DE-FE0031672 "High Performance Circuit Pastes for Solid Oxide Fuel Cell Applications" Kickoff Meeting

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Michigan State University
East Lansing, MI

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The MSU Circuit Paste Team
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Circuit Paste Manufacture

Project Lead

Dr. Timothy Hogan

Electrical Characterization

Dr. Yue Qi

DFT & MD Modeling

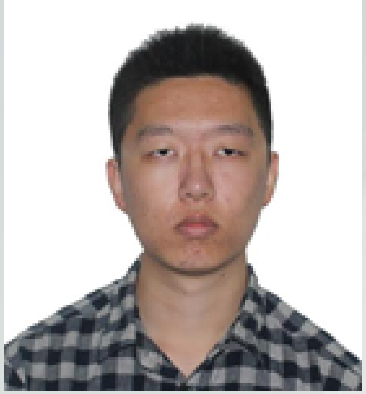
Dr. Thomas Bieler

Mechanical Testing, Metallurgy

Dr. Hui-Chia Yu

Phase Field Modeling

The MSU Circuit Paste Team
Graduate Students



Yuxi Ma

Circuit Paste Manufacture

Aishwarya Bhatlawande

Electrical Characterization

Joe Phongpreecha

DFT & MD Modeling

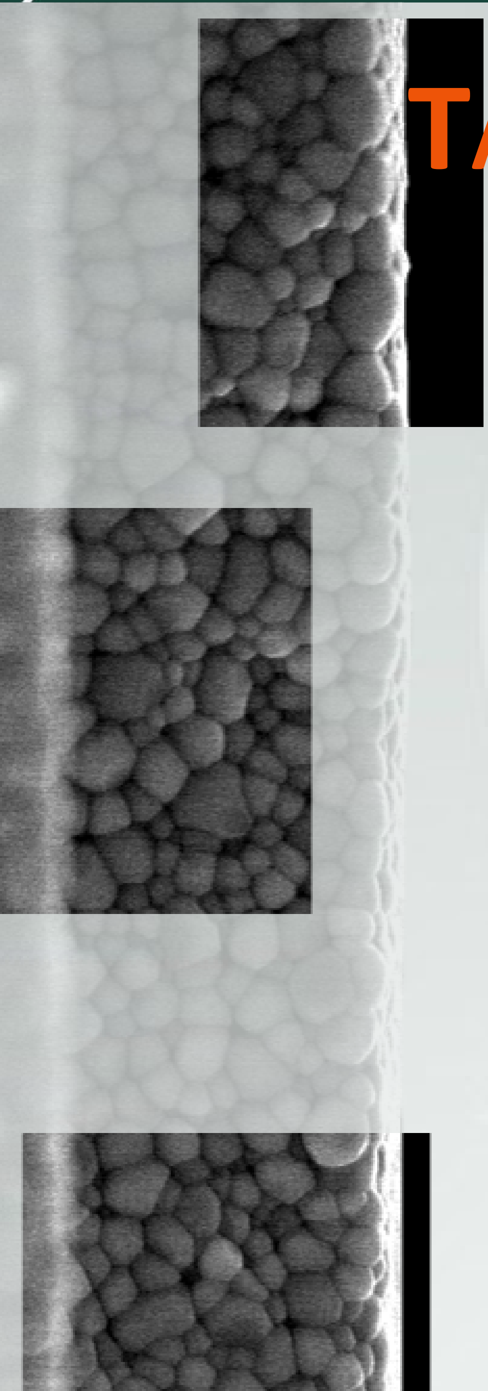
New Student

Circuit Paste Manufacture,

Mechanical Testing

Robert Termuhlen

Phase Field Modeling



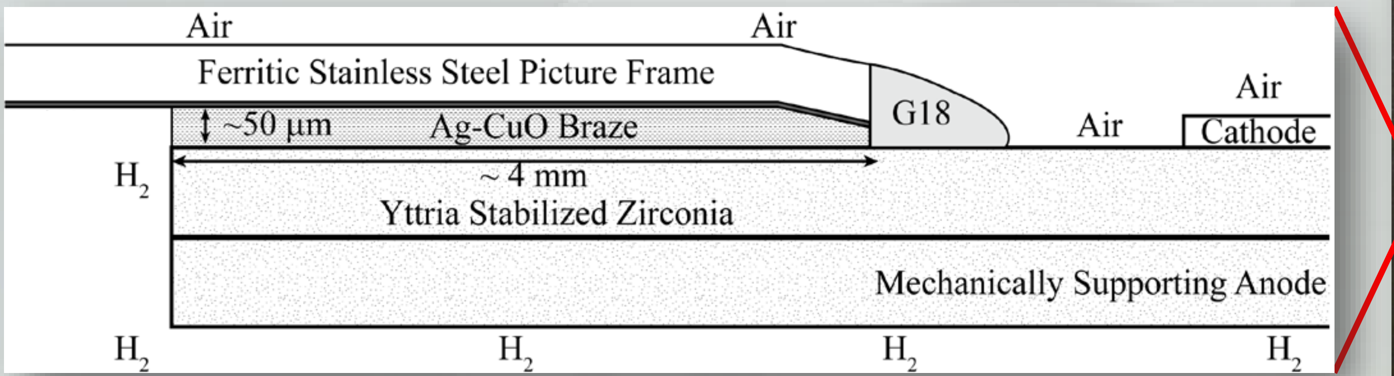
Talk Outline

1. **Background**
    - a) **Results from DE-FE0031250 on Ag-Ni Brazes**

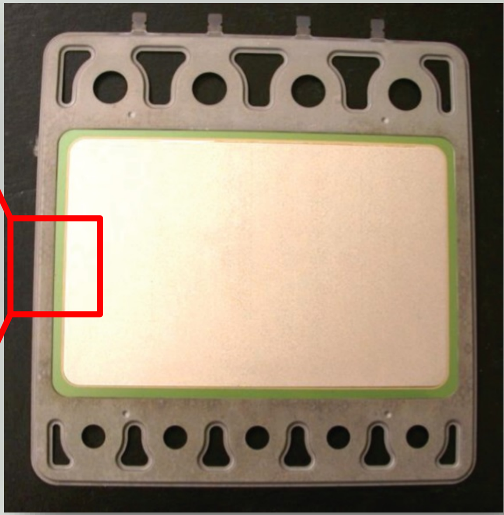
2. Project Approach
    - a) Preliminary Results
    - b) Research Plan

3. Initial Project Progress

Conventional Silver-Copper Oxide Reactive Air Brazes Have many Benefits



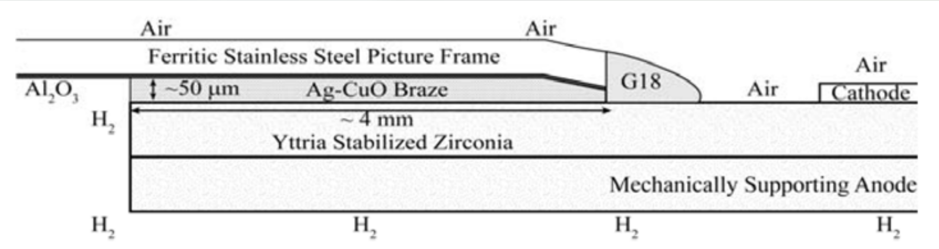
Delphi Technologies Inc, U.S. Patent No US7855030B2



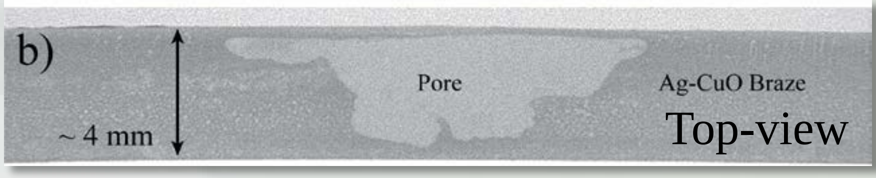
- Less Permeable to H_2 and O_2 than Glass Seals
- Much More Ductile than Glass Seals, So CTE Mismatch is not a concern
- Brazing can be performed in air
- No flux is needed
- The enhanced wetting provided by CuO “allows” Ag-CuO brazes to be used on a variety of ceramics

Reactive Air Brazes Have Several Fatal Flaws

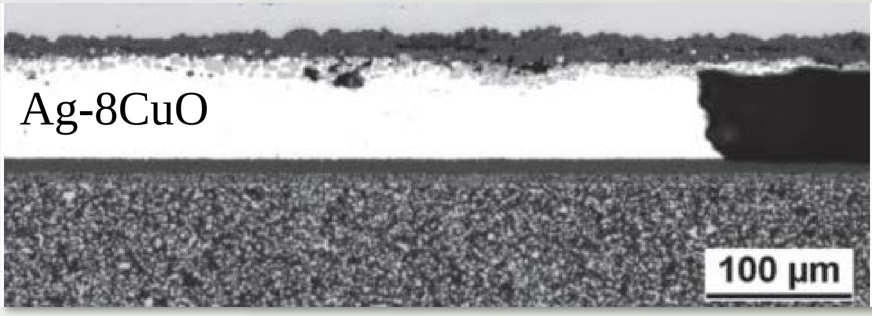
1. Braze joint will be exposed to dual atmospheres (H_2/Air) in SOFC operation.



2. Reactive air silver brazes are only partially wetting, resulting in occasional manufacturing defects (**Type I Pores**);



3. Reduction of reactive air additions (CuO) by hydrogen during SOFC operation can result in **Type II Pores;**



4. **Type III pore** formation due to H_2 and O_2 reaction. CuO additions do not prevent the formation of **Type III Pores** produced when hydrogen and oxygen dissolved in the braze meet and form water pockets.

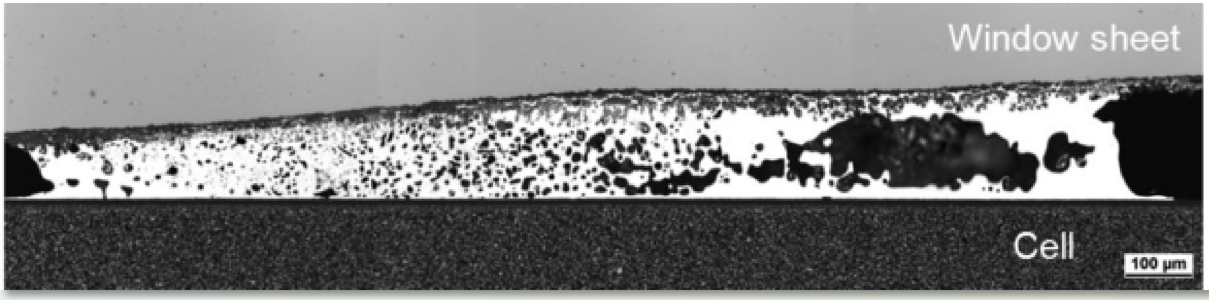
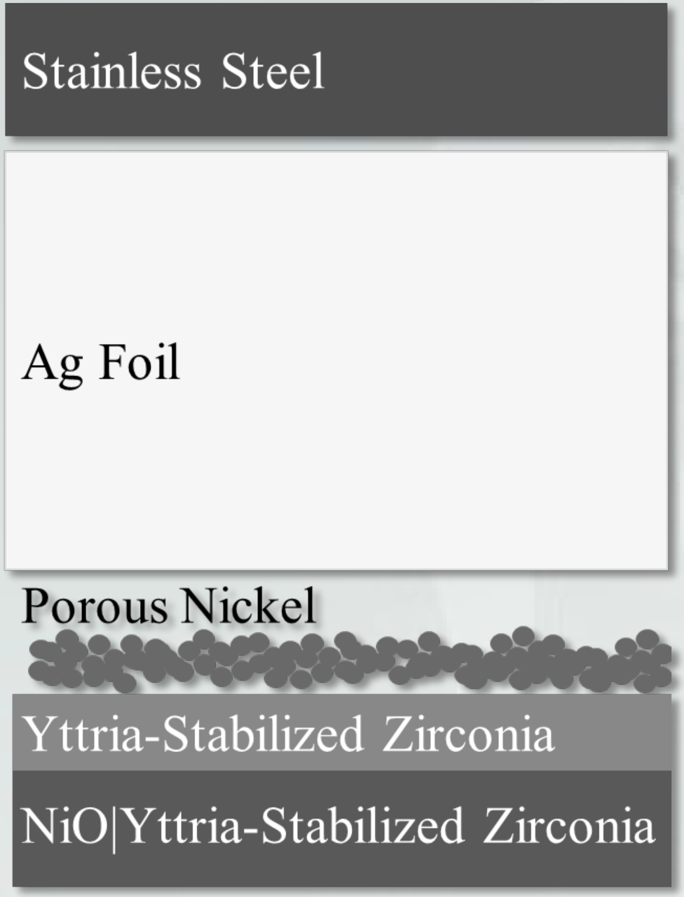


Image b) Courtesy of Delphi Automotive.
Bause, T., et al., Damage and Failure of Silver Based Ceramic/Metal Joints for SOFC Stacks. Fuel Cells, 2013. 13 (4): p. 578-583.

Hypothesis: Porous Nickel Layers Can Be Used Instead of Reactive-Air Elements



Stainless Steel

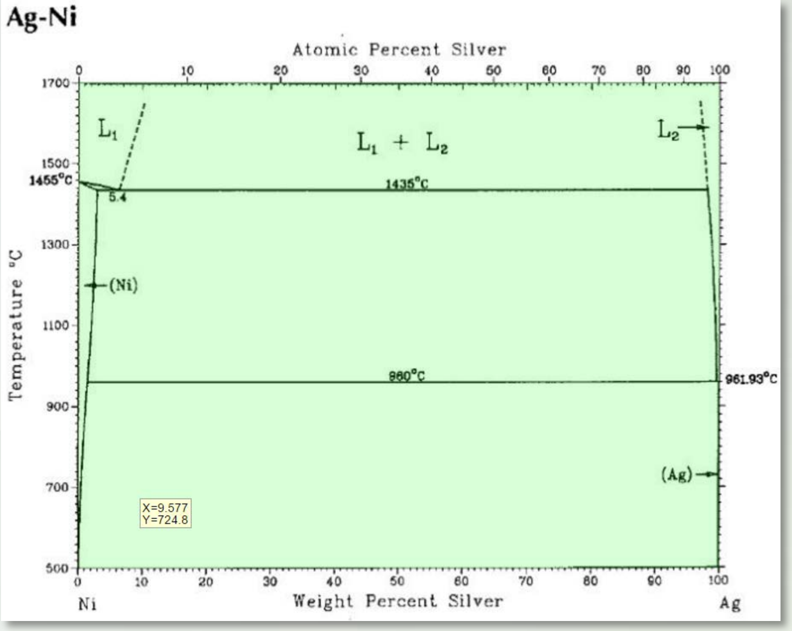
Ag Foil

Porous Nickel

Yttria-Stabilized Zirconia

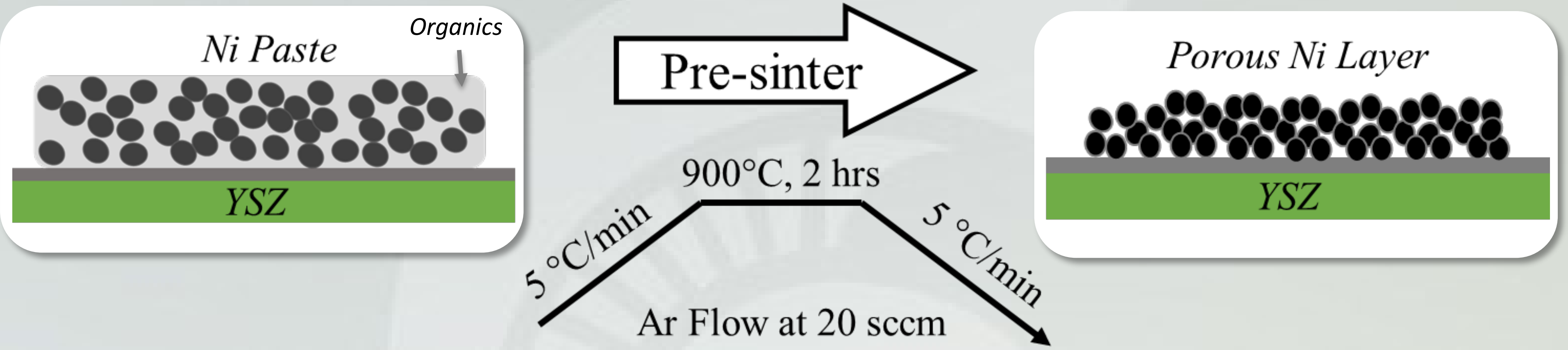
NiO|Yttria-Stabilized Zirconia

- The Ag wetting angle on Ni is ~30° in inert atmosphere
- Ni (T_m=1445C) will not melt before Ag
- Ni will not dissolve in Ag



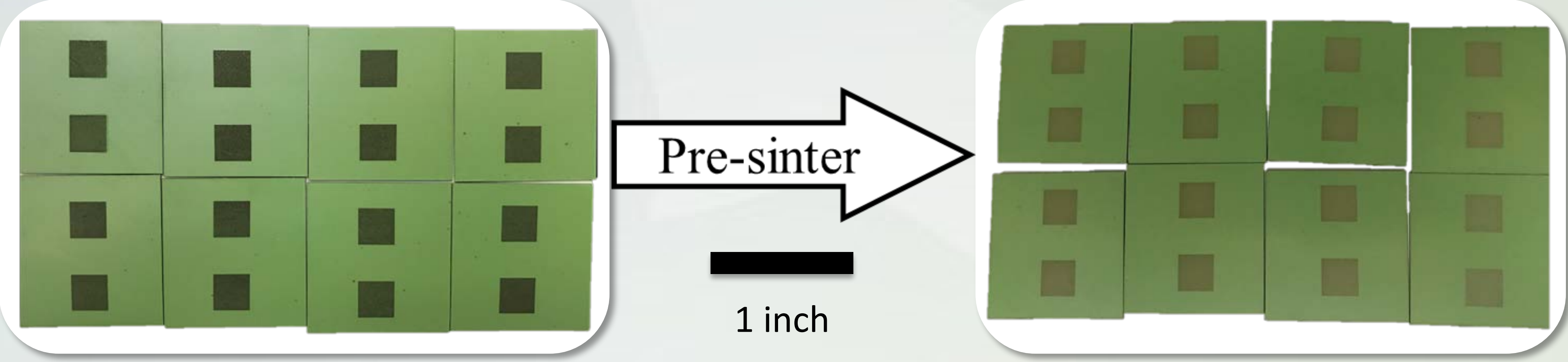
Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.
ASM handbook Volume 03; Nagesh, V.K. and J.A. Pask, Wetting of Nickel by Silver. Journal of Materials Science, 1983. ***18*** *(9): p. 2665-2670.*
Hula, R.C., et al., The Wetting Behaviour of Silver on Carbon, Pure and Carburized Nickel, Cobalt and Molybdenum Substrates. Appl. Surf. Sci., 2010. ***256*** *(14): 4697-4701.*

Porous Nickel Interlayer Fabrication



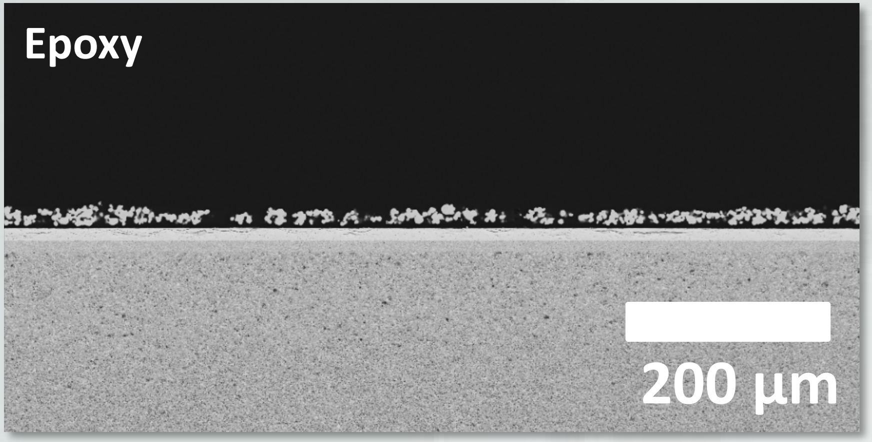
Screen Print Ni Paste onto YSZ Substrates

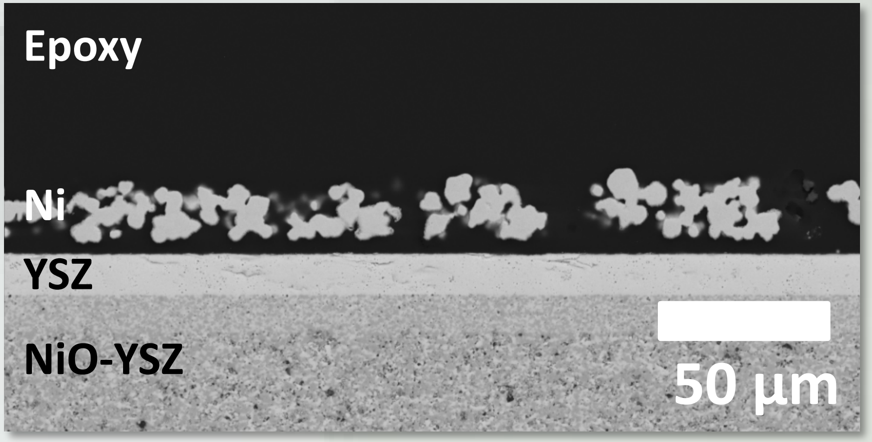
Partially Sintered Ni Interlayer on YSZ

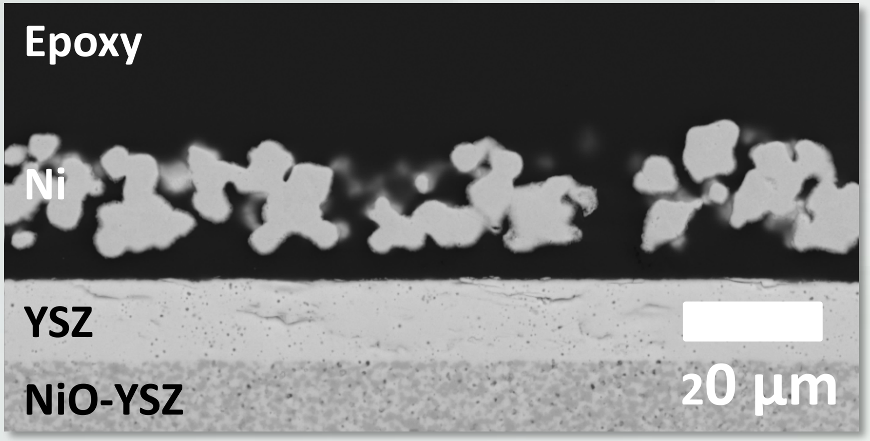


Zhou et al., *Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater*, 2018. 148: p. 156-162.

Porous Nickel Interlayer Microstructure



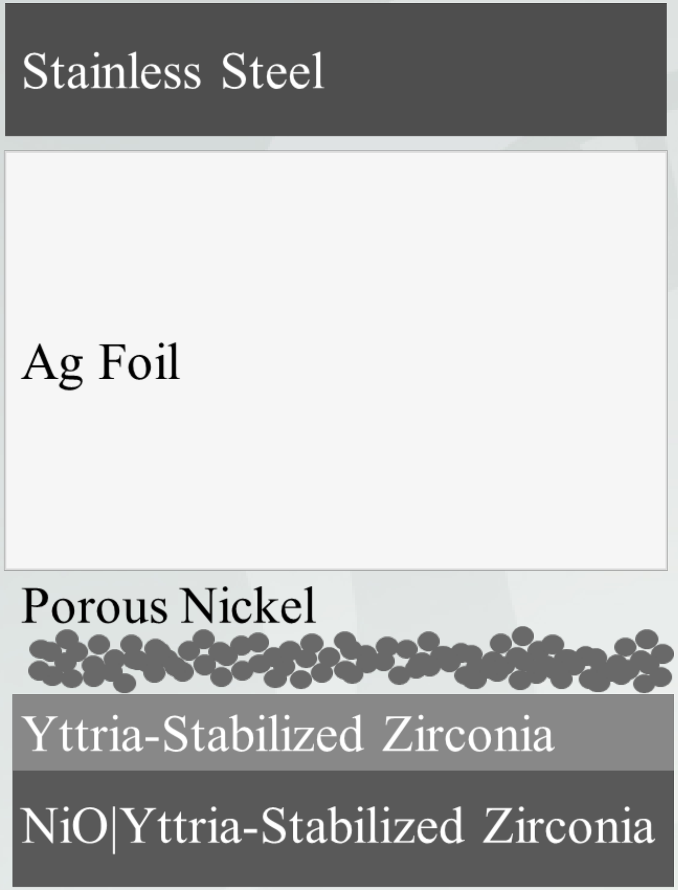




- The screen-printed, pre-sintered Ni layer has a uniform thickness of ~20 µm on the YSZ.
- There are 2~6 particles through the thickness of the porous layer.

Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

Brazing Procedure



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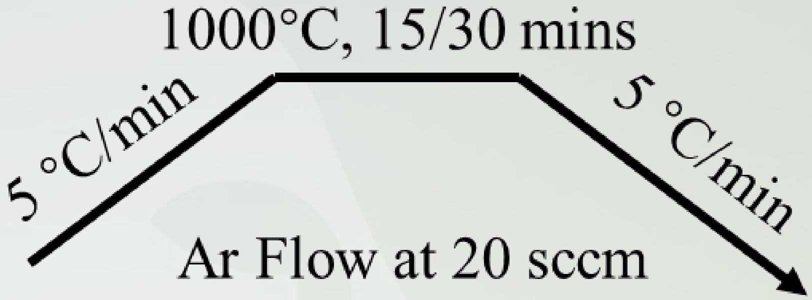
Yttria-Stabilized Zirconia

NiO|Yttria-Stabilized Zirconia



1000°C, 15/30 mins

5 °C/min

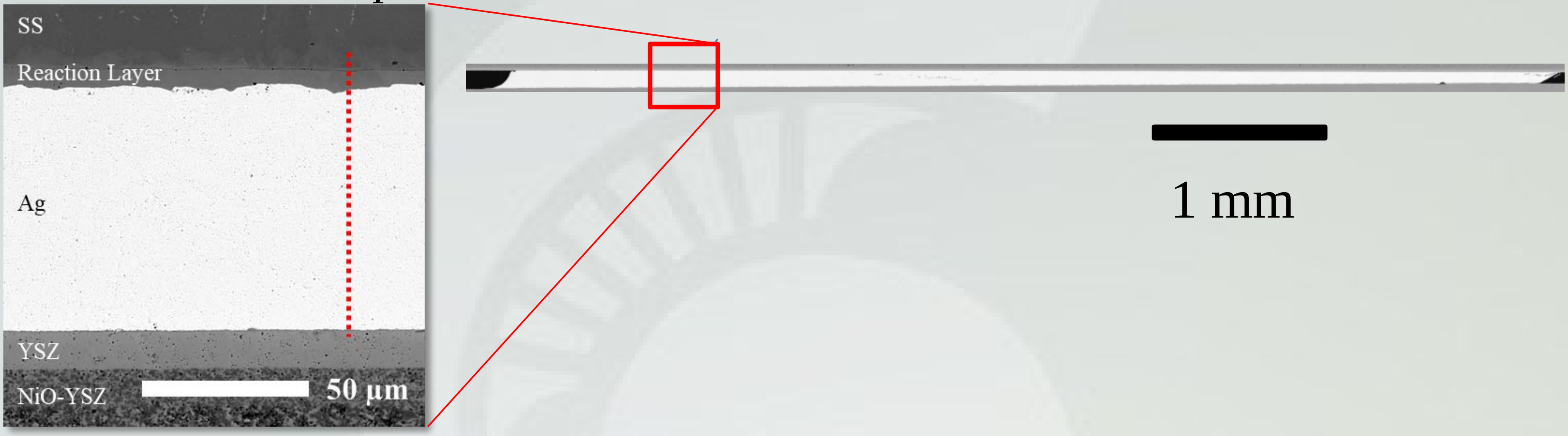
5 °C/min

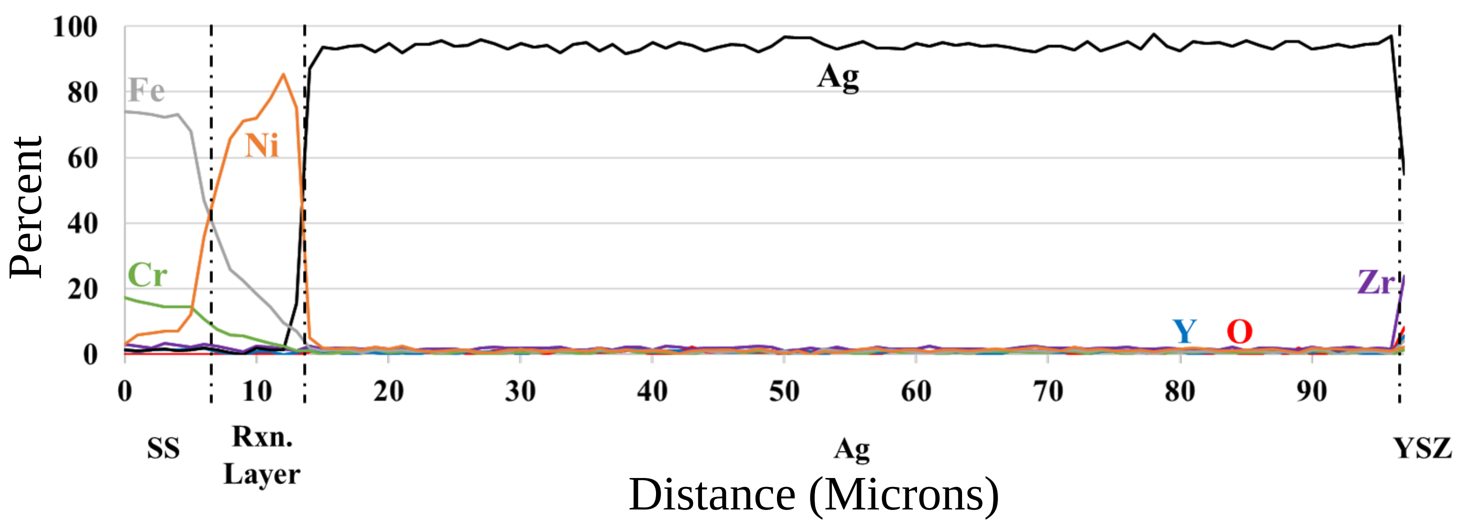
Ar Flow at 20 sccm

Zhou et al., Brazing Method Using Porous Interlayers and Related Articles, USPTO Patent. (Pending, May 10, 2017)
Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

Dense Braze Joints Can be Produced and the Porous Nickel Layer is Transient

30 Mins Brazed Sample





Zhou, Q., T. R. Bieler and J. D. Nicholas. "Transient Porous Nickel Interlayers for Improved Silver-Based Solid Oxide Fuel Cell Brazes." *Acta Materialia* **148**: 156-162, http://dx.doi.org/10.1016/j.actamat.2018.01.061 (2018)

Macroscopically Oxidation Has Negligible Effect On Braze Joint Quality

As Brazed

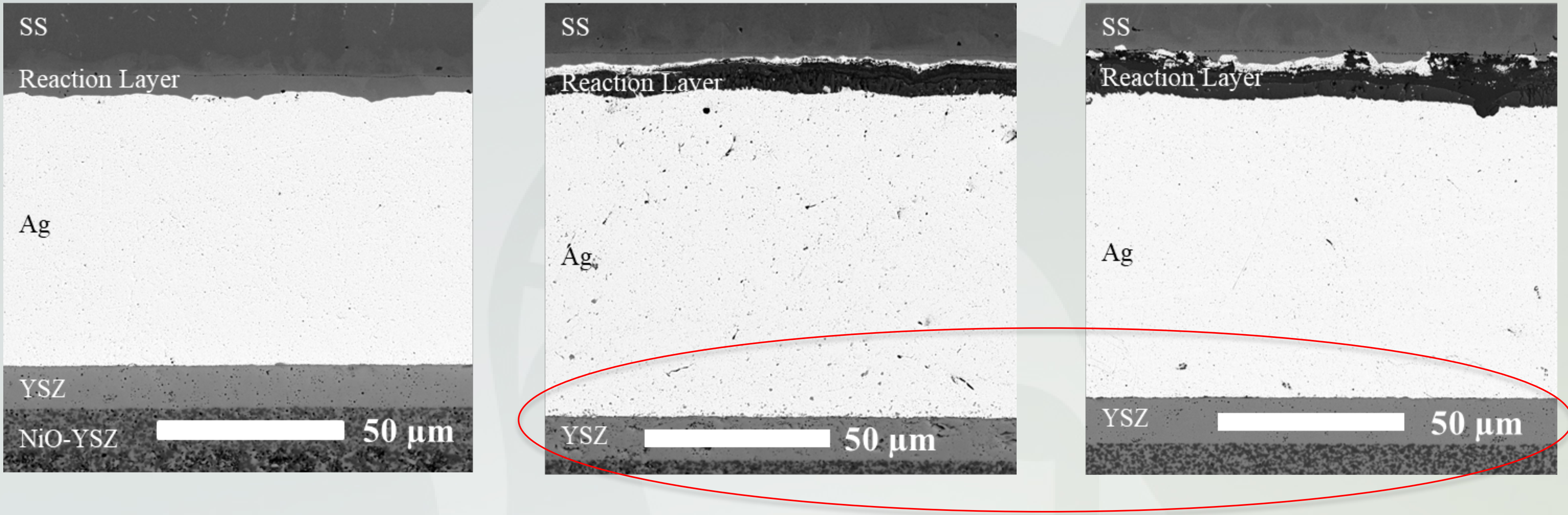
After 120 Hours of Oxidation

After 500 Hours of Oxidation

- Samples were held at 750°C in an air furnace for oxidation.
- No obvious porosity developed after 500 hours of oxidation in air.

Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

Oxidation Does Not Affect The Ag Or The Ag-YSZ Interface



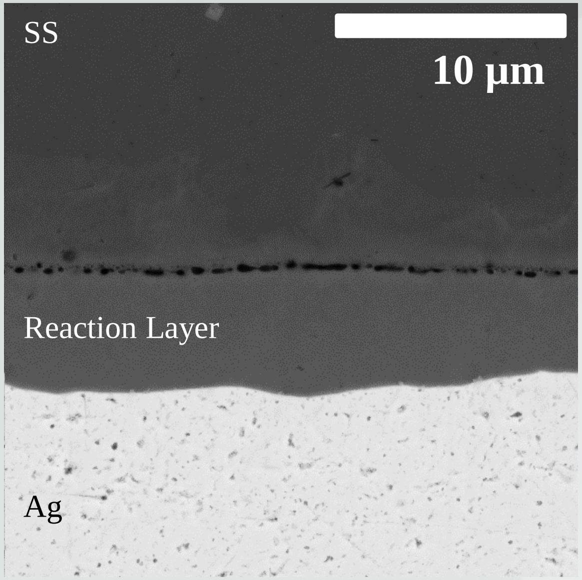
As-Brazed

120 Hour Oxidized

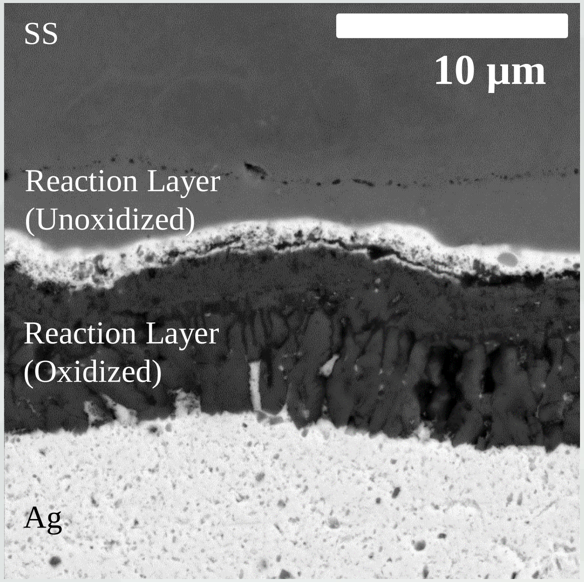
500 Hour Oxidized

Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

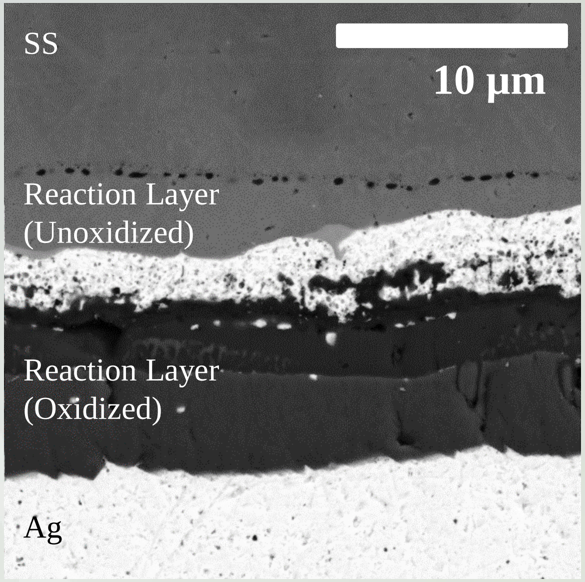
Oxidation affects the Ag-SS Interface



As-Brazed



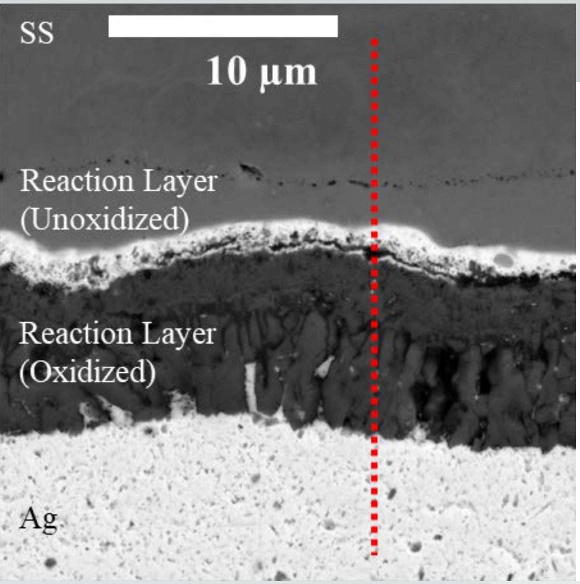
120 Hour Oxidized



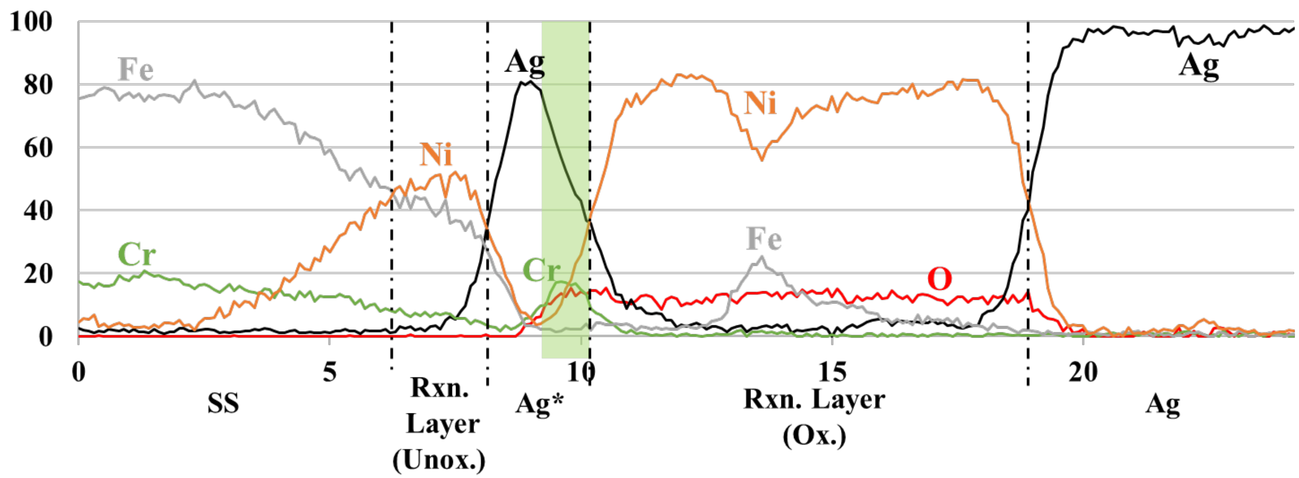
500 Hour Oxidized

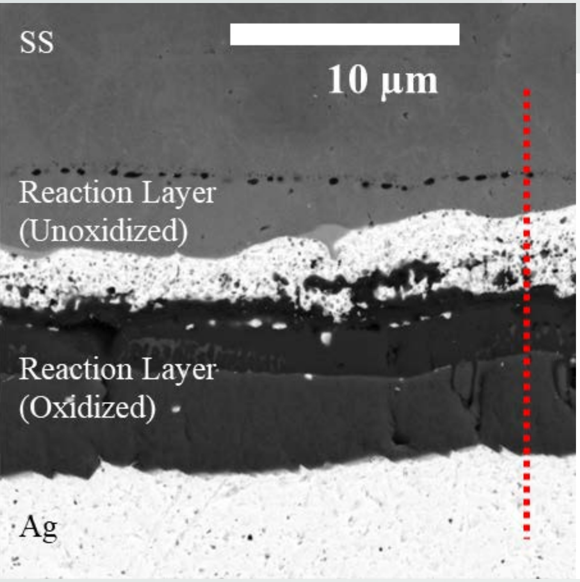
Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

A Protective Chromia layer forms in the Reaction Layer

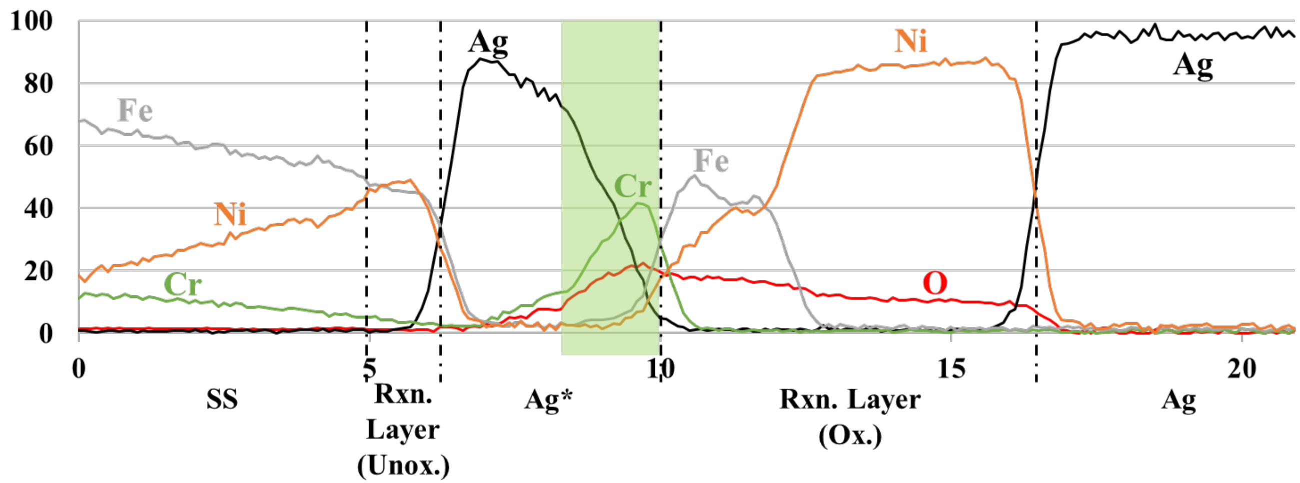


120 Hours of Oxidation



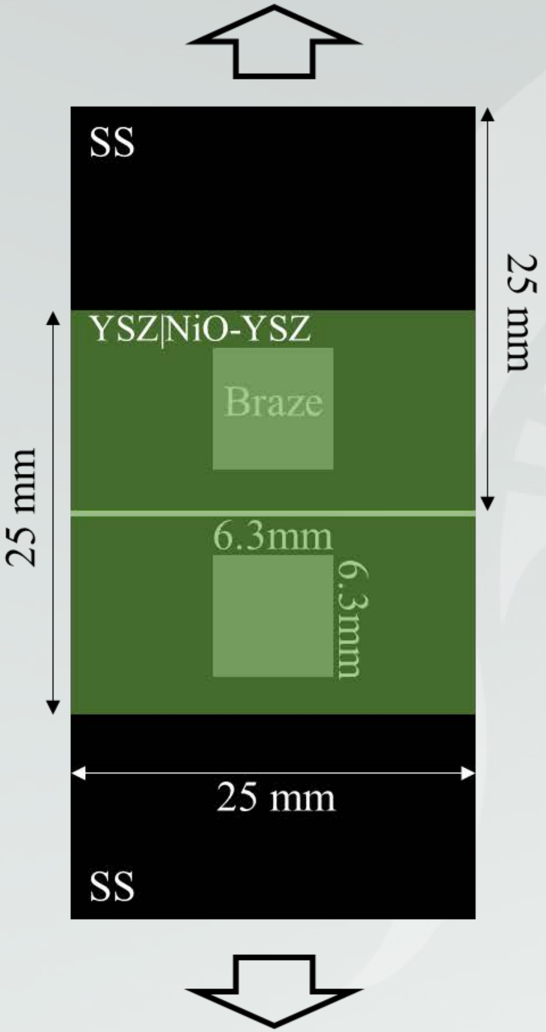


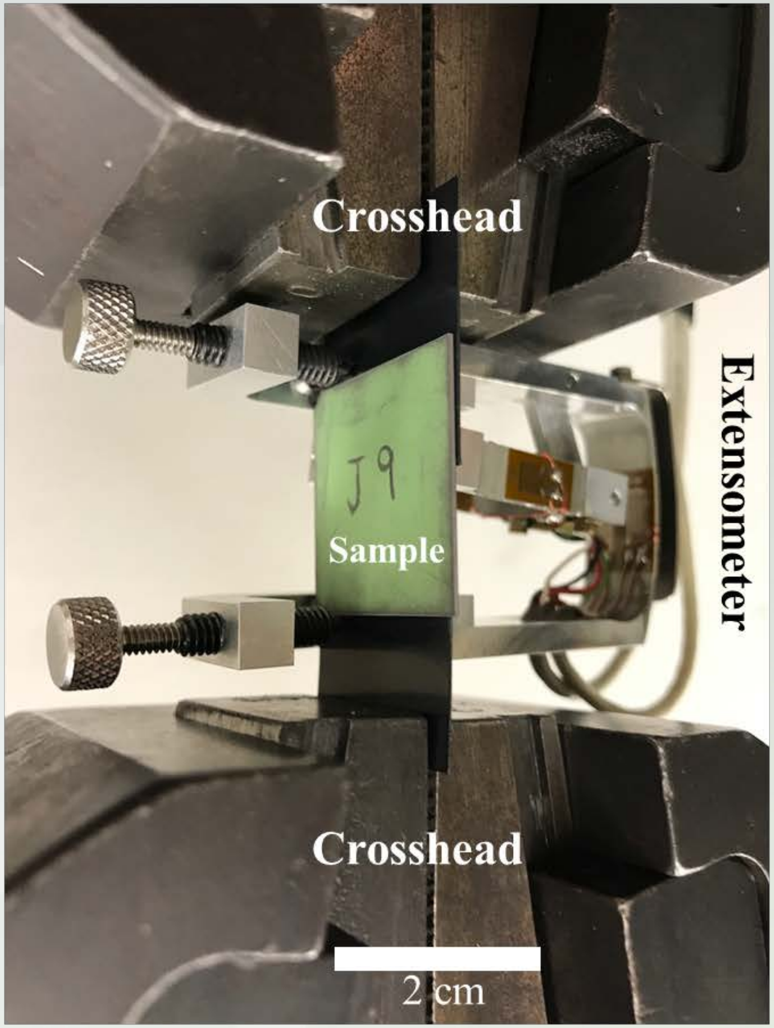
500 Hours of Oxidation



Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

Symmetric Double Shear Lap Tensile Tests

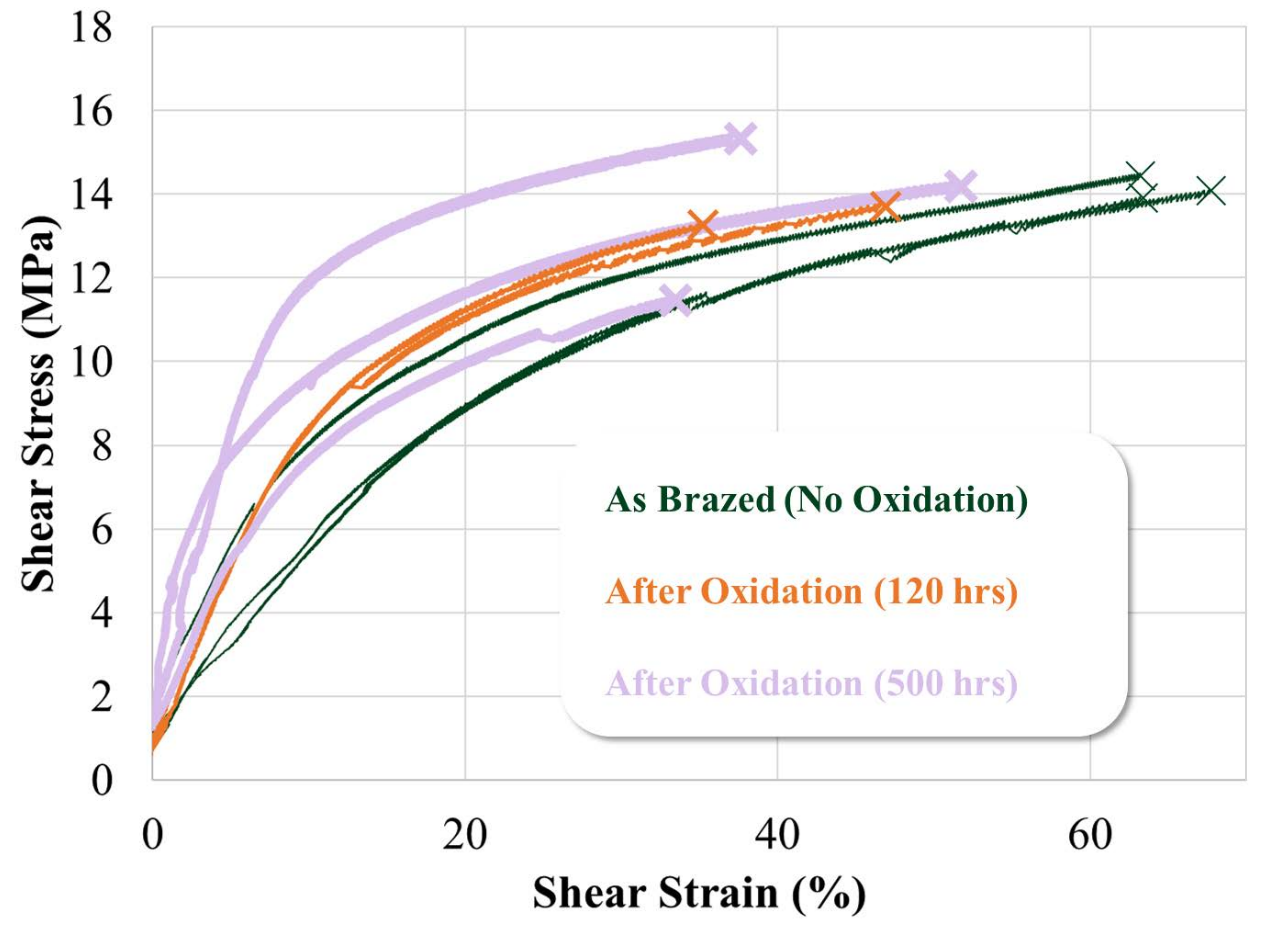




- Displacement Control: 0.009mm/min (~10^{-3} s^{-1})
- Test to Failure

Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

Even oxidized samples show excellent ductility



δ: Displacement per joint; σ_{shear}: Shear stress; ε_{shear}: Shear strain

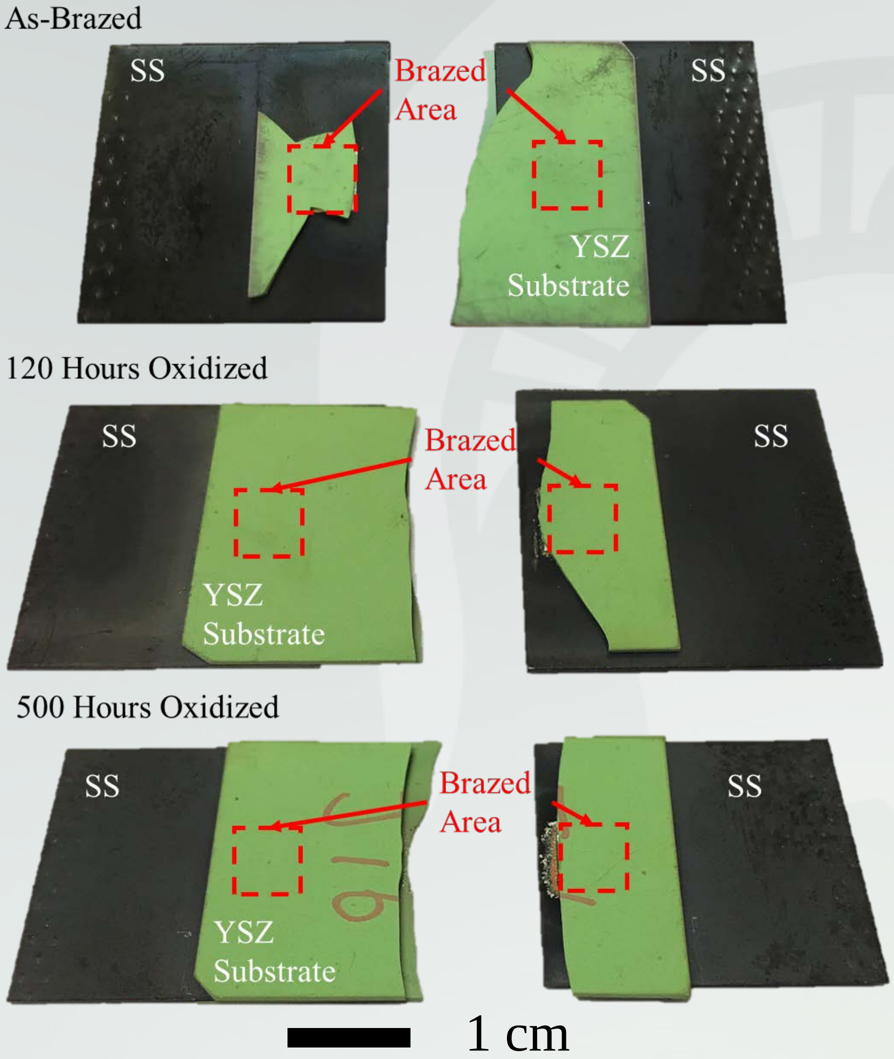
a: ¼'' (lateral length of the joints); F: Load; t: Joint thickness;

δ = Extension/2; $\sigma_{shear} = F/2[a*(a-\delta)]$; $\varepsilon_{shear} = (\delta/2)/t$.

Displacement were measured with extensometers.

Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

Both Braze Interface Strengths are Higher than the Anode Supported YSZ Substrate Strength



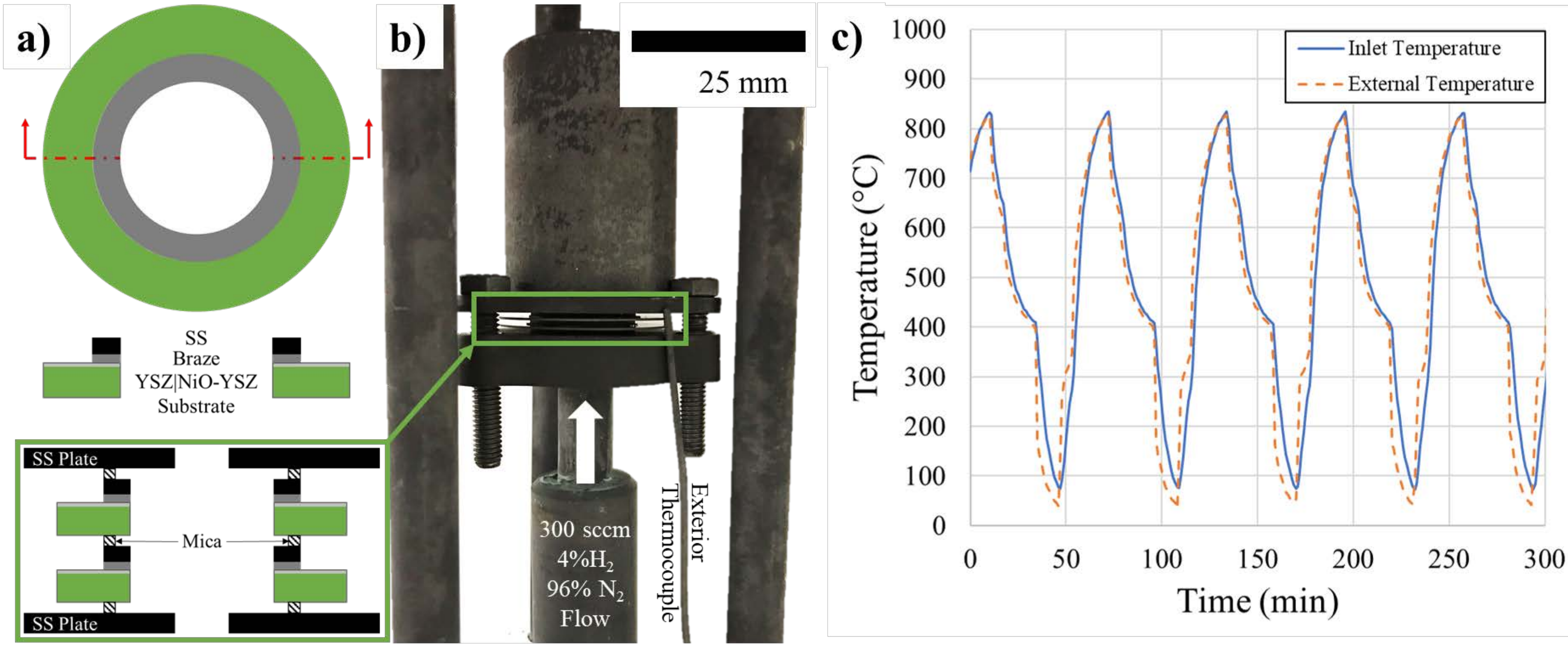
- All the joints broke only in the YSZ substrate. The other one has half of the braze/YSZ bonding area detached.

- In some of the joints, the YSZ substrate cracked around the brazed region, indicating the good bonding at the interfaces.

Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

DUAL ATMOSPHERE ISOTHERMAL TESTS & DUAL ATMOSPHERE RAPID THERMAL CYCLING TESTS

Dual Atmosphere Rapid Thermal Cycling Setup

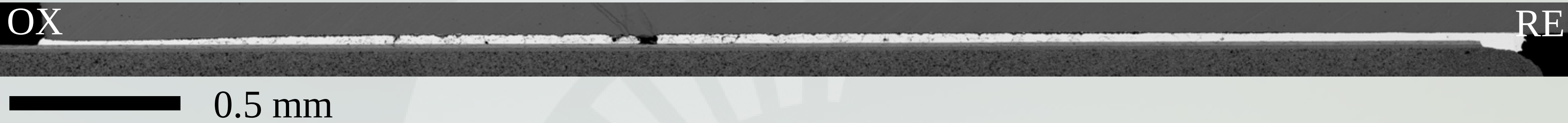


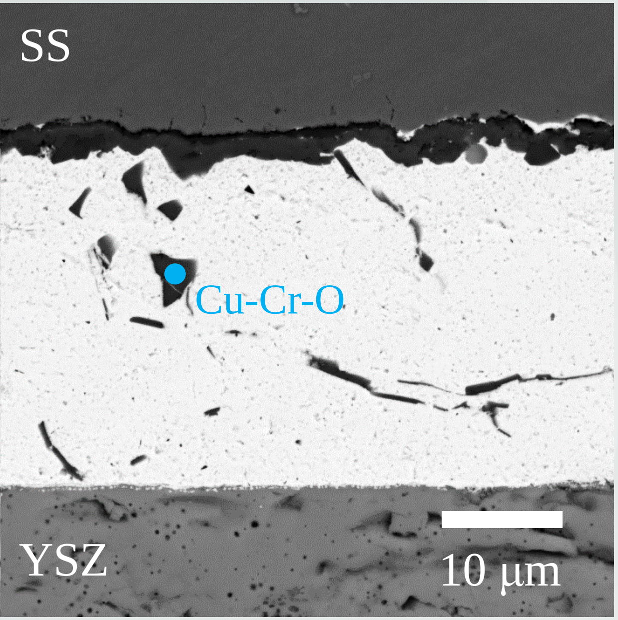
- Dual atmosphere achieved by flowing 300 sccm of 4%H_2 96% N_2 through the center hole of the sample stack;
- Thermal cycling was performed by moving the entire assembly in and out of a three-zone furnace. An average of ~26°C/min heating and cooling rate was applied during the test.

Quan Zhou et al., Dual Atmosphere Thermal Cycling Stability of Stainless-Steel to Yttria-Stabilized-Zirconia Joints Braze with Ag and Porous Nickel Interlayers, Acta Mater, 2018. (In Preparation)

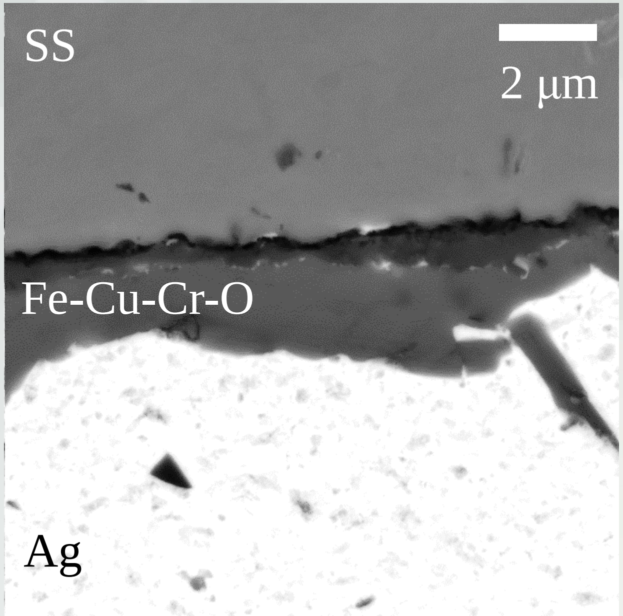
Ag-3CuO Reactive Air Brazes Display Literature-Reported As-Produced Microstructures

Ag3CuO (wt.) Braze Joint, As-Brazed

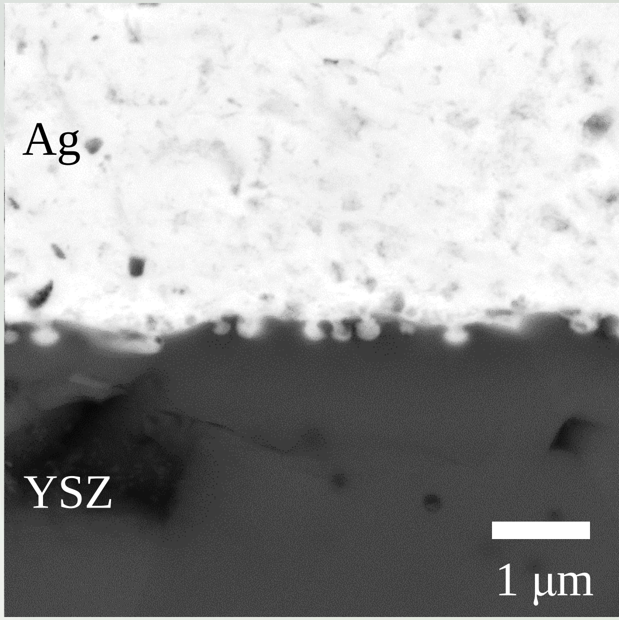




RAB Joint Center (As-Brazed)



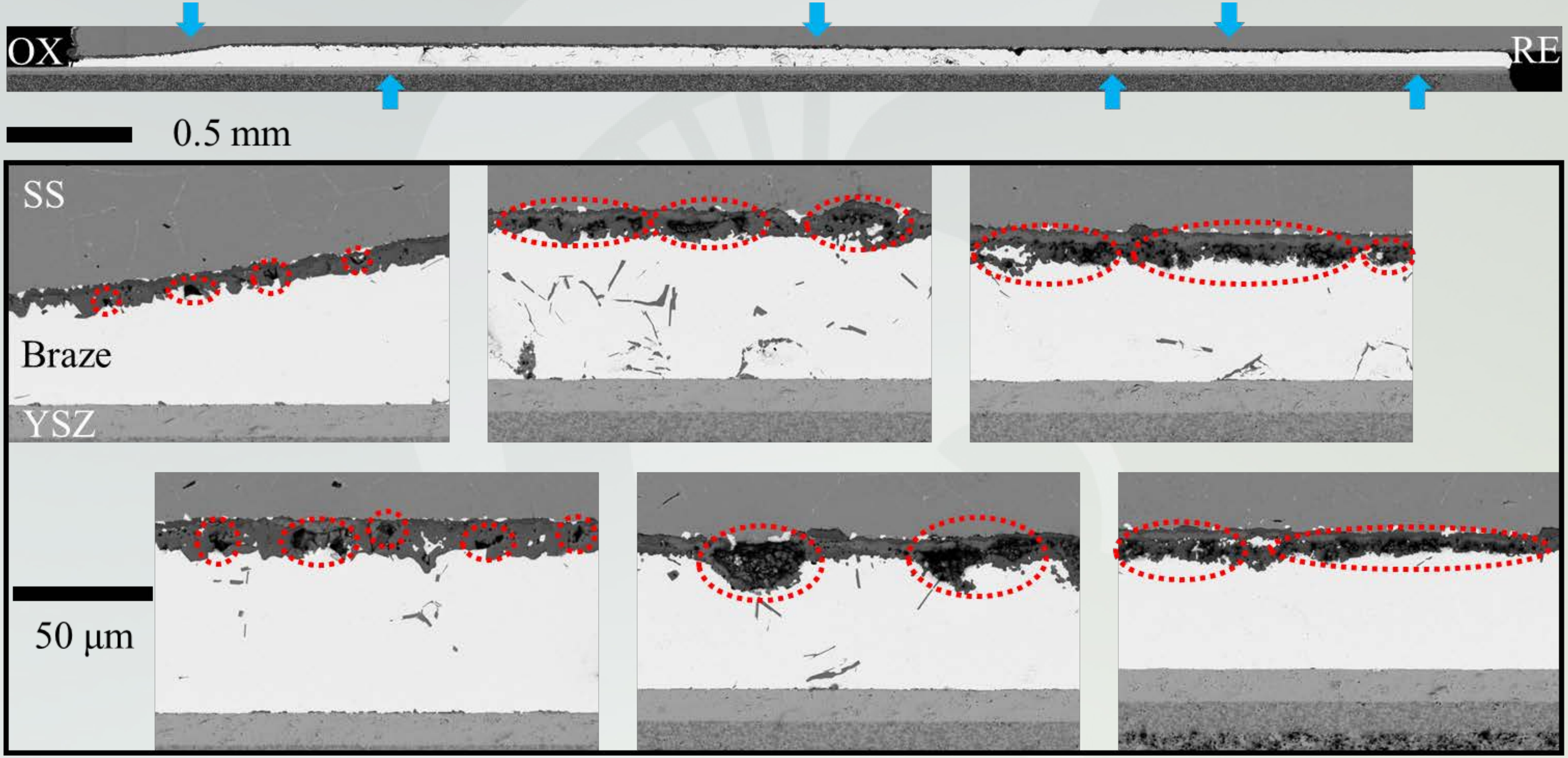
RAB Joint SS Interface (As-Brazed)



RAB Joint YSZ Interface (As-Brazed)

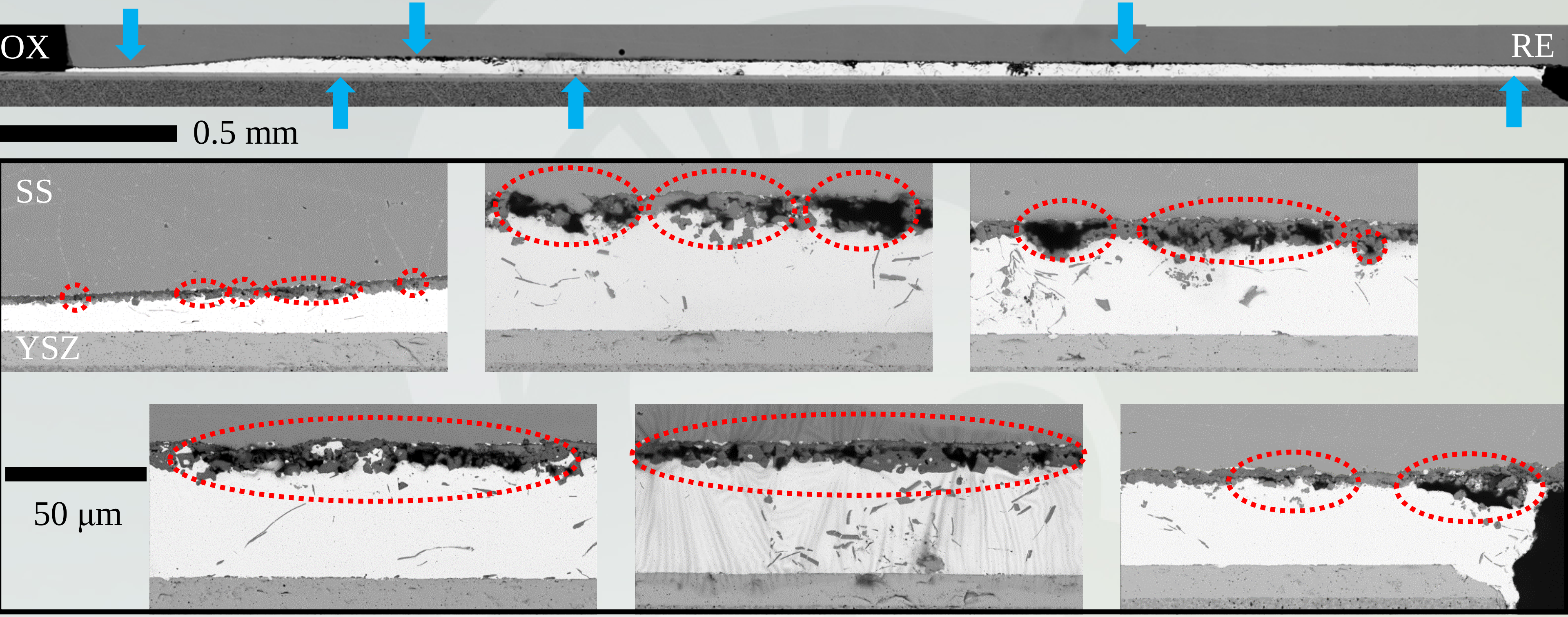
Quan Zhou et al., Dual Atmosphere Thermal Cycling Stability of Stainless-Steel to Yttria-Stabilized-Zirconia Joints Braze with Ag and Porous Nickel Interlayers, Acta Mater, 2018. (In Preparation)

Ag-3CuO Reactive Air Brazes Display Extensive CuO Reduction Pores after 300 Hours of 750°C Dual Atmosphere testing



Quan Zhou et al., Dual Atmosphere Thermal Cycling Stability of Stainless-Steel to Yttria-Stabilized-Zirconia Joints Braze with Ag and Porous Nickel Interlayers, Acta Mater, 2018. (In Preparation)

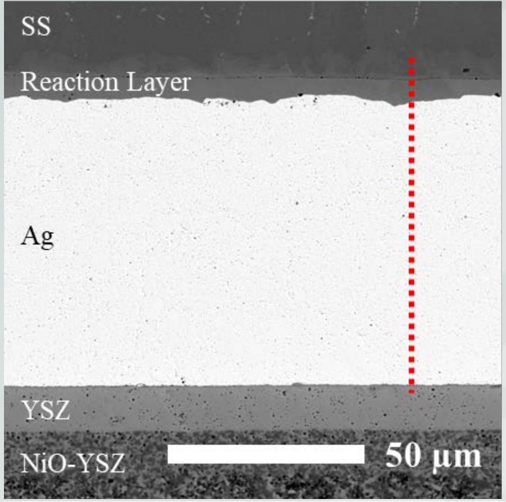
Ag-3CuO Reactive Air Brazes Display Similar Degradation after 300 50-825°C Dual Atmosphere Rapid Thermal Cycles



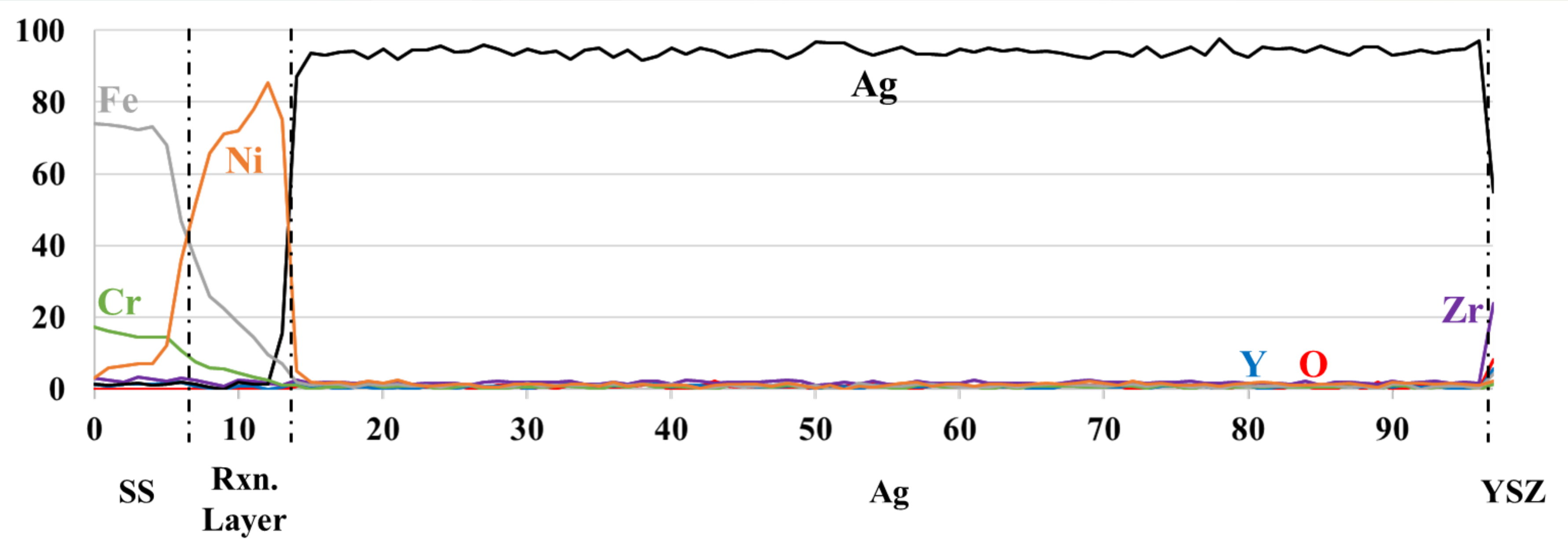
Quan Zhou et al., Dual Atmosphere Thermal Cycling Stability of Stainless-Steel to Yttria-Stabilized-Zirconia Joints Braze with Ag and Porous Nickel Interlayers, Acta Mater, 2018. (In Preparation)

Reminder of the As-Produced Ag-Ni Braze Microstructure

30 Mins Brazed Sample

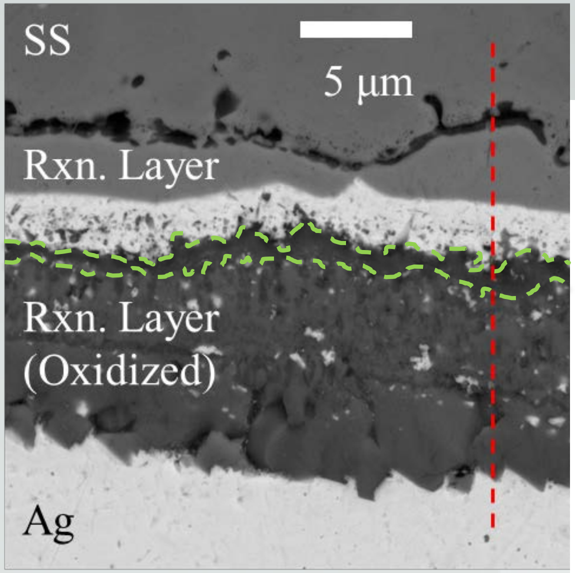


- There is a reaction layer at the SS interface, comprising Ni, Fe and Cr.
- After 30 mins of brazing, the Ni interlayer will be totally transient.

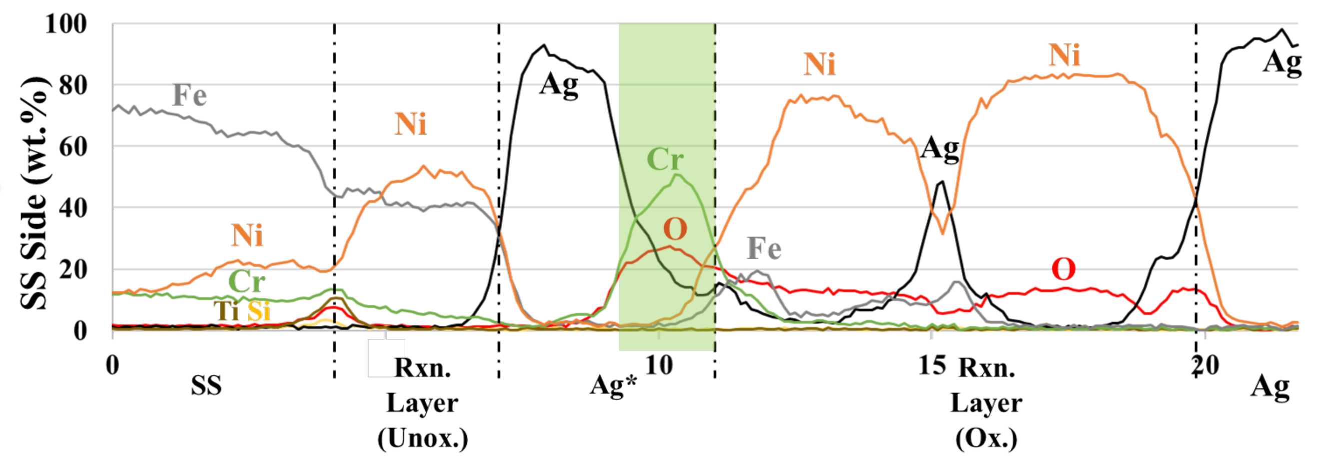


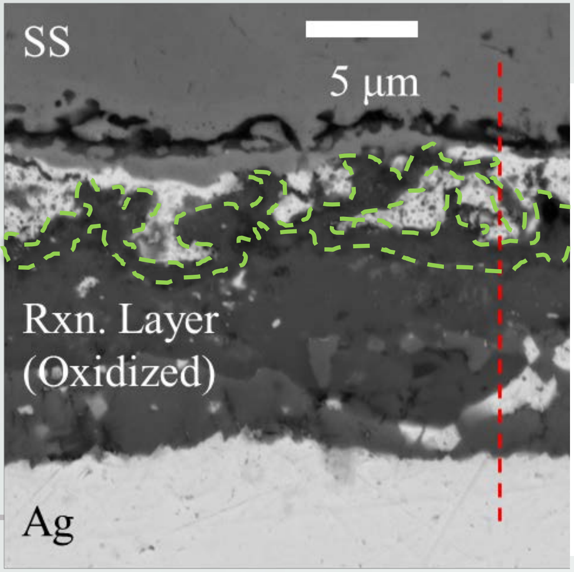
Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

No pores form in Ag-Ni Brazes after 300 hours of 750ºC Dual Atmosphere Exposure

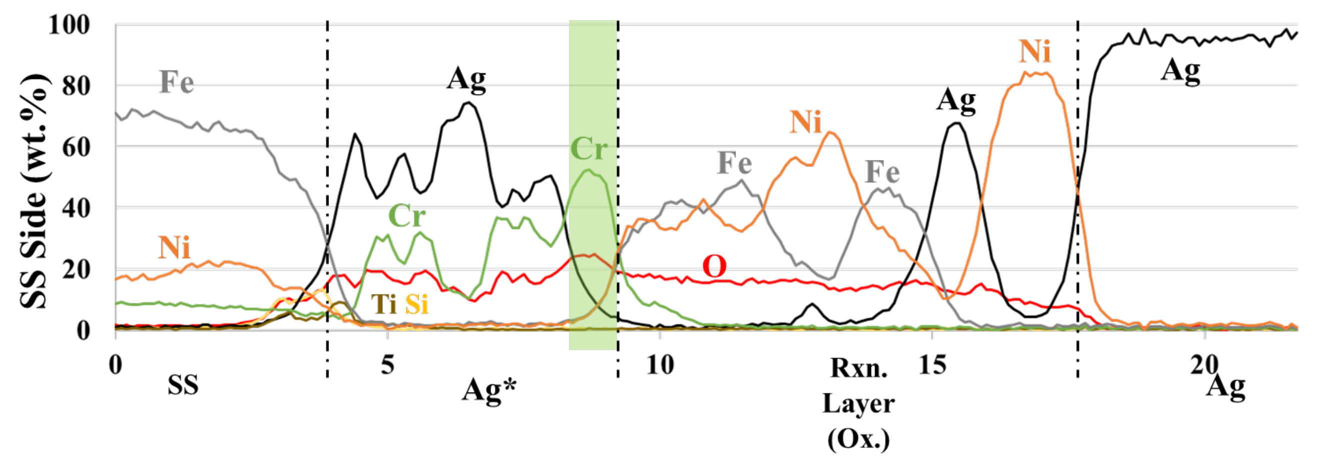


OX Side

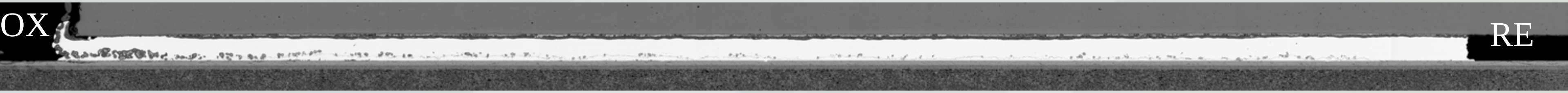




RE Side



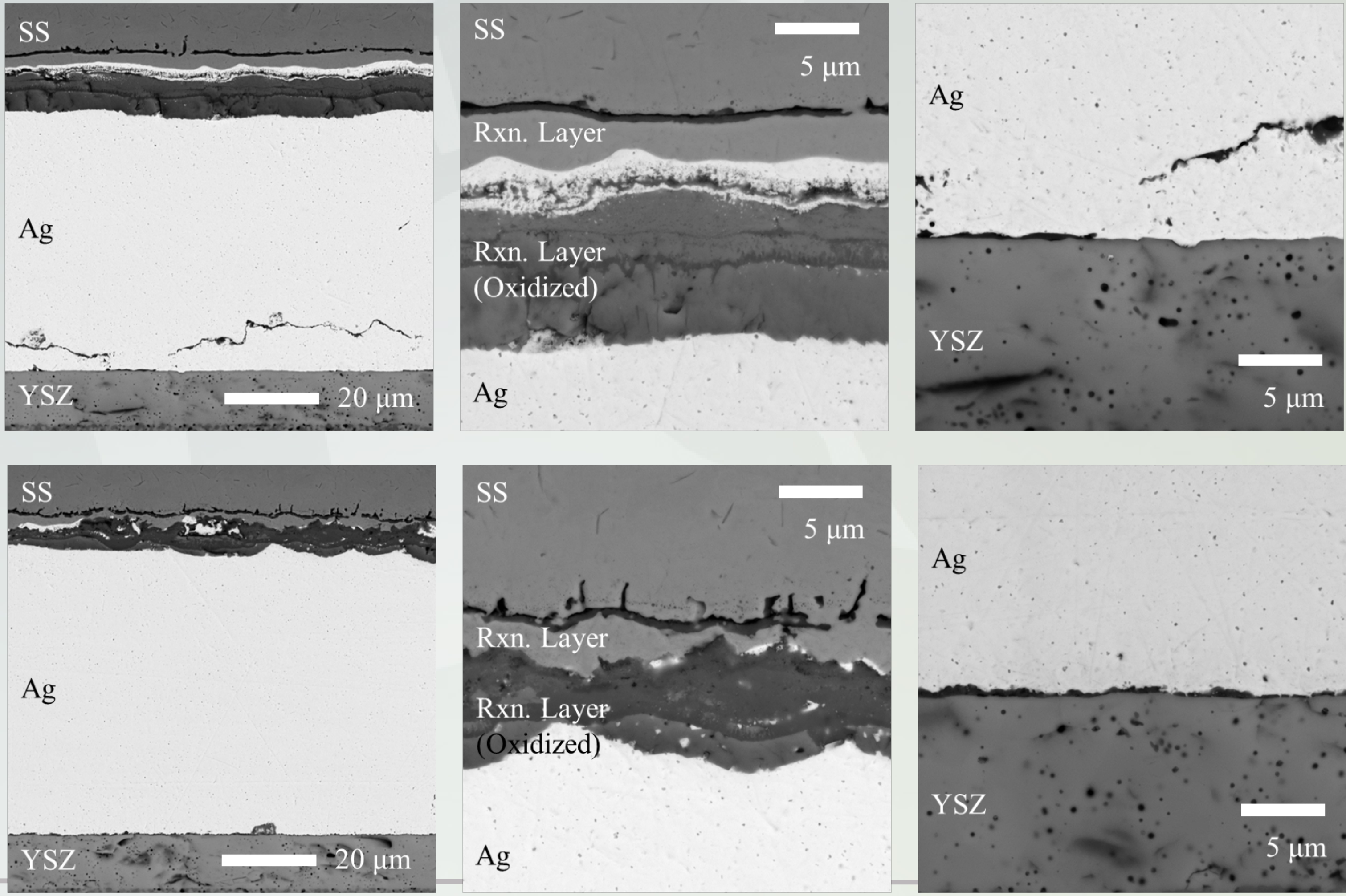
No pores form in Ag-Ni Brazes after 300 80-825°C Dual Atmosphere Rapid Thermal Cycles



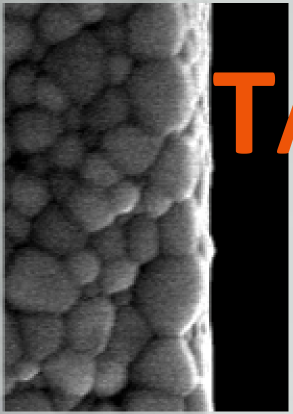
Oxidation Side

~74 hours total @ >700 ℃

Reduction Side



Through Thickness *SS Interface* *YSZ Interface*



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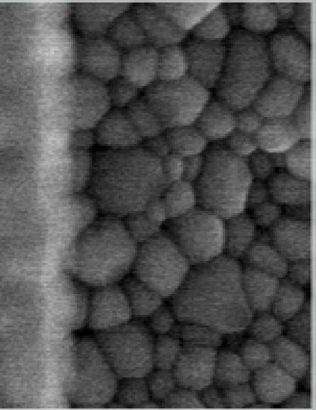
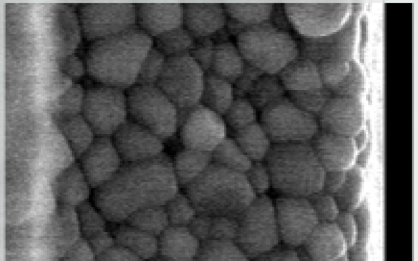
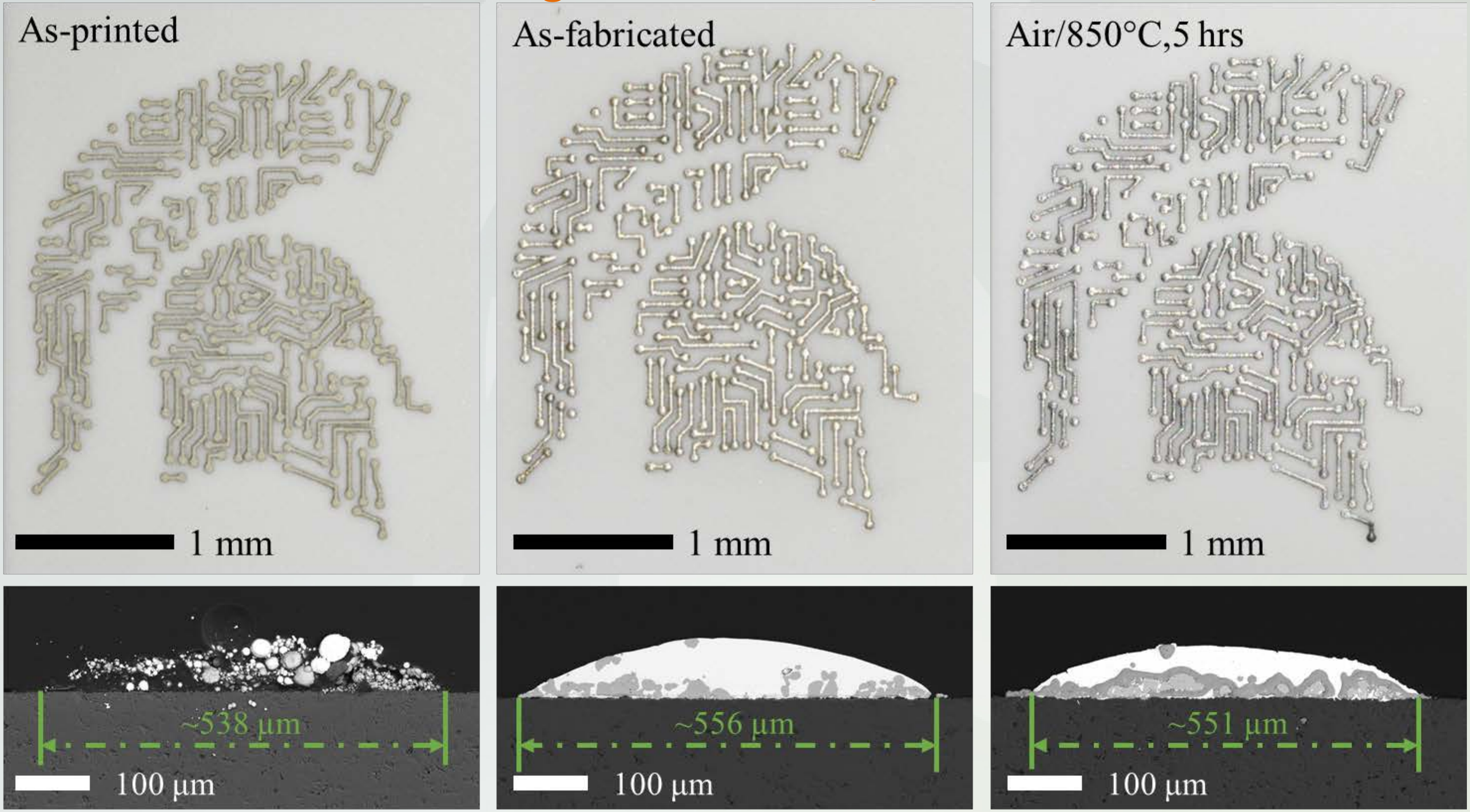




The Controlled Wetting and Spreading of Ag can be used for High Temp Semiconductors, High Power SOFCs, Etc.



Zhou et al., Controlled Wetting and Spreading of Metals on Substrates Using Porous Interlayers and Related Articles, USPTO Provisional Patent (Submitted April 17, 2018)
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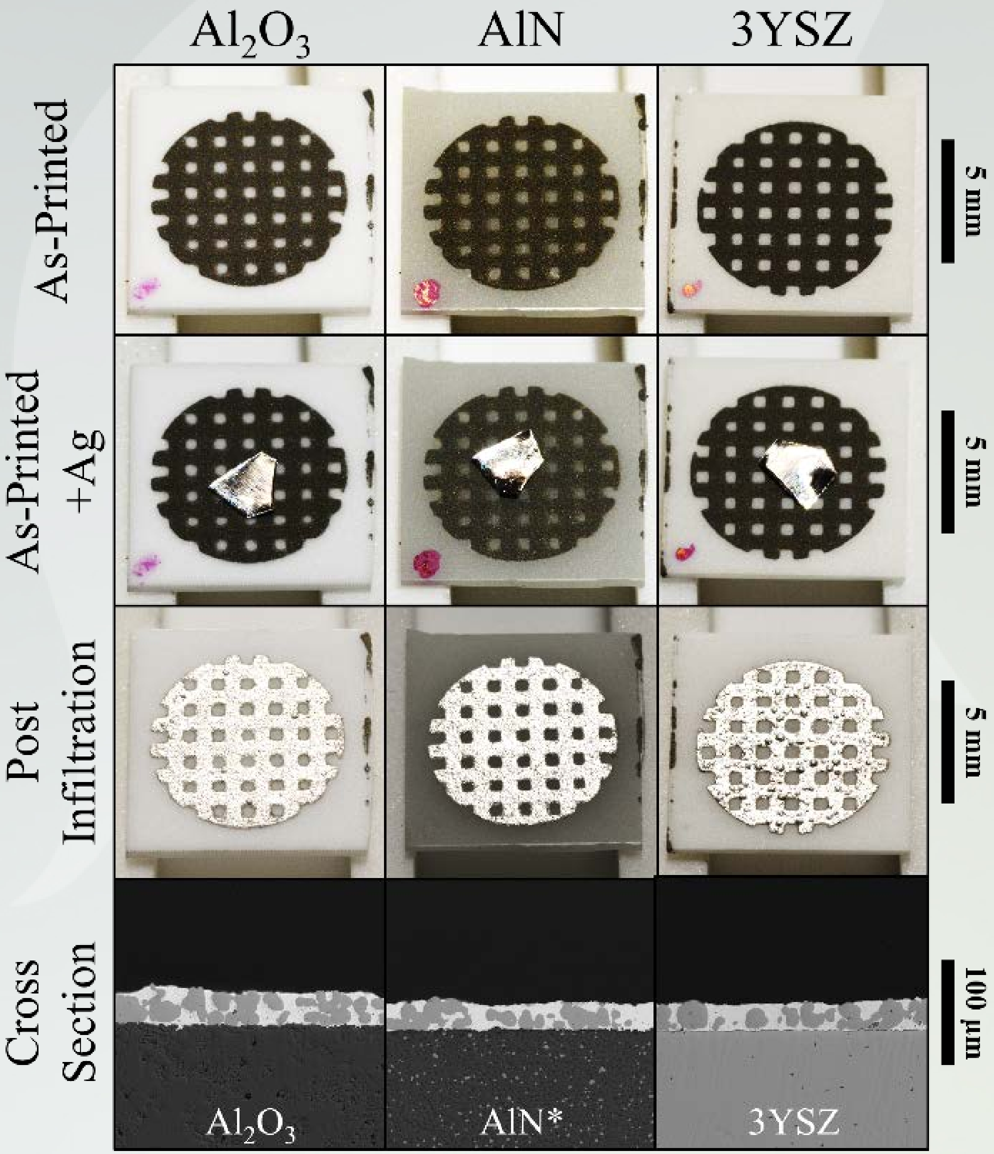
Molten Ag Will Also Infiltrate and Spread Through a Contiguous Ni Pattern



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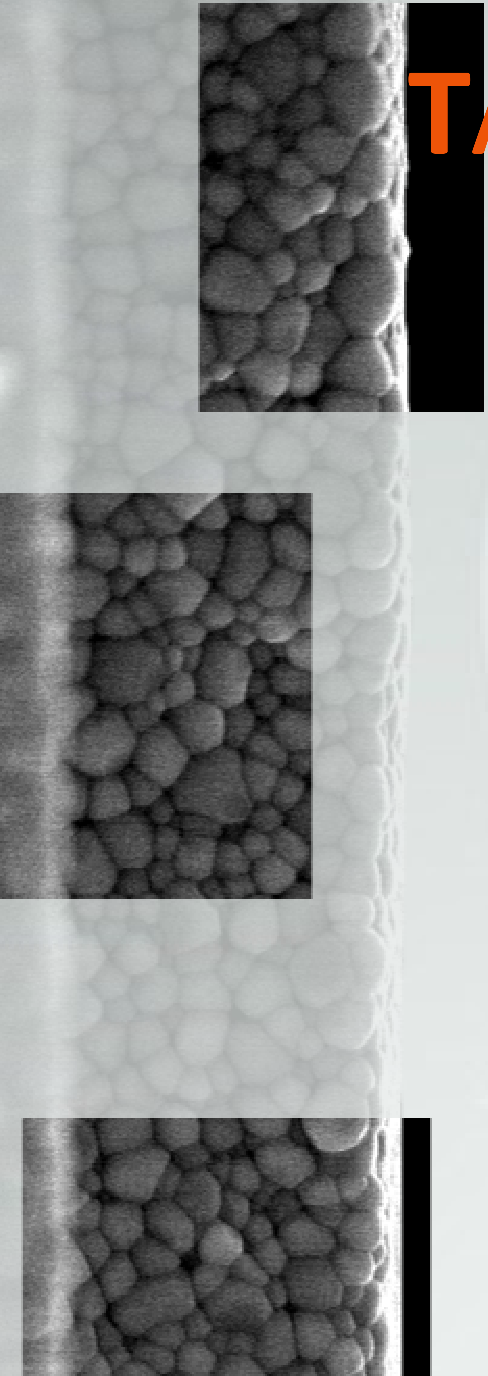


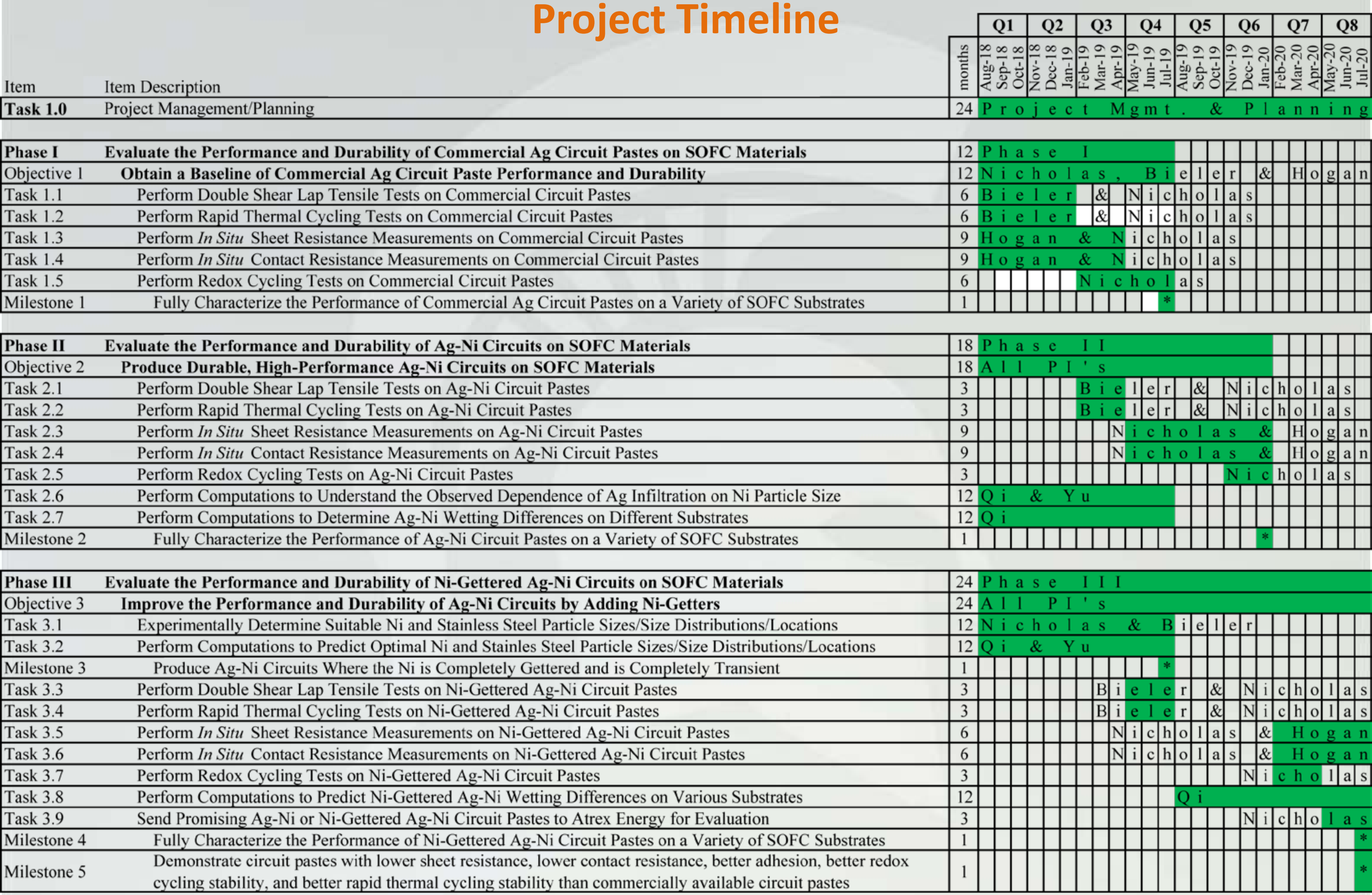
TALK Outline

1. Background
    a) Results from DE-FE0031250 on Ag-Ni Brazes

2. **Project Approach**
    a) Preliminary Results
    b) Research Plan

3. Initial Project Progress

Project Timeline



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Phase I	**Evaluate the Performance and Durability of Commercial Ag Circuit Pastes on SOFC Materials**	12	🟩 Phase I	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩												
Objective 1	**Obtain a Baseline of Commercial Ag Circuit Paste Performance and Durability**	12	🟩 Nicholas, Bieler & Hogan	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩												
Task 1.1	Perform Double Shear Lap Tensile Tests on Commercial Circuit Pastes	6	🟩 Bieler & Nicholas	🟩	🟩	🟩	🟩	🟩																		
Task 1.2	Perform Rapid Thermal Cycling Tests on Commercial Circuit Pastes	6	🟩 Bieler & Nicholas	🟩	🟩	🟩	🟩	🟩																		
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Milestone 1	Fully Characterize the Performance of Commercial Ag Circuit Pastes on a Variety of SOFC Substrates	1												🟩 *												
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Objective 2	**Produce Durable, High-Performance Ag-Ni Circuits on SOFC Materials**	18	🟩 All PI's	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩						
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Objective 3	**Improve the Performance and Durability of Ag-Ni Circuits by Adding Ni-Getters**	24	🟩 All PI's	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
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Task 3.9	Send Promising Ag-Ni or Ni-Gettered Ag-Ni Circuit Pastes to Atrex Energy for Evaluation	3																	Nicholas					🟩	🟩	🟩
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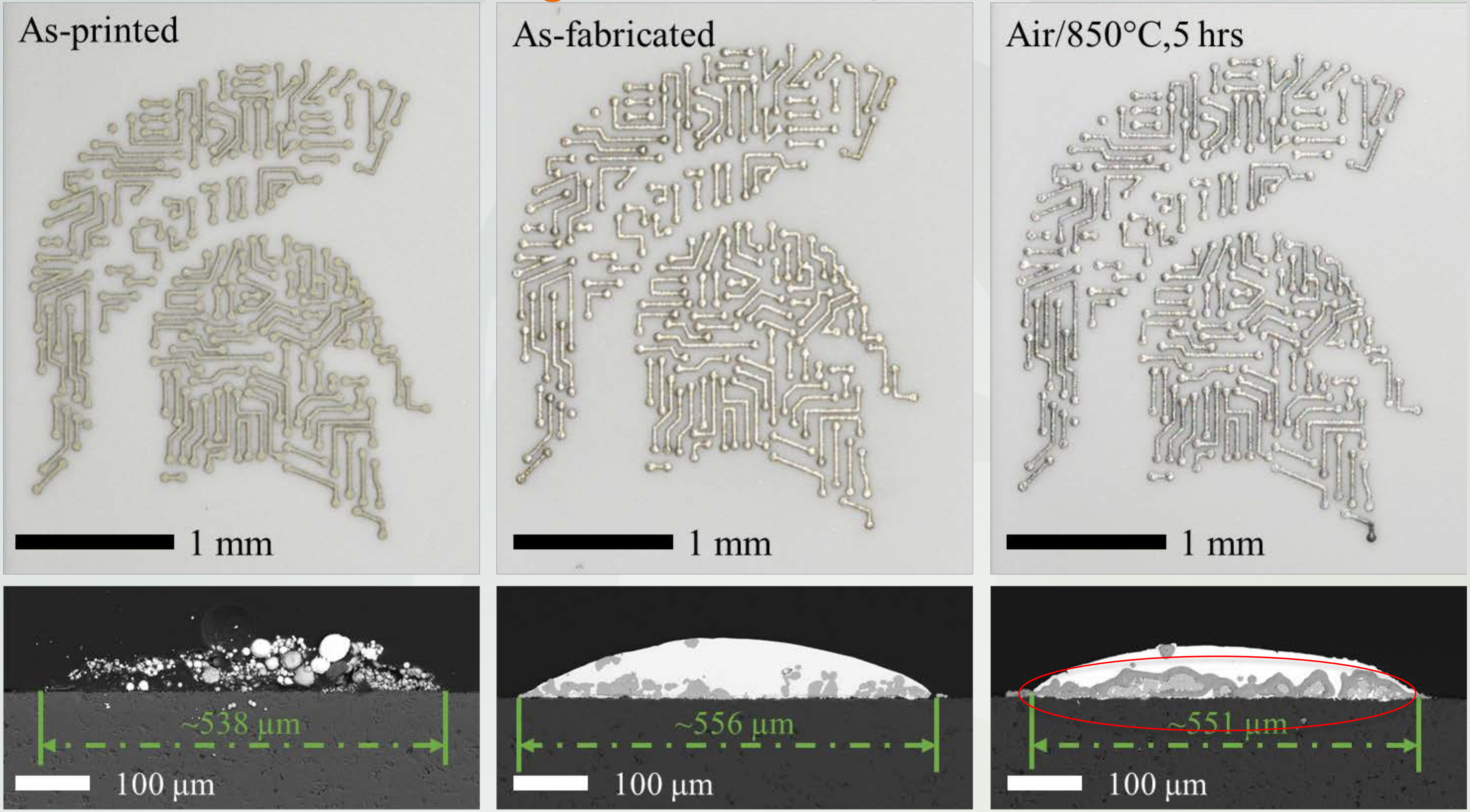

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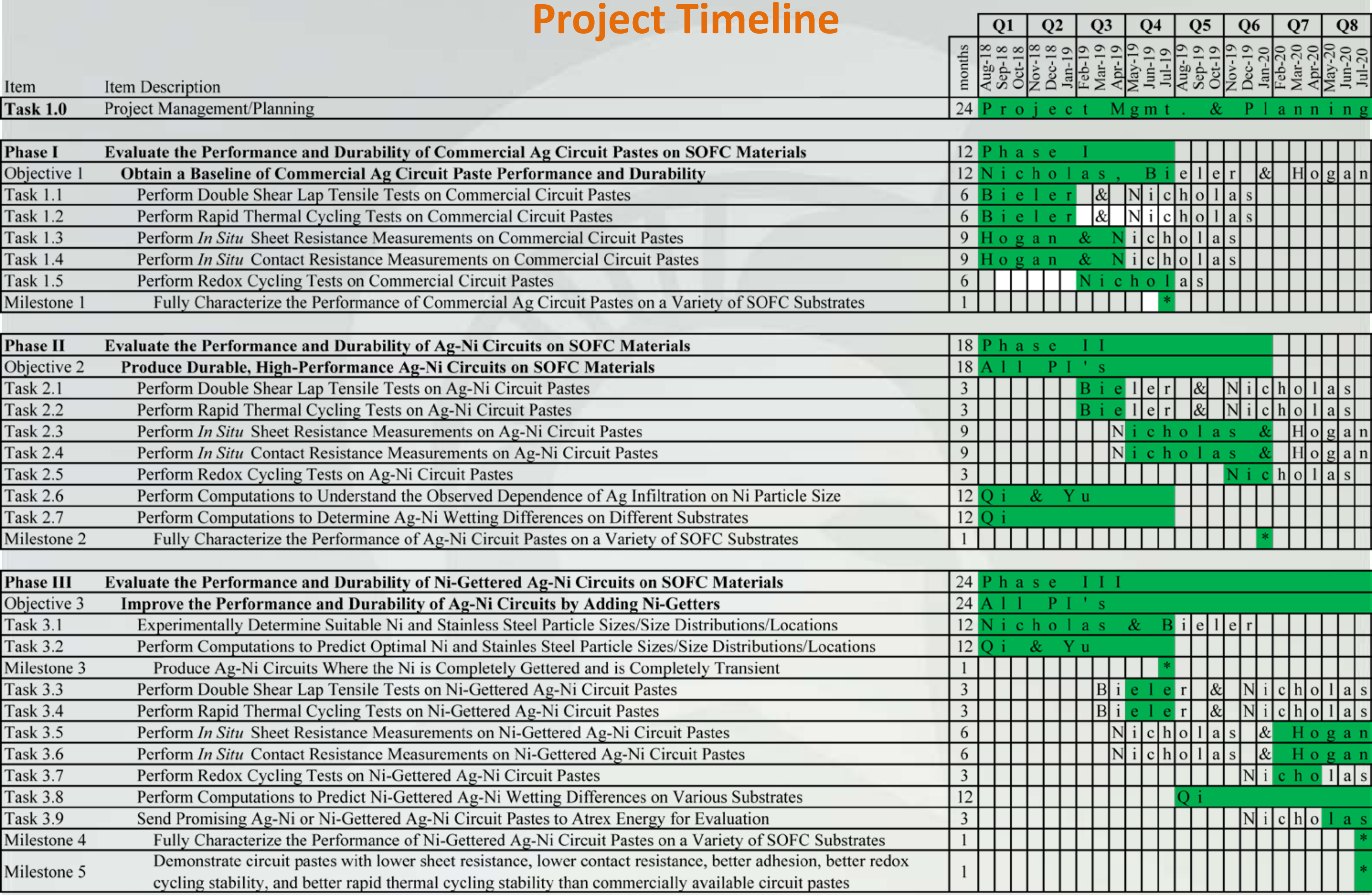

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In situ Electrical Measurements

Characterization Capabilities (6 independent measurement systems)

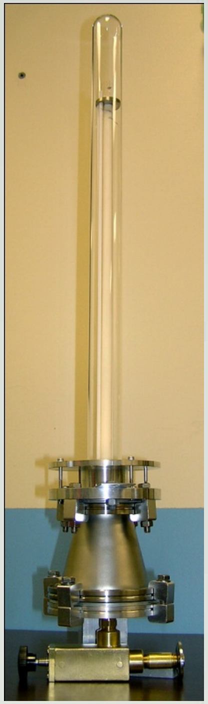
- Electrical Conductivity (4.2 K - 1000 K)
- Thermoelectric Power (4.2 K - 1000 K)
- Thermal Conductivity (4.2 K - 400 K)
- Hall Effect (100 K - 800 K)
- ZT meter – Impedance Spectroscopy
- Scanning voltage probe (50µm resolution) (room temp)

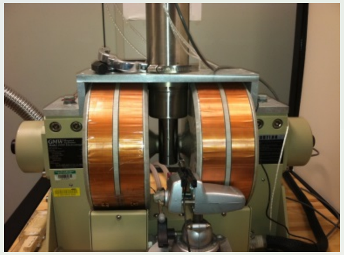
Verification of Measurements

- Multiple Techniques for Same Properties
  - Scanning Voltage Probe & 4-Probe Techniques for Electrical Conductivity
  - Independent Property Measurements & ZT Direct Measurements
- Round Robin Measurements between Groups
  - Reference Materials (stable, wide T range, readily available)
  - Exchange of Samples (MSU, UofM, NU, JPL, Ames, ORNL, NIST)
- Large Number of Samples Measured
  - Trends
  - Range of Property Values

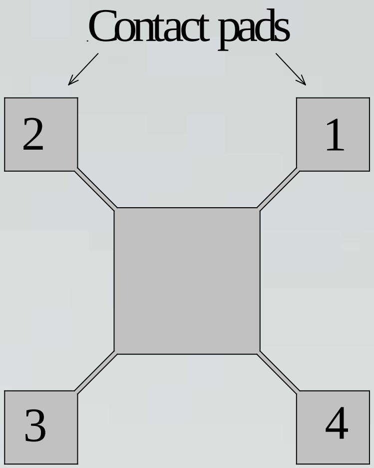
Other Equipment

- Pulsed Laser Deposition and Micromachining System





Sheet Resistance Measurements



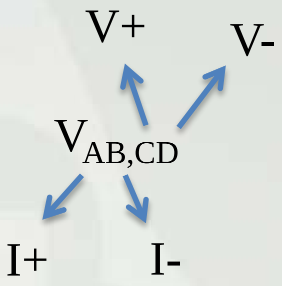
Van der Pauw
(VdP)

In-plane measurements.

$$\rho_A = \frac{1.1331 f_A t}{I}\left[V_{21,34} - V_{12,34} + V_{32,41} - V_{23,41}\right]$$

$$\rho_B = \frac{1.1331 f_B t}{I}\left[V_{43,12} - V_{34,12} + V_{14,23} - V_{41,23}\right]$$

I **= Current (A)**
t **= Thickness (cm)**



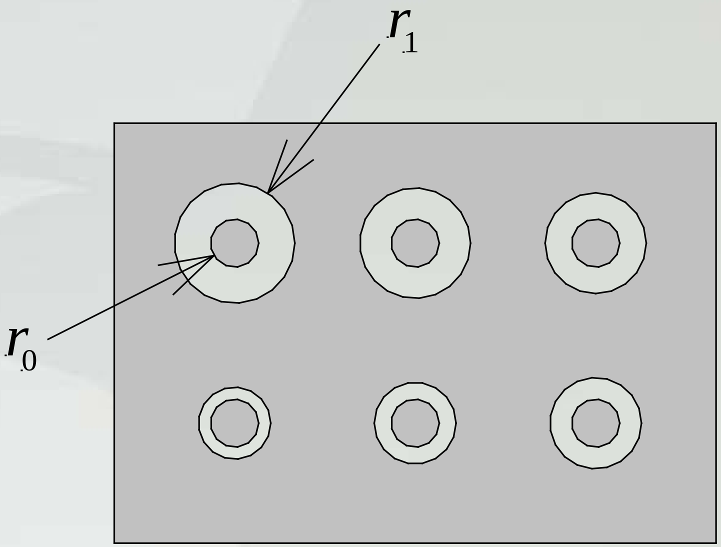
Sheet resistance: $R_s = \dfrac{\pi}{ln2}\dfrac{V}{I}$

Where geometrical factors f_A and f_B are dependent on measured voltages.

If ρ_A is not equal to ρ_B within 10%, the specimen is inhomogeneous and a more uniform specimen is required. If they are within 10%, then they are averaged for the sample resistivity.

Contact Resistance Measurements

Circular transmission line measurements for contact resistance between the the circuit pastes and various SOFC electrode substrates (lanthanum strontium manganite, lanthanum strontium cobalt iron oxide, ceria, and Ni-YSZ)



The measured resistance, R_M, is given by

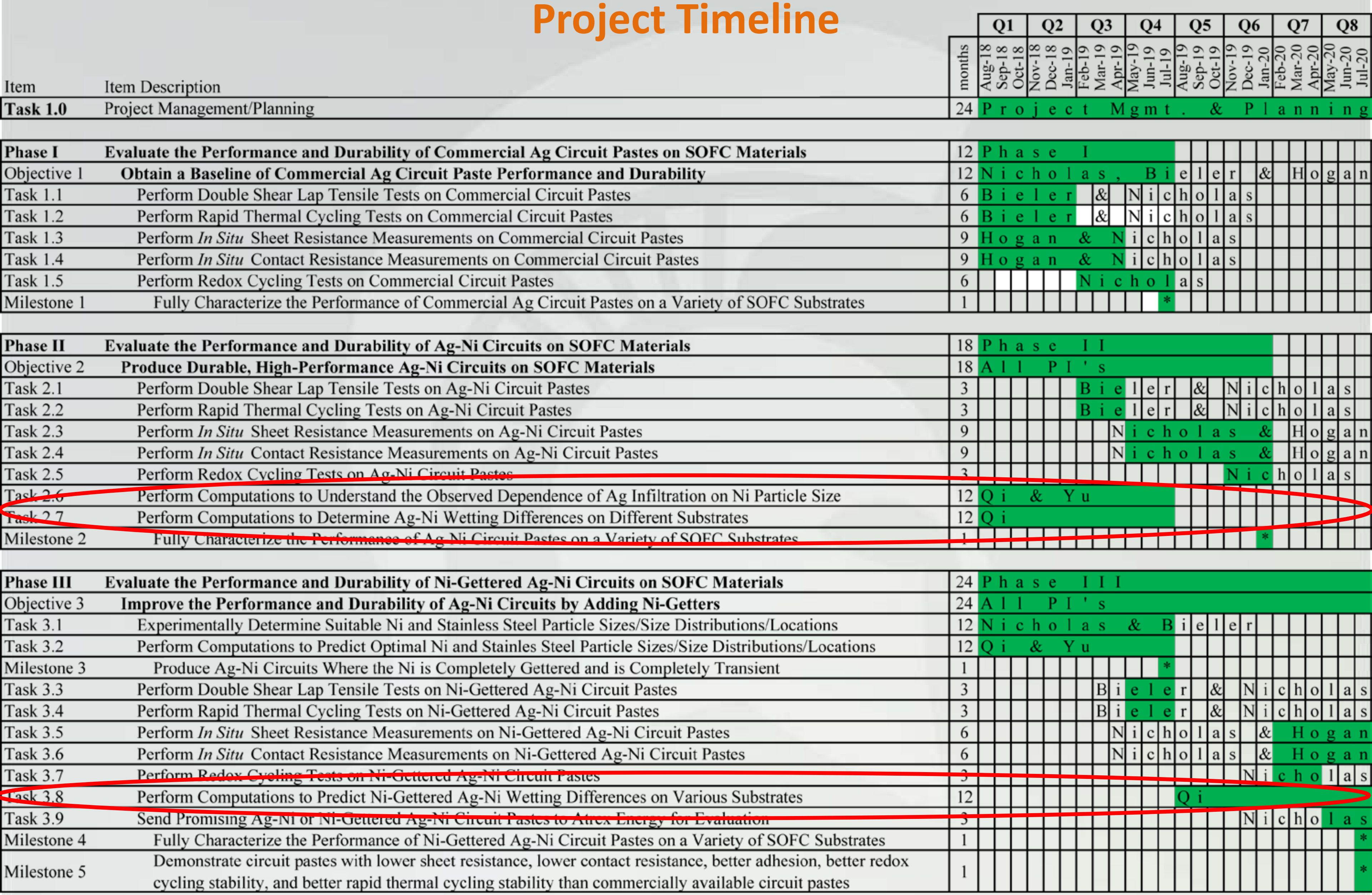
$$R_M = \frac{R_{SH}}{2\pi}\left[ln\left(\frac{r_1}{r_0}\right) + \frac{1}{kr_0} + \frac{1}{kr_1}\right]$$

where R_{SH} is the sheet resistance of the SOFC substrate under the contact, and $k = \sqrt{\frac{R_{SH}}{\rho_C}}$.

Using $d = r_1 - r_0$ then R_M versus d can be plotted and a least squares fit can be made to determine k and the specific contact resistivity, ρ_C.

Temperature dependent measurements of the specific contact resistivity will be taken from room temperature to 700ºC in air and in 4% hydrogen.

Project Timeline



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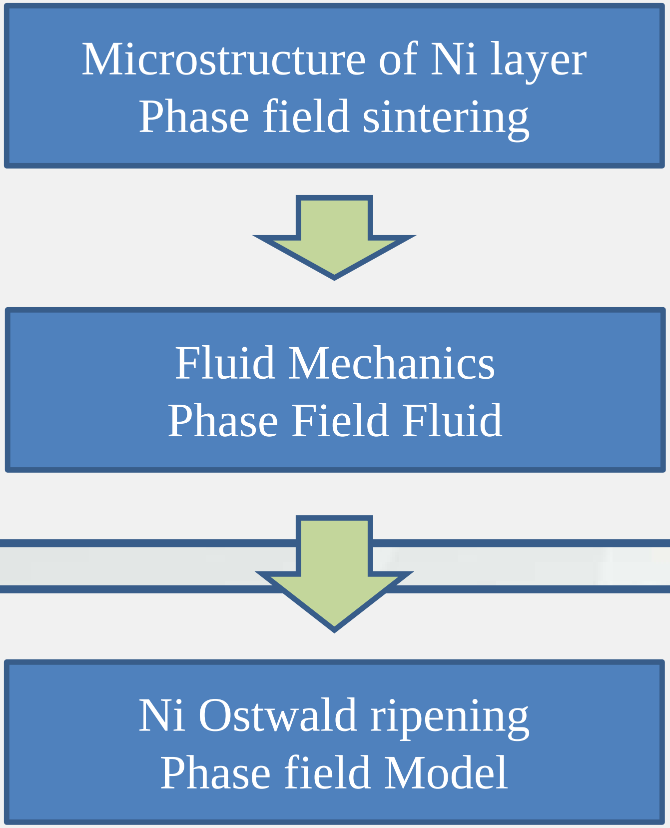
Task 2.7	Perform Computations to Determine Ag-Ni Wetting Differences on Different Substrates	12	Qi	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩												
Milestone 2	Fully Characterize the Performance of Ag-Ni Circuit Pastes on a Variety of SOFC Substrates	1																		*						
Phase III	**Evaluate the Performance and Durability of Ni-Gettered Ag-Ni Circuits on SOFC Materials**	24	Phase III	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Objective 3	**Improve the Performance and Durability of Ag-Ni Circuits by Adding Ni-Getters**	24	All PI's	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Task 3.1	Experimentally Determine Suitable Ni and Stainless Steel Particle Sizes/Size Distributions/Locations	12	Nicholas & Bieler	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩												
Task 3.2	Perform Computations to Predict Optimal Ni and Stainles Steel Particle Sizes/Size Distributions/Locations	12	Qi & Yu	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩												
Milestone 3	Produce Ag-Ni Circuits Where the Ni is Completely Gettered and is Completely Transient	1												*												
Task 3.3	Perform Double Shear Lap Tensile Tests on Ni-Gettered Ag-Ni Circuit Pastes	3								Bieler & Nicholas		🟩	🟩	🟩												
Task 3.4	Perform Rapid Thermal Cycling Tests on Ni-Gettered Ag-Ni Circuit Pastes	3								Bieler & Nicholas		🟩	🟩	🟩												
Task 3.5	Perform *In Situ* Sheet Resistance Measurements on Ni-Gettered Ag-Ni Circuit Pastes	6									Nicholas & Hogan										🟩	🟩	🟩	🟩	🟩	🟩
Task 3.6	Perform *In Situ* Contact Resistance Measurements on Ni-Gettered Ag-Ni Circuit Pastes	6									Nicholas & Hogan										🟩	🟩	🟩	🟩	🟩	🟩
Task 3.7	Perform Redox Cycling Tests on Ni-Gettered Ag-Ni Circuit Pastes	3																	Nicholas		🟩	🟩	🟩			
Task 3.8	Perform Computations to Predict Ni-Gettered Ag-Ni Wetting Differences on Various Substrates	12													Qi	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Task 3.9	Send Promising Ag-Ni or Ni-Gettered Ag-Ni Circuit Pastes to Atrex Energy for Evaluation	3																	Nicholas					🟩	🟩	🟩
Milestone 4	Fully Characterize the Performance of Ni-Gettered Ag-Ni Circuit Pastes on a Variety of SOFC Substrates	1																								*
Milestone 5	Demonstrate circuit pastes with lower sheet resistance, lower contact resistance, better adhesion, better redox cycling stability, and better rapid thermal cycling stability than commercially available circuit pastes	1																								*

Continuum (Microstructural) Scale Simulations: Phase Field Modeling

1. **Understand the microstructural effects on Ag infiltration through Ni structure**
2. **Extract design guidelines for Ni brazing paste (e.g., Ni particle size distribution)**
3. **Extract guidelines for heat treatment (temperature, duration) for Ni removal**

Task 2.6



Microstructure of Ni layer
Phase field sintering

Fluid Mechanics
Phase Field Fluid

Generate porous layers with assigned **particle size distribution**, **sintering duration** etc. on computers.

Identify **optimal porous microstructures** for Ag (1) **infiltration** and (2) **spread** on substrates.

Parameters for other particles and substrates can be tested for **other candidate materials**.

Task 3.2

Ni Ostwald ripening
Phase field Model

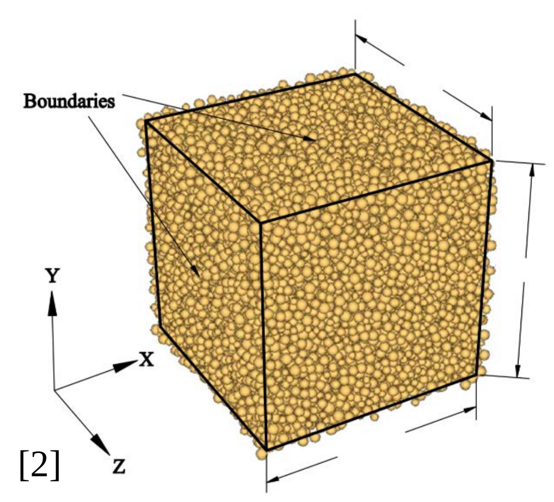
Design **heat treatment protocols** (e.g., temperature and duration) for Ni gettering.

Phase Field Modeling

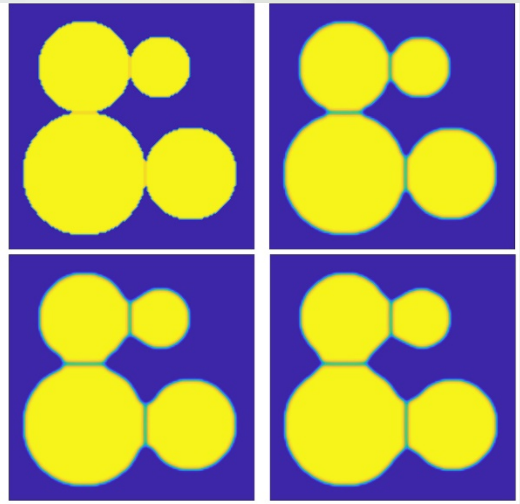
I: Ni particle sintering

1. **Discrete Element Method [2]:** Generate packed hard spheres with assigned particle size distribution as the initial configuration
2. **Phase Field Model [3]:** Simulate Ni particle sintering at brazing temperature over brazing duration to obtain connected Ni porous structures

Objective: generate porous microstructures realistically mimicking Ni layer, which will be used as the input geometries for fluid mechanics simulation.



Closed packed configuration generated using DEM



Preliminary sintering simulation using the model in [3]

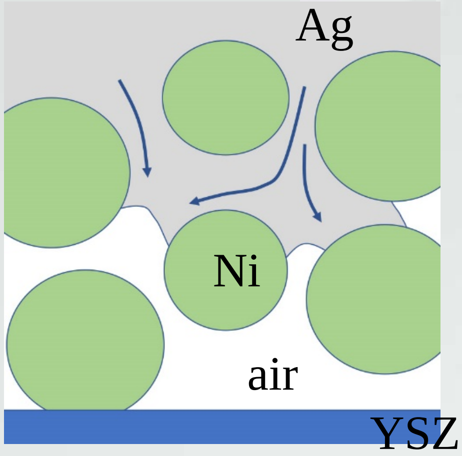
[2] U. El Shamy et al., Int J Geomech **13**, 57-64 (2013); [3] Y. U. Wang, Acta Mater **54**, 953-961 (2006)

Phase Field Method: Binary Fluid Through the Porous Nickel Layer

II: Molten Ag infiltration

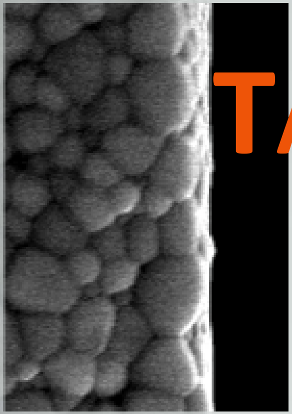
1. **Phase Field Method for multiphase fluid [4,5]:** Solve the Navier-Stokes-Cahn-Hillard equations to simulate Ag infiltration through Ni porous structure
2. **Smoothed Boundary Method [5,6]:** Incorporate Ni porous structure, and contact angles of Ag-Ni interface and Ag-YZS interface
3. **Adaptive Mesh [7]**: Increase numerical accuracy for the SBM

Objective: Incorporate phase field fluid model into the SBM frame to simulate the Ag **infiltration** through porous layer and **spread** on ceramic substrate.



- Binary fluid: molten Ag + air
- Complex microstructure: Porous Ni layer
- Contact angle: capillary force on (1) Ni and (2) substrate

[4] D. Jacqmin, J Comput Phys 155, 96-127 (1999); [5] S. Aland, Comput Model Eng Sci **57**, 77-107 (2010);
[6] H.-C. Yu et al., Model Simul Mater Sci Eng **20**, 075008 (2012); [7] C. Min et al., J Comput Phys 218, 123-140 (2006);

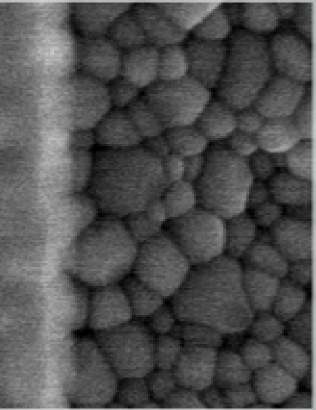


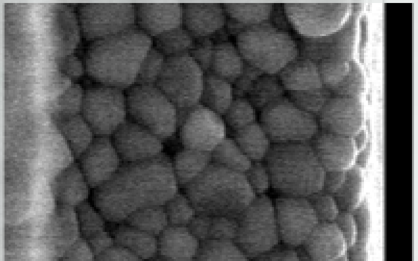
Talk Outline

1. Background
    a) Results from DE-FE0031250 on Ag-Ni Brazes

2. Project Approach
    a) Preliminary Results
    b) Research Plan

3. **Initial Project Progress**





Phase Field Method: Initial Results

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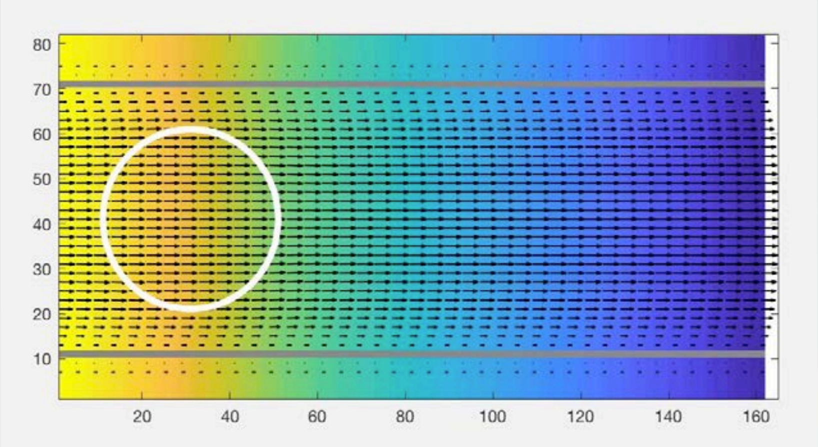
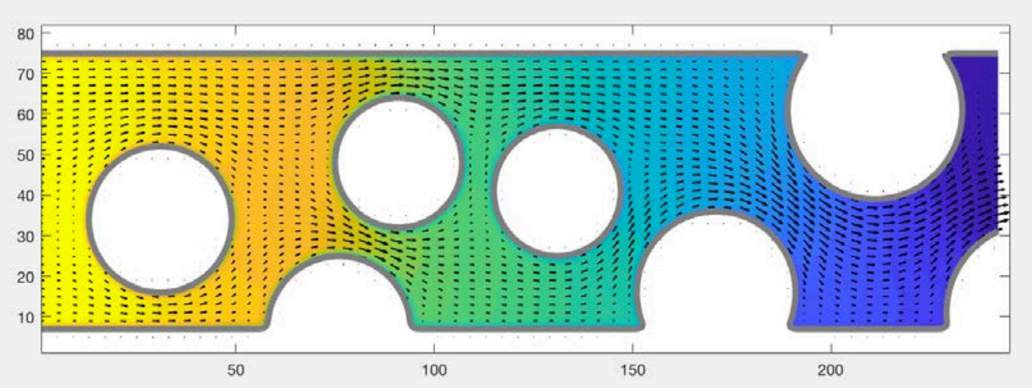
2. **Smoothed Boundary Method [5,6]:** Incorporate Ni porous structure, and contact angles of Ag-Ni interface and Ag-YZS interface
3. **Adaptive Mesh [7]:** Increase numerical accuracy for the SBM



Preliminary result for channel flow with binary fluid using PFMF



Preliminary result for solving the Navier-Stokes equation in a complex geometry in the SBM framework.

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[4] D. Jacqmin, J Comput Phys 155, 96-127 (1999); [5] S. Aland, Comput Model Eng Sci **57**, 77-107 (2010);
[6] H.-C. Yu et al., Model Simul Mater Sci Eng **20**, 075008 (2012); [7] C. Min et al., J Comput Phys 218, 123-140 (2006);

Phase Field Method: Initial Results

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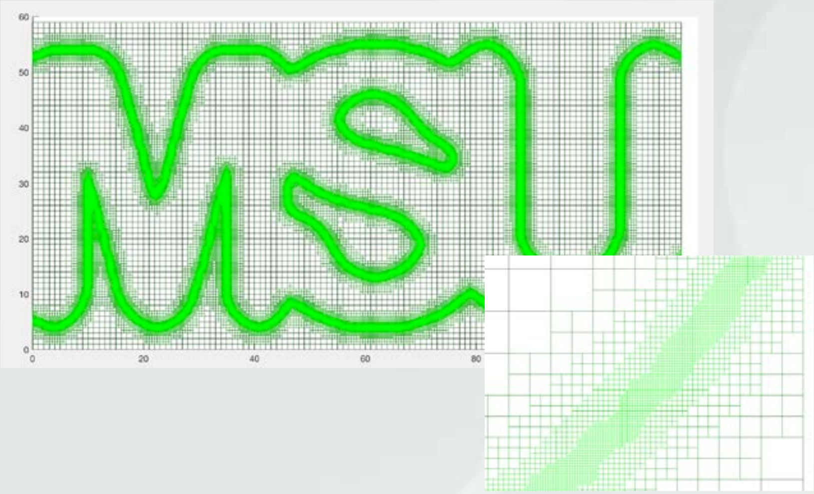
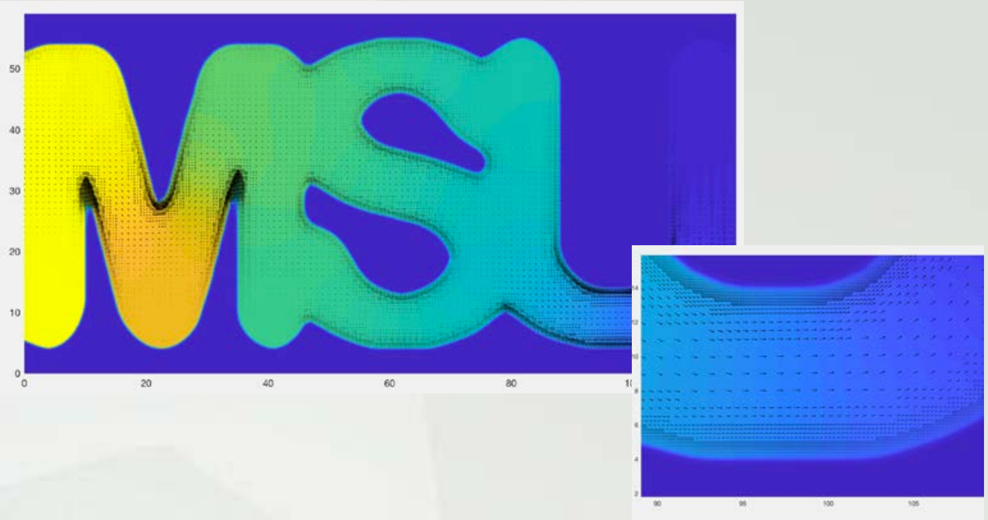


2D Non-uniform grid system generated using in-house developed code



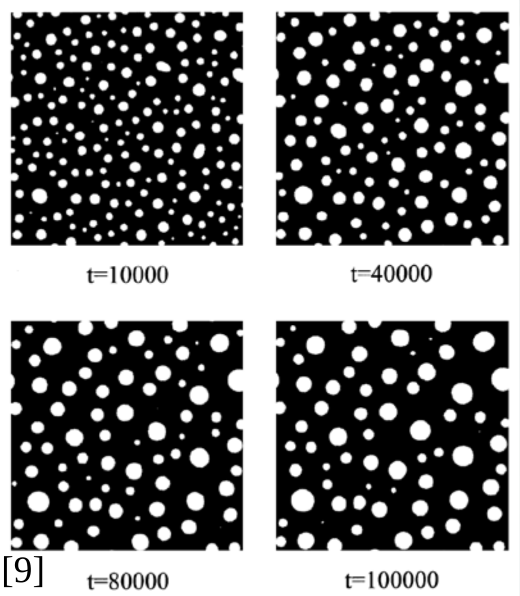
Preliminary 2D Fluid mechanics simulation using SBM on non-uniform the grid system

[4] D. Jacqmin, J Comput Phys 155, 96-127 (1999); [5] S. Aland, Comput Model Eng Sci **57**, 77-107 (2010);
[6] H.-C. Yu et al., Model Simul Mater Sci Eng **20**, 075008 (2012); [7] C. Min et al., J Comput Phys 218, 123-140 (2006);

Phase Field Method: Ostwald Ripening

III: Ostwald ripening of Ni

Ostwald ripening is the phenomena in which smaller particles in solution dissolve and deposit on larger particles in order to reach a more thermodynamically stable state wherein the surface to area ratio is minimized.[8]



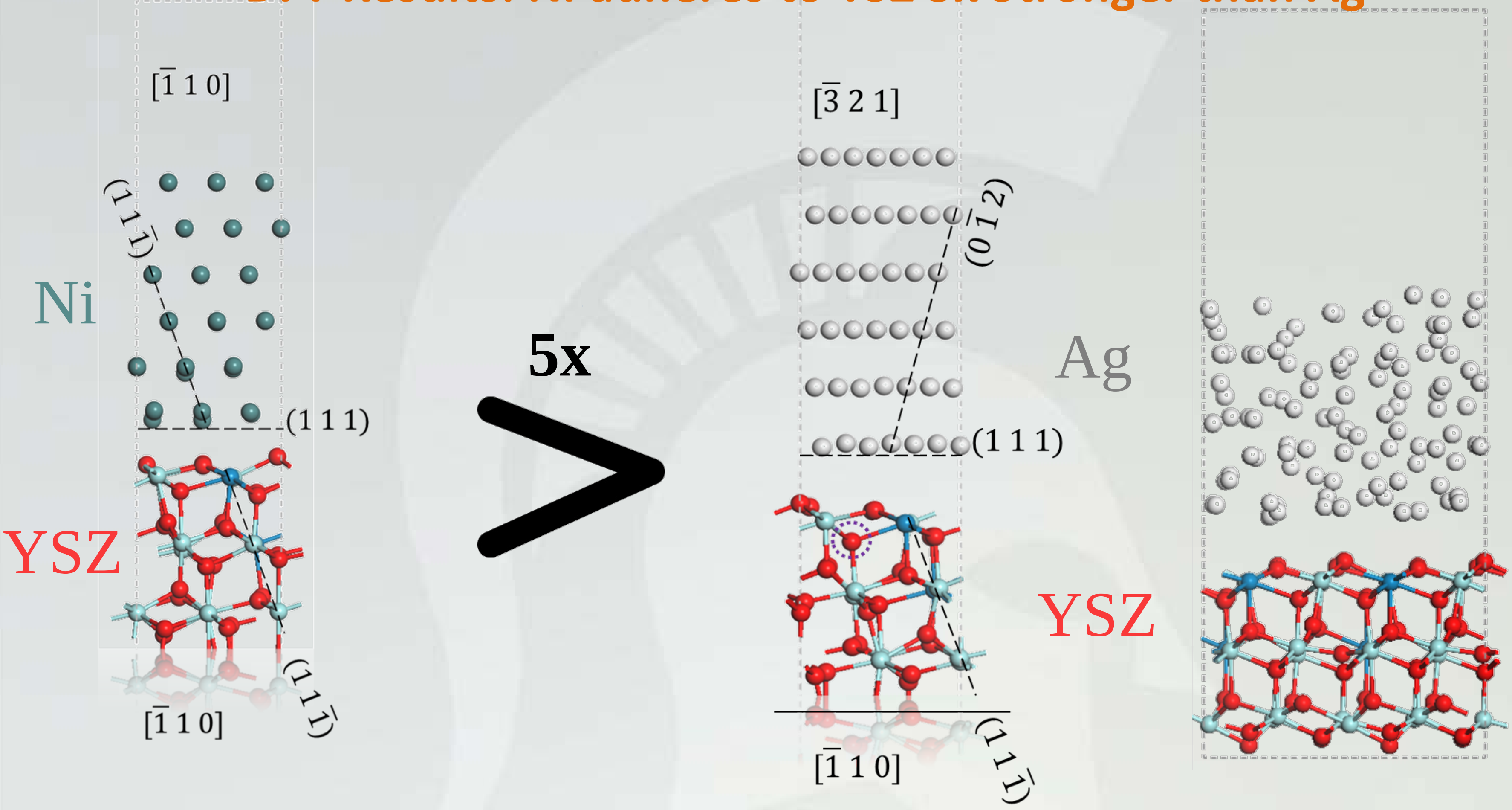
[9]

PFM simulation of Ostwald ripening

- Quantitative phase field simulations for Ostwald ripening dynamics of Ni in Ag, validified with experiments.
- Parameters: temperature-dependent diffusivity, surface tension, and free energy functions for the Ni-Ag-SS system .
- Extract design guidelines for heat treatment via simulations.

[8] http://pssnicomp.com/definitions/ostwald-ripening/; [9] D. Fan et al., Acta Mater **50**, 1895-1907 (2002)

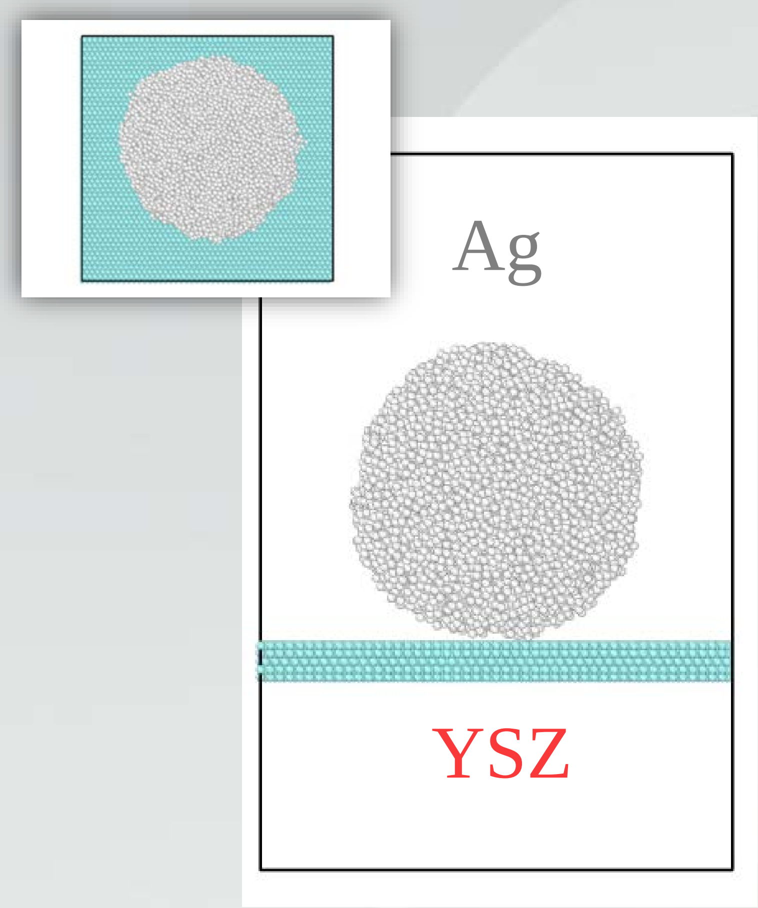
DFT Results: Ni adheres to YSZ 5x Stronger than Ag

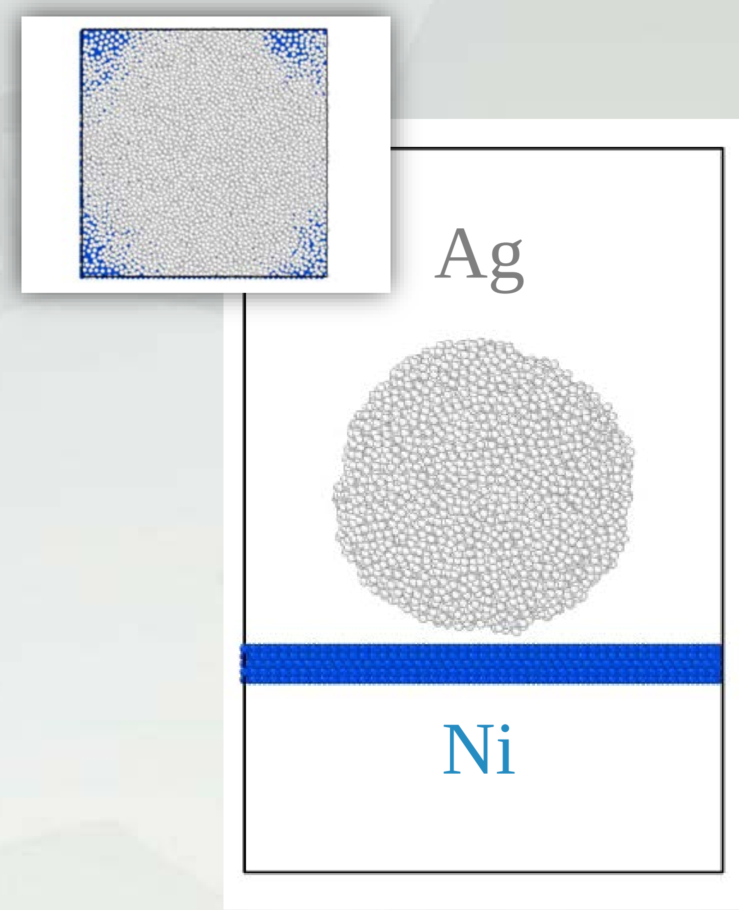


$W_{adh} = 0.49\ J/m^2$ $W_{adh} = 0.10\ J/m^2$ $W_{adh} = 0.11\ J/m^2$

- Preliminary results show that Ni could adhere strongly to the YSZ surface as measured by work of adhesion (W_{adh}).
- It also shows that solid and liquid Ag have roughly the same W_{adh}.

Classical MD Results:
Ag Does Not Wet YSZ, Ag Does Wet Nickel

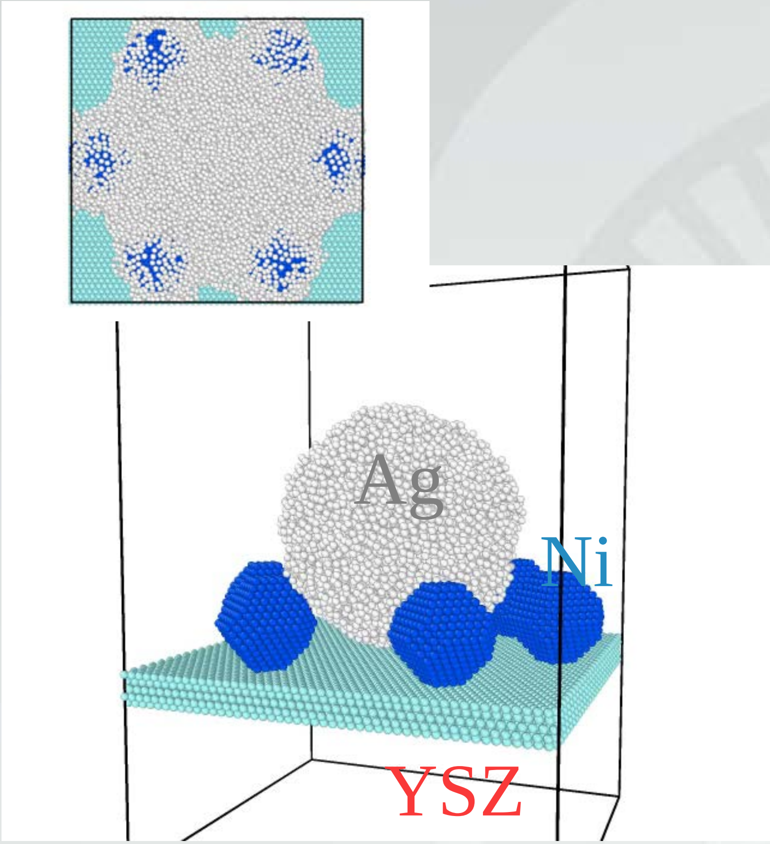




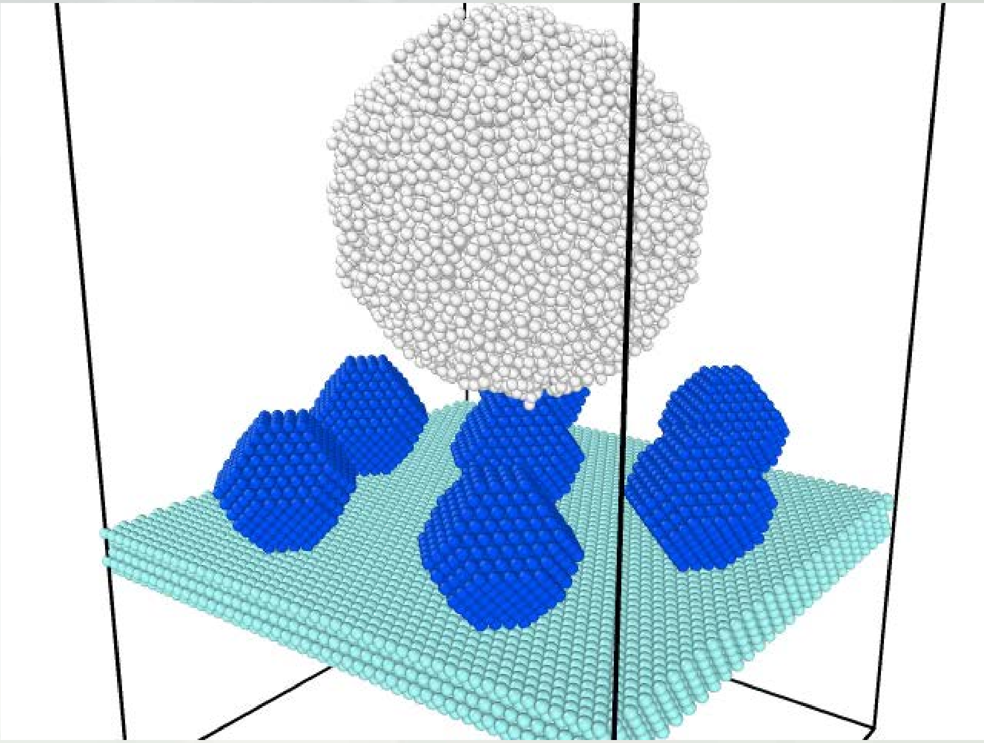
- Silver forms a non-wetting droplets on YSZ surface as shown on the left.
- Changing the substrate to Ni allows silver to wet on it. This is important as it implies how Ni particle may help Ag wetting on YSZ.

Classical MD Results:
Nickel Particles Help Ag Wet YSZ

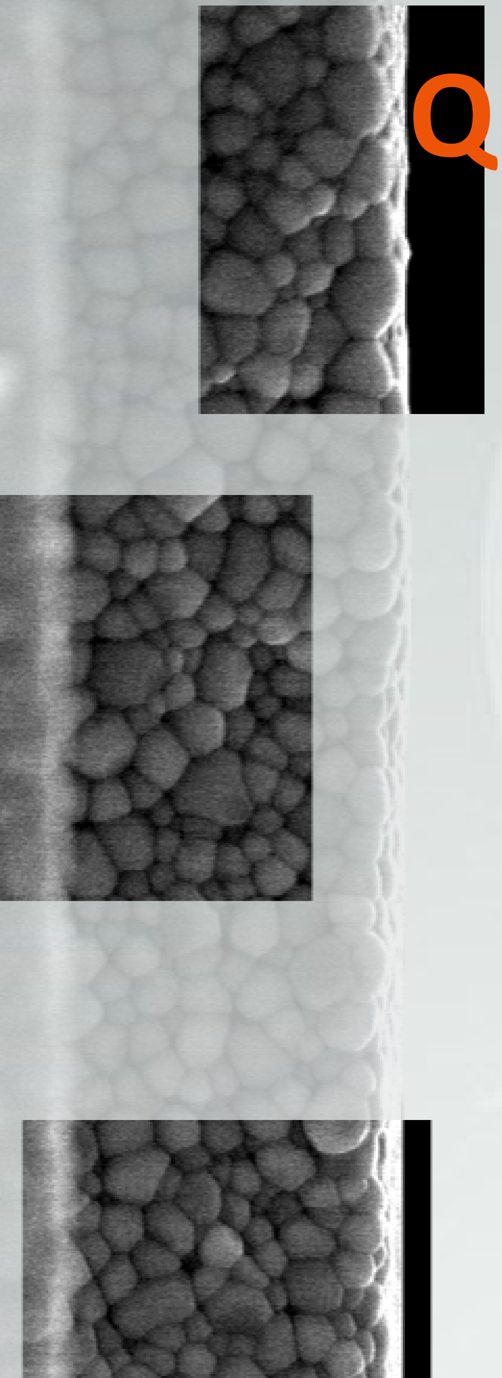
Surrounding Ag by Ni particles



Placing Ag on Top of Ni particles



- The molecular dynamics results clearly show that Ni particle can help Ag to wet on YSZ surface. Ag will expand according to the distribution of Ni particles (top left).
- These raise a lot of interesting questions for future study, such as the effect of Ni sintering, particle size, and pore distribution on the wetting enhancement capability as well as how these will interplay with the substrate’s surface properties.

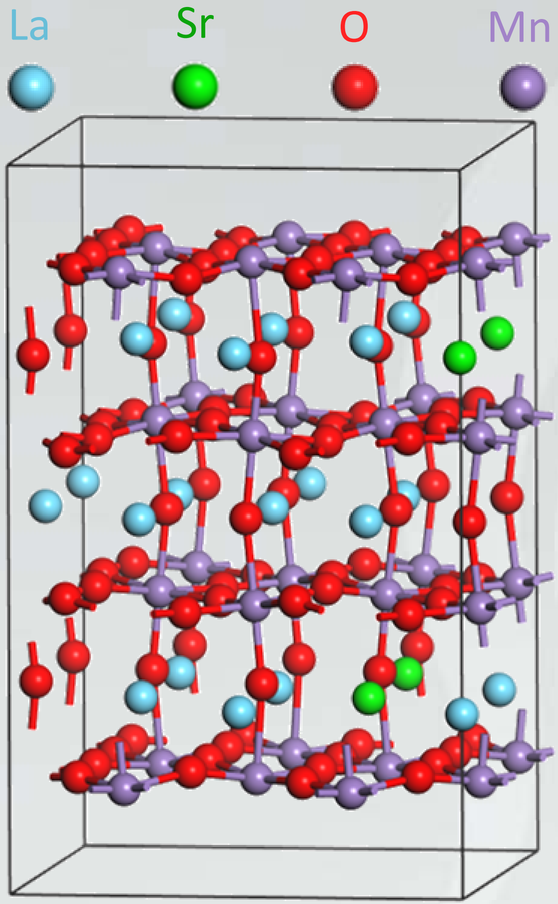


Questions?

This work was made possible by the Department of Energy Solid Oxide Fuel Cell Core Technology Program through Agreement Number DE-FOA-0001853

Backup Slides

DFT Calculation Method: Moving Forward to Other Interfaces



$La_{1-x}Sr_xMnO_3$ (001) surface with Sr and oxygen vacancy aggregate at the surface as have been shown in previous studies to be the most stable.[2]

- There are other challenging interfaces related to SOFC that its interaction with Ag-Ni needs to be evaluated including, lanthanum strontium manganite ($La_{1-x}Sr_xMnO_3$), lanthanum strontium cobalt iron oxide, ceria, alumina, manganese cobalt oxide, stainless steel, and/or Ni-YSZ

- For example, studies have shown that $La_{1-x}Sr_xMnO_3$, one of the widely used SOFC electrodes, behaves differently at SOFC operating temperatures.[1] Therefore we aim to study the effects of its
  - 1. Antiferromagneticity and charge redistribution
  - 2. Oxygen vacancy
  - 3. Different surface terminations (and compositions) due to change in temperature and atmosphere

on the adhesion between $La_{1-x}Sr_xMnO_3$ and Ag-Ni system.

[1] Pavone, Michele, et al. *The Journal of Physical Chemistry C* (2014)
[2] Piskunov, Sergei, et al. *Physical Review B* (2008)

Ag-Ni Brazes Have Several Key Benefits

Pore Type	Reactive Air Brazing	Ag-Ni Brazing
Type I (wetting) Pore Formation	• ***$\theta = 45°$*** (for Ag-4CuO) occasionally leads to pores during manufacturing [1,2]. • Organics in the braze paste can also lead to pores during manufacturing [3].	• $\theta = 30°$ leading to a fully infiltrated porous Ni network [5]. • Since ***no organics*** are used during brazing (these are removed by heating the nickel paste in Ar to obtain the porous nickel network) binder burnout ***cannot cause pores*** during brazing
Type II (interfacial) Pore Formation	• With the ***reduction of CuO*** along the braze/YSZ and braze/SS interface, micro-pores will form during SOFC operation near the H_2 side of the joint [4].	• Even after 5 days of oxidation a strong, intimate SS-braze joint is maintained (the reaction layer oxides are suspended within the braze and hence do not impact the braze-ss bonding). Also, no reducible oxides form during brazing so that ***no Type II pores*** will be formed.
Type III (H_2+O_2) Pore Formation	• H_2 and O_2 diffuse through Ag and form water pockets (Type III pores) that mechanically compromise the braze joint after ~10,000 hours of SOFC operation [4].	• Since Type II pores form much faster than Type III pores and thereby provide a short-circuit path for H_2 invasion into the center of the braze [6], the elimination of Type II pores can increase joint reliability by ***delaying the onset*** of Type III pores.

[1] Kim, J.Y. et. al, Journal of the American Ceramic Society, 2005.

[2] Kim, J.Y. et. al, Journal of Materials Research, 2005.

[3] Bobzin, K. et. al, Advanced Engineering Materials, 2014.

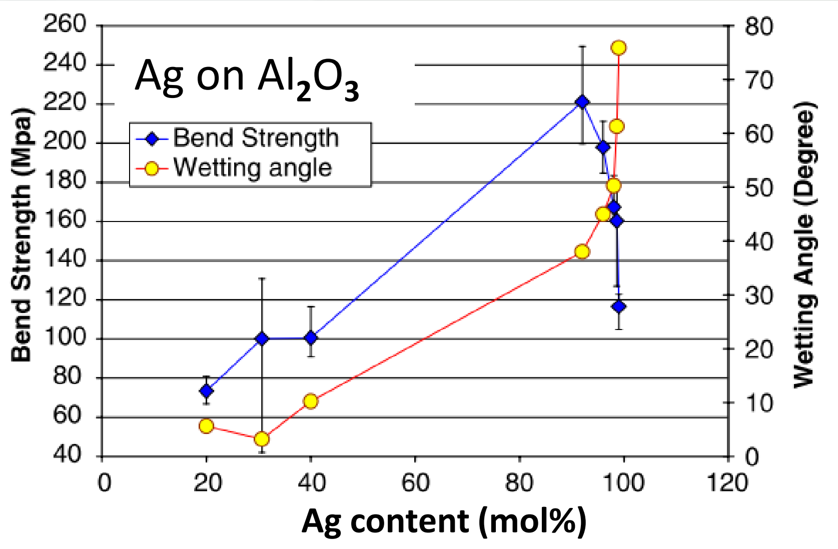
[4] Bause, T., et al., Fuel Cells, 2013.

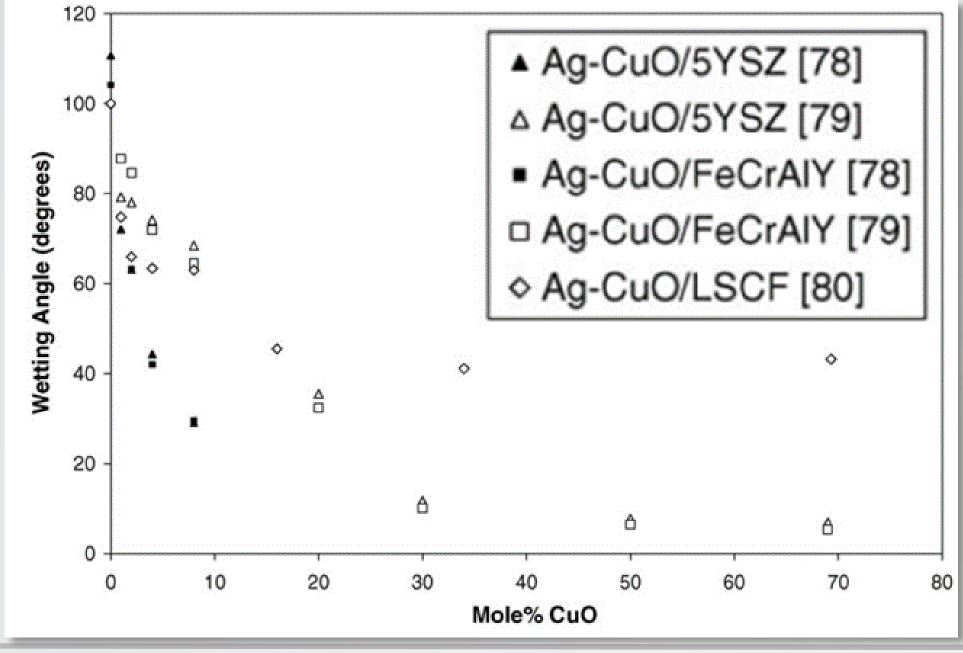
[5] Trumble, K.P., Acta Materialia, 1998.

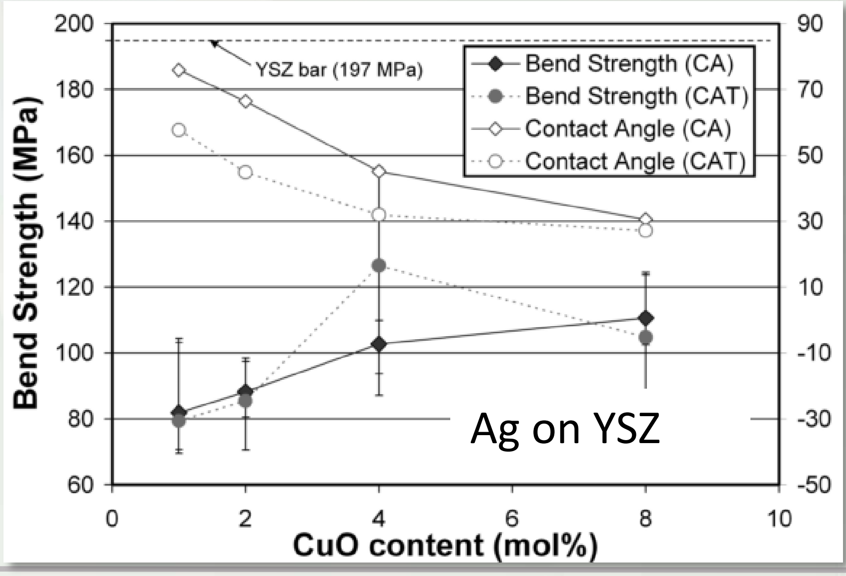
[6] Kim, J.Y. et. al, International Journal of Hydrogen Energy, 2007.

Ag-Based Reactive Air Brazes (RAB) Seem Promising at 1st

1. Reactive air braze additions improve silver on YSZ and silver on aluminized stainless steel ***wetting*** angles.
    - CuO additions to reduce Ag on YSZ in air θ to ~30° (θ = ~45° for commonly employed Ag-4CuO).
2. Reactive air braze additions improve Ag-Al_2O_3 and Ag-YSZ ***bond strengths***.
3. Silver reactive air brazing can be done in ***air***.







Kim, J.Y., J.S. Hardy, and K.S. Weil, Journal of the American Ceramic Society, 2005. 88 (9): p. 2521-2527.
Kim, J.Y., J.S. Hardy, and K.S. Weil, Journal of Materials Research, 2005. 20 (3): p. 636-643.
Fergus, J.W., Materials Science and Engineering A, 2005. 397 (1-2): p. 271-283.