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# Aluminization Coatings and Glass Seals for a High Temperature Hydrogen Reactor

October 27, 2022

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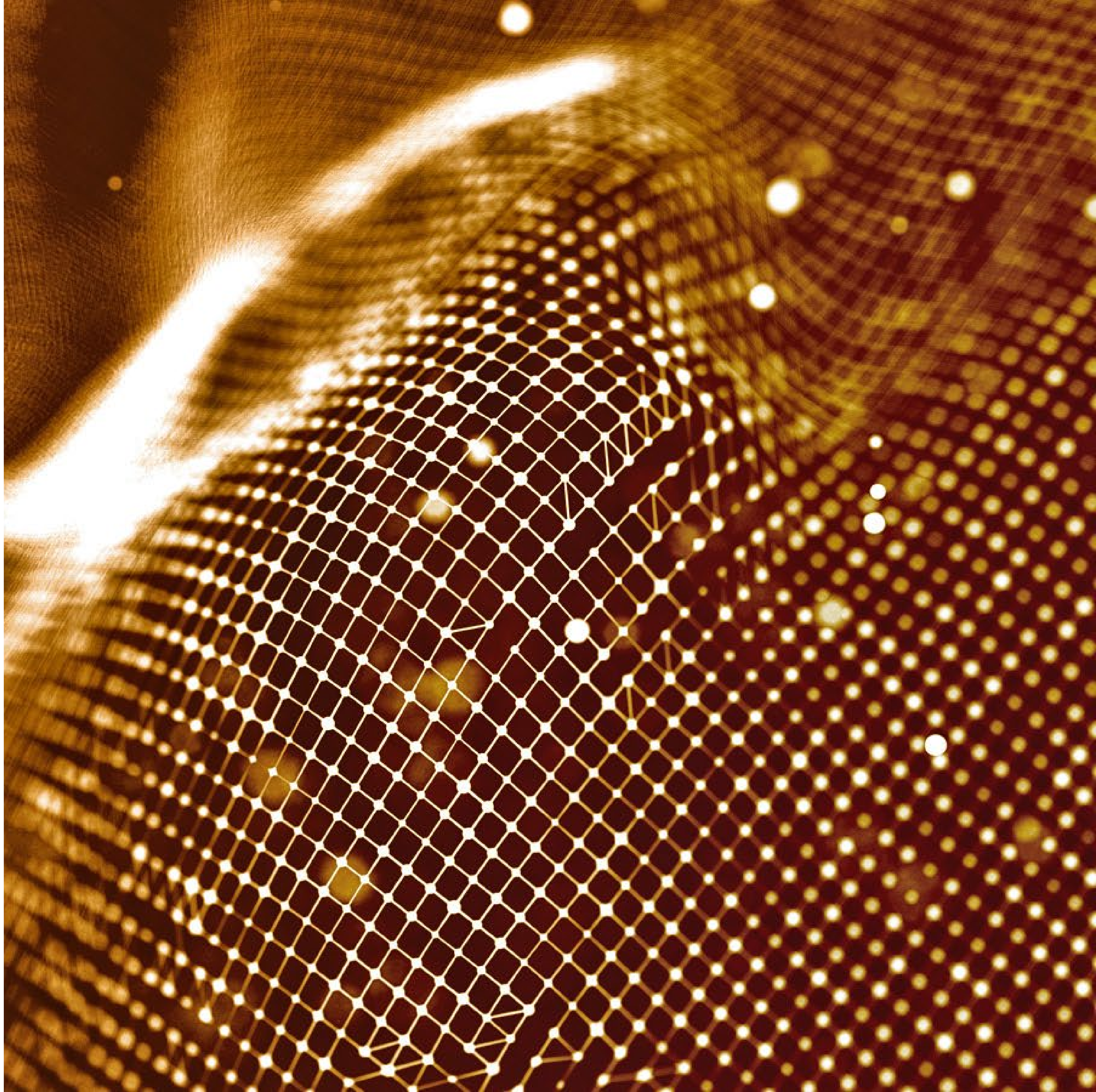

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# Background & Project Objective

- Our industrial partner is developing innovative electrolyzer technology for use in high temperature processes (e.g., steel plants) utilizing tubular cells.
- A critical challenge they are facing is creating stable, hermetic seals between the tubular cells (CTE ~ 12.8 $x10^{-6}/^{o}C$) and Inconel 617 manifolds (CTE ~ 15.8 $x10^{-6}/^{o}C$)
- Partnered to evaluate PNNL's sealing and coating IP (US Patent Numbers 10,577,694, 10,378,094, and 9,481,923) to overcome this challenge and demonstrate hermetic sealing in a full-scale reactor test.

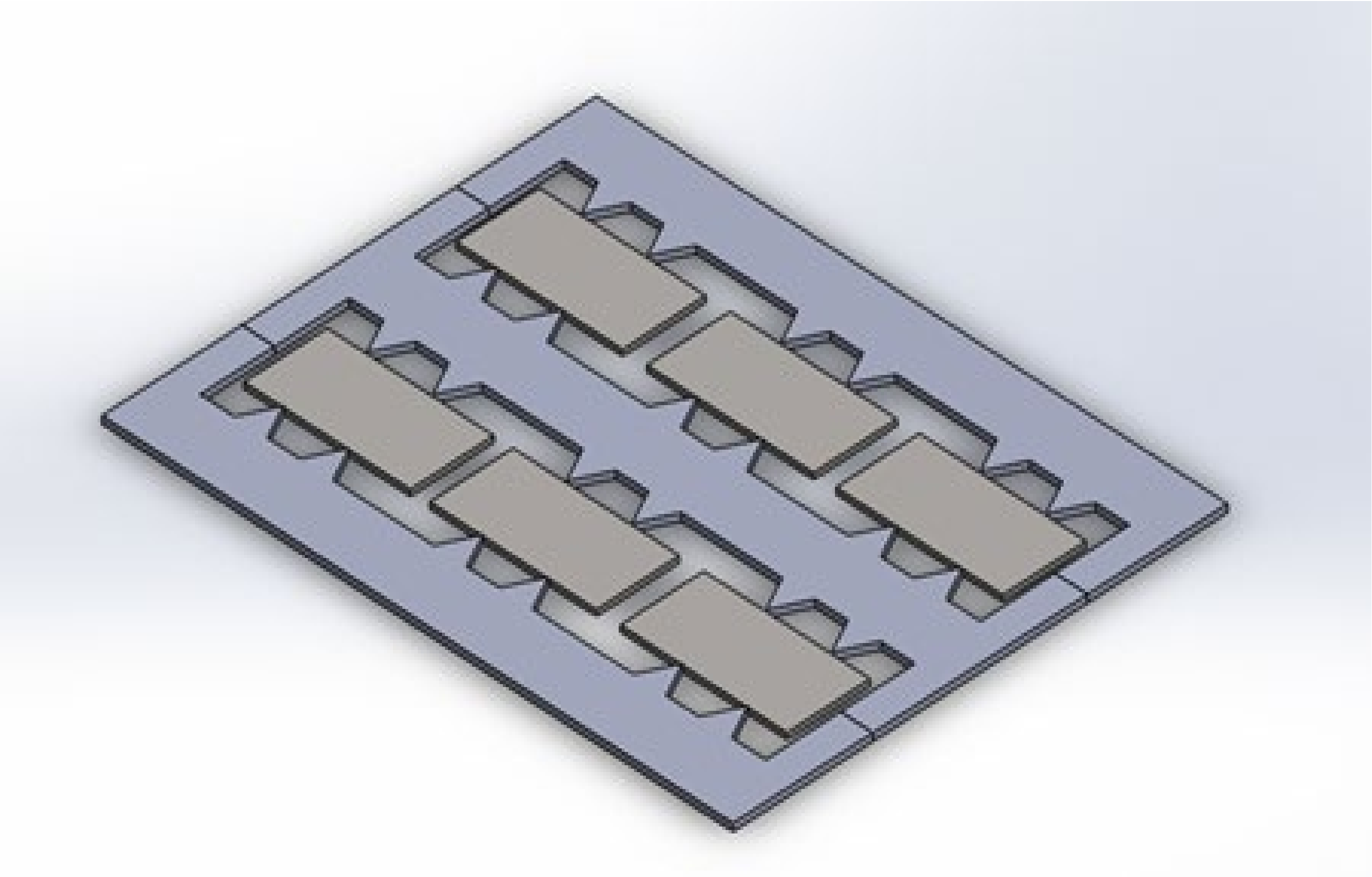
# Reactive Air Aluminization (RAA) Coating Deposition


**RAA coating applied with ultrasonic spray coater**

# Spray Coating Challenges

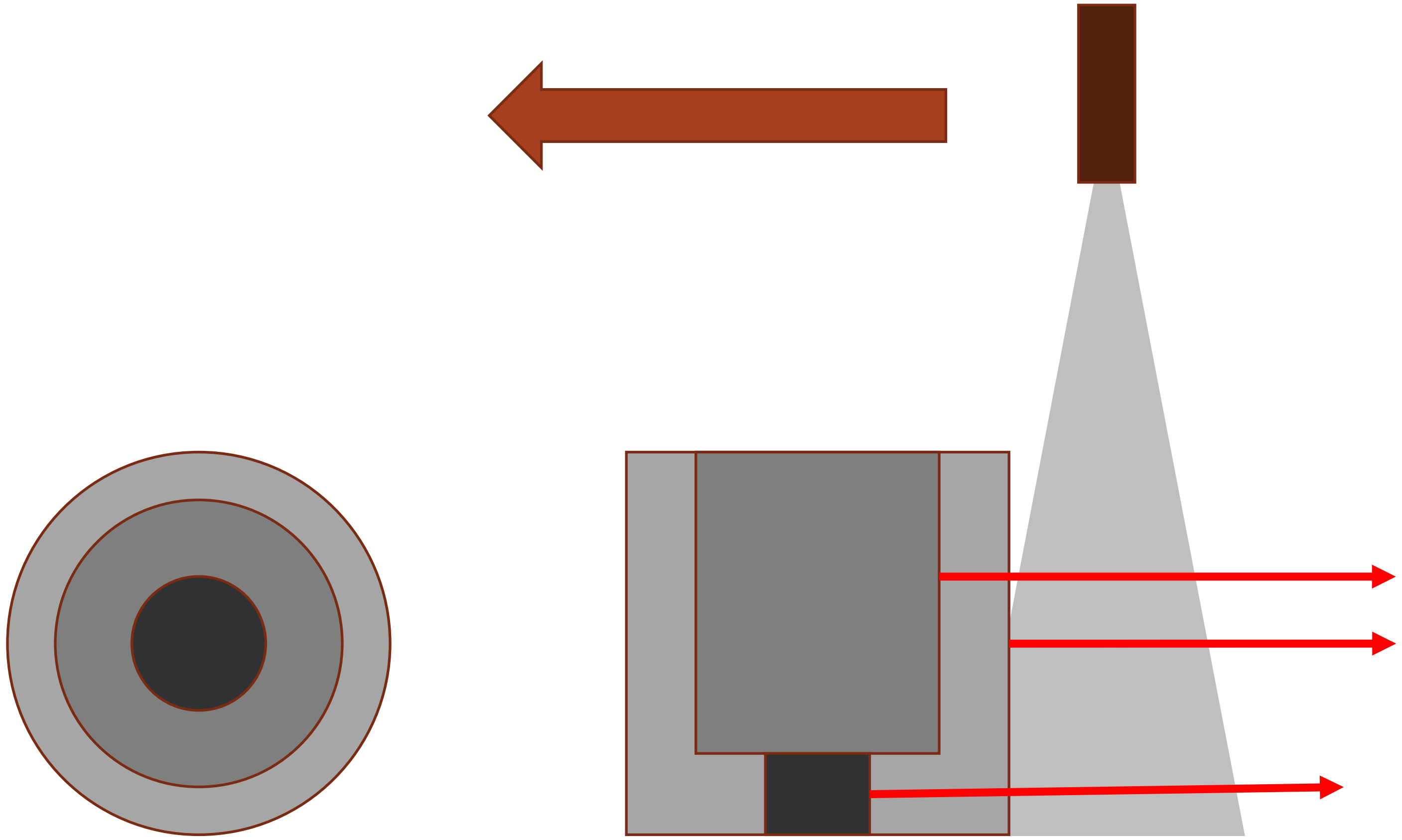
**Issue: Inconel 617 is not magnetic, and therefore not magnetically held down.**

**Solution: Designed a magnetic fixture to hold coupons down without shielding.**



# Spray Coating Challenges

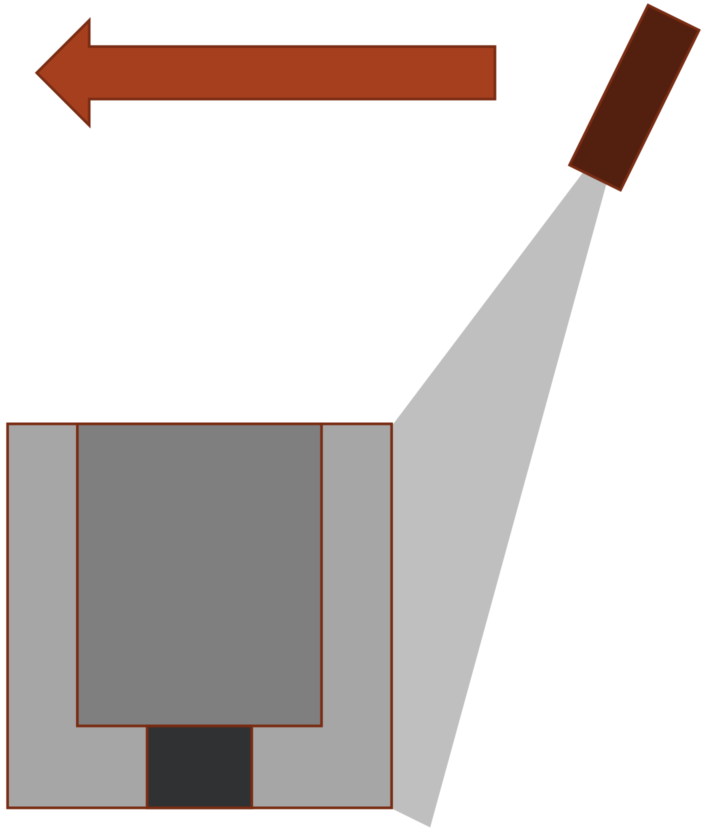
**Issue: Spray coater works best for surfaces that are largely perpendicular to spray direction, but our parts are shaped like:**



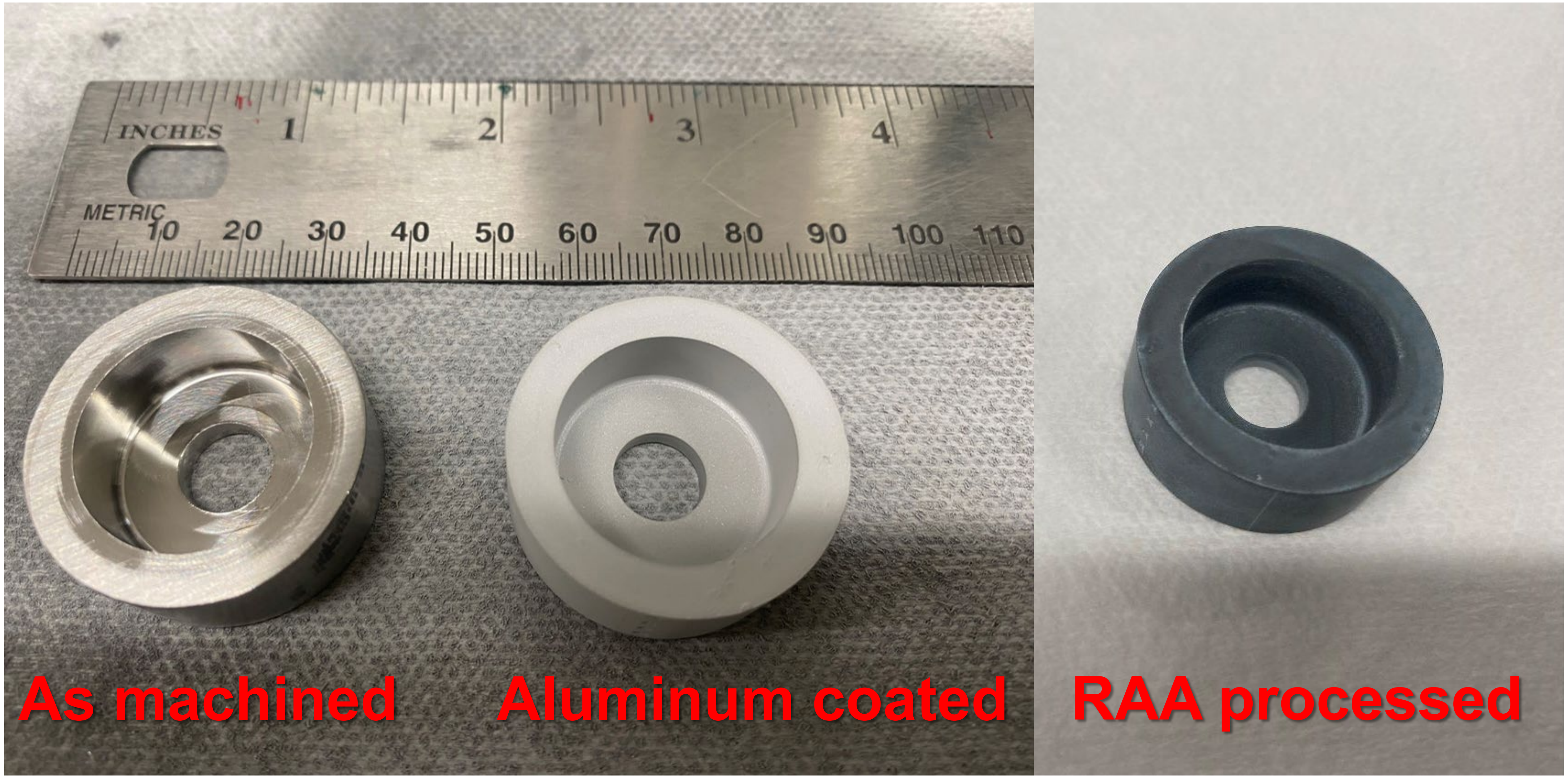
**Vertical walls are not coated well**

# Solution to Spray Coating Challenge #2

**Working with the vendor, we were able to solve some calibration issues related to the rarely implemented tilted head configuration**



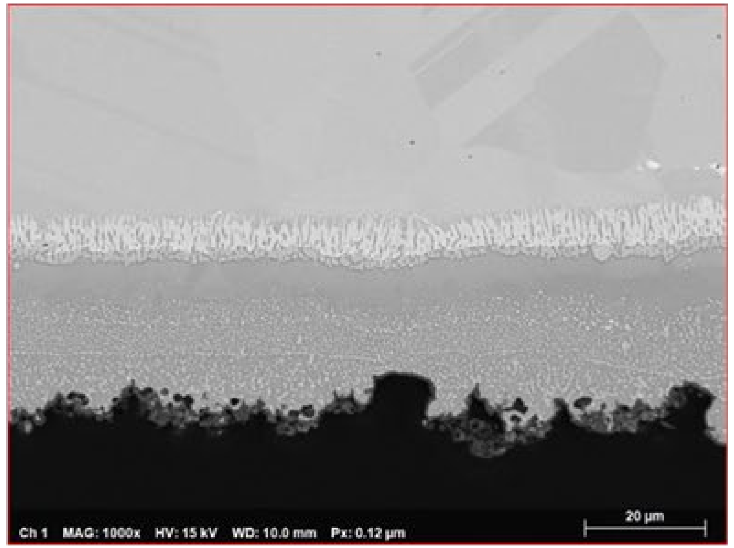
# Resulting Parts

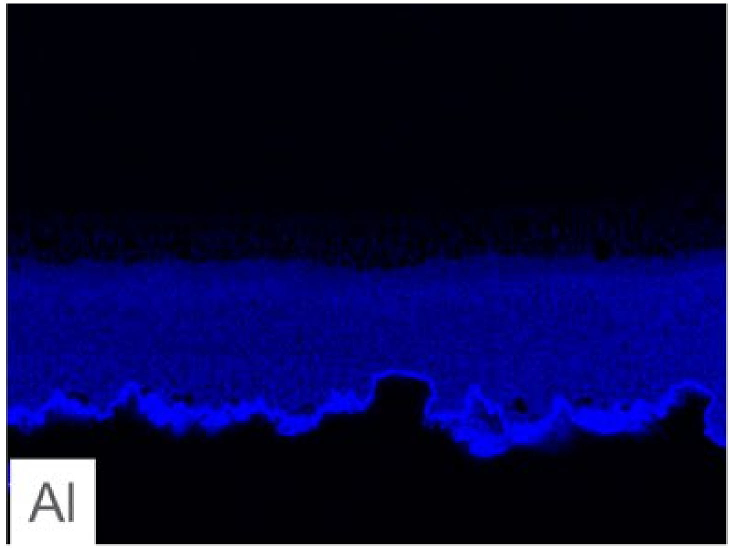


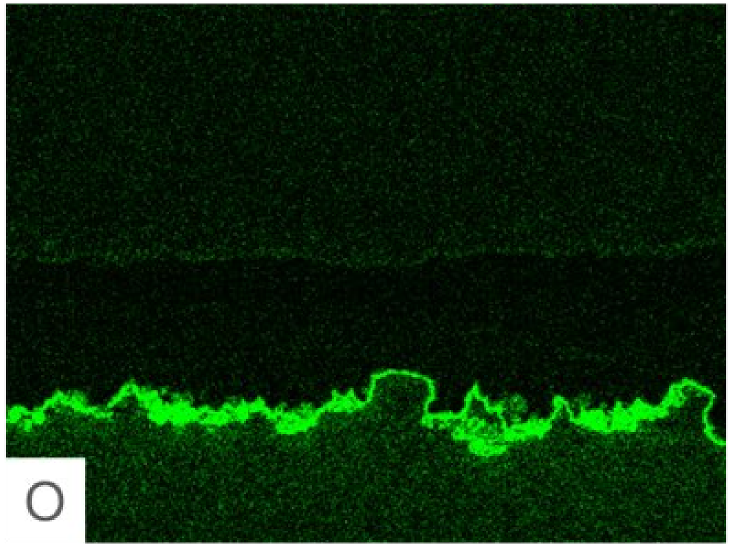
# RAA Coating Microstructure on Inconel 617

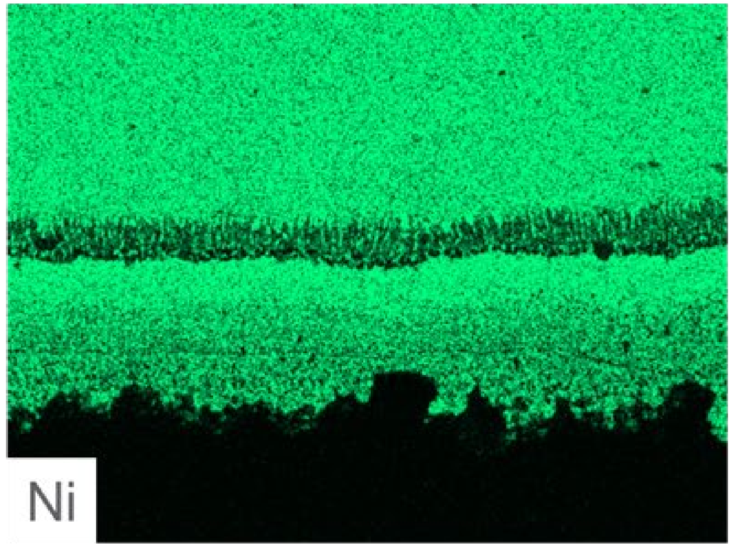
## RAA-6

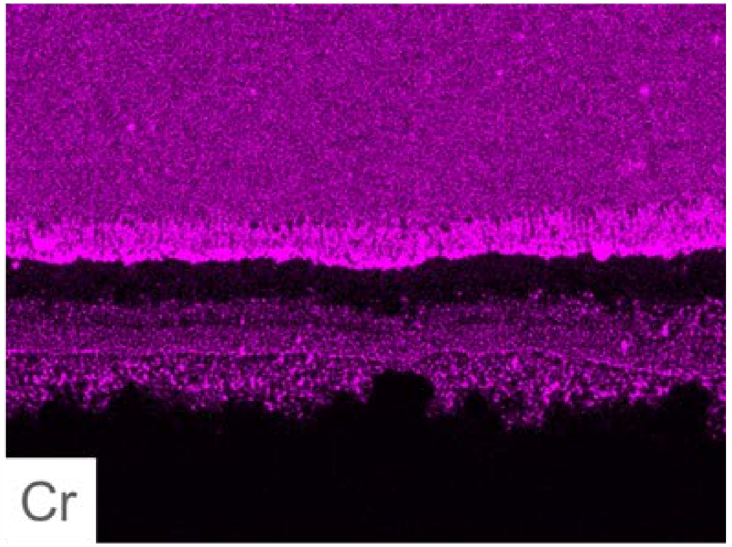
**The reaction band is composed of Ni, Cr, Co, Fe and Mo.**



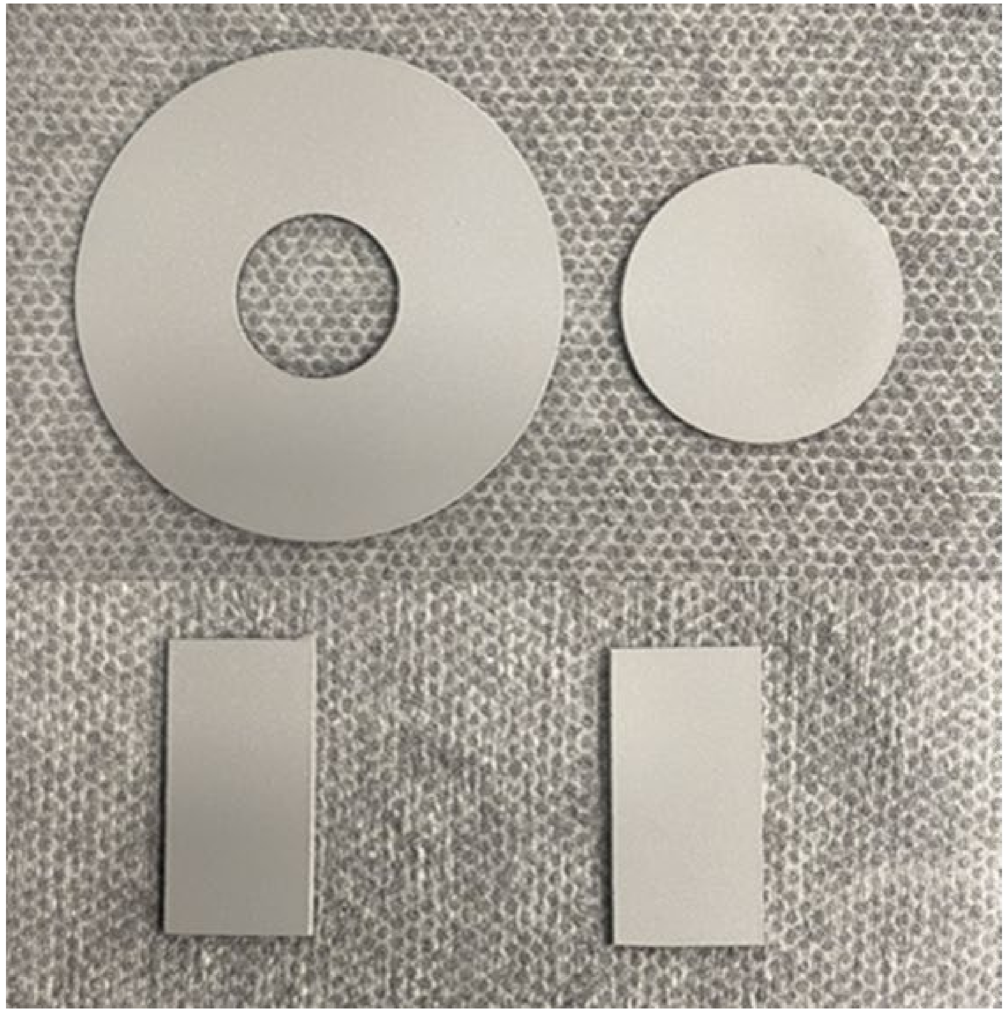



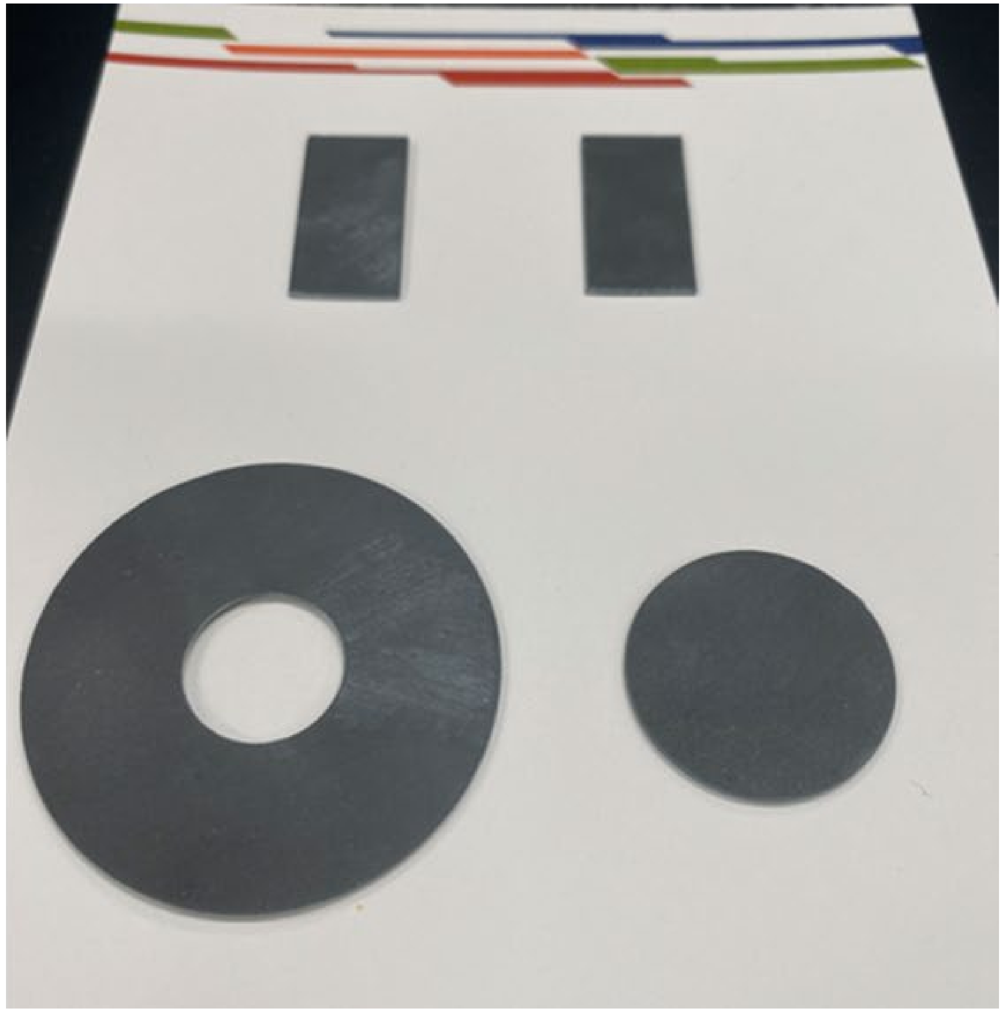



# RAA Coatings will be Pop-gun Rupture Tested

## Pop-Gun washer & disc pair is RAA processed





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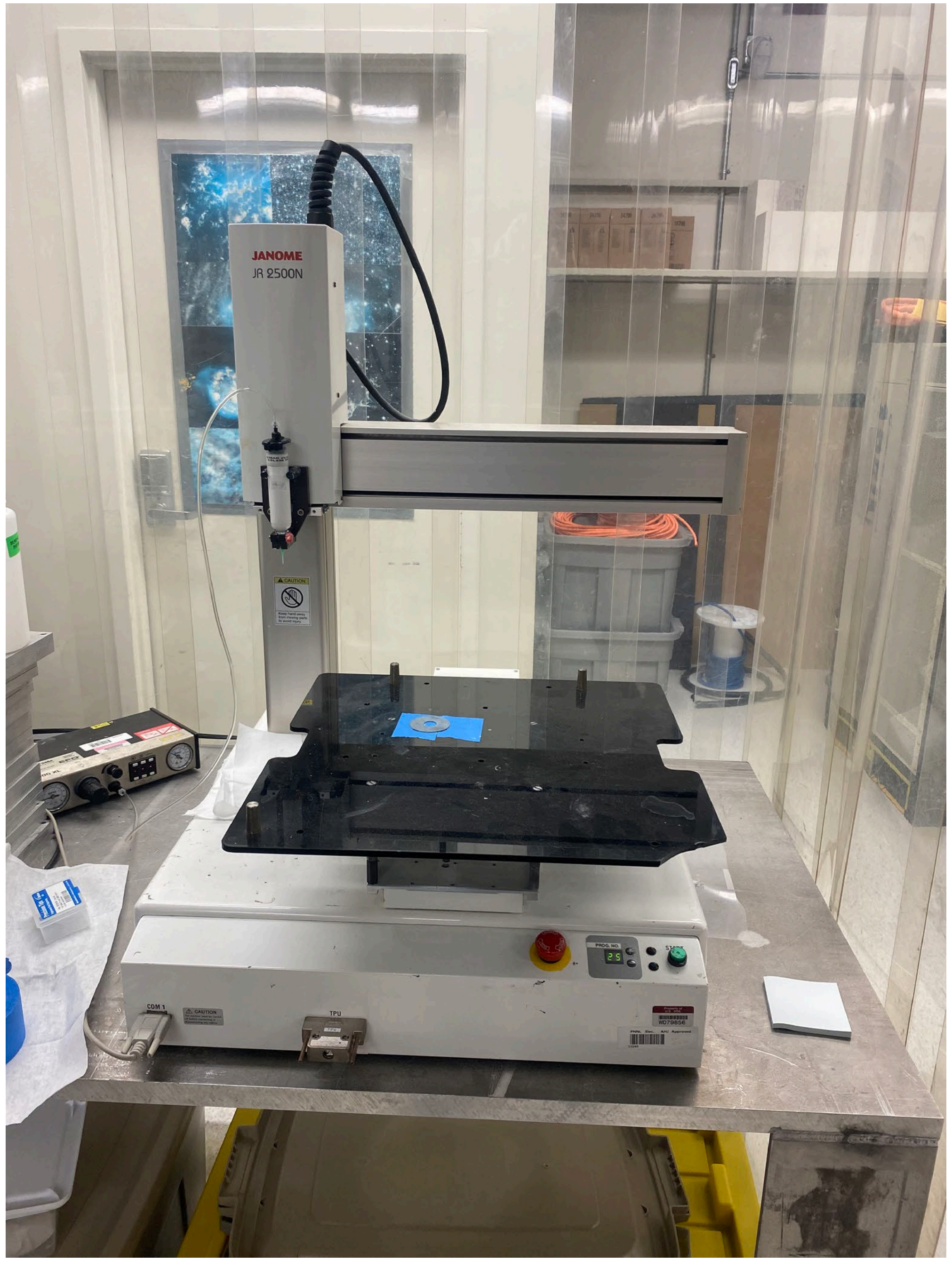
# Glass sealant applied via Robotic Dispenser


G18-20%LSCF
-17% binder


G18-4%YSZ
-17% binder

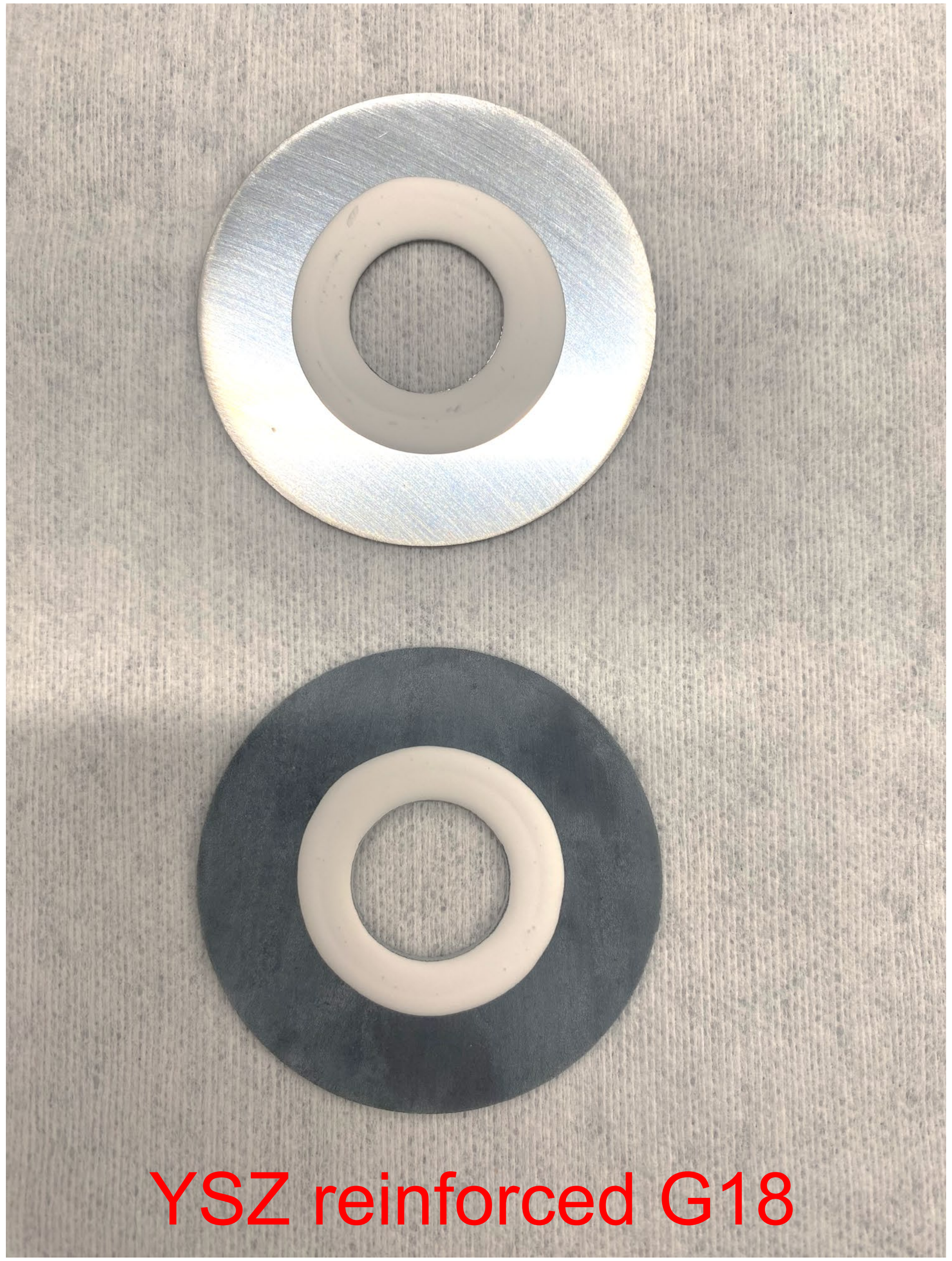


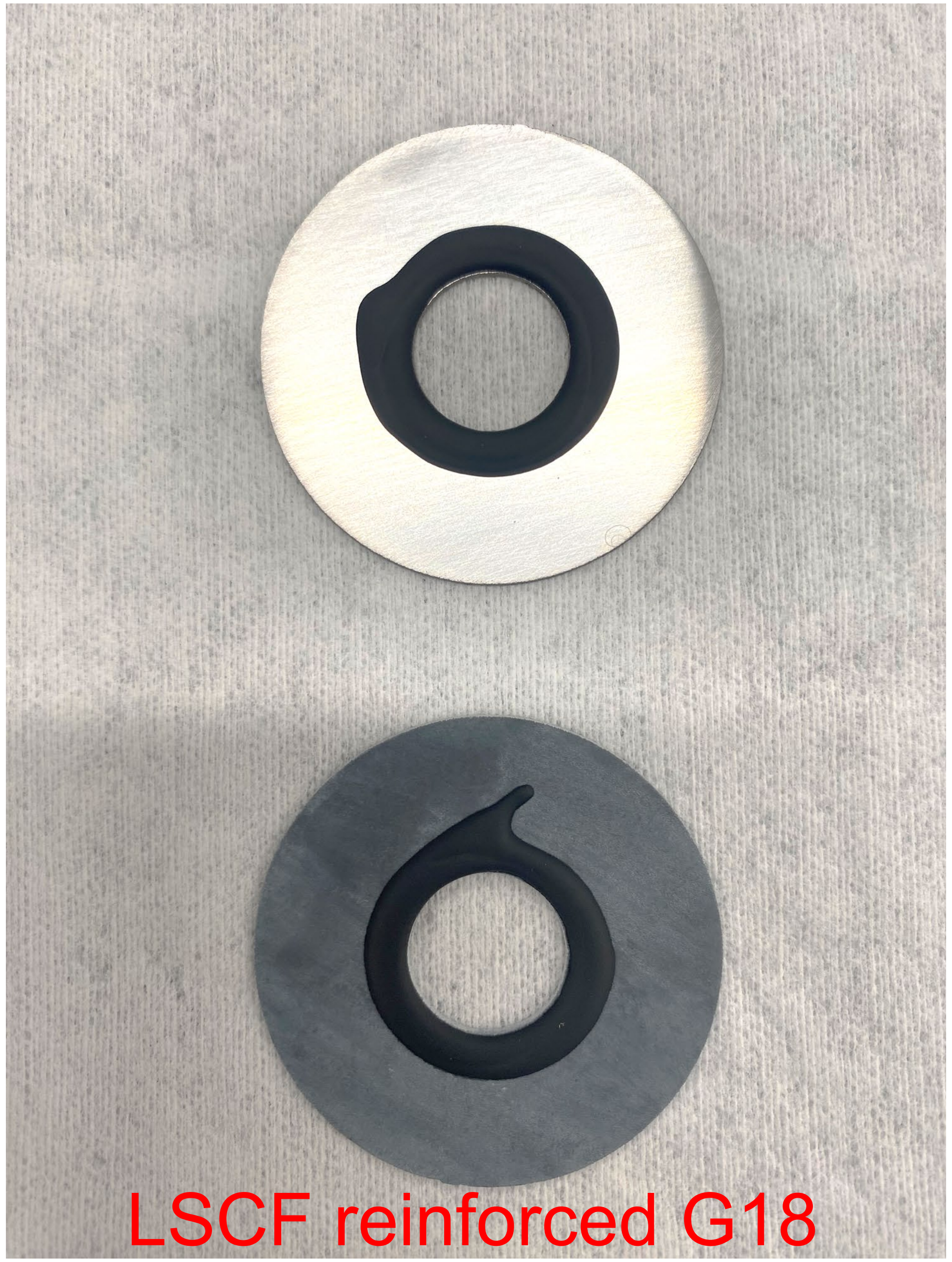

20psi condition

~0.67g of G18+YSZ

~0.8g of G18+LSCF

# Simple 2x2 test matrix




**Without RAA**

**With RAA**

# Glass sealing discs to washers

Test samples sealing in the furnace

Pop-gun tests are currently underway

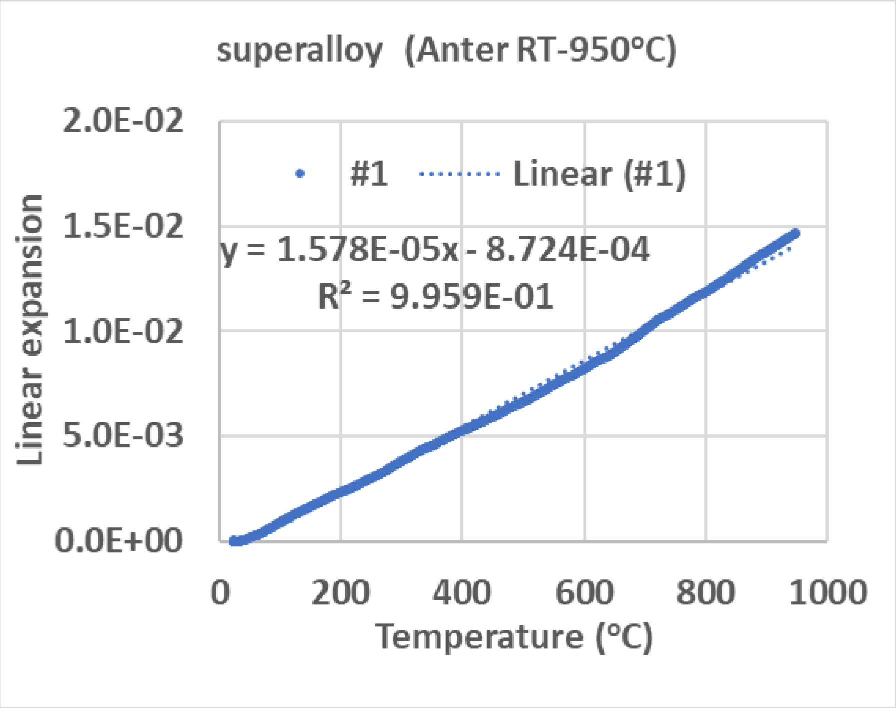
# Objective and Tasks for Glass Seal Development

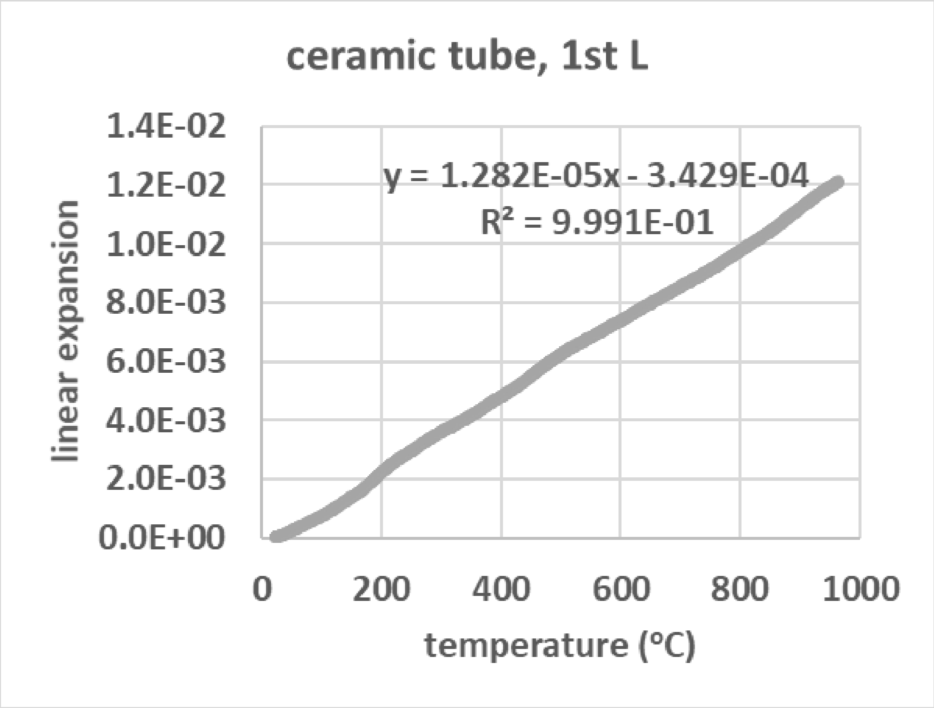
***Objective**: To develop glass sealant for client's tubular cells in electrolysis application at high temperature (900$^oC$) and high steam (> 90% $H_2O$)*

- **Glass Formulation and Thermal Property Characterization: plain glass and composite glass approach, as-made and crystallized state**
- **Ageing Effect on Thermal Properties and Wetting Study: aged in air and reducing/humid environment at 900$^oC$**
- **Bonding Strength and Interfacial Reaction Study: tensile testing on YSZ; cup sealing leak test, and interfacial characterization**
- **Validation of Candidate Glass and Aluminization Coating in a mini-tube reactor under dual environment**

# Mating Materials and Configuration for Glass Development

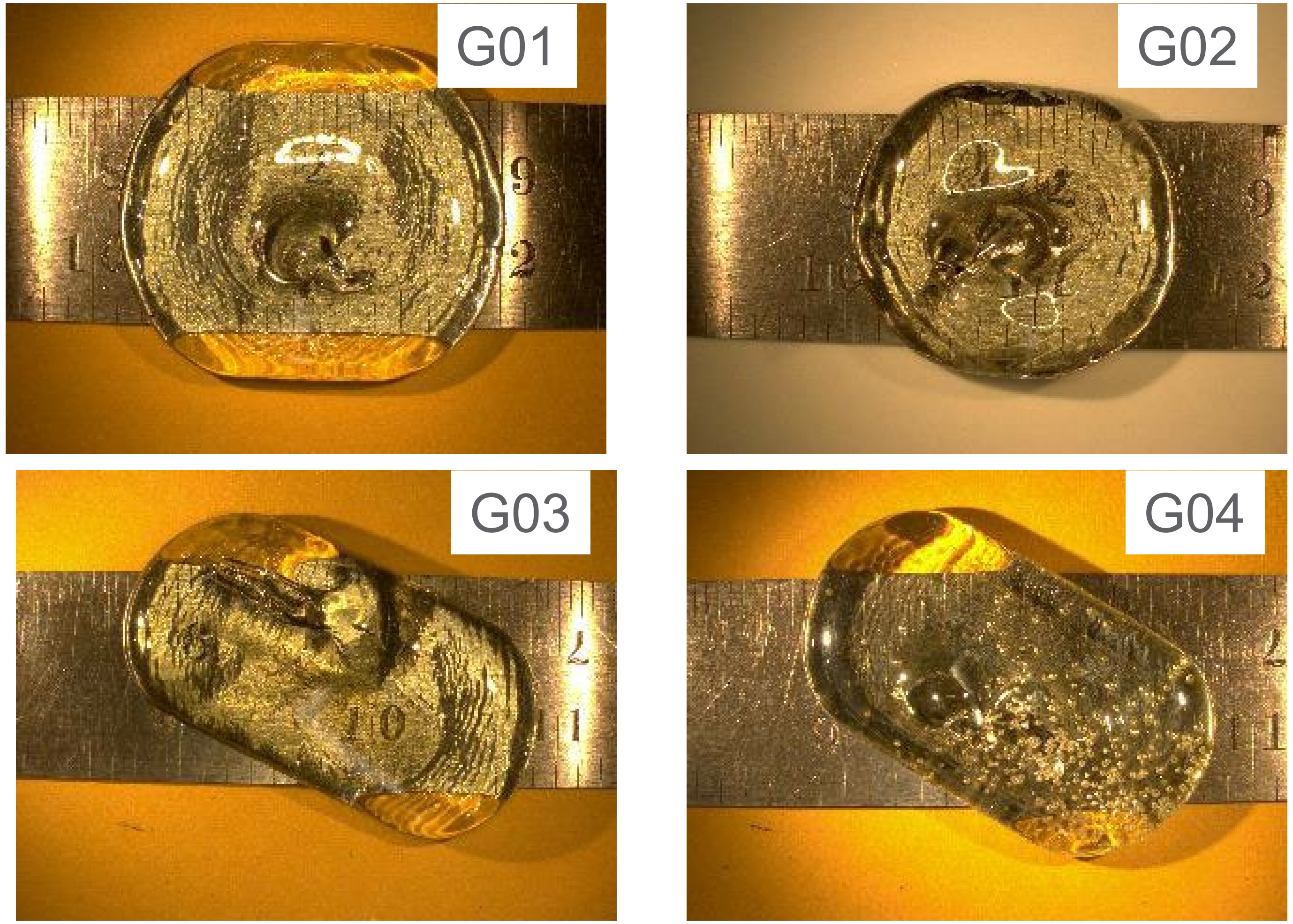
- Superalloy cup manifold & ceramic tubular cell
- Operating condition: 900°C with >90-95%$H_2O$
- Very large CTE mismatch (~$3x10^{-6}$/°C) between superalloy ($15.8x10^{-6}$/°C) & tube 12.8 $x10^{-6}$/°C
- Targeting ~$14x10^{-6}$/°C for sealant CTE




# Glass formulation and thermal property characterization: plain glass approach

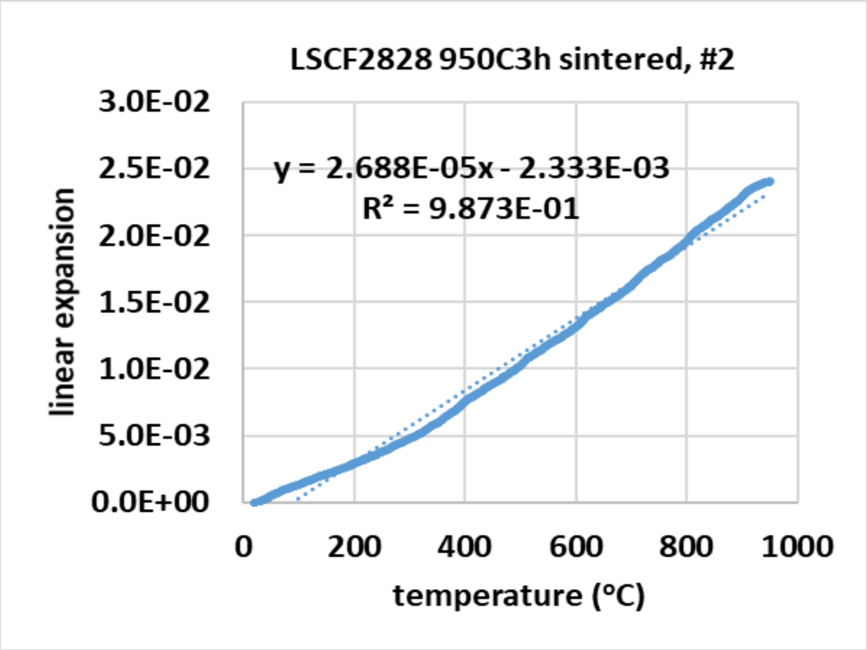
| mole% | SiO2 | B2O3 | Al2O3 | BaCO3 | SrCO3 | Y2O3 | La2O3 | as-made |
|---|---|---|---|---|---|---|---|---|
| **G01** | 39.0 | 10.0 | 9.0 | 33.0 | 9.0 | 0.0 | 0.0 | transparent |
| **G02** | 39.0 | 10.0 | 9.0 | 36.0 | 6.0 | 0.0 | 0.0 | transparent |
| **G03** | 39.0 | 10.0 | 9.0 | 39.0 | 3.0 | 0.0 | 0.0 | transparent |
| **G04** | 39.0 | 10.0 | 9.0 | 42.0 | 0.0 | 0.0 | 0.0 | transparent |
| **G05** | 39.0 | 10.0 | 0.0 | 33.0 | 9.0 | 9.0 | 0.0 | opaque |
| **G06** | 39.0 | 10.0 | 0.0 | 33.0 | 9.0 | 0.0 | 9.0 | transparent |

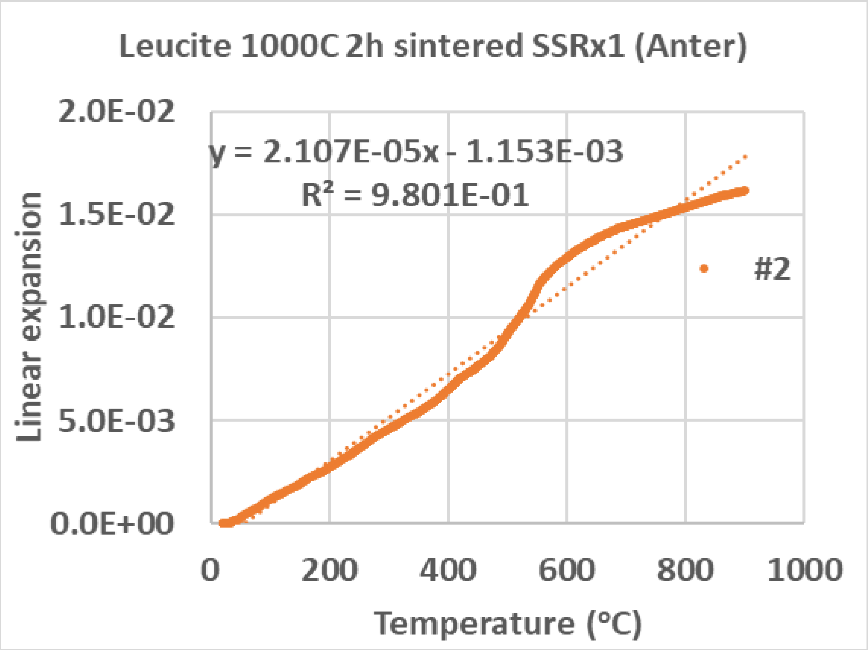


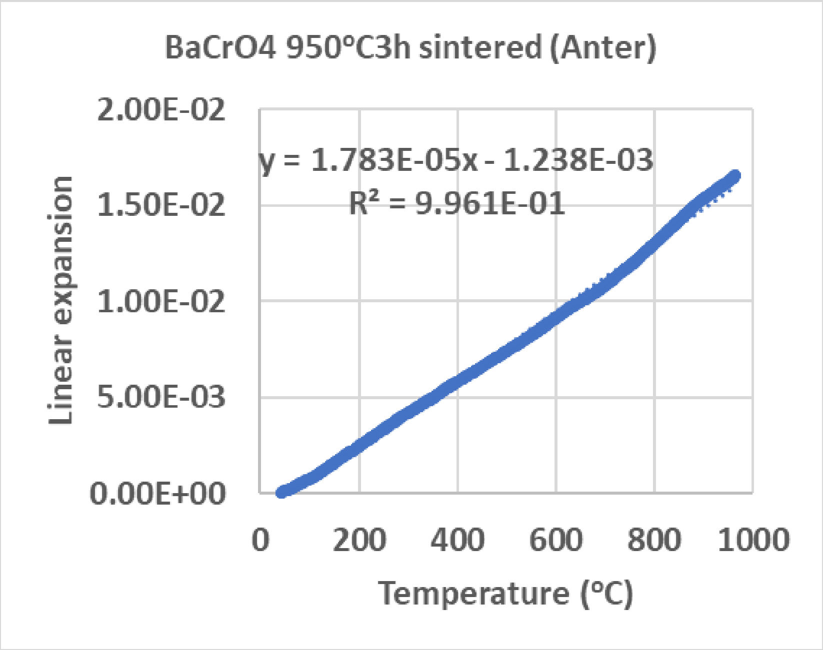

- All glasses except G05 were homogeneous and transparent in as-made state.
- Among all glasses only G04 showed a desirable CTE of ~14.2x$10^{-6}$/$^{o}$C after firing (930-950$^{o}$C/2h); however, the wetting behavior was not promising.

# Glass formulation and thermal property characterization: composite glass approach

- Identified 3 high CTE ceramic phases: LSCF2828, Leucite ($KAlSiO_4$), and $BaCrO_4$ to add to the matrix G18 glass (Ba-Ca-Al-B-Si) - and YSZ fibers for reinforcement
- Potential issues: chemical compatibility, volatility, electrical conductivity, thermal stability in red./H2O, commercial availability
- CTE tailorable by rule of mixtures: $\alpha_{comp} = (\alpha_1 K_1 V1 + \alpha_2 K_2 V_2)/(K_1 V_1 + K_2 V_2)$



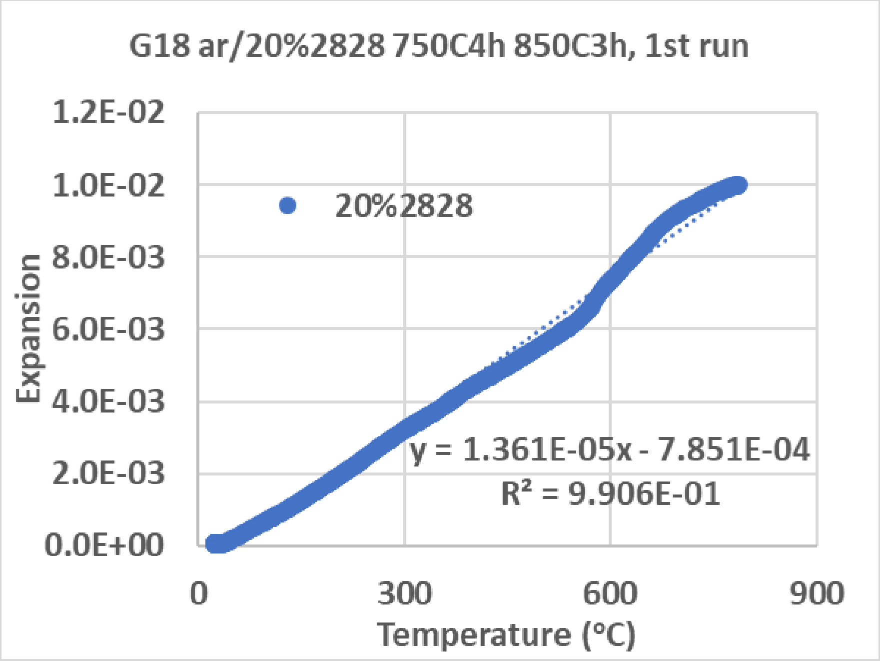



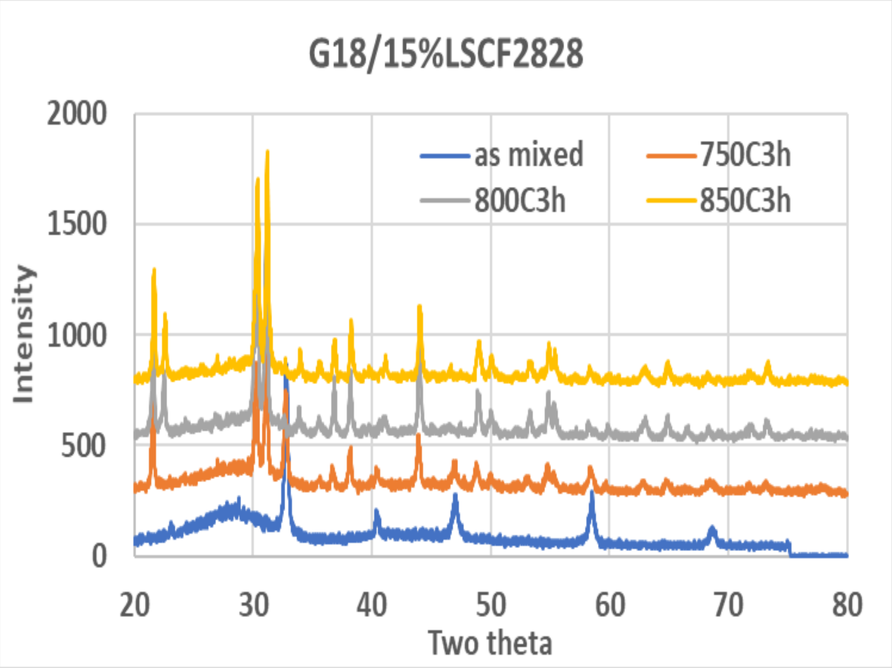
# Dissolution of LSCF2828 in G18 glass

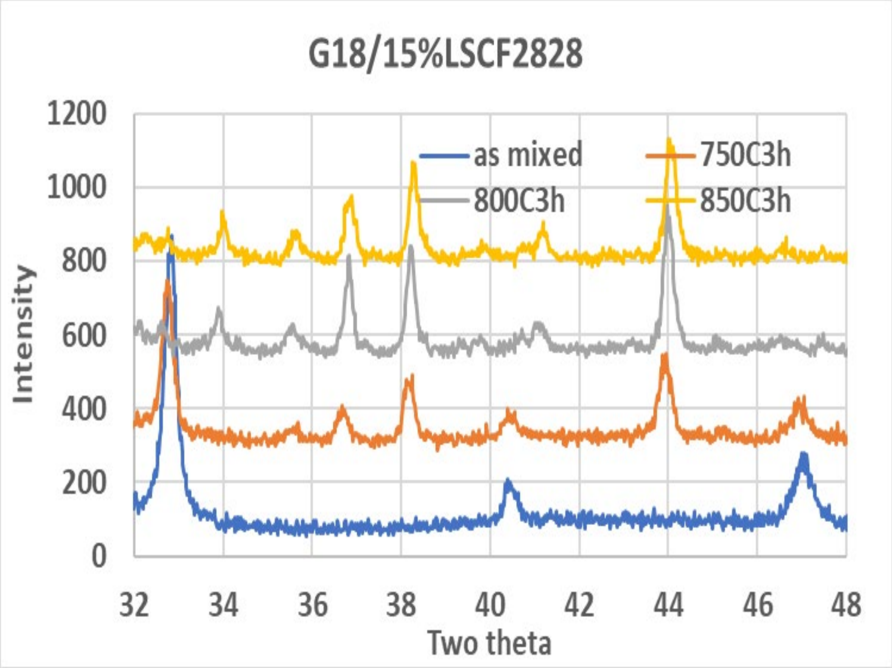
- **G18 glass highly reactive with LSCF2828 (sub-micron sized mixed conductor active phase)**
- **CTE of G18/LSCF2828 composite was much lower than model prediction, consistent with XRD results indicating G18 reacted with/dissolved LSCF2828**

**CTE prediction of composite by rule of mixture**

| Vf | CTE (G18/2828) | CTE (G18/leucite) | CTE (G18/BaCrO4) |
|---|---|---|---|
| 0.00 | 12.5 | 12.5 | 12.5 |
| 0.05 | 14.2 | 13.0 | 12.7 |
| 0.10 | 15.6 | 13.4 | 12.8 |
| 0.15 | 16.9 | 13.9 | 13.0 |
| 0.20 | 18.0 | 14.4 | 13.2 |
| 0.25 | 19.0 | 14.8 | 13.4 |
| 0.30 | 19.9 | 15.2 | 13.6 |

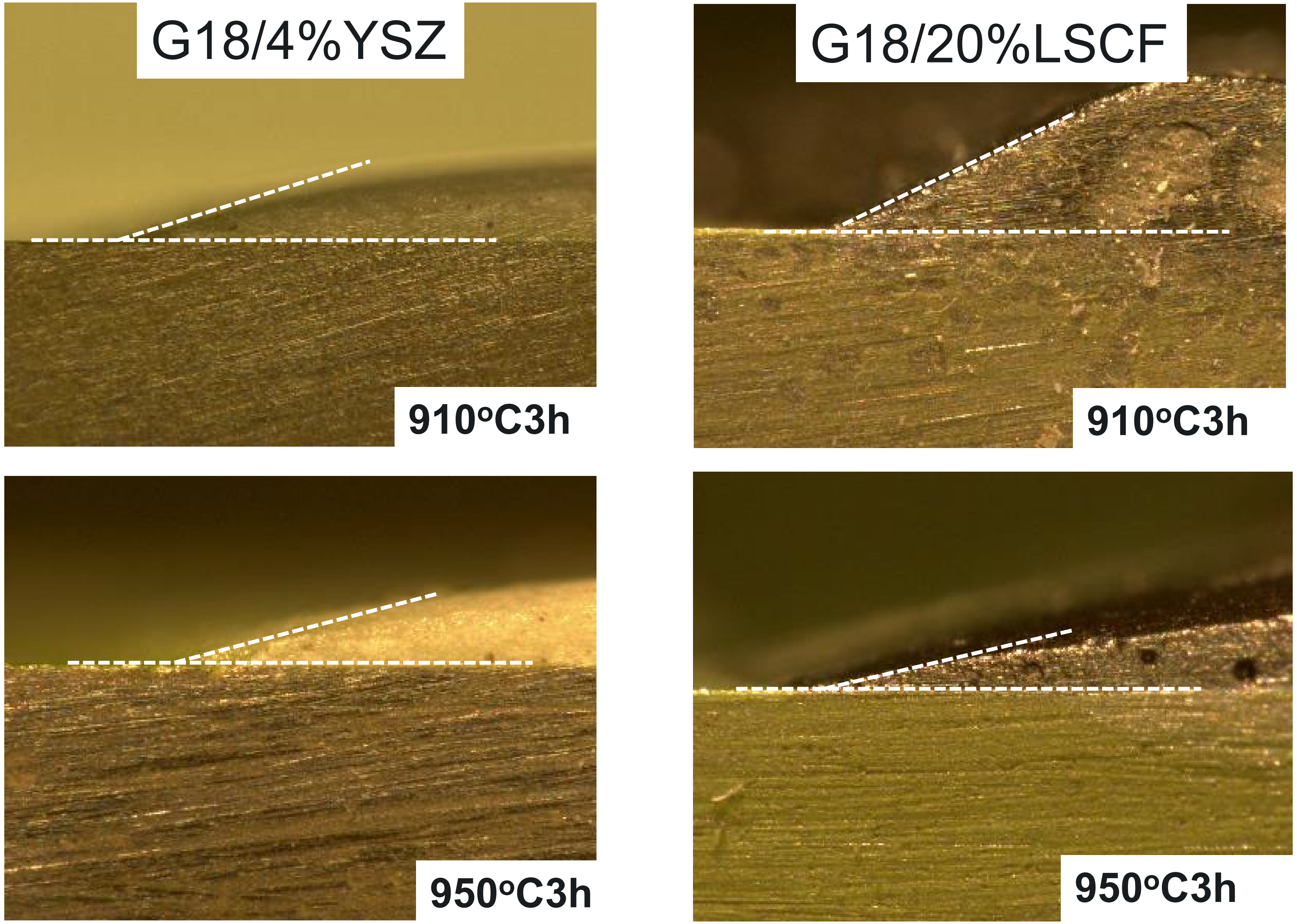


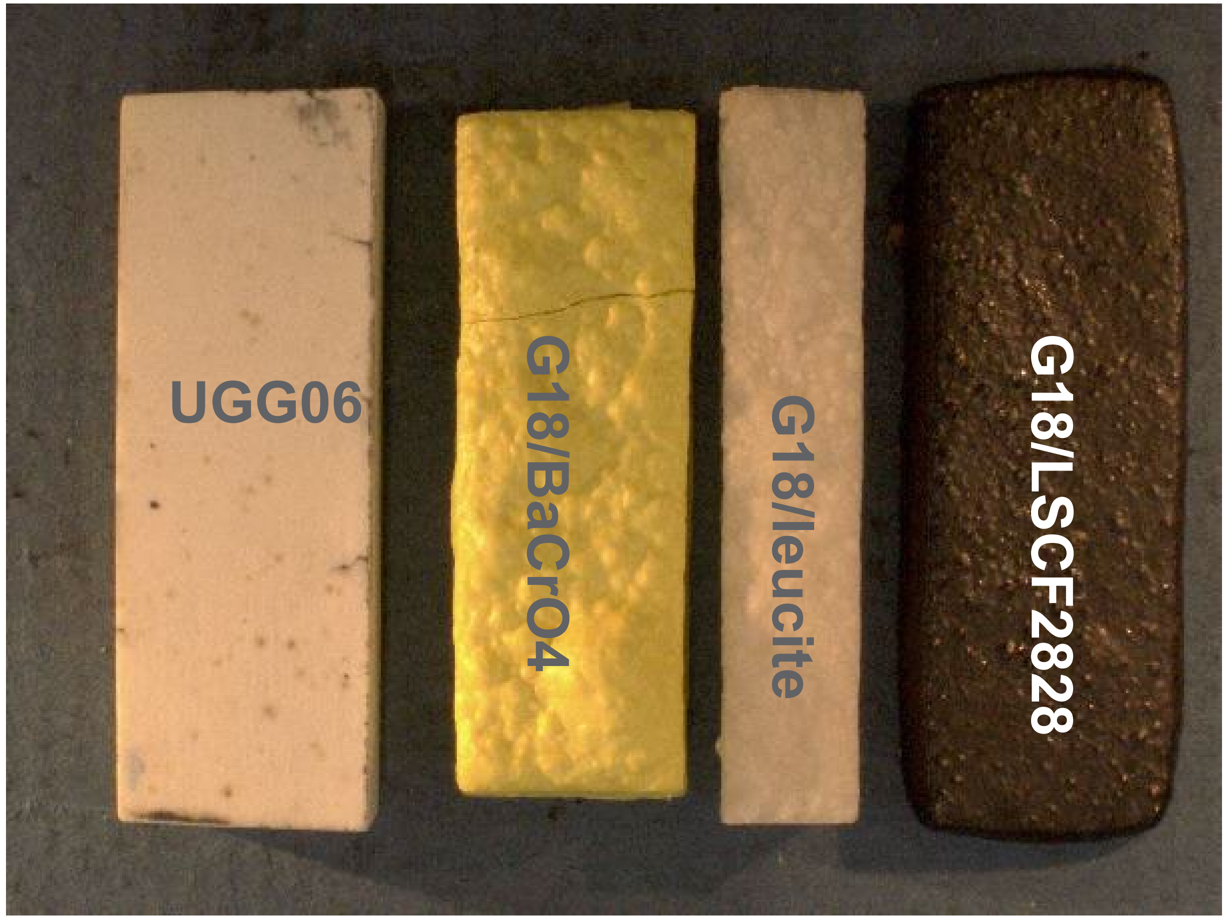
# Wetting behavior on YSZ

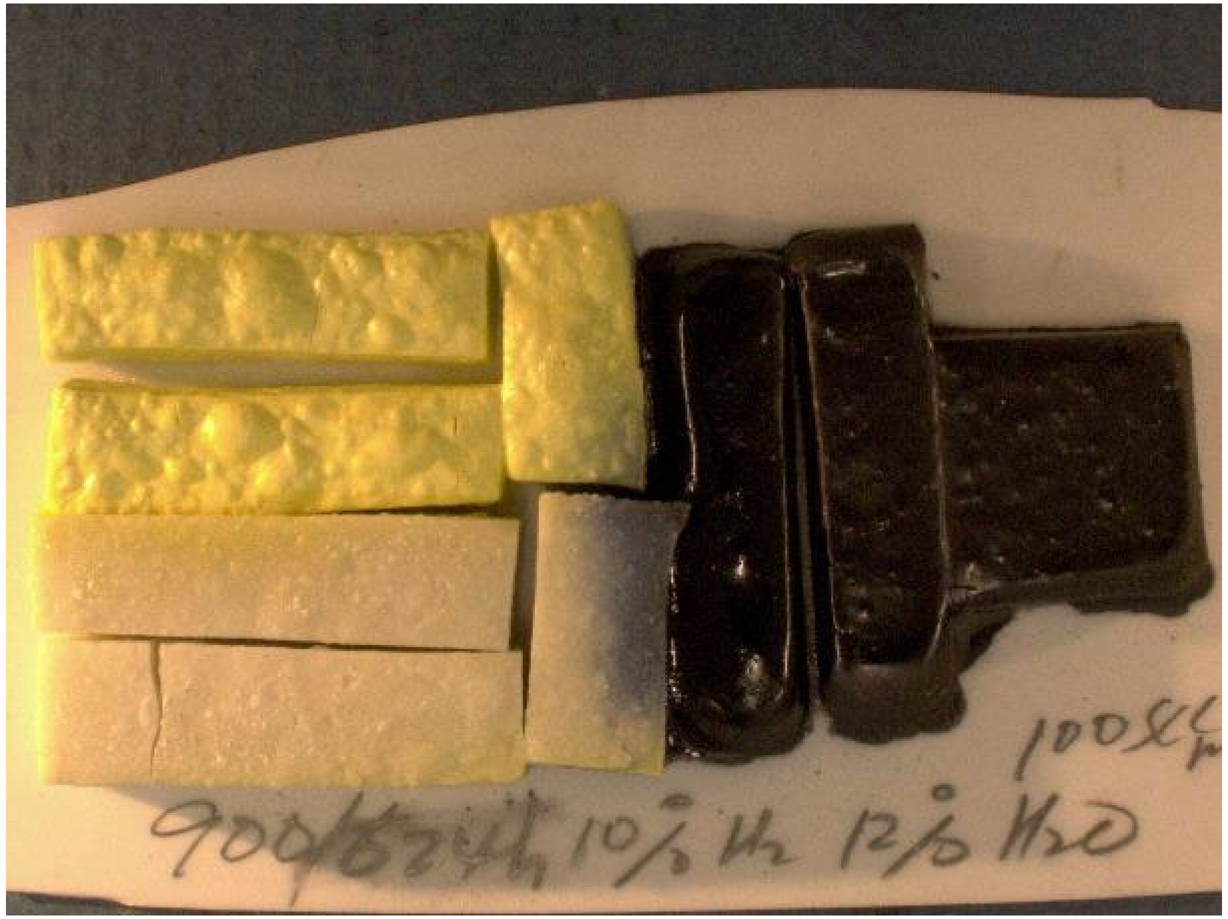
**Good wetting observed for both G18/4%YSZ and G18/20%LSCF2828 composite glasses on YSZ layer with wide working temperature range**



# Isothermal ageing of composite glass in air and reducing environment

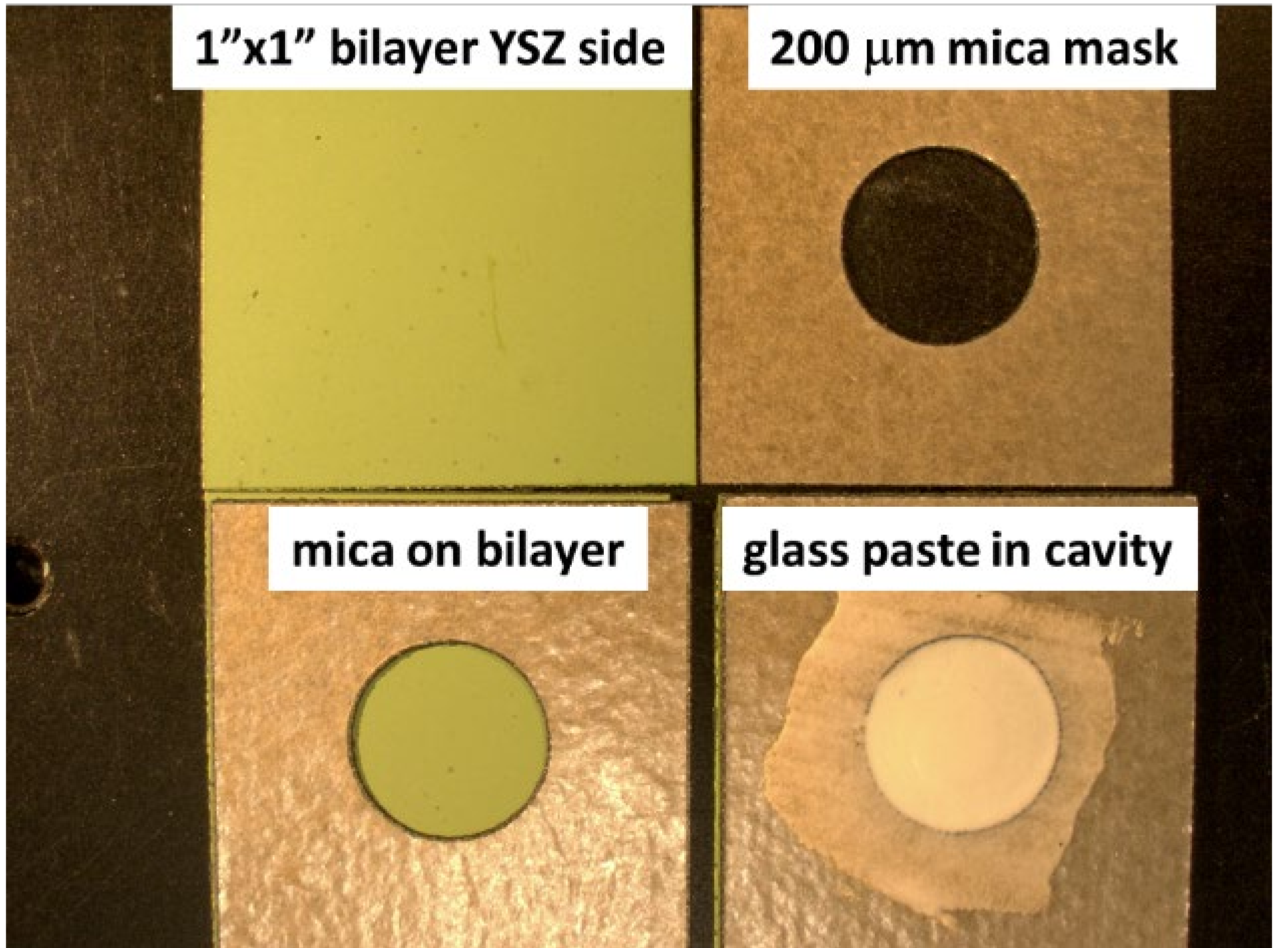
- G18/20%LSCF2828, G18/20%leucite, G18/20%$BaCrO_4$
- Aged at 900$^{o}$C 500h in air or 10%$H_2$/10%$H_2O$
- Microscopy of samples aged in air or reducing environment showed no distinct difference, suggesting good thermal/environmental stability

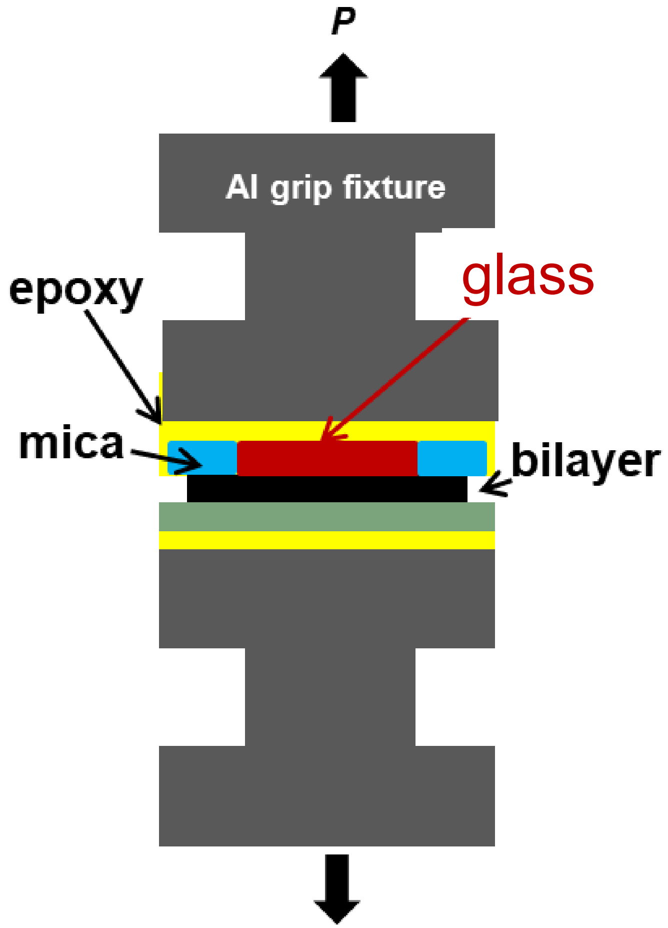


# Seal bond strength: sample preparation

- Candidate  composite glass made as paste using organic binders
- 200-micron thick mica mask (with a central hole) glued onto 1”x1” bilayer on YSZ side
- Apply glass paste to central cavity and smooth with razor blade
- After drying fire to 950°C 3h in air, then epoxy glued to Al fixture and tensile tested
- 8 samples for as-fired, 8 samples for air aged+10 TC, 8 samples for red. aged+10 TC



# No substantial bond strength reduction after 900°C/500h ageing + 10 thermal cycles in air or reducing environment

## As-fired

| | MPa | | MPa | |
|---|---|---|---|---|
| as-fired | 20%2828 | Note | 4%YSZ | Note |
| 1 | 9.68 | epoxy/Al | 9.64 | epoxy/Al |
| 2 | 9.59 | epoxy/Al | 10.82 | epoxy/Al |
| 4 | 9.65 | epoxy/Al | 7.87 | epoxy/Al |
| 5 | 8.72 | epoxy/Al | 10.52 | epoxy/Al |
| 6 | 8.17 | epoxy/Al | 8.93 | epoxy/Al |
| 7 | 9.96 | epoxy/Al | 11.01 | epoxy/Al |
| 8 | 8.02 | epoxy/Al, l | 9.84 | epoxy/Al |
| 3 | 2.80 | bilayer | 6.15 | bilayer |
| **avg** | **9.29** | **avg** | **9.80** | |
| **std** | **0.69** | **std** | **1.12** | |

- **G18/YSZ showed slightly higher strength, likely due to strong fiber reinforcement.**
- **Small reduction in bond strength after ageing is likely attributed to crystallized microstructure from as-fired state.**

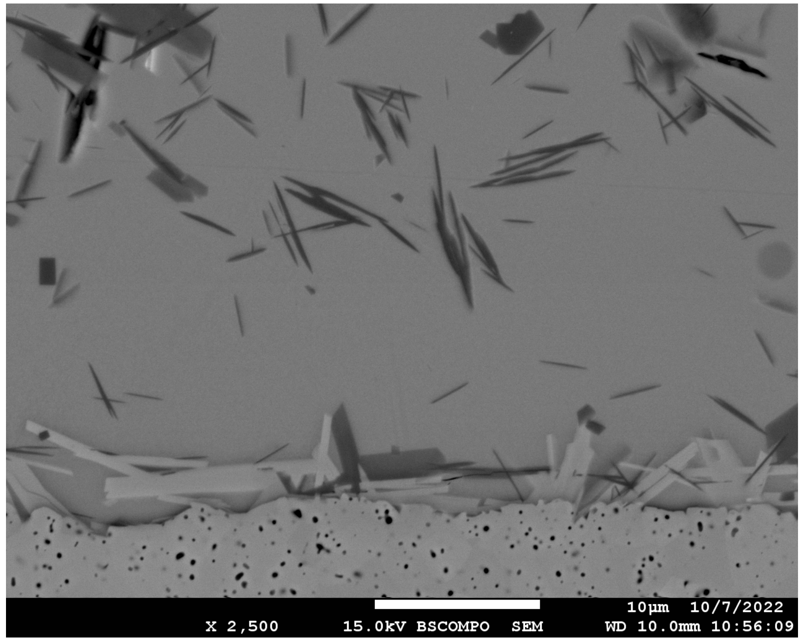
## Aged in air

| | MPa | | MPa | |
|---|---|---|---|---|
| air aged | 20%2828 | Note | 4%YSZ | Note |
| 1 | 4.97 | epoxy/Al | 7.08 | epoxy/glass |
| 2 | 3.30 | epoxy/Al | 6.18 | epoxy/Al |
| 5 | 7.28 | epoxy/Al | 7.58 | epoxy/Al |
| 6 | 6.05 | epoxy/Al | 6.58 | epoxt/glass |
| 8 | 8.53 | in bilayer | 9.46 | glass/ysz |
| 7 | 3.73 | in bilayer | 4.43 | bilayer |
| 3 | 3.06 | in bilayer | 5.83 | bilayer |
| 4 | 3.31 | in bilayer | 5.09 | mixed |
| **avg** | **6.02** | **avg** | **7.37** | |
| **std** | **2.03** | **std** | **1.28** | |

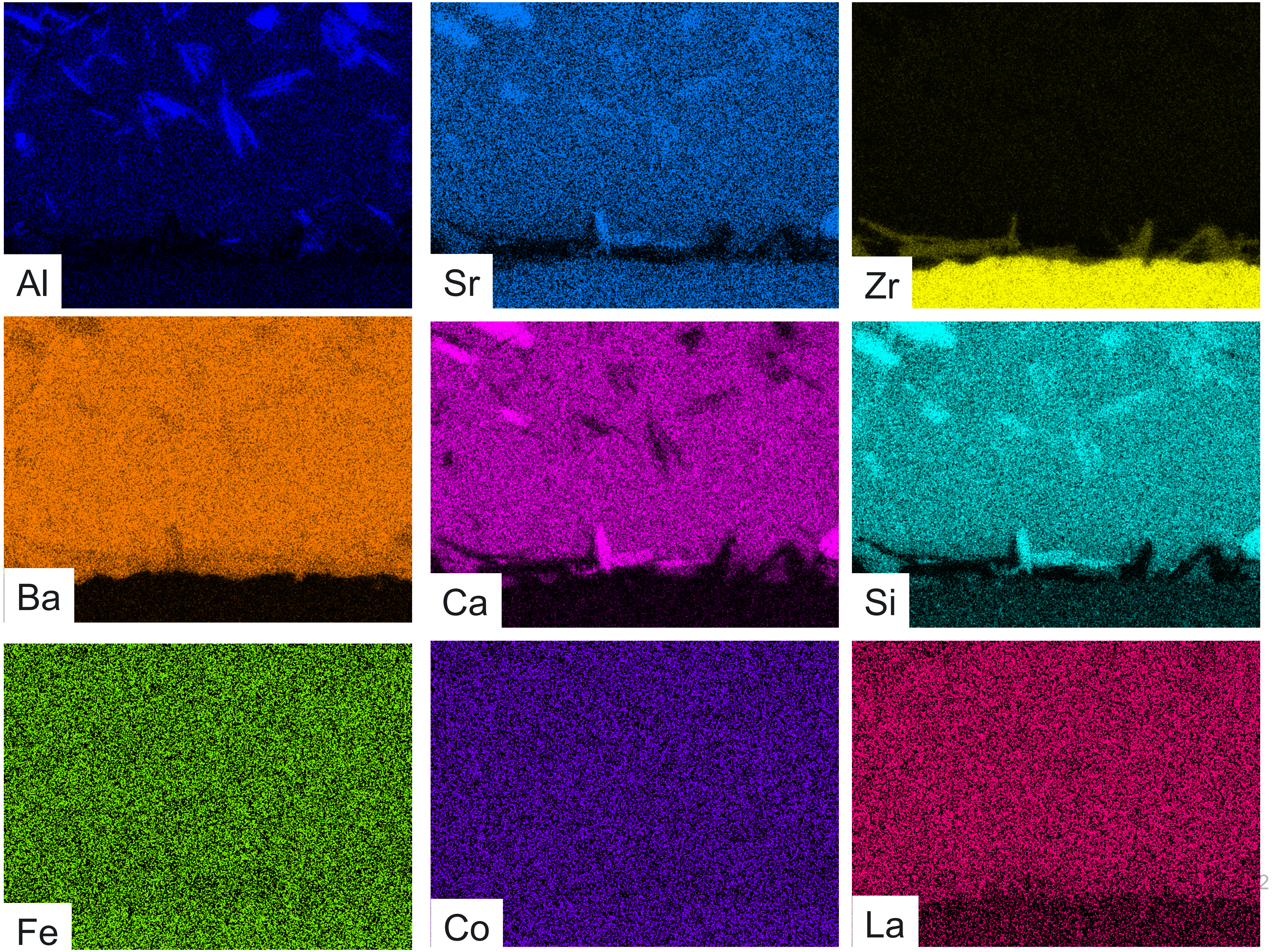
## Aged in 10%$H_2$ 20%$H_2O$

| | MPa | | MPa | |
|---|---|---|---|---|
| red. aged | 20%2828 | Note | 4%YSZ | Note |
| 1 | 8.17 | epoxy/Al | 7.65 | epoxy/glass |
| 2 | 7.37 | epoxy/glas | 8.01 | mixed bil/epo |
| 5 | 9.18 | mixed | 10.21 | epoxy/Al |
| 6 | 5.92 | epoxy/Al | 11.29 | epoxt/Al |
| 8 | 7.37 | mixed | 7.14 | epoxt/Al |
| 4 | 8.00 | in bilayer | 7.78 | mixed bil/epo |
| 7 | 4.06 | in bilayer | 5.11 | epoxy/Al |
| 3 | 4.71 | in bilayer | 9.18 | bilayer |
| **avg** | **7.67** | **avg** | **8.30** | |
| **std** | **1.08** | **std** | **1.92** | |

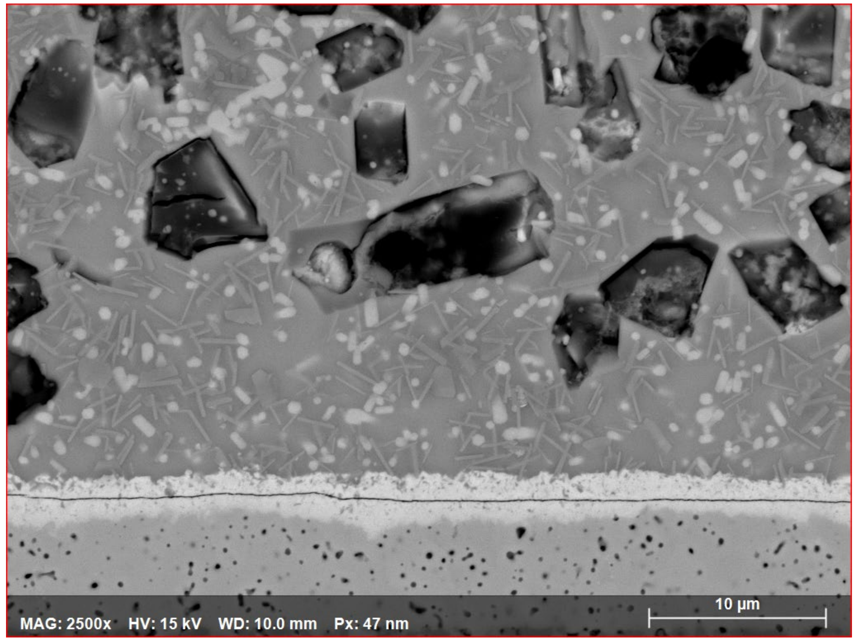
# EDS of as-fired YSZ/glass (G18/20%LSCF2828)



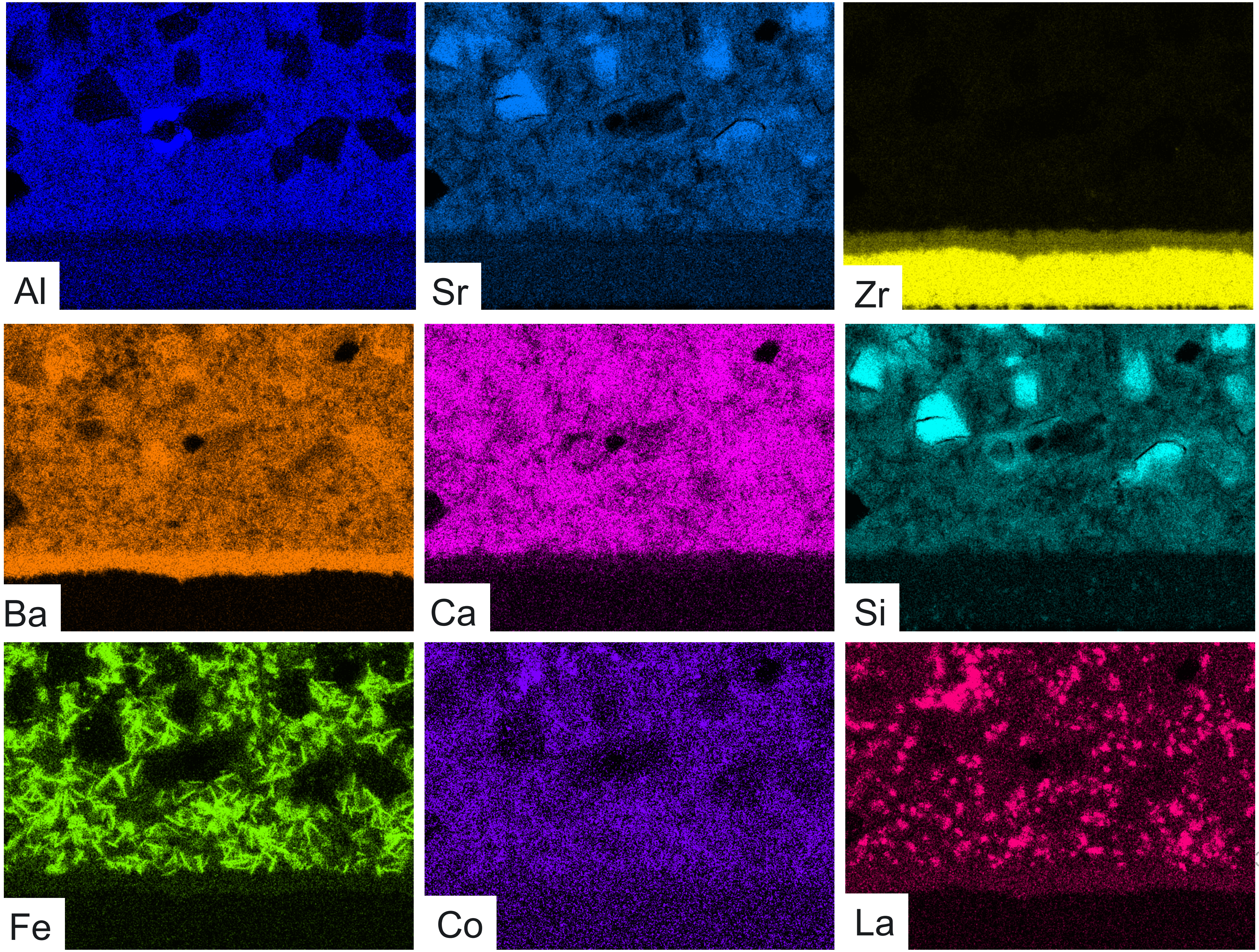

- Some discrete crystal formed along interface: Sr-Ca-silicate, $BaZrO_3$.
- Al-Ca-silicate and Sr-Ca-silicate in matrix.
- LSCF appeared well dissolved within glass matrix, no crystalline phase identified along interface.



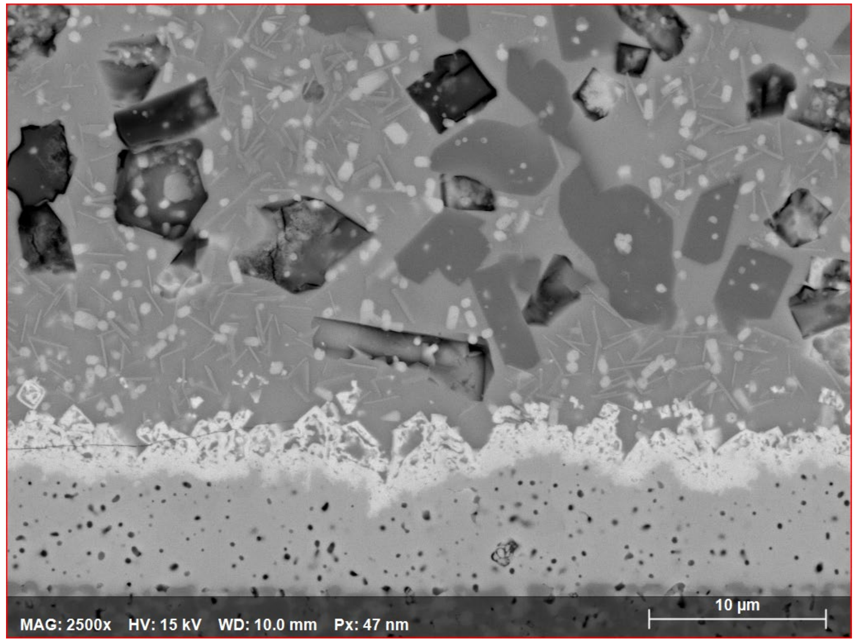
# EDS of air-aged (900°C/500h) YSZ/glass

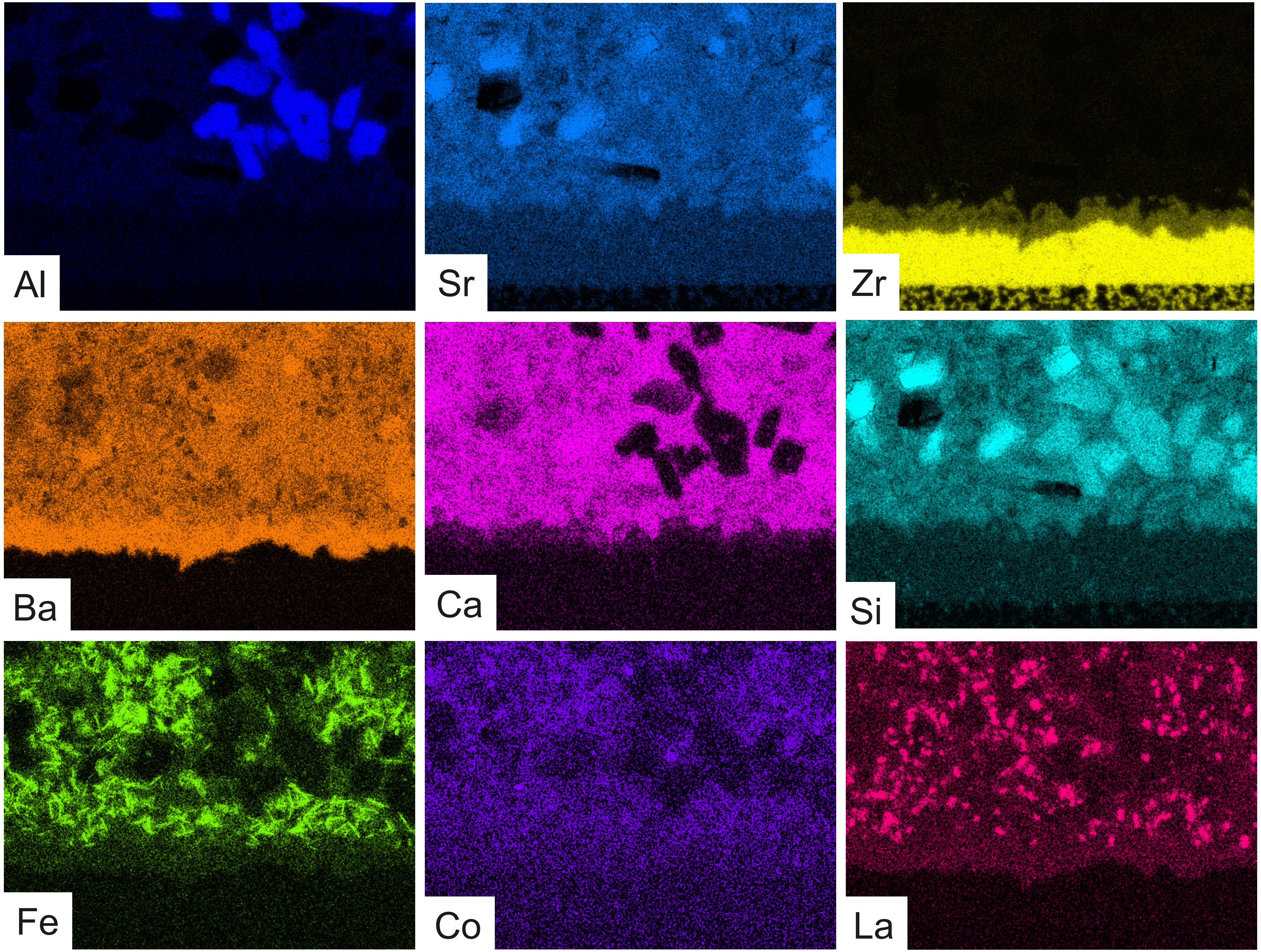



- **Dense layer, ~3 $\mu$m $BaZrO_3$ formed at interface.**
- **Interfacial $BaZrO_3$ cracked during metallography.**
- **Uniformly distributed La- or Fe-enriched precipitates.**
- **Microstructural evolution resulted in some irregular voids, likely due to redissolution.**



# EDS of reducing-aged (900°C/500h) YSZ/glass

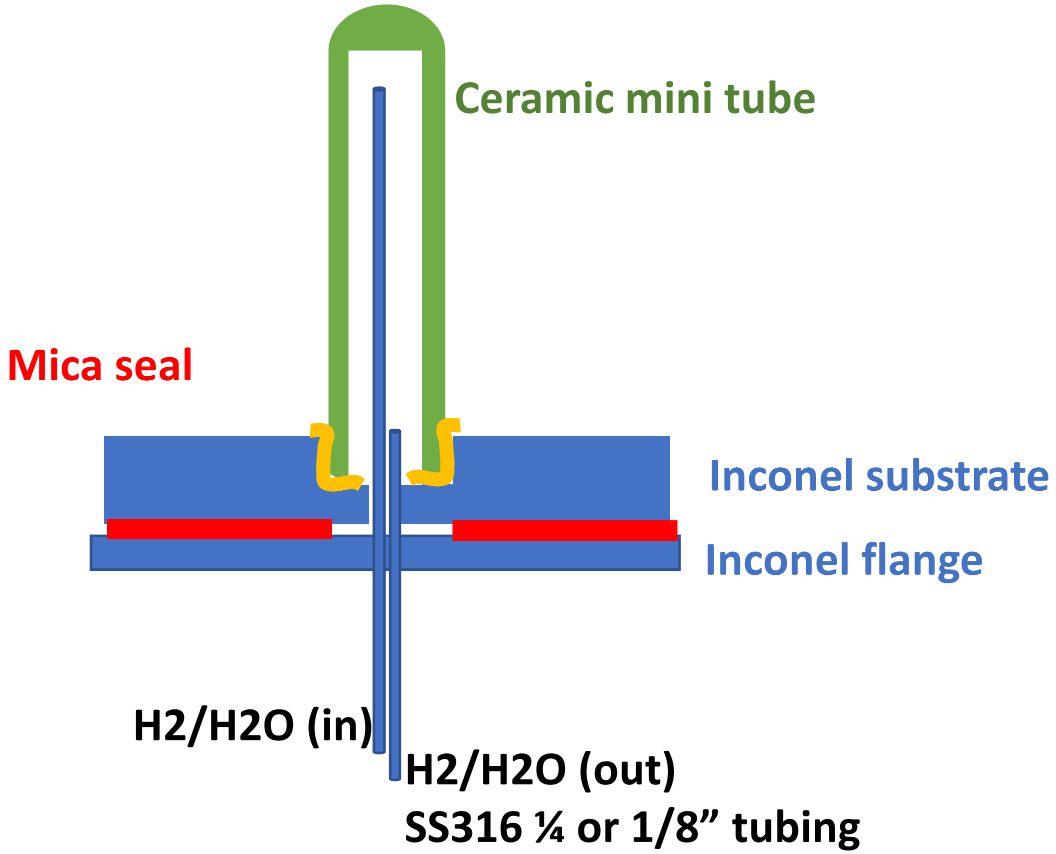



- Dense layer, ~2 µm $BaZrO_3$ formed at interface.
- Uniformly distributed La- or Fe-enriched precipitates
- Microstructural evolution resulted in some irregular voids, likely due to redissolution.
- No distinct difference from ageing in air.

# Validation with mini-tube reactor

- Objective is to test glass seal integrity in dual environment at 900ºC for ~300-500h followed by ~10 thermal cycles
- Tests underway for both G18/YSZ and G18/LSCF composite glasses




# Summary and Conclusions

- Formulated 6 glasses - 5 showed good glass behavior, one crystallized upon casting.
- CTE of as-made plain glasses were lower than the targeted values - crystallized G04 glass has the closest match; however, its sealing behavior was undesirable due to rapid crystallization.
- 3 high CTE ceramic phases were identified to form composites with G18 matrix glass.
- Chemical compatibility was assessed for high CTE ceramic phases with G18. $BaCrO_4$ was the least reactive, while leucite and LSCF reacted readily with G18 glass melt.
- Composite G18/20%LSCF2828 and G18/4%YSZ(f) were chosen for dual atmosphere testing. Both glasses showed good wetting on YSZ over a wide temperature range for sealing.
- Interfacial EDS analysis of G18/LSCF on YSZ showed BaZrO3 formation which grows over time at 900$^o$C to form a dense and continuous layer. No distinct microstructure difference between ageing in air or reducing/humid environment.
- Tensile testing showed strong bonding of candidate composite glasses to YSZ while YSZ fiber-reinforcement resulted in a slightly greater strength, due to higher elasticity and toughness. Bond strength showed a small reduction after 900$^o$C/500h ageing in air or reducing environment.
- Composite glass validation testing in a mini-tube reactor under dual environment is underway.

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# Acknowledgments


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# Thank you