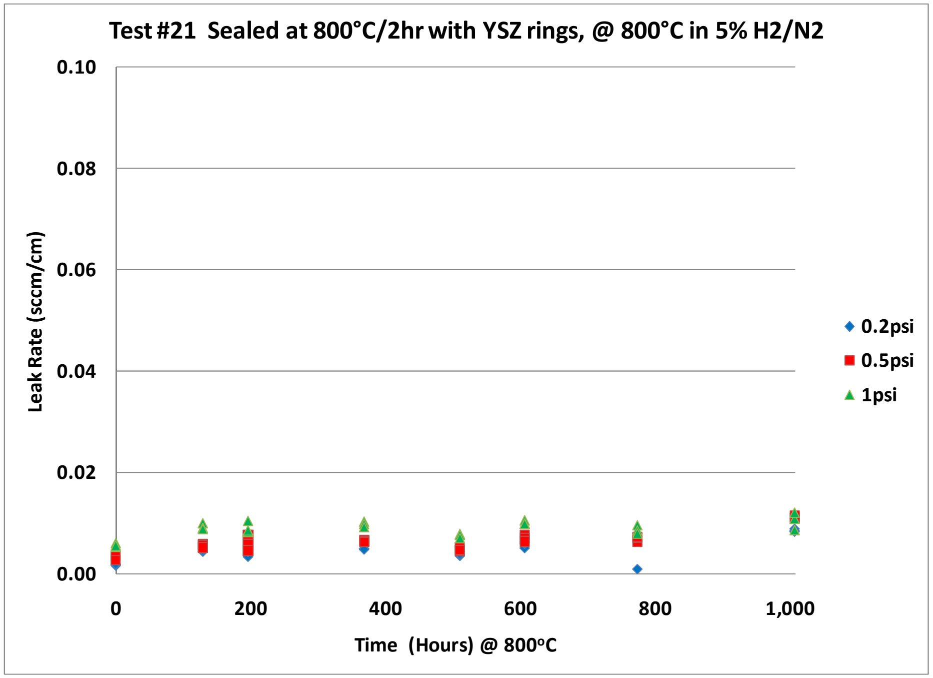
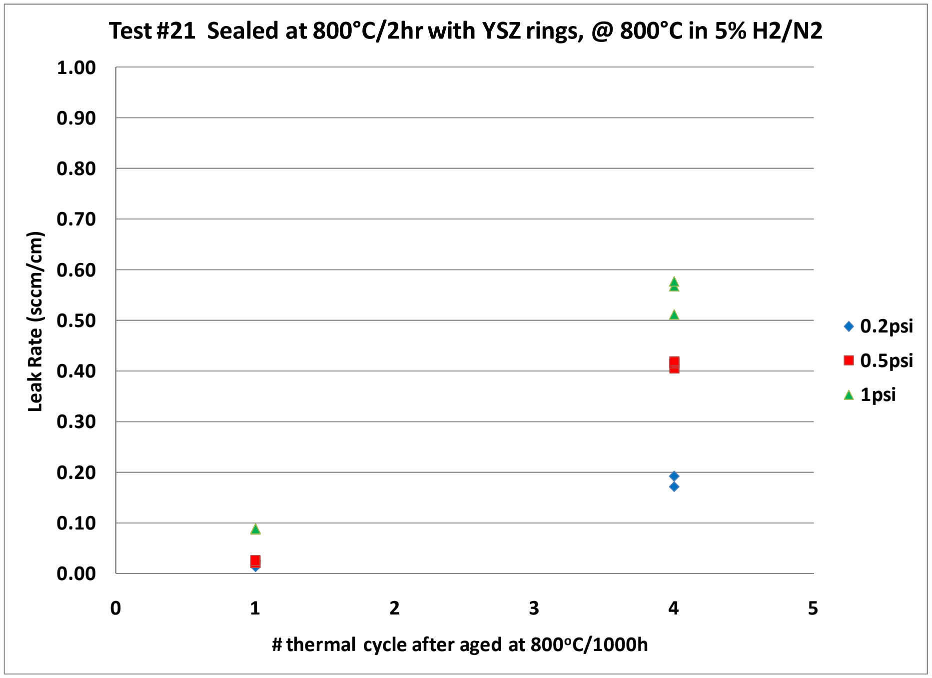
Q2: thermal stability in dual environment 800°C/1000h then 5 thermal cycles

Very stable during isothermal ageing test
Sample failed after 4 deep thermal cycles





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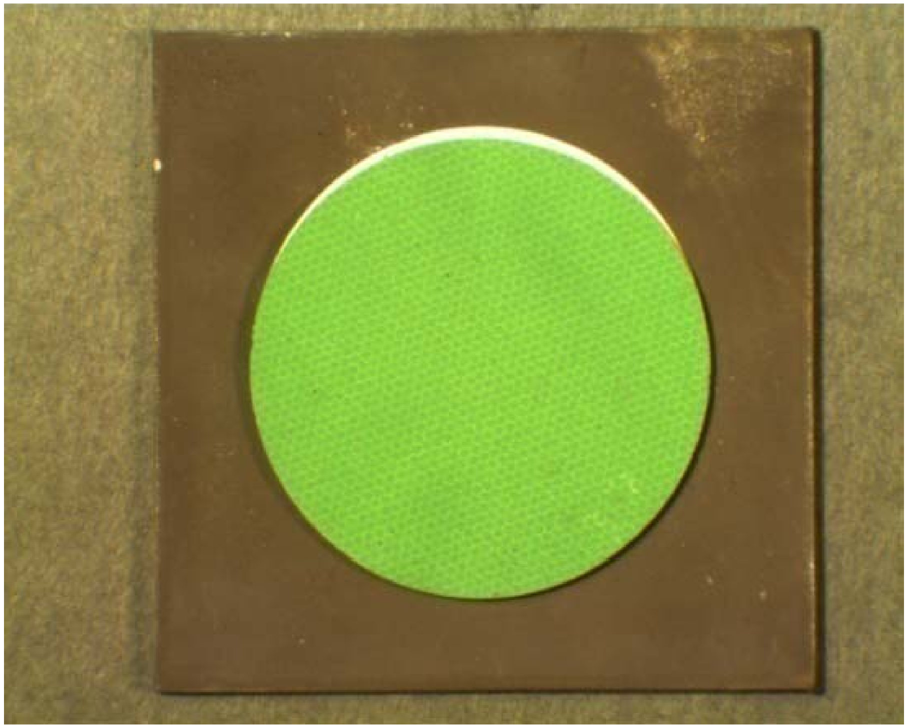
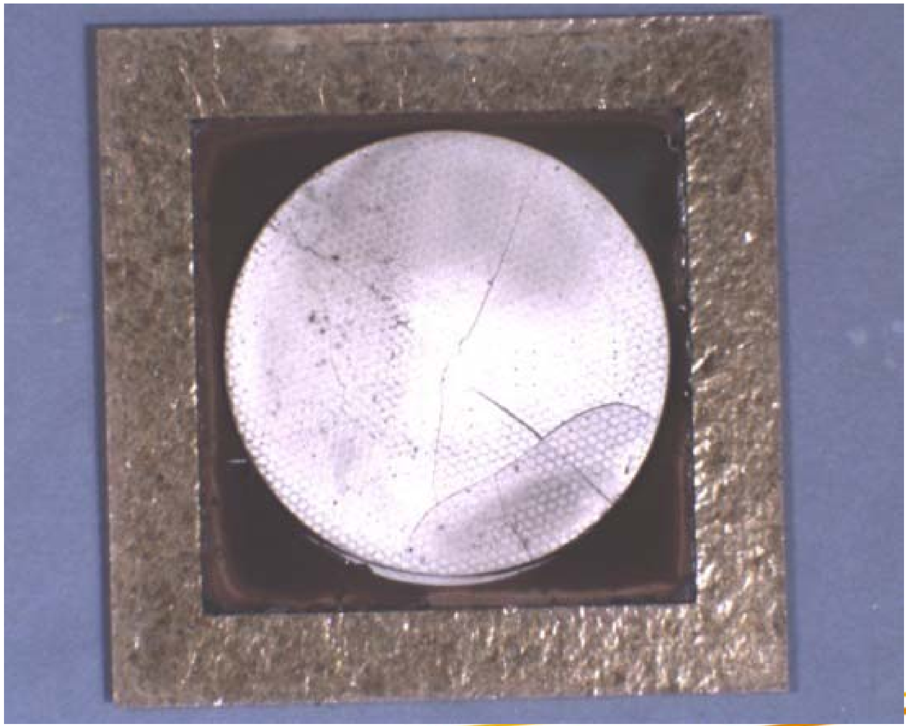
Post-mortem analysis: 800ºC/1000h+4 cycles

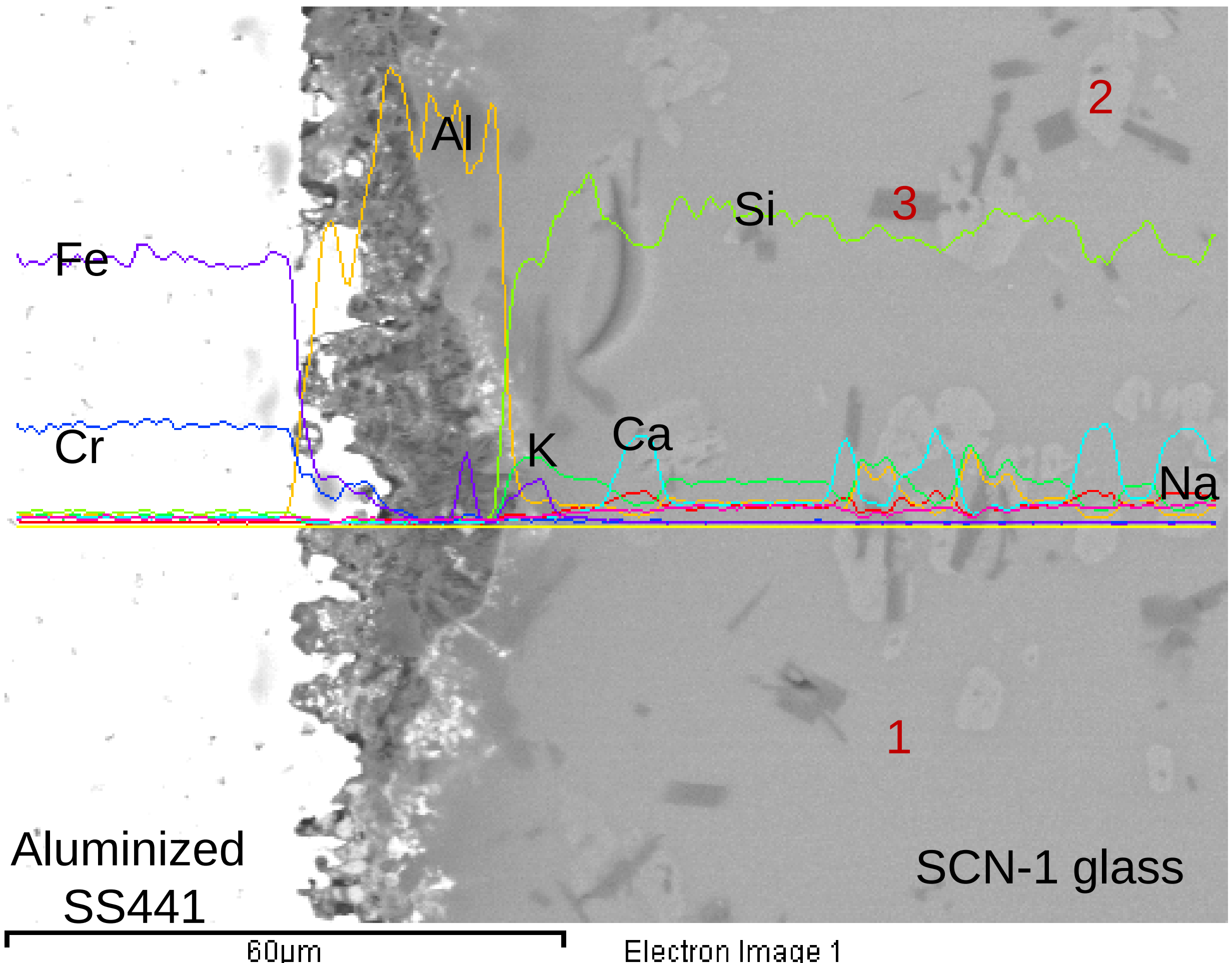
As-sealed



After 1000h and 4 cycles



Glass/aluminized SS441 interface (800ºC1000h)



Element	#1	#2	#3
O K	63.0	61.9	63.9
Na K	3.0	6.0	0.9
Mg K	0.9		0.4
Al K	1.3	0.3	5.5
Si K	25.9	22.2	23.4
K K	3.2	0.9	5.7
Ca K	1.4	7.6	
Ba L	1.4	1.2	0.3

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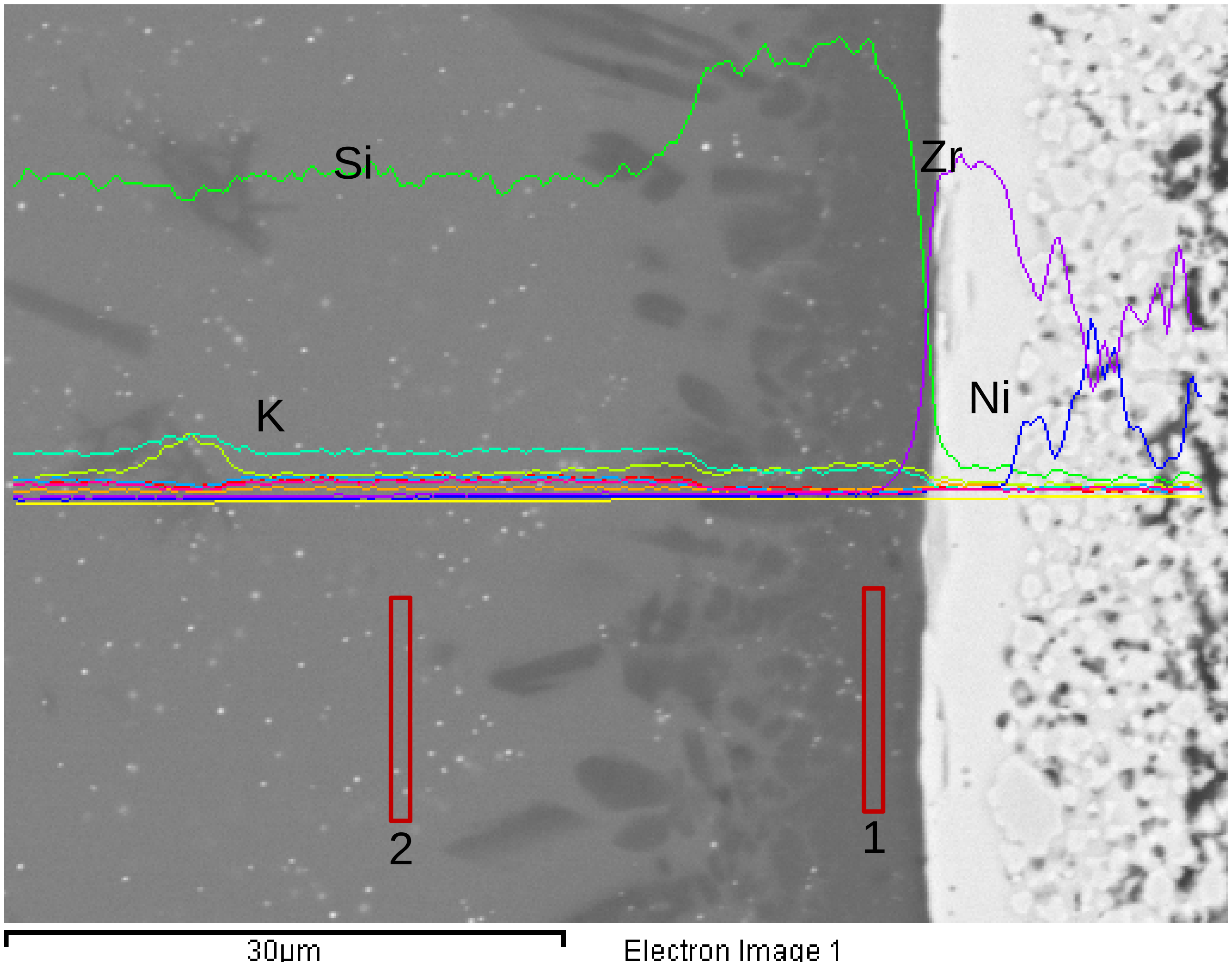
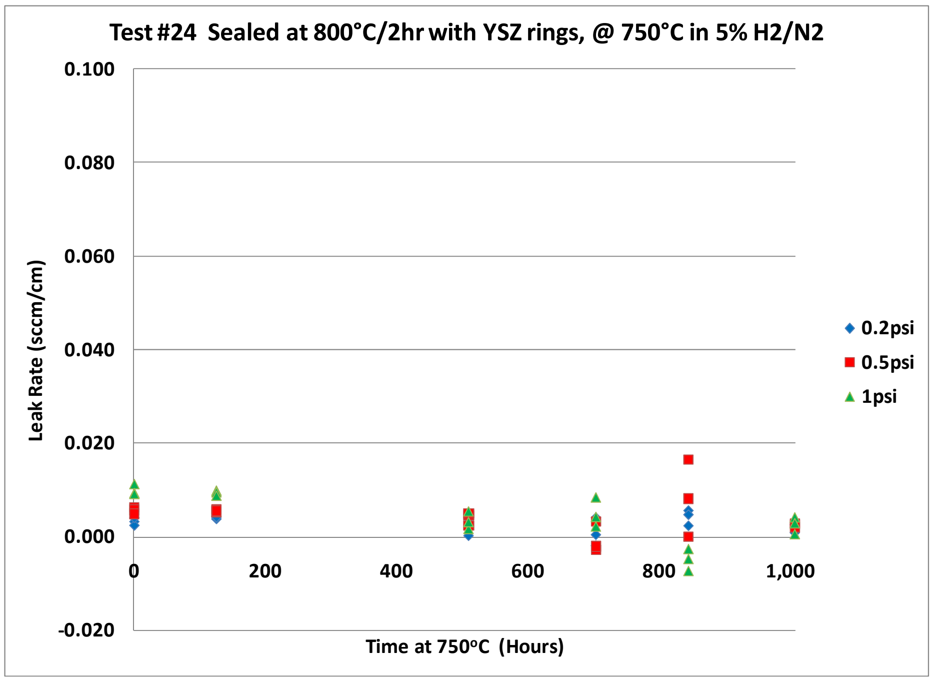
Glass/YSZ electrolyte interface (800ºC1000h)

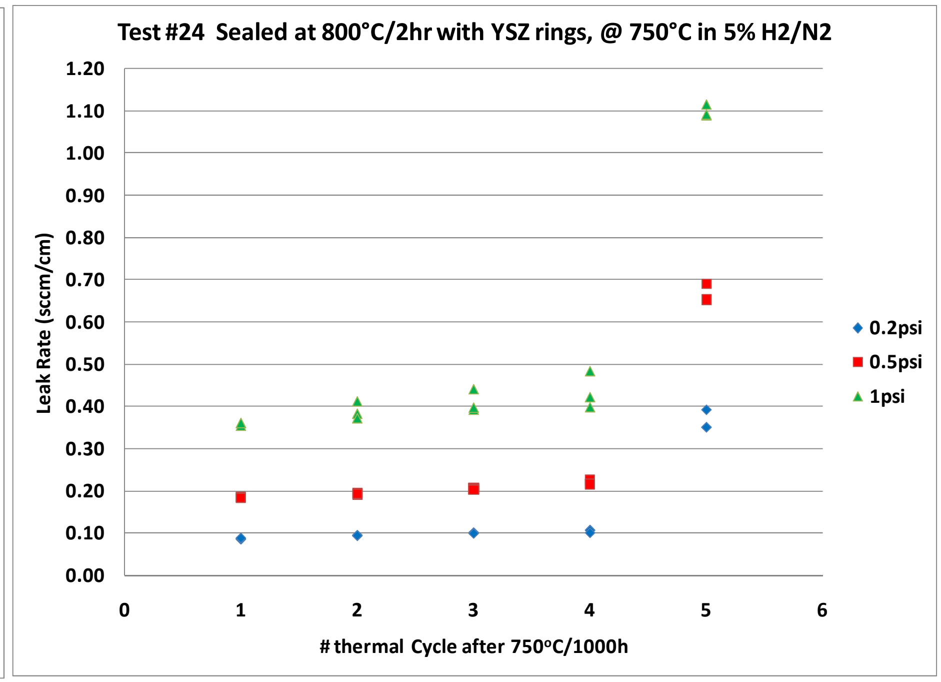


Element	#1	#2
O K	66.2	62.9
Na K	0.6	3.2
Mg K	0.2	0.7
Al K	1.7	1.5
Si K	29.0	25.9
K K	1.8	3.4
Ca K		1.2
Ba L		1.2
Ti K	0.1	
Zr L	0.3	

Q2: thermal stability in dual environment 750ºC/1000h then 5 thermal cycles

Very stable during isothermal ageing test
Sample failed after 1 cycle and more damages after 5 cycles





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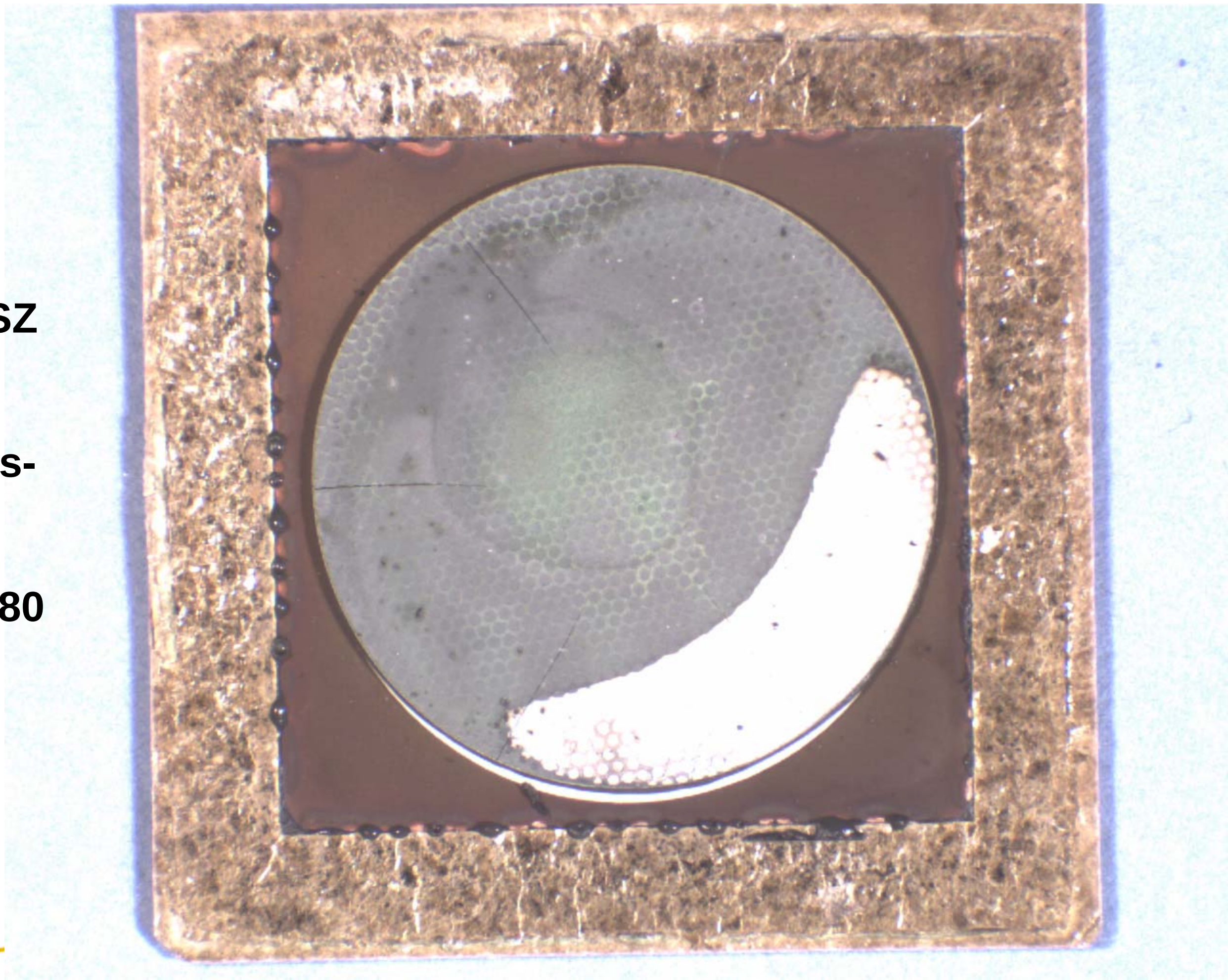
Post-mortem analysis: 750^oC/1000h+5 cycles

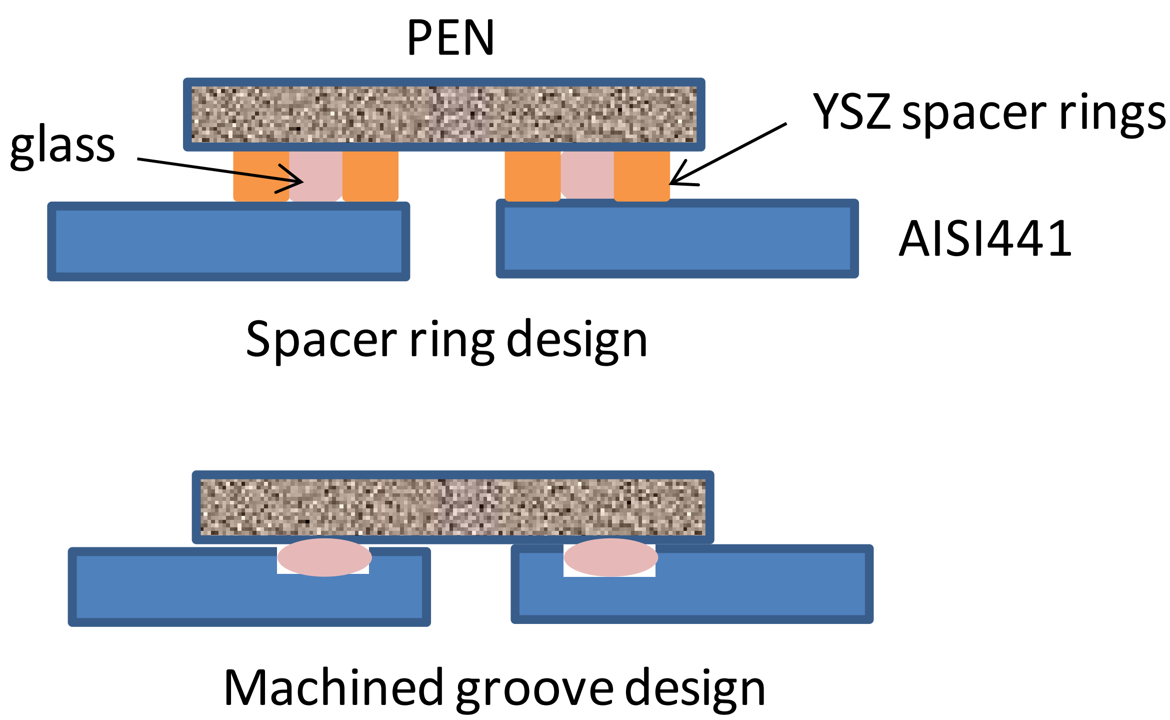
Consistent radial fractures of bi-layers as previous (800^oC/1000h) sample

<u>Cause for fracture</u>

- **High stress from thick YSZ spacer rings**
- **Lower strength after reduced (~60 MPa from as-sealed of ~240 MPa).**
- **Lower modulus after reduced (~45 GPa from ~80 GPa as-sealed)**
- **Increased flaw size and distribution**



Other containment geometry

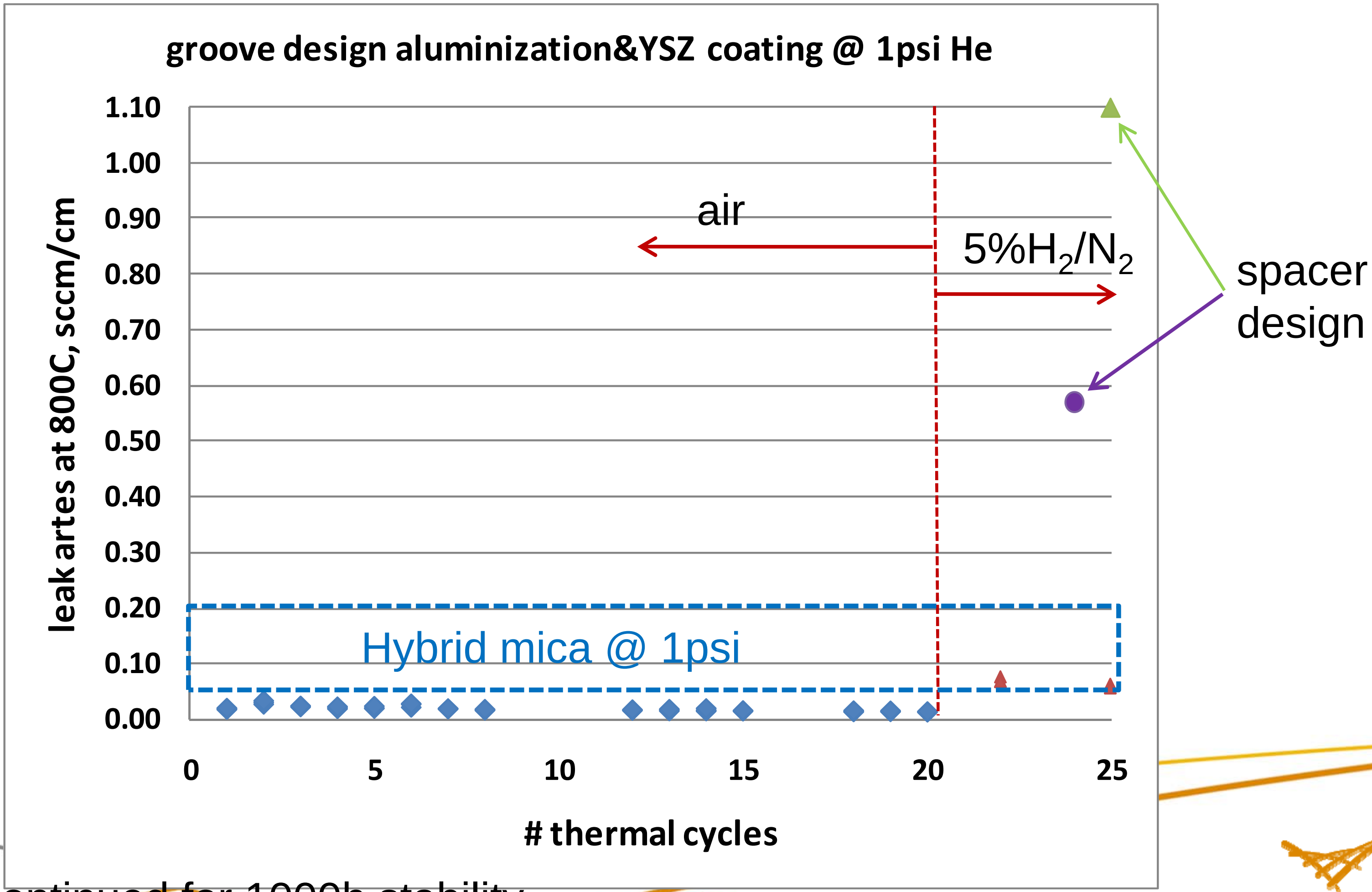


YSZ coating on SS441

- Vapor deposition at PNNL showed poor adhesion on plain SS441
- Double coating: YSZ coating (15-20 μm) by ultrasonic sprayer on aluminized SS441
- Single coating by high velocity cold spray on plain SS441 without heat treatment (S. Dakota School of Mines)

Low leak rates suggest no bi-layer fracture

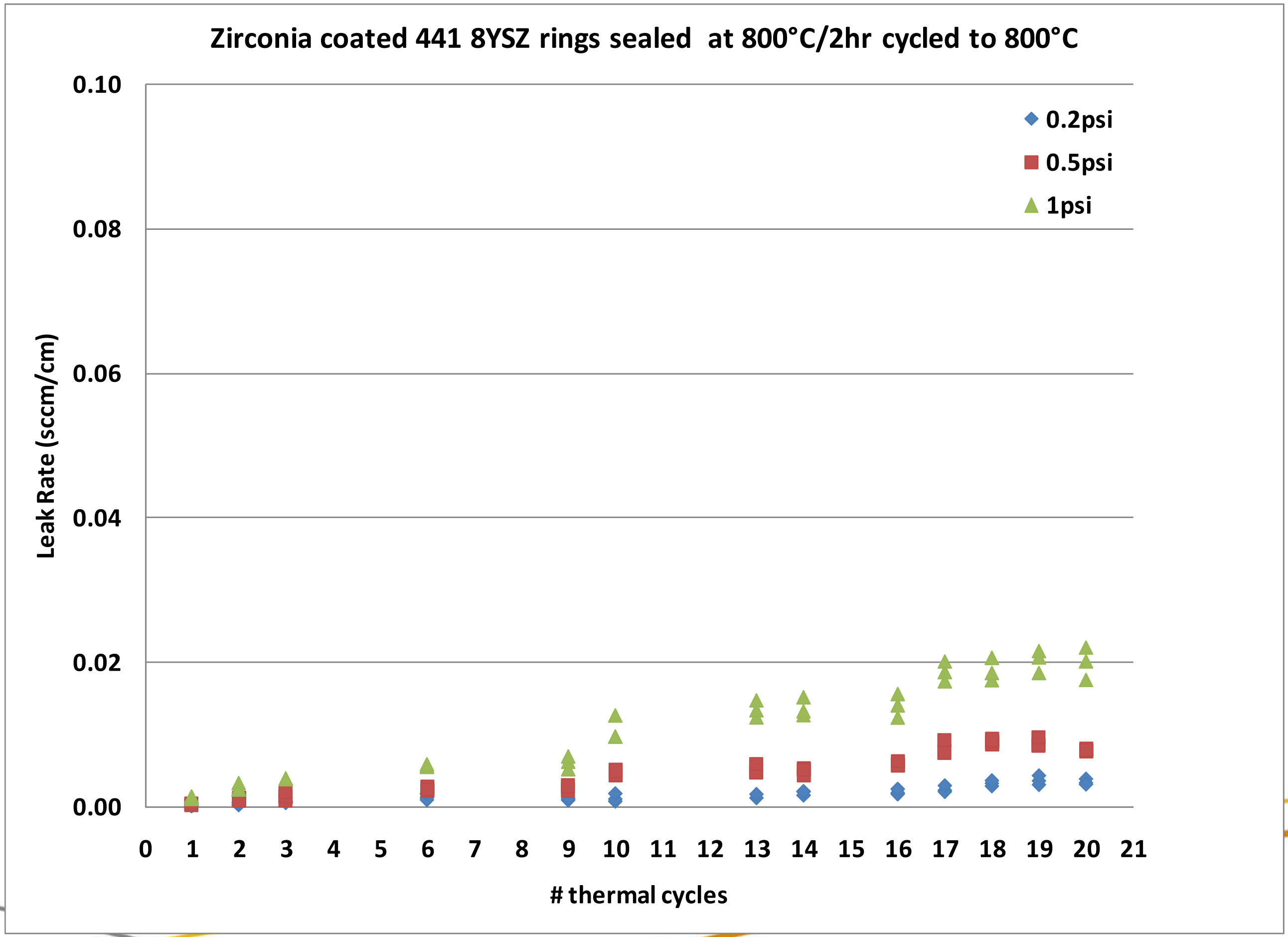
SS441 was aluminized then coated with YSZ with ultrasonic sprayer



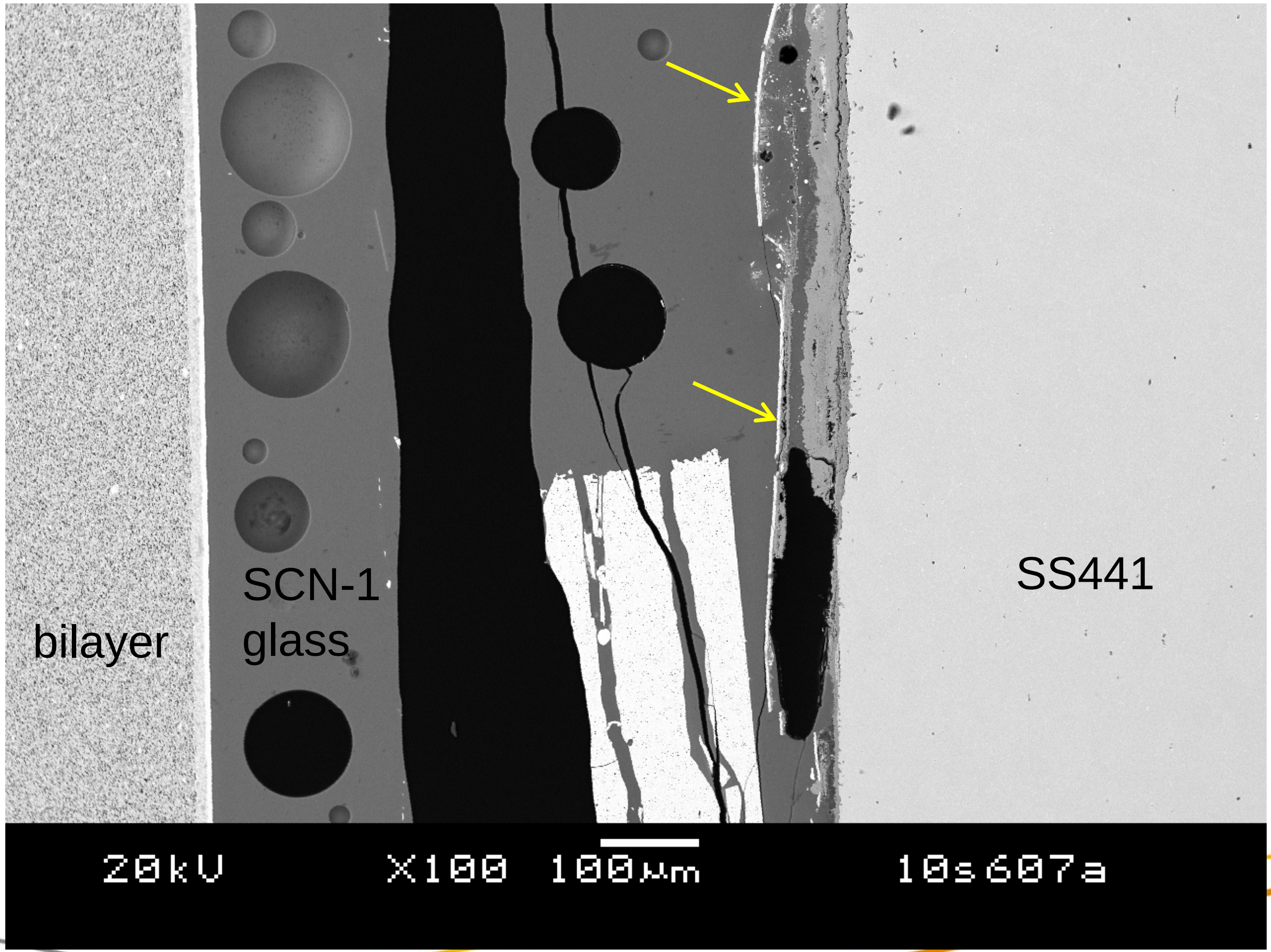
Test continued for 1000h stability

Thermal cycle stability of YSZ-coated SS441

SS441 substrate was coated with high velocity cold spray in collaboration with S. Dakota School of Mines



Poor adhesion of YSZ coating on plain SS441



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Summary and conclusion

- SCN-1 glass showed good thermal cycle stability between RT and T=700-850^{o}C when sealed between a ceramic bi-layer and an aluminized SS441 substrate.
- SCN-1 glass was able to stand back pressure to 1.0 psi and remained hermetic after thermal cycling.
- Current spacer ring design resulted in bi-layer fracture after anode reduction. Using groove design low leak rates were obtained suggesting no bi-layer fracture.
- SCN-1 glass appeared thermally stable for 1000h at 750-800^{o}C in dual environment and 1psi.
- Microstructure analysis showed more precipitates along YSZ/glass interface than glass/aluminized SS41 interface. There were also two types of precipitates/crystallites observed in glass matrix.
- The adhesion of direct coating of YSZ on SS441 was poor.

Future work

1. Incorporate compliant glass into stack fixture testing.
2. Continue stability test (750-800ºC/1000h) in dual environment for aluminized+YSZ coated SS441. Conduct post-mortem interfacial characterization and optimize YSZ coating and process.
3. Conduct volatility (K+Na ~13 at%) and electrical stability study in dual environments with high water content to assess long-term durability.
4. Continue development / evaluation of coatings for seal / interconnect interfaces.
5. Optimize compliant glass-based seal designs for long-term and thermal cycle stability
6. Evaluate other compliant glasses developed under SECA programs with PNNL leak test fixtures.

Acknowledgements

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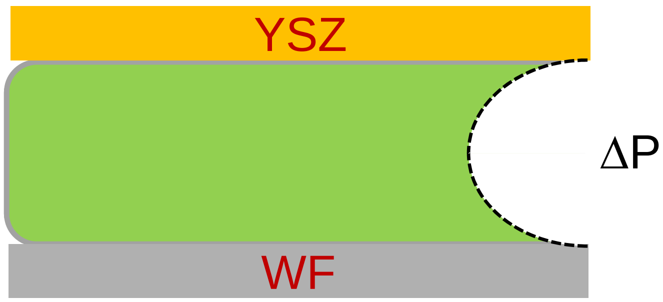
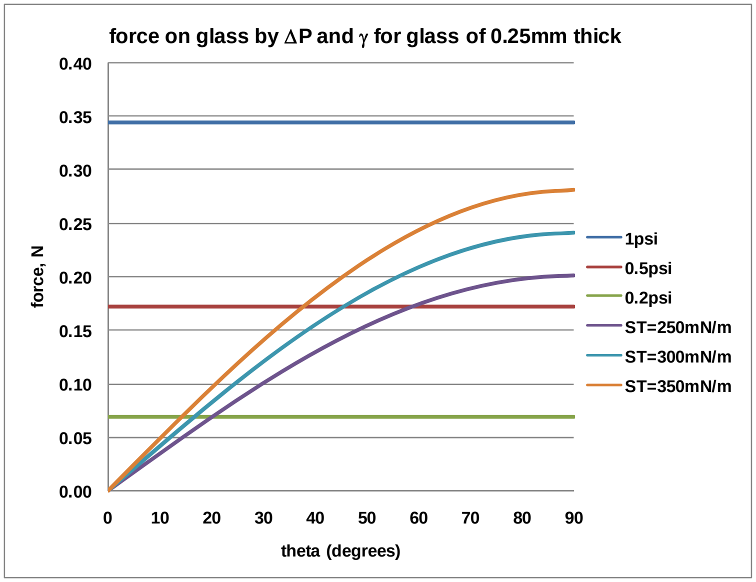
- ORNL: Edgar Lara-Curzio, Amit Shyam
- South Dakota School of Mines: Prof. West
- PNNL: Jim Coleman, Shelley Carlson, Nat Saenz

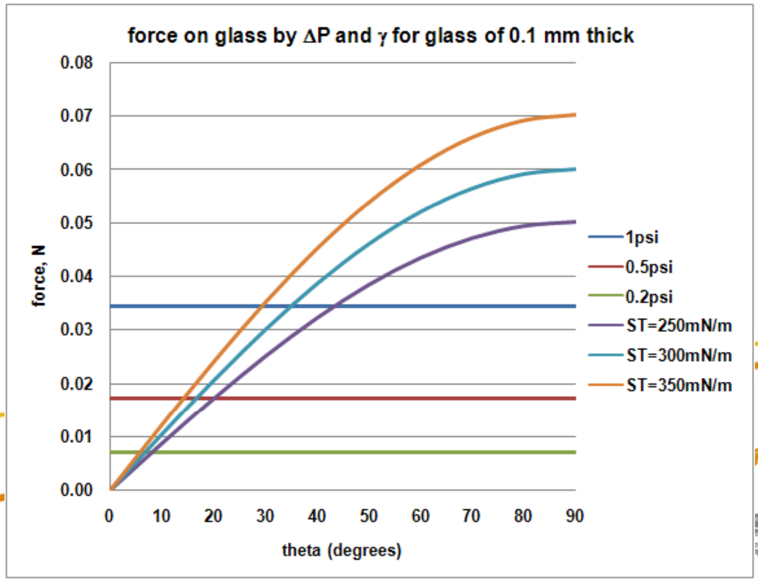
Will the glass be pushed out by back pressure

$\eta = 10^5$ Pa s (800°C), $10^{5.5}$ Pa s (750°C)
γ = 250-350 mN/m as liquid, ? 750-800°C

Force to push-out =area x ΔP
Force to resist push-out = length x γ

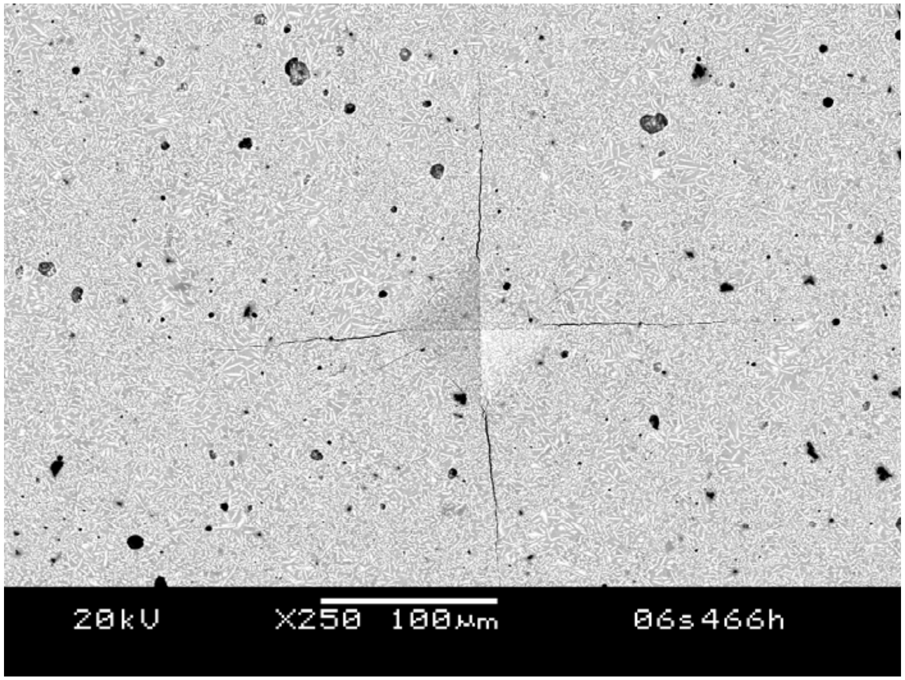




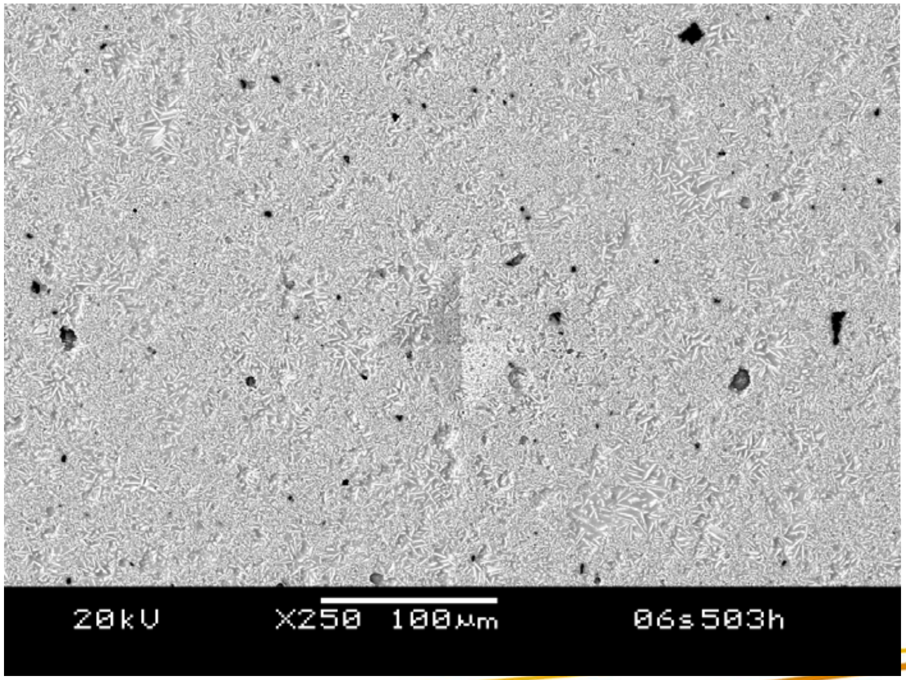


Crack healing

- Commonly observed in glass at elevated temperatures.
- 3 mechanisms proposed: diffusion-driven thermal healing, adhesion from intermolecular forces, and chemical reaction at crack-tip



G18 indented 2 kg



Fired at 750°C

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