Durable, Impermeable Brazes for Solid Oxide Fuel Cells

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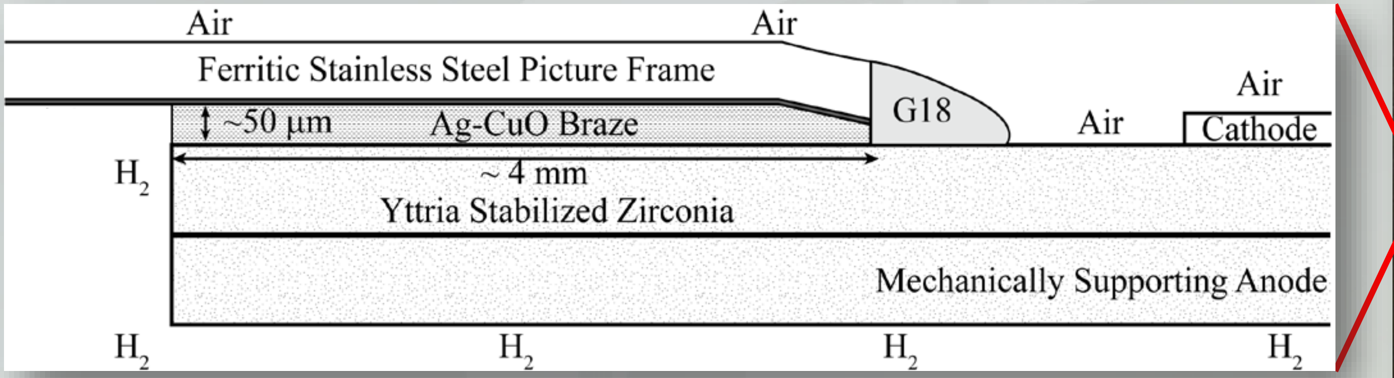
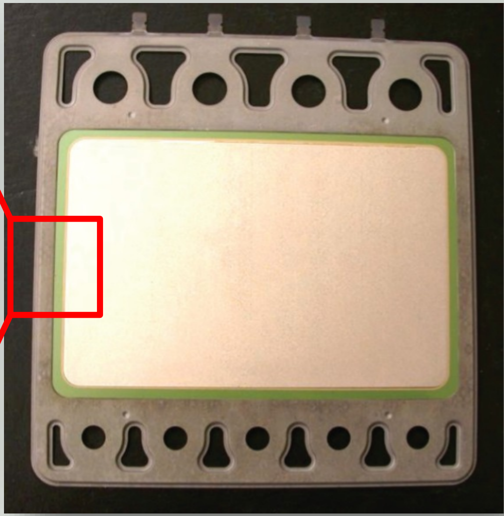
Outline

- **Background and Motivation**
  - Benefits of Silver-Copper Brazes
  - Problems with Silver-Copper Brazes
  - Proposed Strategy
- **Results and Discussion**
  - Partially Sintered Ni Layers
  - As Brazed Joint Microstructures
  - Oxidized Braze Joints
  - Mechanical Properties with/without Oxidation
  - Dual Atmosphere Isothermal Test
  - Dual Atmosphere Thermal Cycling Test
  - Other Applications
- **Conclusions**

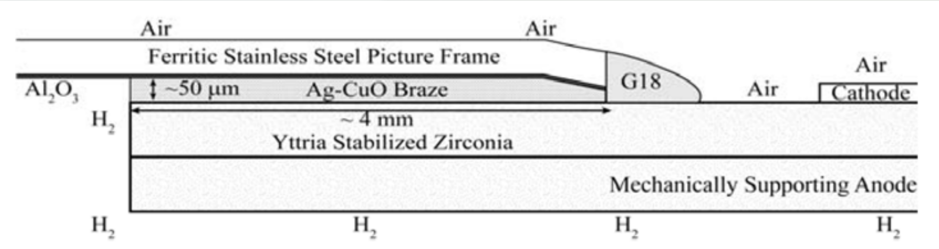
Conventional Reactive Air Brazes Has Many Benefits



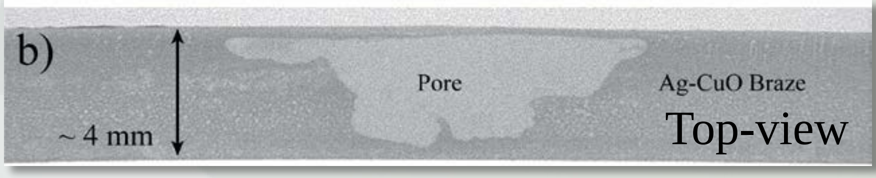


- CuO improves the wetting properties
- Brazing can be performed in air
- No flux is needed
- Can be used on a variety of ceramics

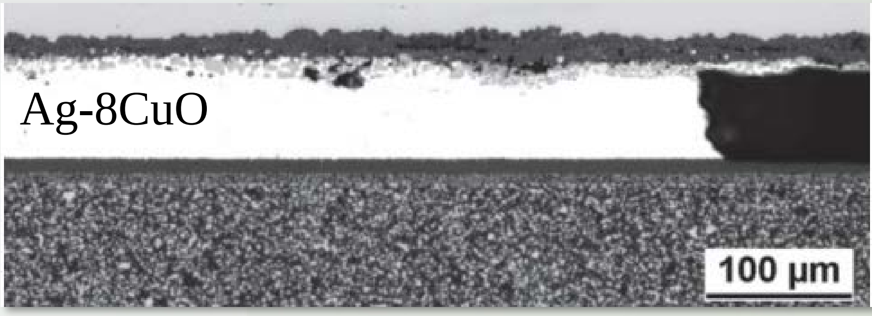
Reactive Air Brazes Have Several Fatal Flaws



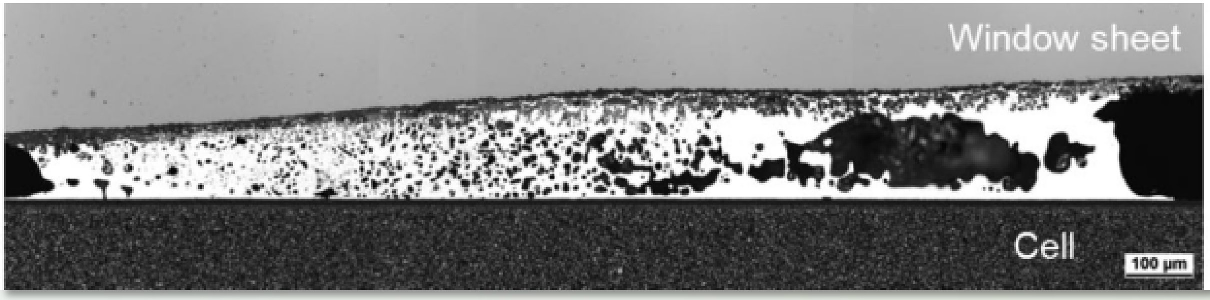
Braze joint will be exposed to dual atmospheres (H_2/Air) in SOFC operation.



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



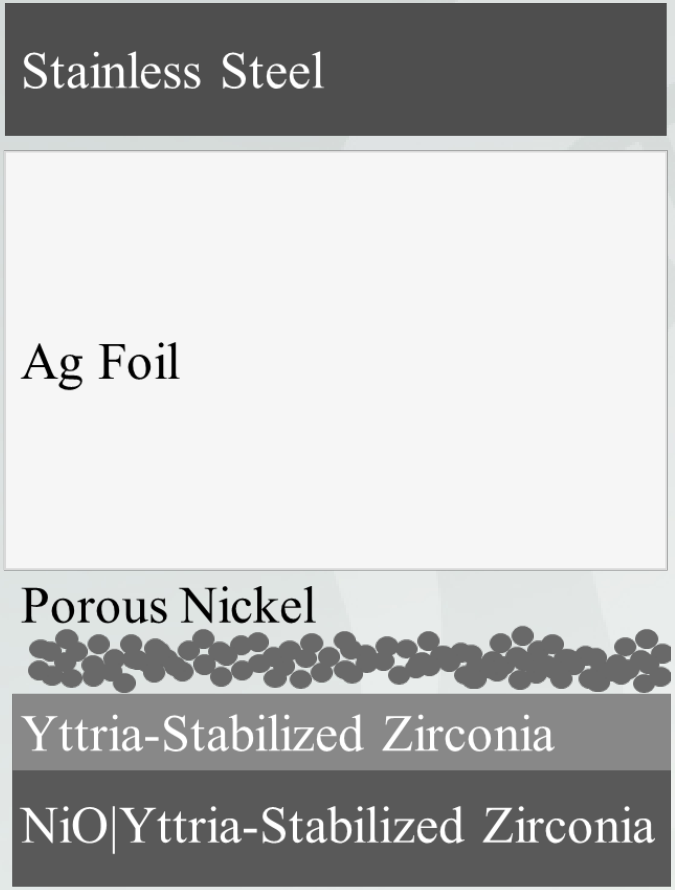
2. Reduction of reactive air additions (CuO) by hydrogen during SOFC operation can result in **Type II Pores;**



3. **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.

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

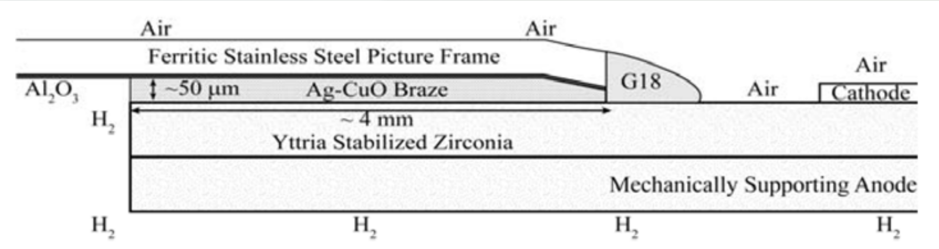


- Ni will not melt before Ag;
- Ni will not dissolve in Ag;
- The Ag wetting angle on Ni is ~30° in inert atmosphere.

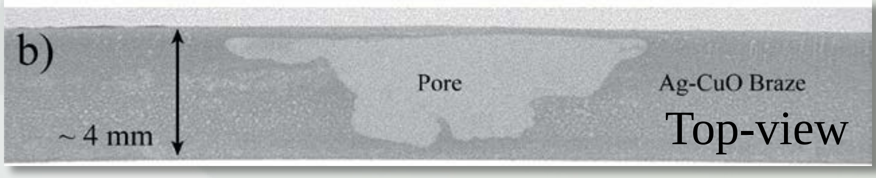
Zhou et al., Brazing Method Using Porous Interlayers and Related Articles, USPTO Patent. (Pending, May 10, 2017)
Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

Porous Nickel Layers Could Lead to Increased Braze Lifetimes

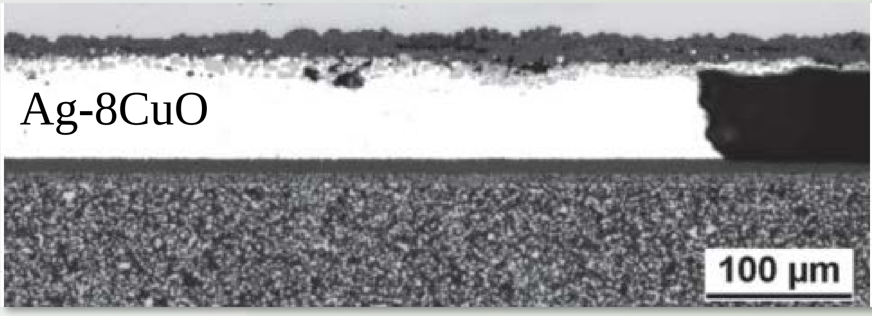
Braze joint will be exposed to dual atmospheres (H_2/Air) in SOFC operation.



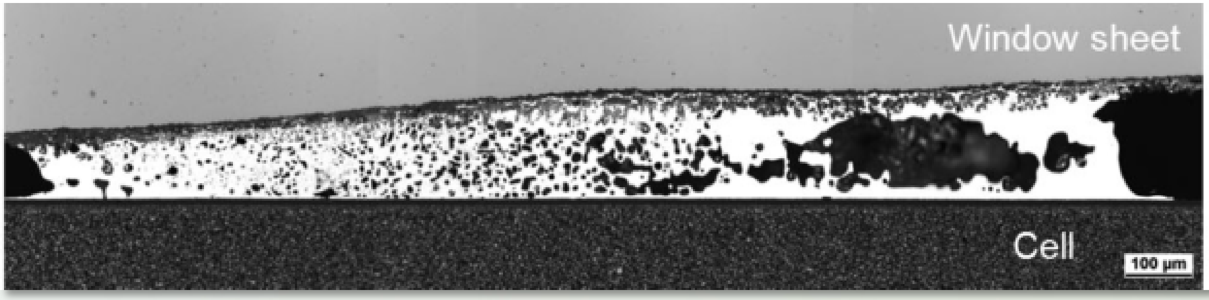
1. **No Type I Pores** with improved wetting characteristics;



2. **No Type II Pores** since no oxides will form during brazing**;**



3. **Delayed onset of Type III pore formation** without Type I and Type II pores



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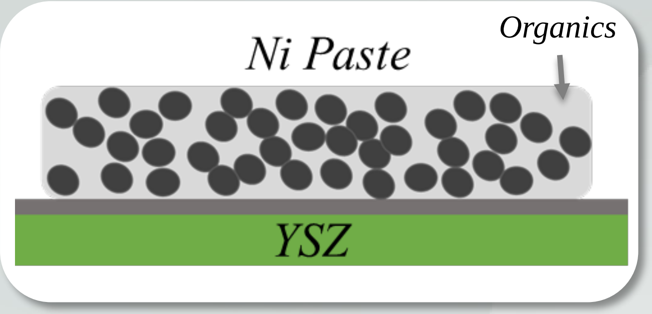
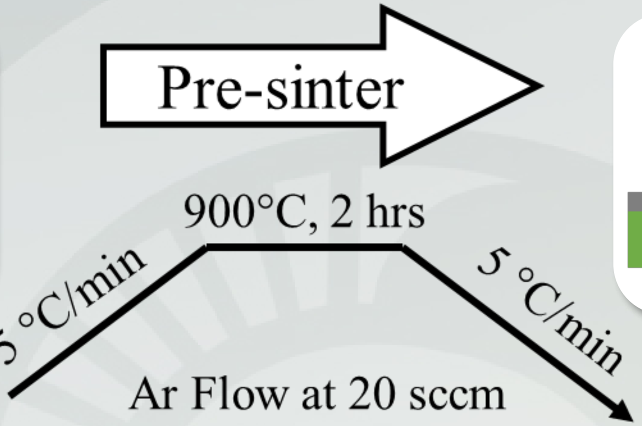
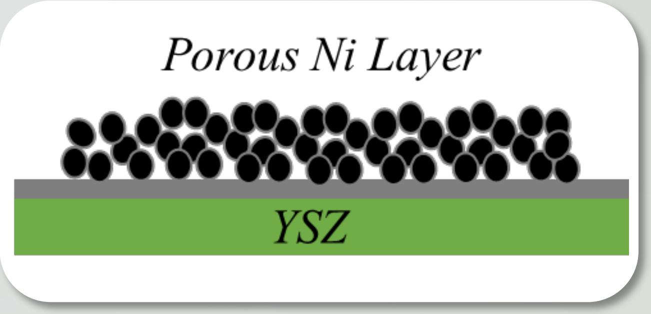
Porous Ni Interlayer Fabrication







Screen Print Ni Paste onto YSZ Substrates

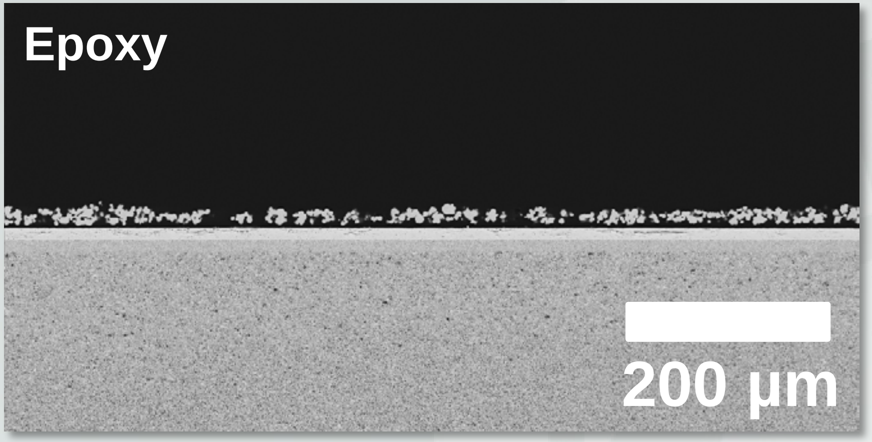
Partially Sintered Ni Interlayer on YSZ

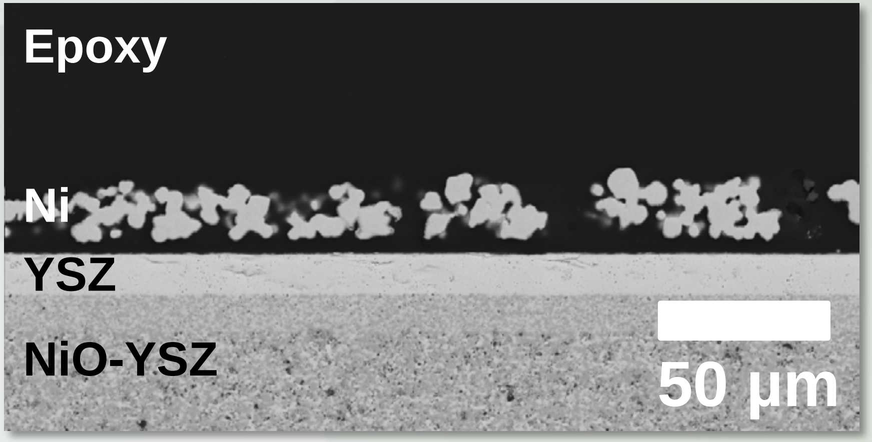
Pre-sinter

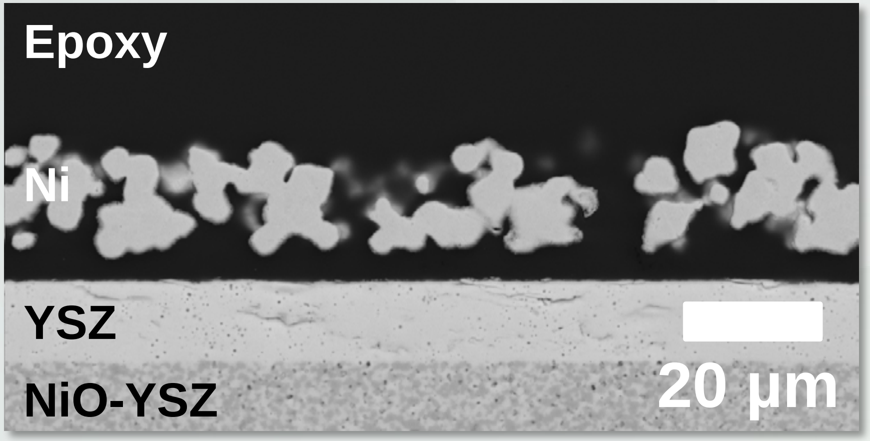
1 inch

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

Porous Ni Interlayers with Uniform Thickness





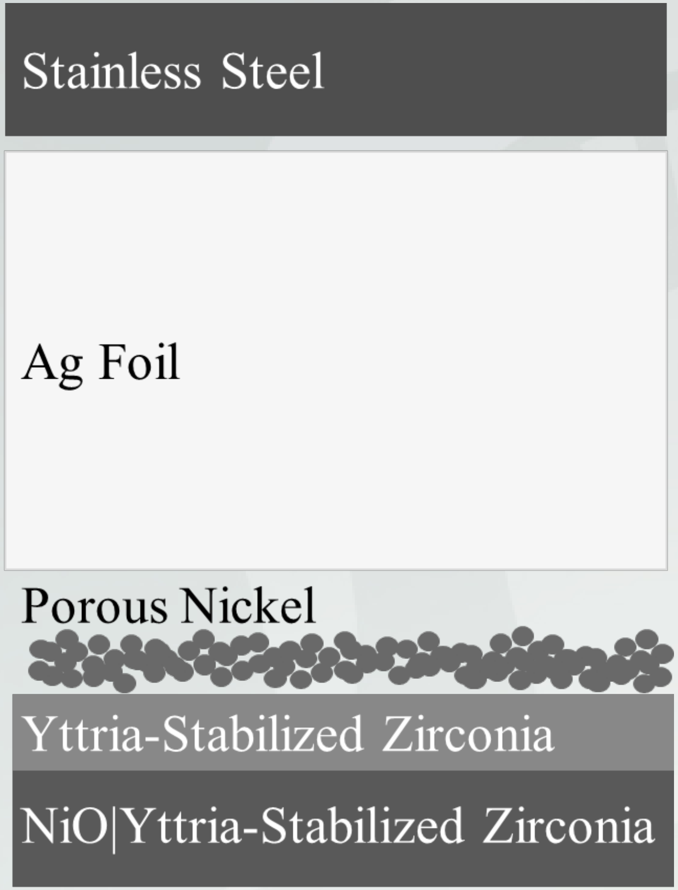


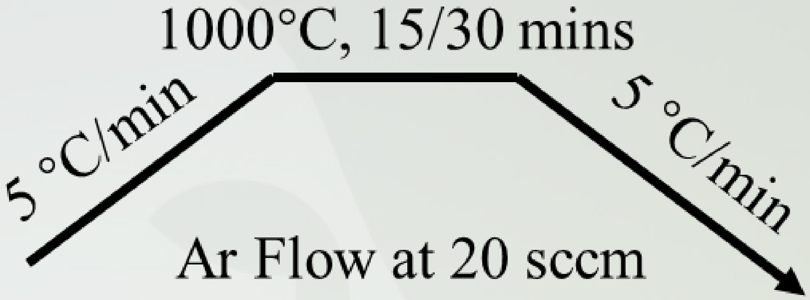
- The screen-printed, pre-sintered Ni layer has a uniform thickness of ~20 µm on the YSZ.
- There are 2~6 particles through the thickness of the porous layer.

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

As Brazed Joint Microstructure

Brazing Set-up





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Ag-Ni Brazing Eliminates Type I Pores

As Brazed Sample

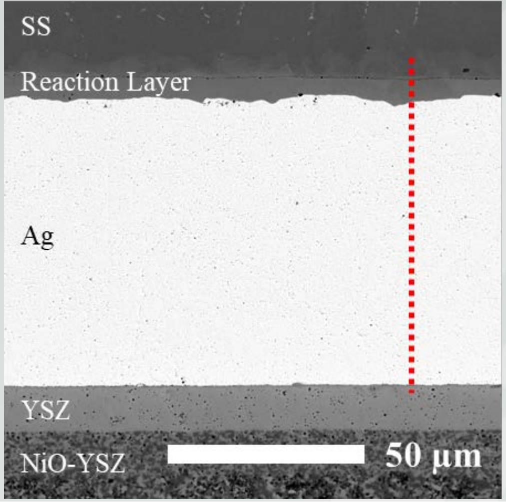
- Solid, dense joints were achieved with the Ag/Ni method using Ag foils.

- Whereas organics (binder) used in the paste form of braze filler materials often lead to large pores.

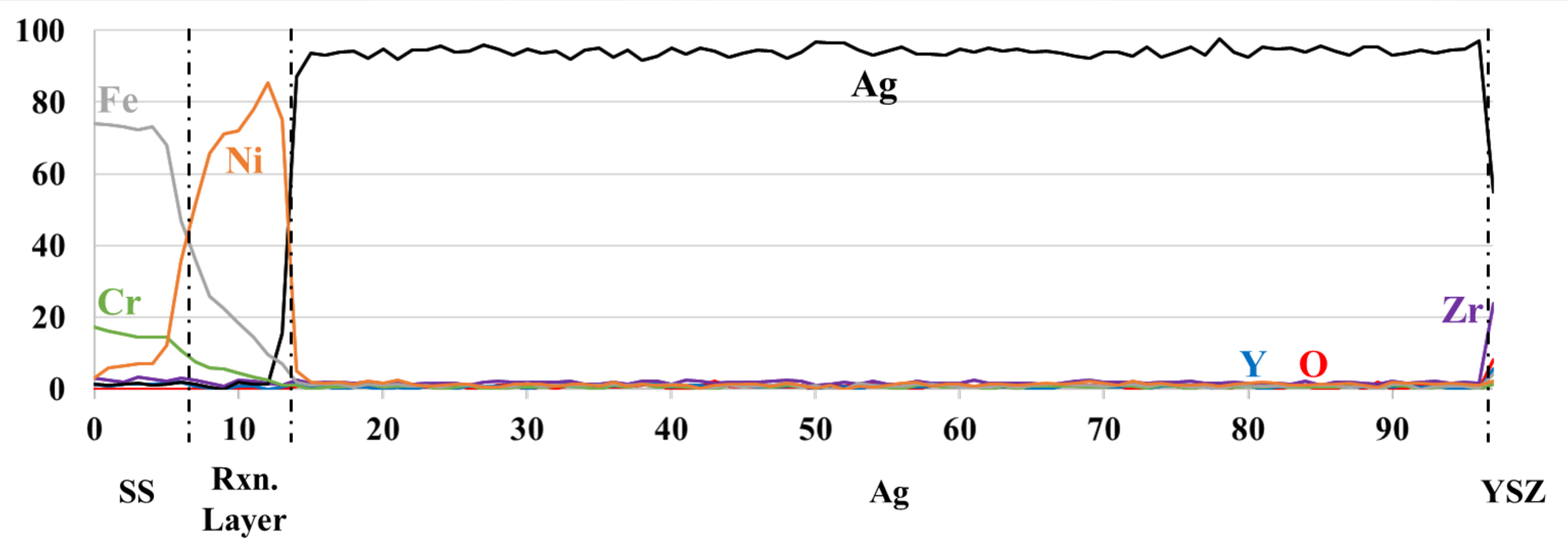
Zhou et al., Transient Porous Nickel 1nterlayers for Improved Silver-based Solid Oxide Fuel Cell Brazes, Acta Mater, 2018. 148: p. 156-162.

Ni Relocates to the Stainless Steel Side of the Joint During Brazing

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.



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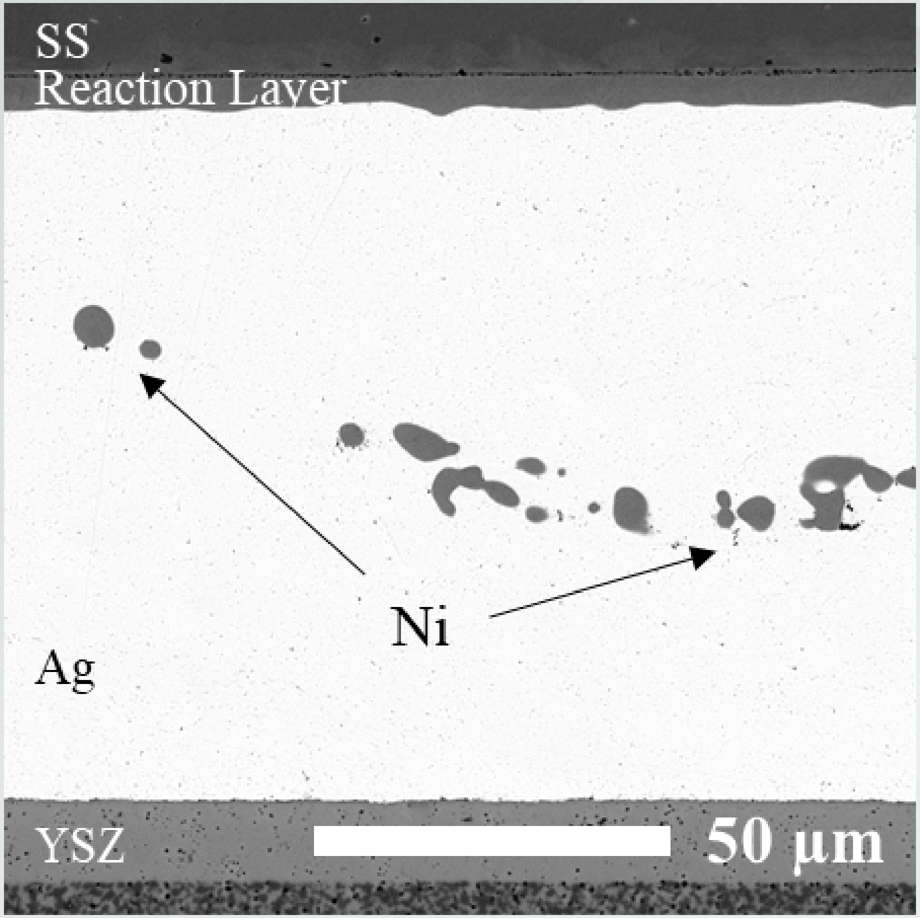
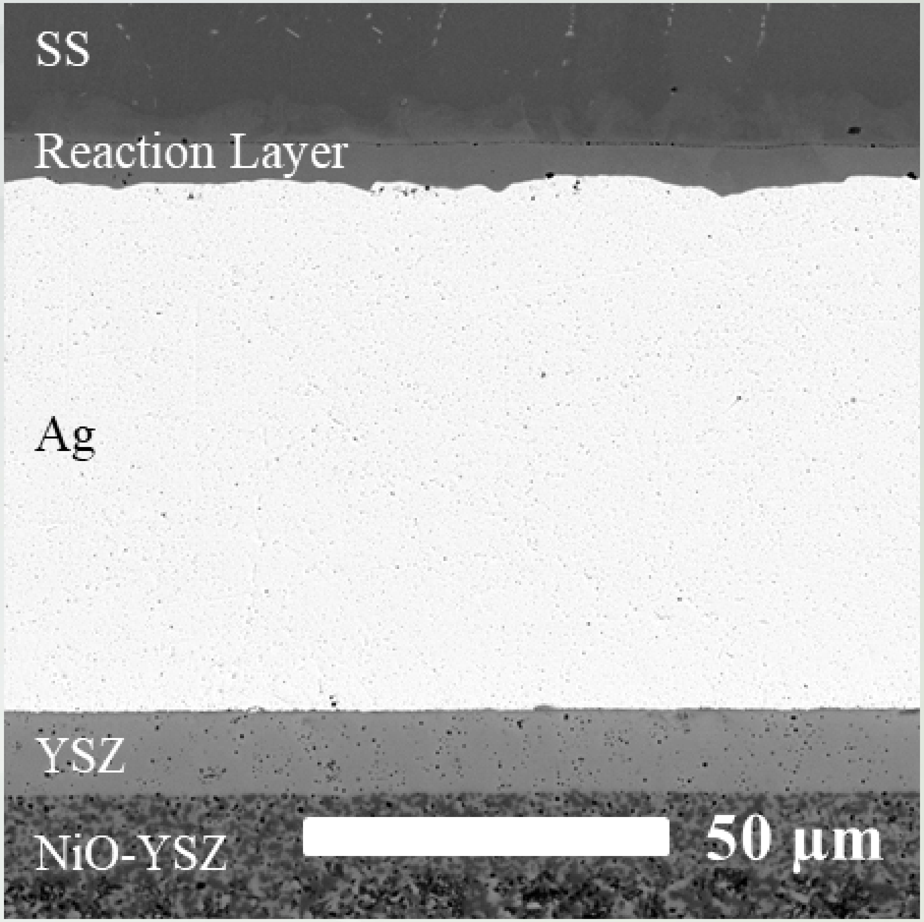
Nickel is Likely Transported via Diffusion and Convective Transport



15 Mins Brazed Sample



30 Mins Brazed Sample

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

POST OXIDATION

Most of the Joint is Unaffected by Oxidation

As Brazed

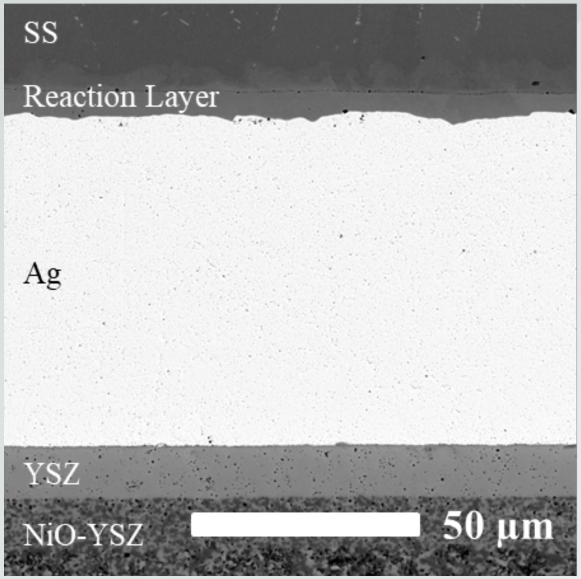
After 120 Hours of Oxidation

After 500 Hours of Oxidation

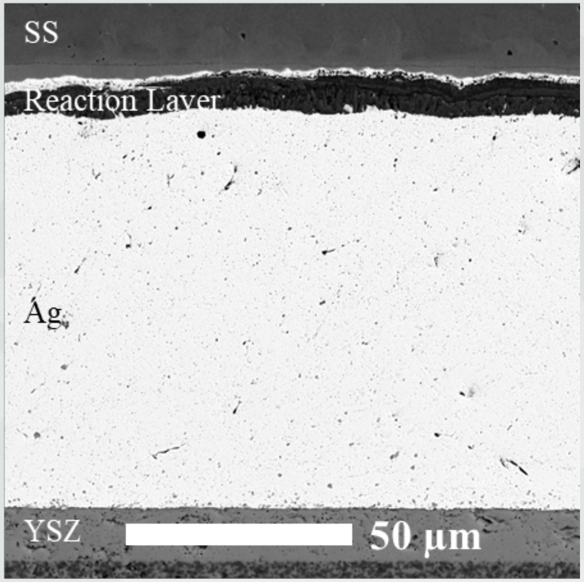
- Samples were held at 750°C in an air furnace for oxidation.
- No obvious porosity developed after 500 hours of oxidation in air.

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

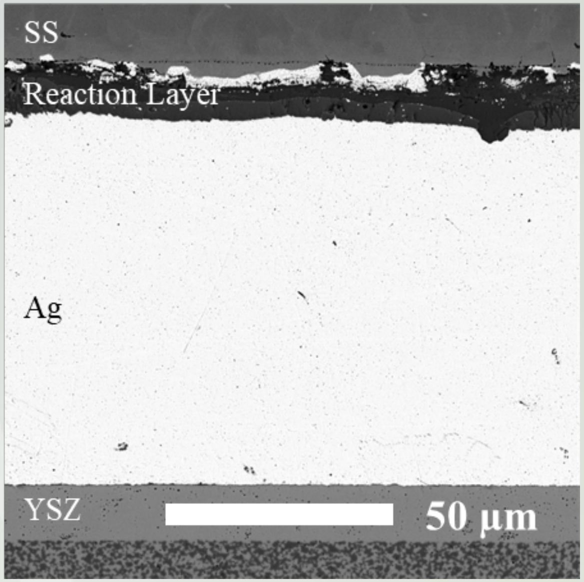
Most of the Joint is Unaffected by Oxidation



As-Brazed



120 Hour Oxidized



500 Hour Oxidized

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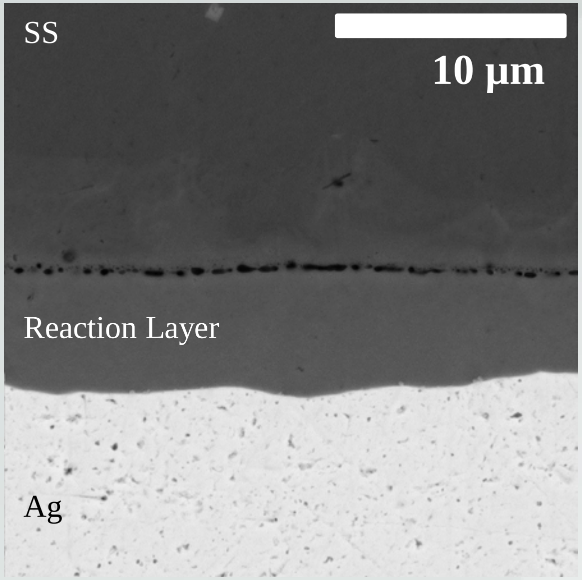
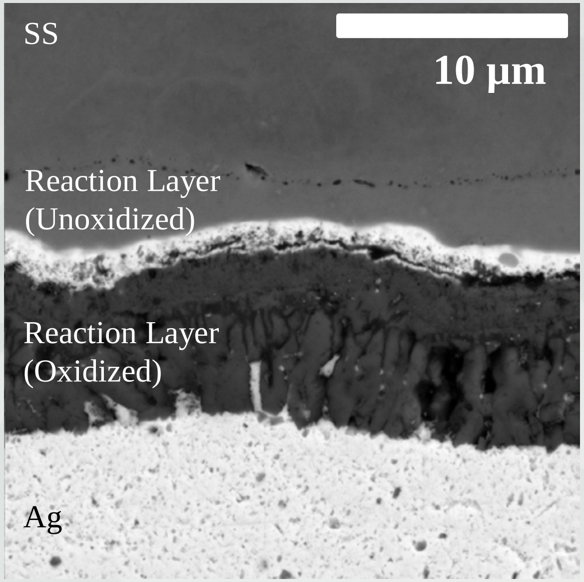
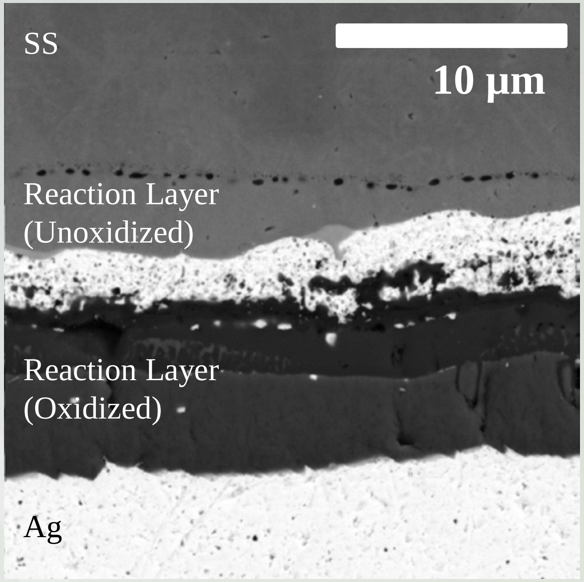
Oxidation Occurs at the Stainless Steel Side of the Joint



As-Brazed



120 Hour Oxidized



500 Hour Oxidized

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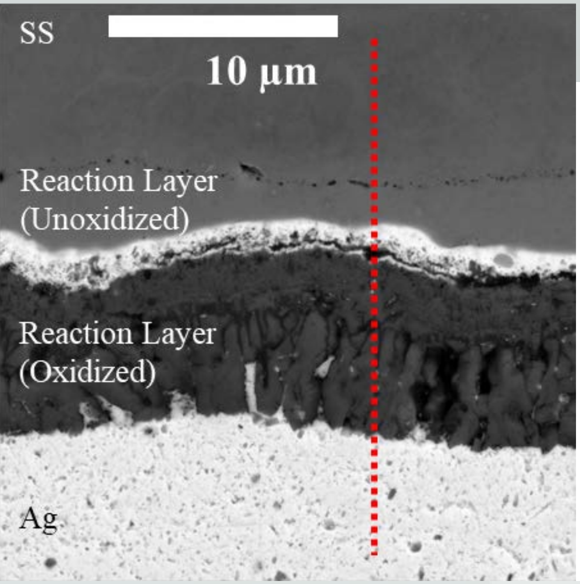
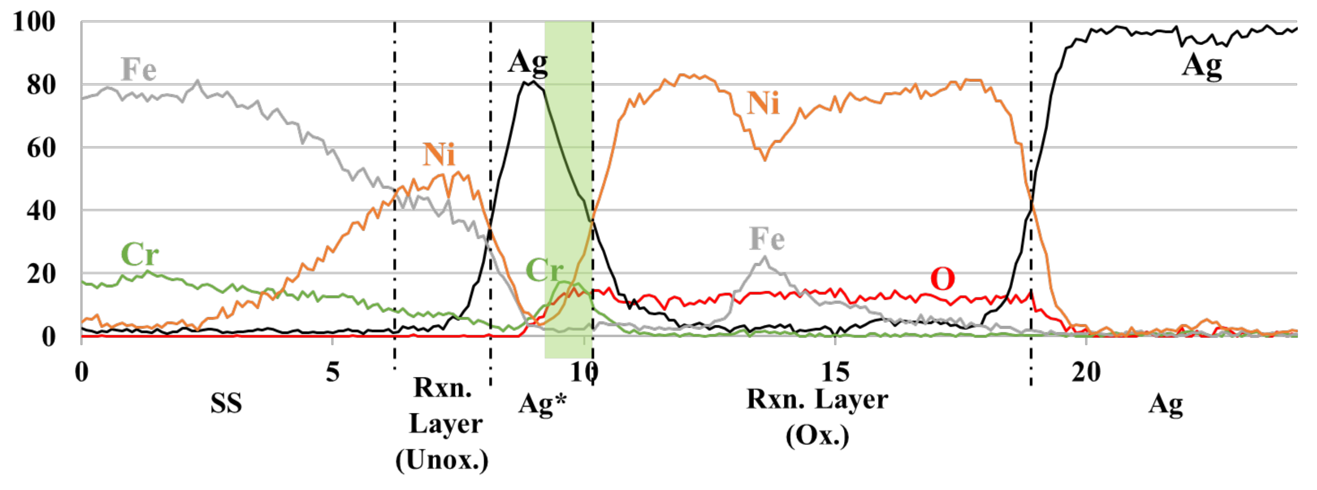
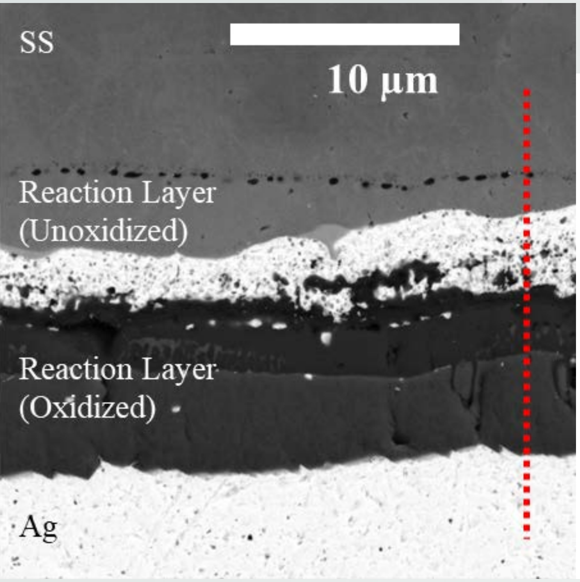
A Protective Chromia Scale Forms Whithin the Rxn. Layer

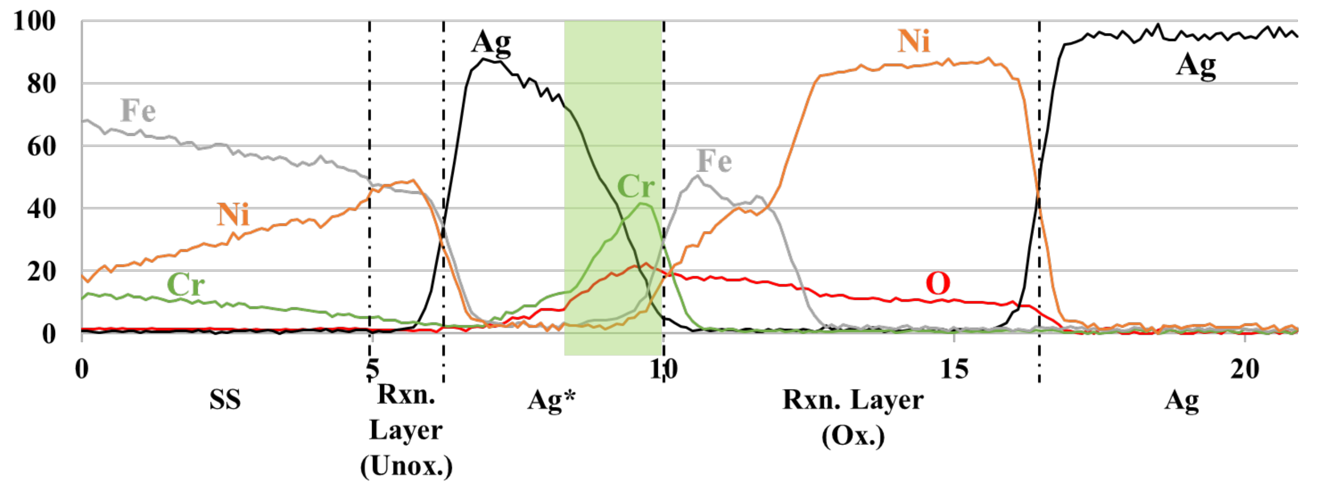


120 Hours of Oxidation





500 Hours of Oxidation



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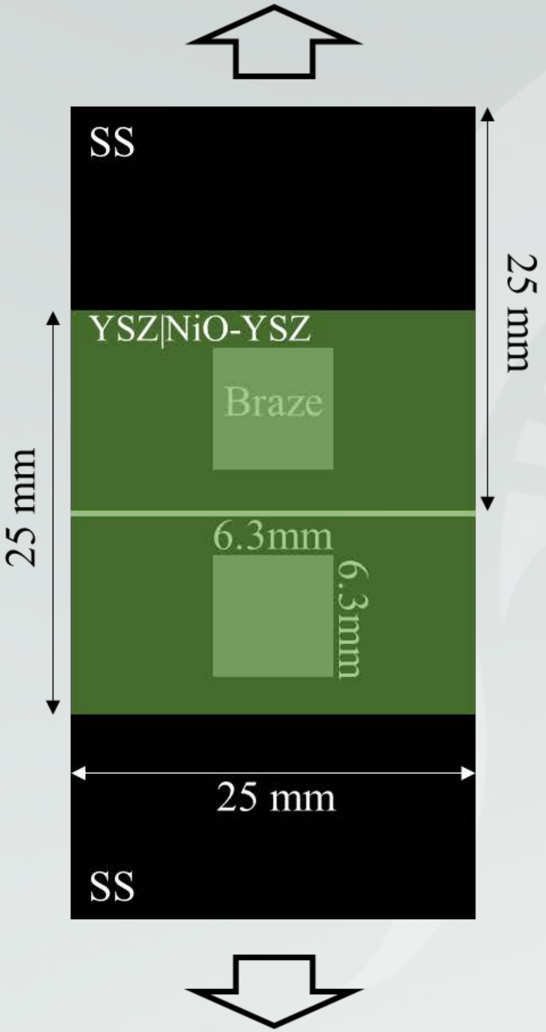
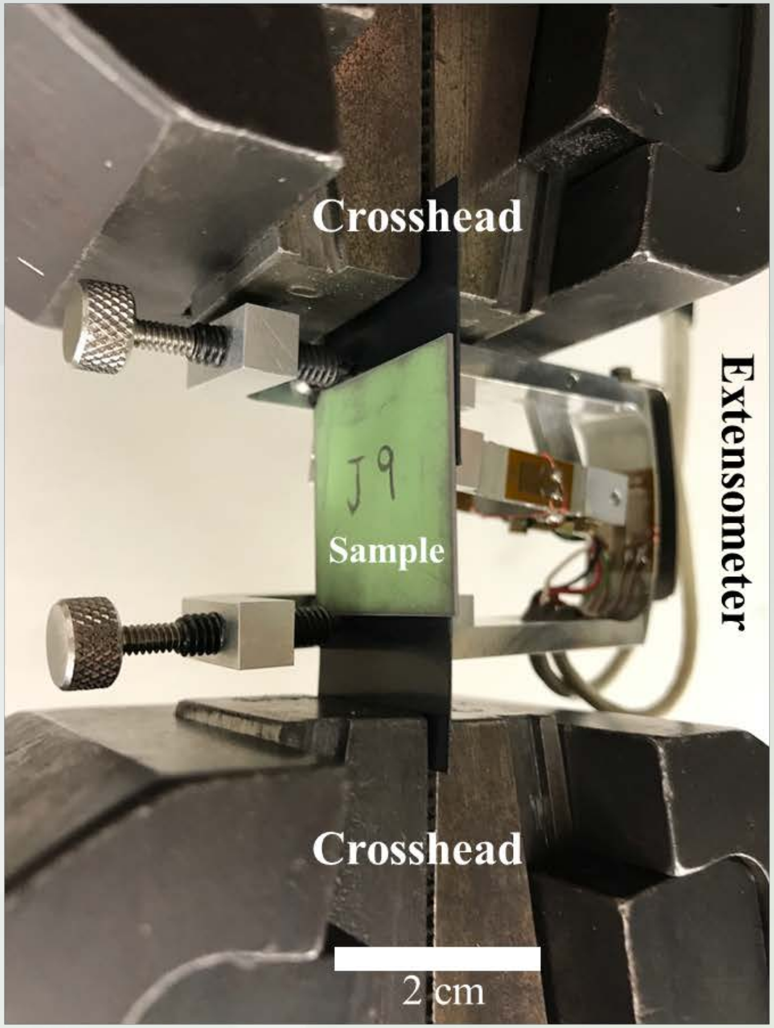
MECHANICAL TESTS

Symmetric Double Shear Lap Set-up with Tensile Loading

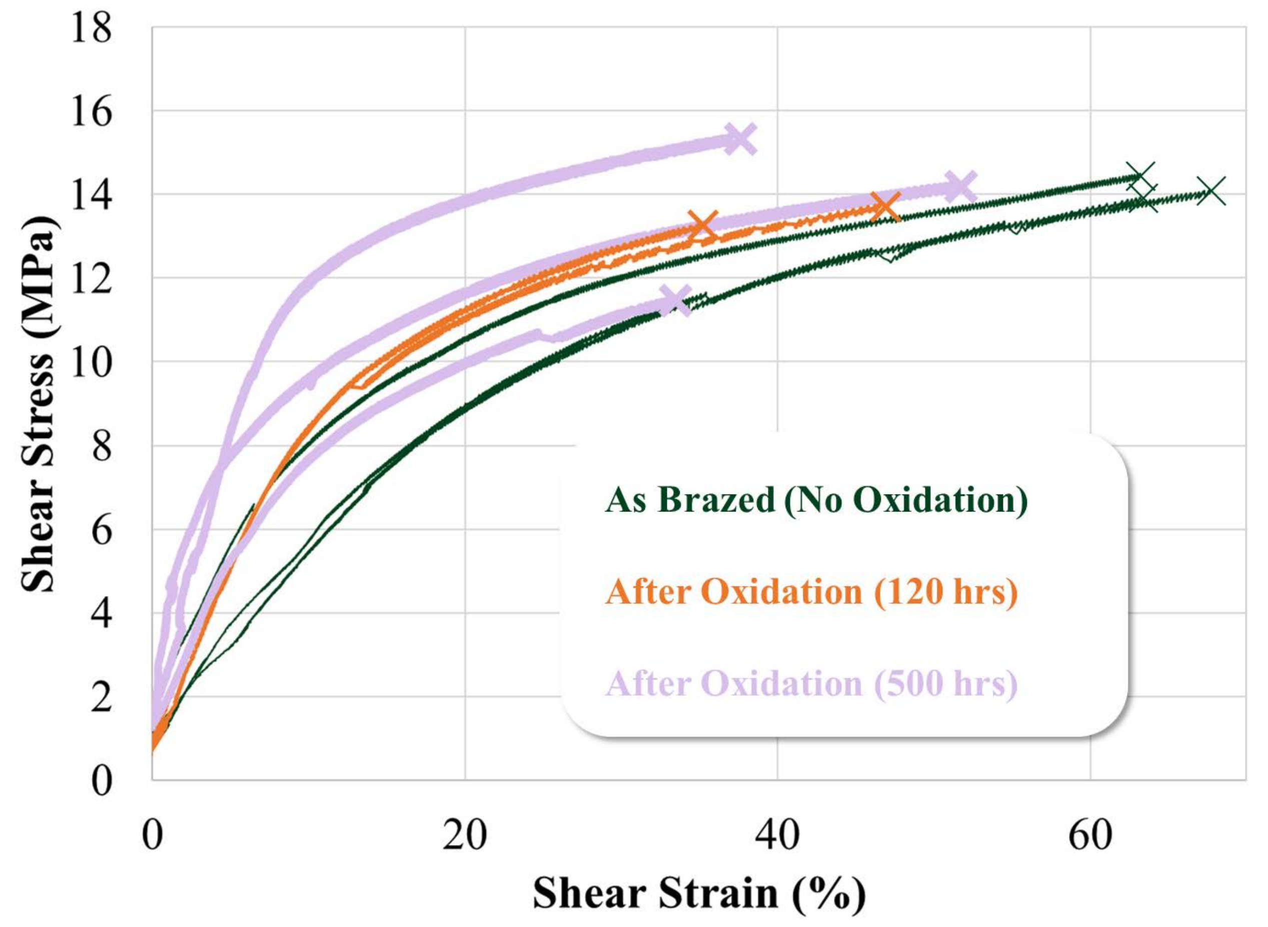




- Displacement Control: 0.009mm/min (~10^{-3} s^{-1})
- Test to Failure

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

Tests Show Good Ductility Followed by “Brittle Fracture”



δ: Displacement per joint;
a: ¼’’ (lateral length of the joints);
δ = Extension/2;

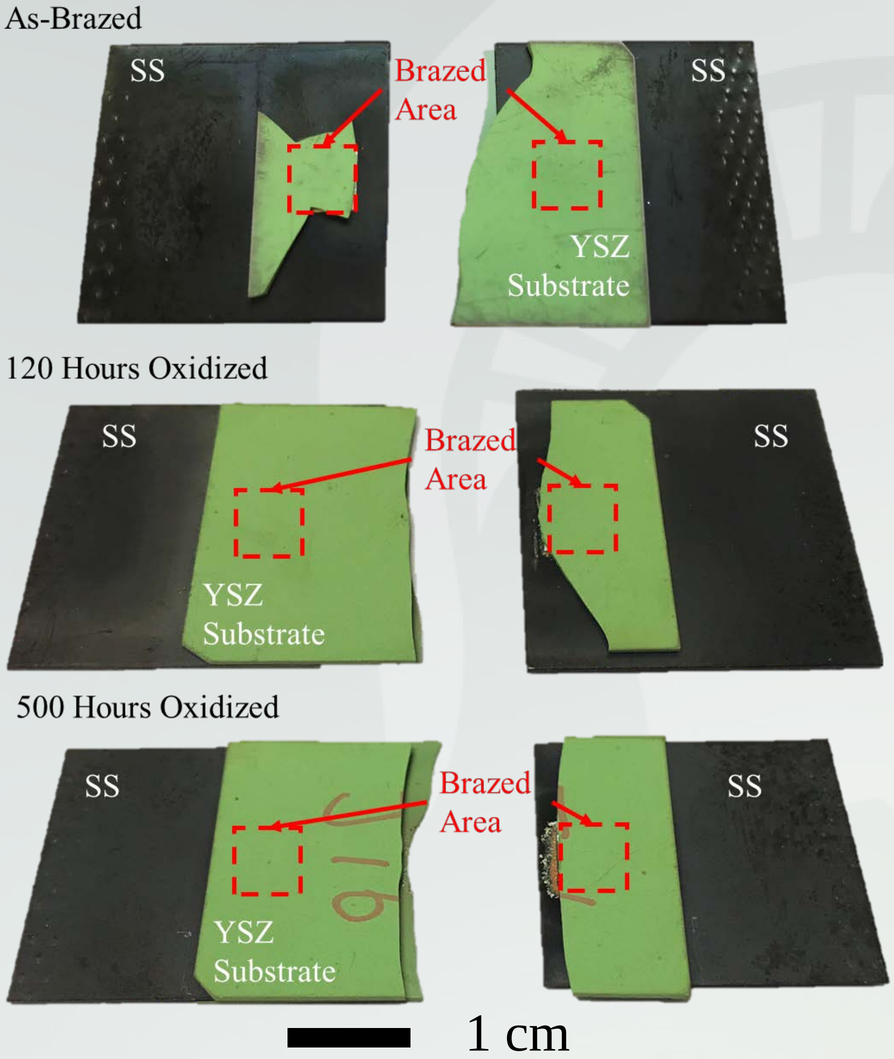
σ_{shear}: Shear stress;
F: Load;
$\sigma_{shear} = F/2[a*(a- \delta)]$;

ε_{shear}: Shear strain
t: Joint thickness;
$\varepsilon_{shear} = (\delta/2)/t$.

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.

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



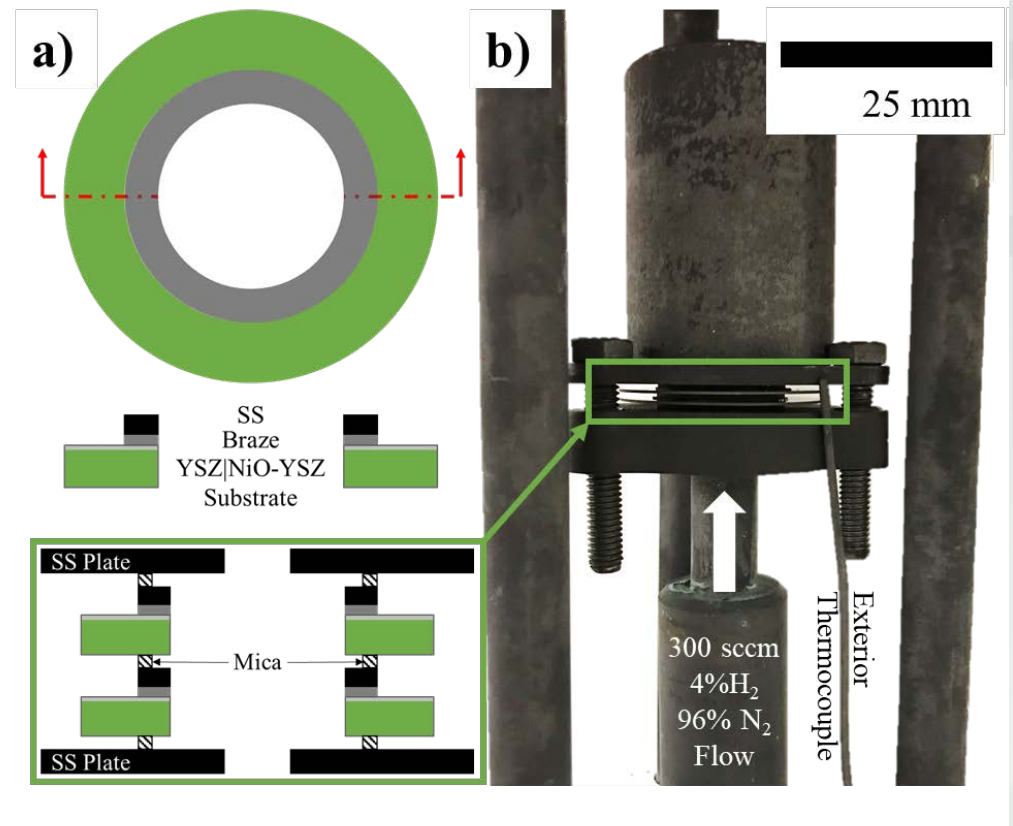
- All the joints broke only in the YSZ substrate. The other one has half of the braze/YSZ bonding area detached.

- 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 Isothermal Test Setup

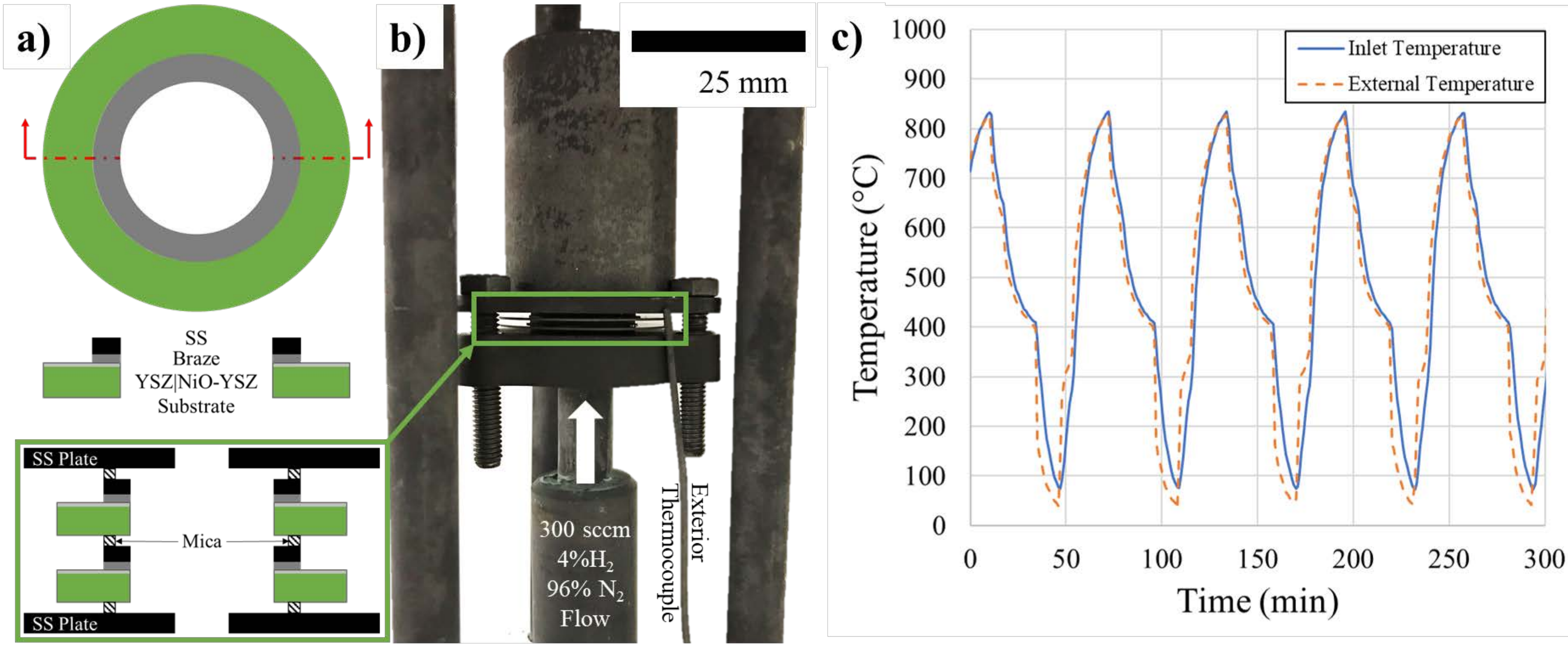


Dual Atmosphere Test Assembly

- Dual atmosphere achieved by flowing 300 sccm of 4%H_2 96% N_2 through the center hole of the sample stack;
- The assembly was sent up into a furnace to hold at 750°C for 300 hours.

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)

Dual Atmosphere Thermal Cycling Test

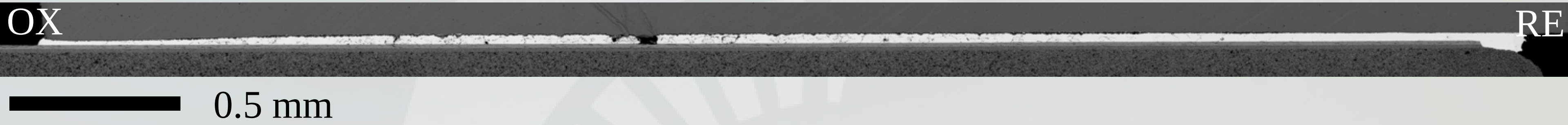


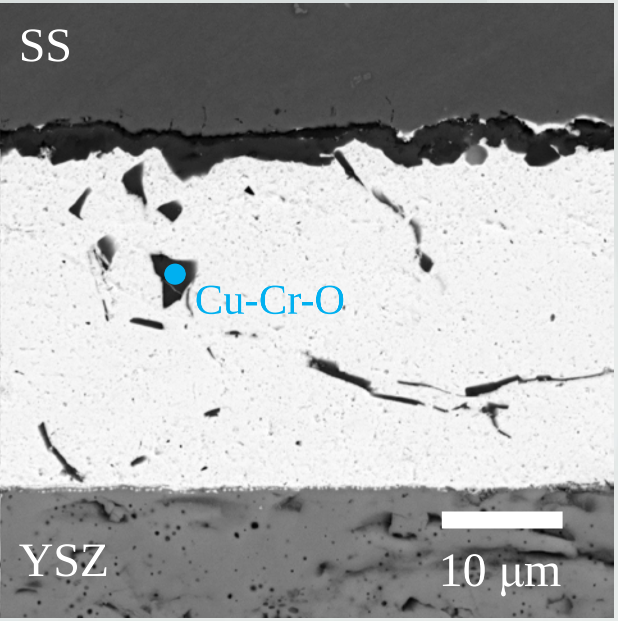
- Dual atmosphere achieved by flowing 300 sccm of 4%H_2 96% N_2 through the center hole of the sample stack;
- Thermal cycling was performed by moving the entire assembly in and out of a three-zone furnace. An average of ~26°C/min heating and cooling rate was applied during the test.

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)

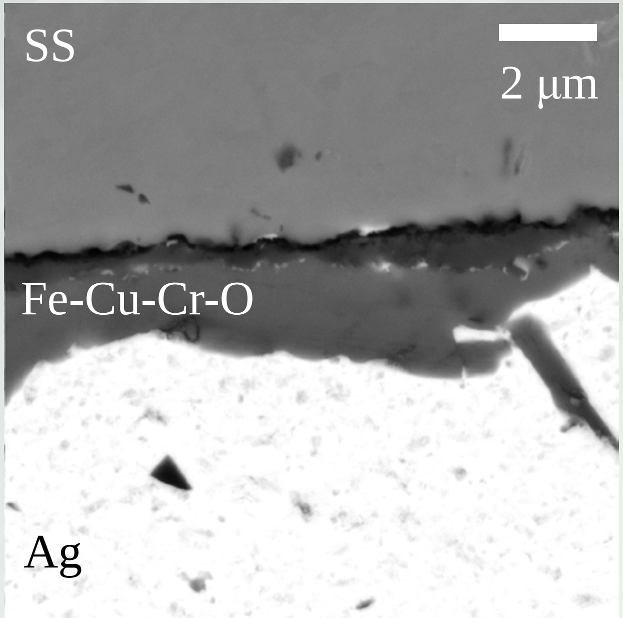
Microstructure of As-brazed Ag3CuO (RAB) Samples Are Consistent with Literature Reports

Ag3CuO (wt.) Braze Joint, As-Brazed

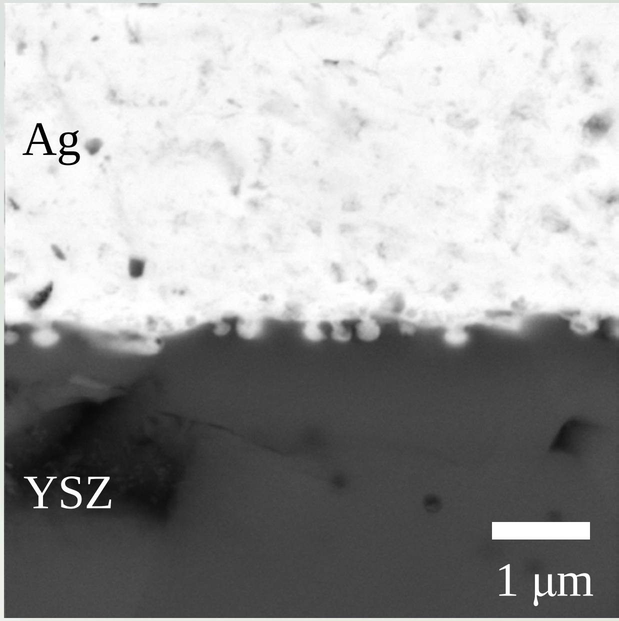




RAB Joint Center (As-Brazed)



RAB Joint SS Interface (As-Brazed)



RAB Joint YSZ Interface (As-Brazed)

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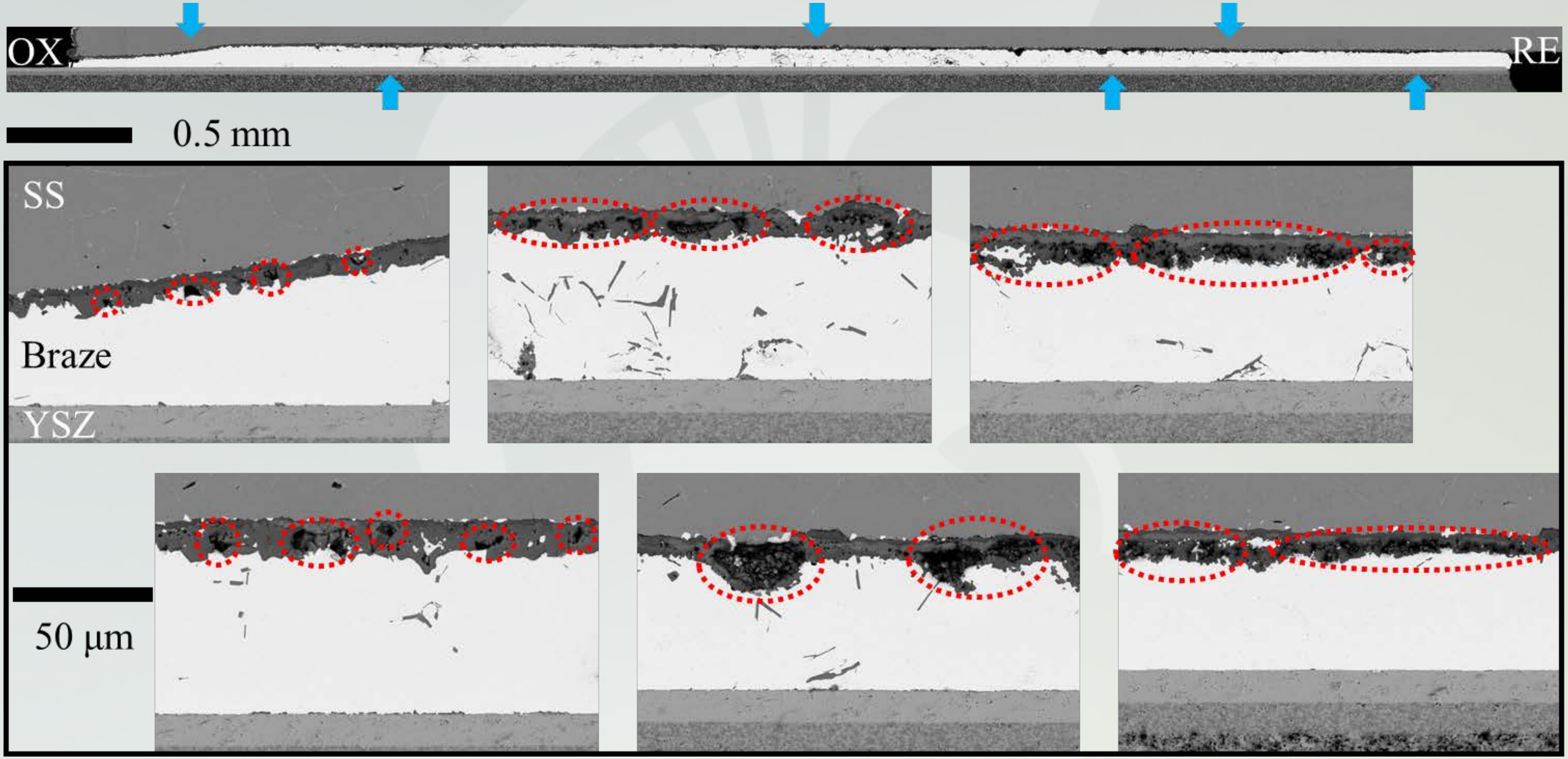
Ag3CuO (RAB) Brazes Show Degradation After 300 hours of Isothermal, 750°C Dual Atmosphere Testing



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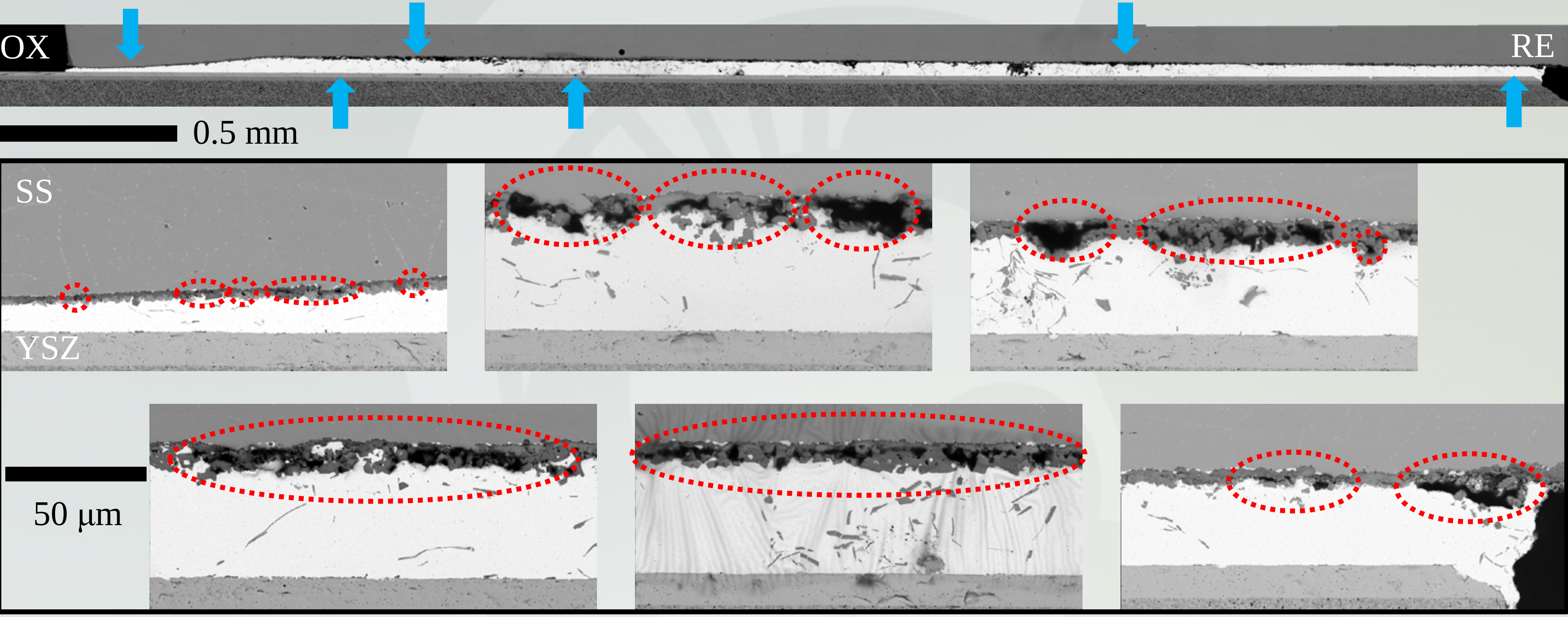
Ag3CuO (RAB) Braze Showed Similar Degradation After 300 Rapid Thermal Cycles to/from 825ºC



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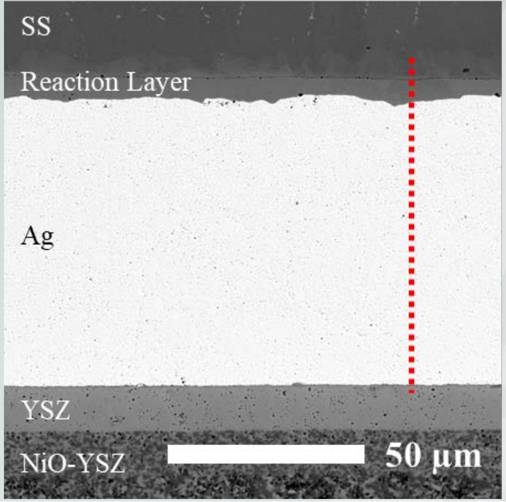
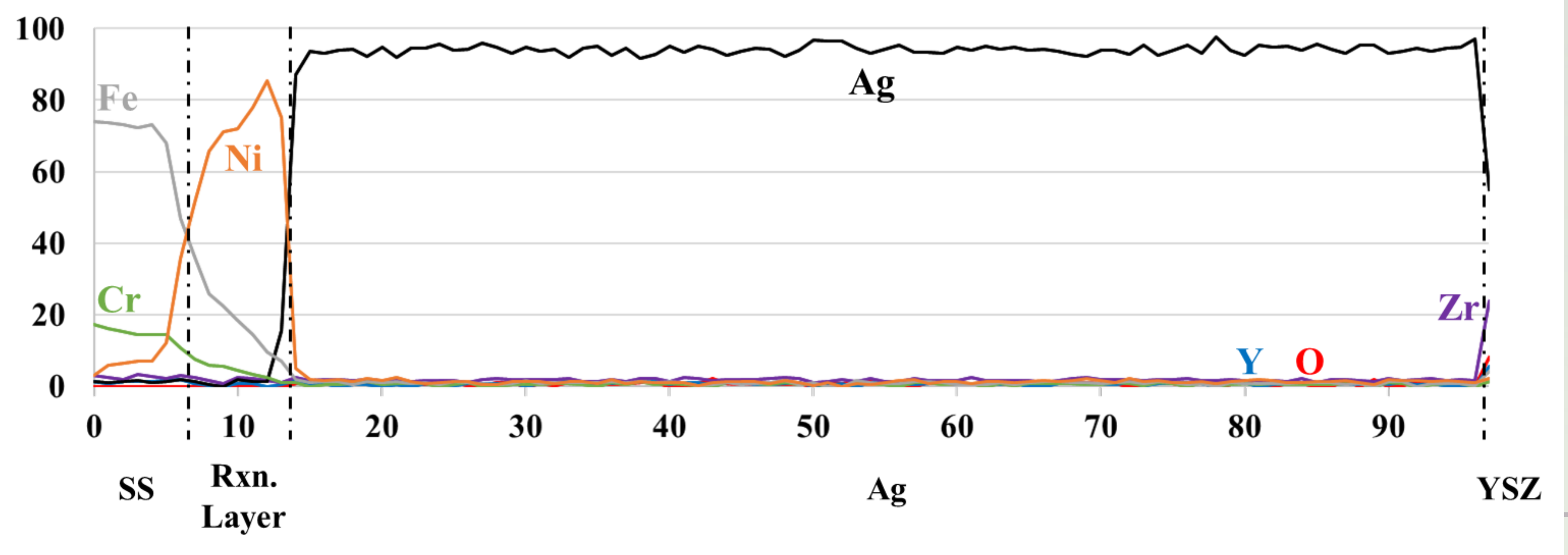
Reminder of the As-brazed Ag-Ni Braze Microstructure

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.



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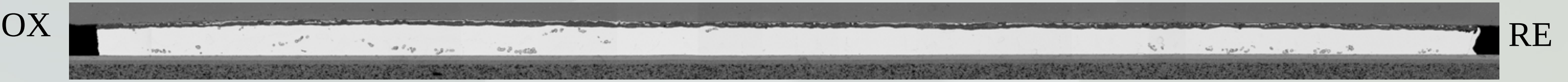
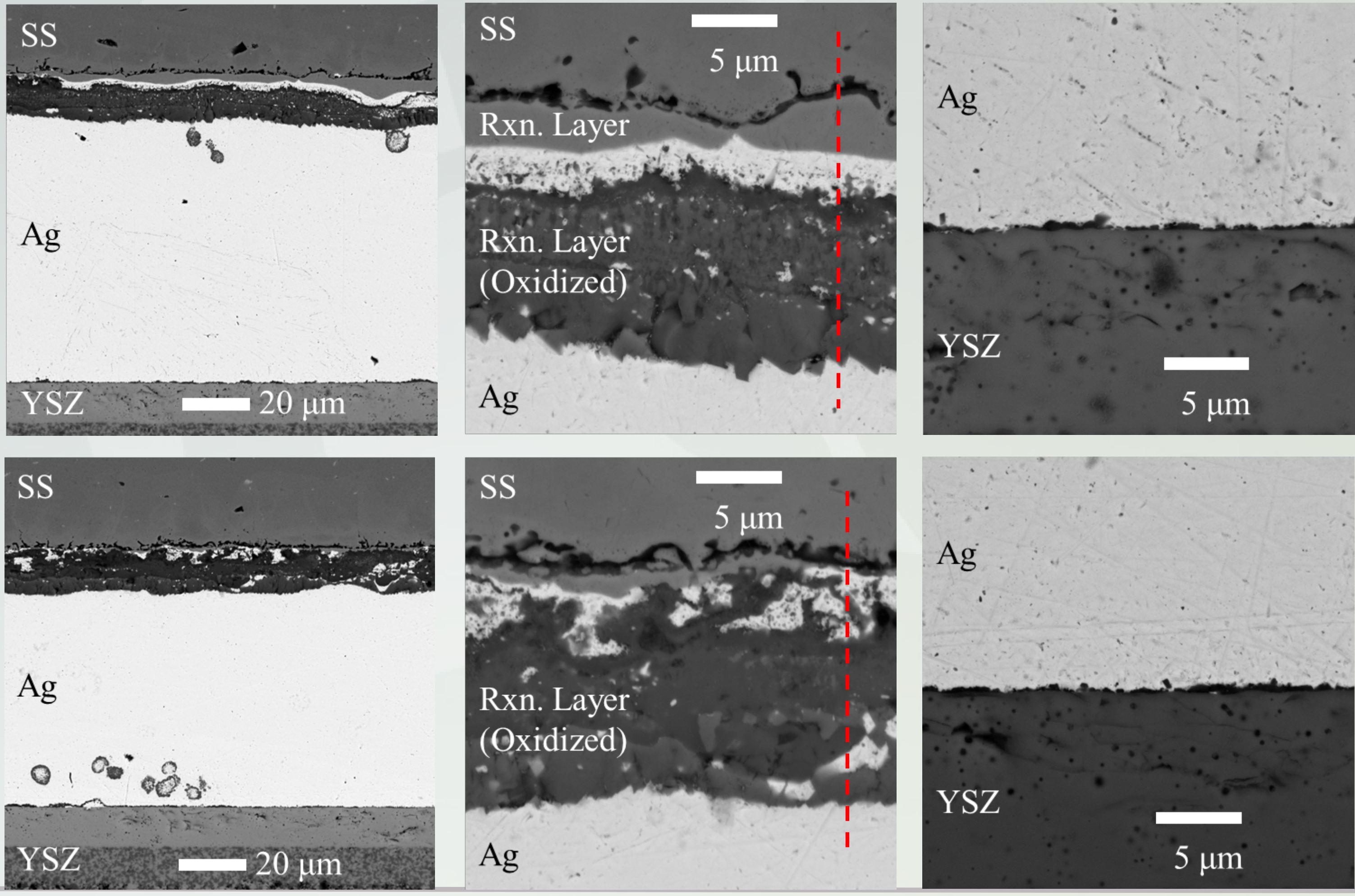
Ag-Ni Braze Joints Remain Dense After 300 hours of Isothermal, 750ºC Dual Atmosphere Testing



0.5 mm

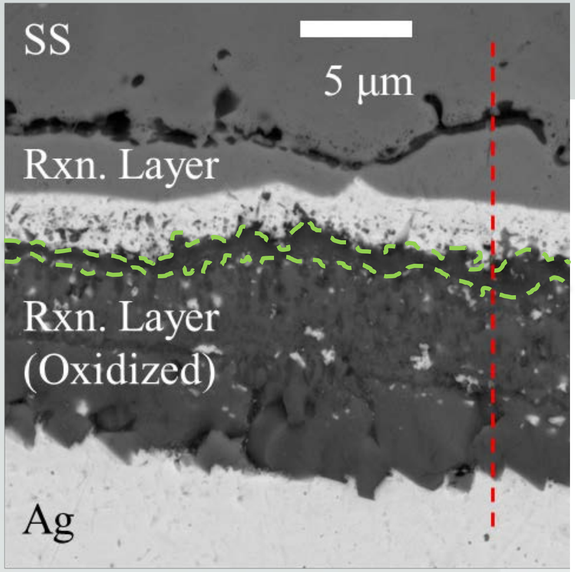


Oxidation Side

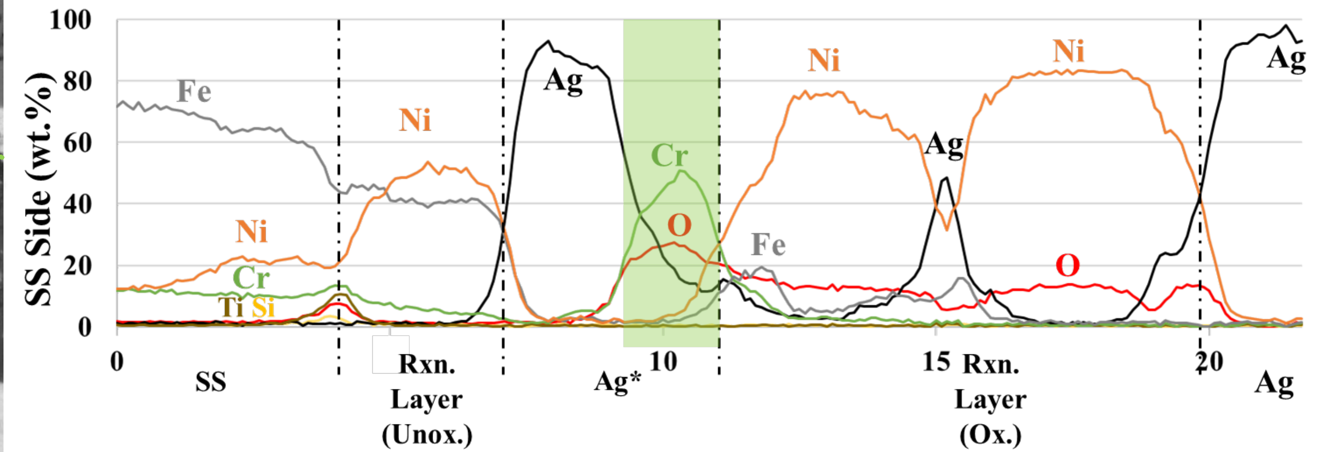
Reduction Side

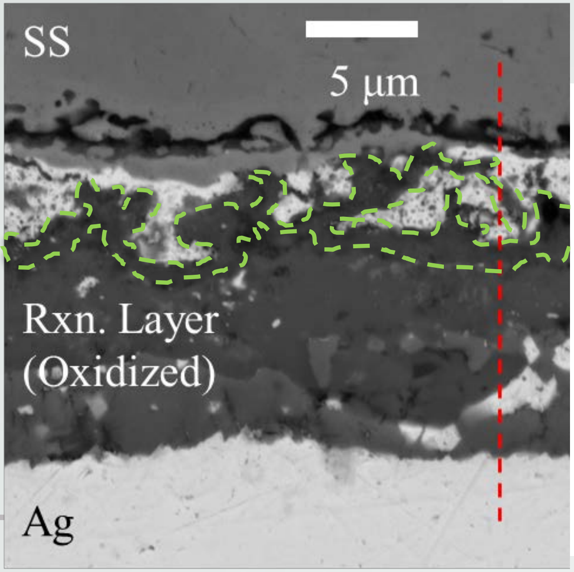
Through Thickness *SS Interface* *YSZ Interface*

More Rxn. Layer Oxidation on the RE Side than the Ox Side May be Caused by a NonPassivating Chromia Layer

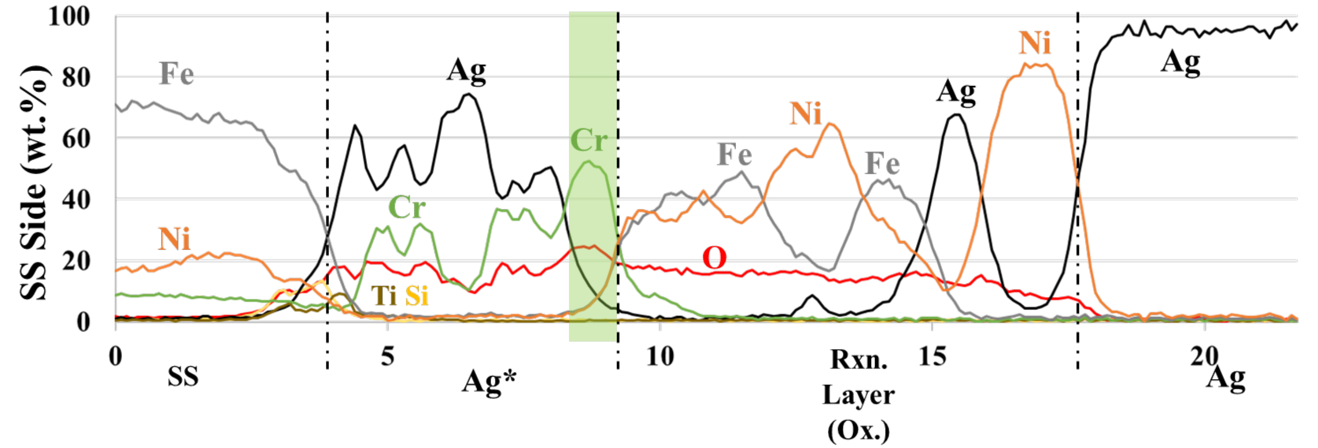


OX Side

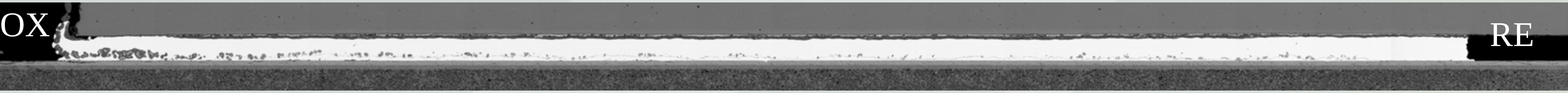




RE Side



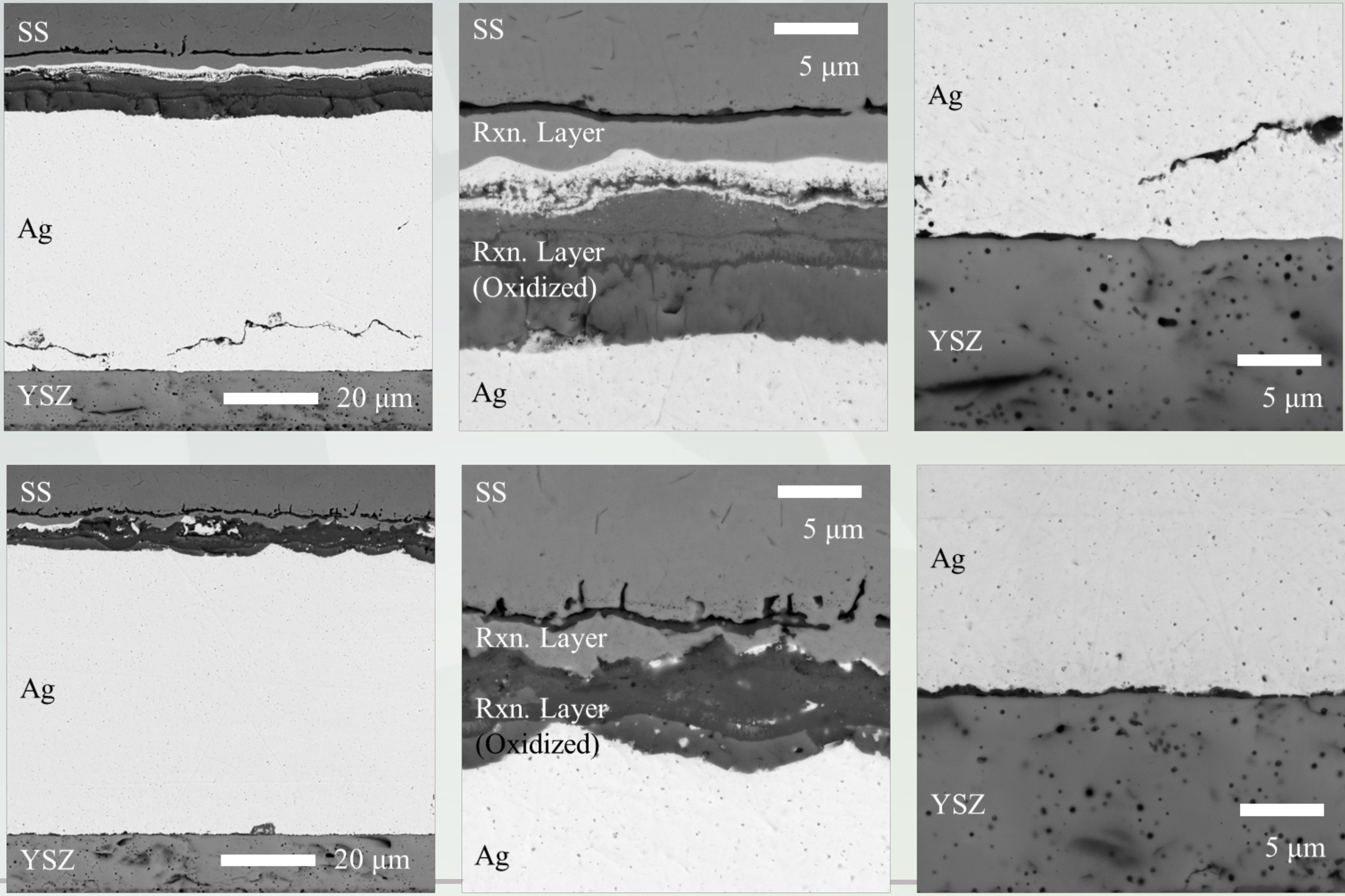
Ag-Ni Braze Joints Remain Dense After After 300 Rapid Thermal Cycles to/from 825ºC



Oxidation Side

~74 hours total @ >700 ℃

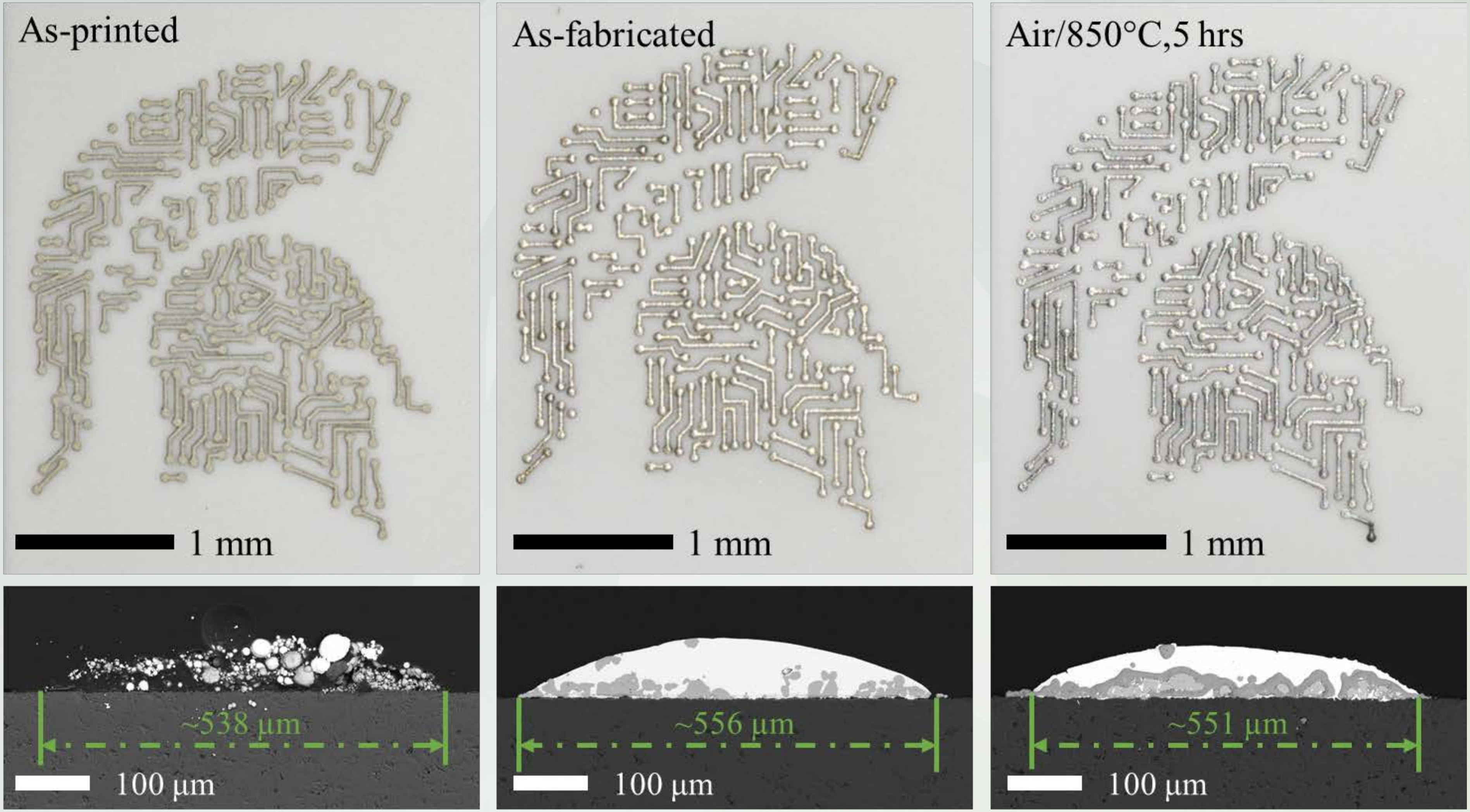
Reduction Side



Through Thickness *SS Interface* *YSZ Interface*

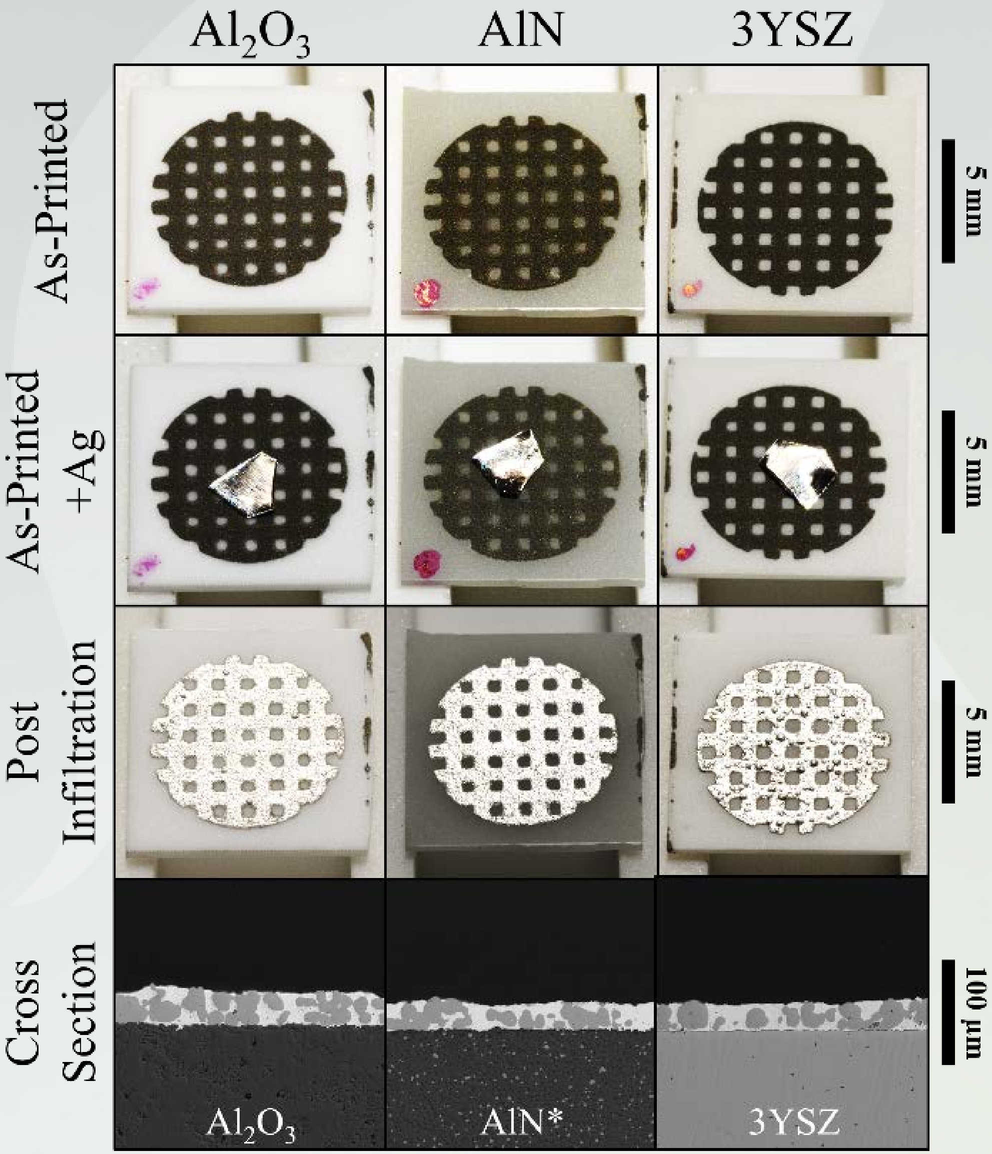
OTHER APPLICATIONS

Controlled Wetting/Spreading of Silver and be Used for High Power/High Temperature Circuits/Current Collectors



Zhou et al., Controlled Wetting and Spreading of Metals on Substrates Using Porous Interlayers and Related Articles, USPTO Provisional Patent (Submitted April 17, 2018)
Zhou et al., Controlled Wetting and Spreading of Ag on Various Ceramic Substrates with Porous Ni Interlayers, Scr. Mater, 2018. (In Preparation)

Molten Ag Will Also Infiltrate And Spread Through A Contiguous Porous Ni Pattern



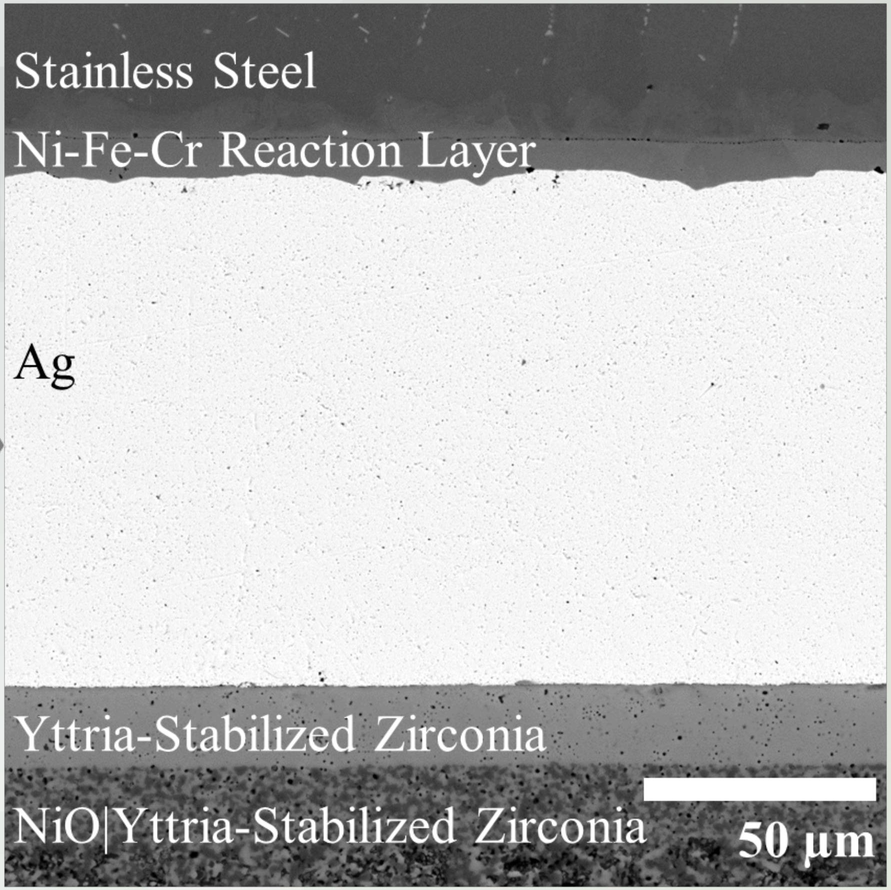
Zhou et al., Controlled Wetting and Spreading of Metals on Substrates Using Porous Interlayers and Related Articles, USPTO Provisional Patent (Submitted April 17, 2018)

Zhou et al., Controlled Wetting and Spreading of Ag on Various Ceramic Substrates with Porous Ni Interlayers, Scr. Mater, 2018. (In Preparation)

Outline

- **Background and Motivation**
    - Benefits of Silver-Copper Brazes
    - Problems with Silver-Copper Brazes
    - Proposed Strategy
- **Results and Discussion**
    - Partially Sintered Ni Layers
    - As Brazed Joint Microstructures
    - Oxidized Braze Joints
    - Mechanical Properties with/without Oxidation
    - Dual Atmosphere Isothermal Test
    - Dual Atmosphere Thermal Cycling Test
    - Other Applications
- **Conclusions**

Ag-Ni Summary



Quan Zhou et al., Brazing Method Using Porous Interlayers and Related Articles, USPTO Provisional Patent. (Submitted 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.

Conclusions

1. A new porous-Ni-enabled Ag brazing approach for improved YSZ-to-stainless steel joining was developed.
2. This technique reduces the porosity commonly found in conventional, dual-atmosphere, Ag-based YSZ-stainless steel braze joints, and hence should produce SOFC braze joints with enhanced lifetimes and operational robustness.
3. Using this new technique, braze joints with good mechanical strength can be produced.
4. The interfacial bonding strength with this new technique is stronger than commercial YSZ substrates, even after prolonged oxidation.
5. Preliminary isothermal aging and rapid thermal cycling tests showed that these brazes are more durable than conventional Ag-CuO brazes.
6. Porous nickel enhanced silver wetting may also be useful for enabling Ag (or other) brazes in other ceramic-ceramic and metal-ceramic applications.

Research Team

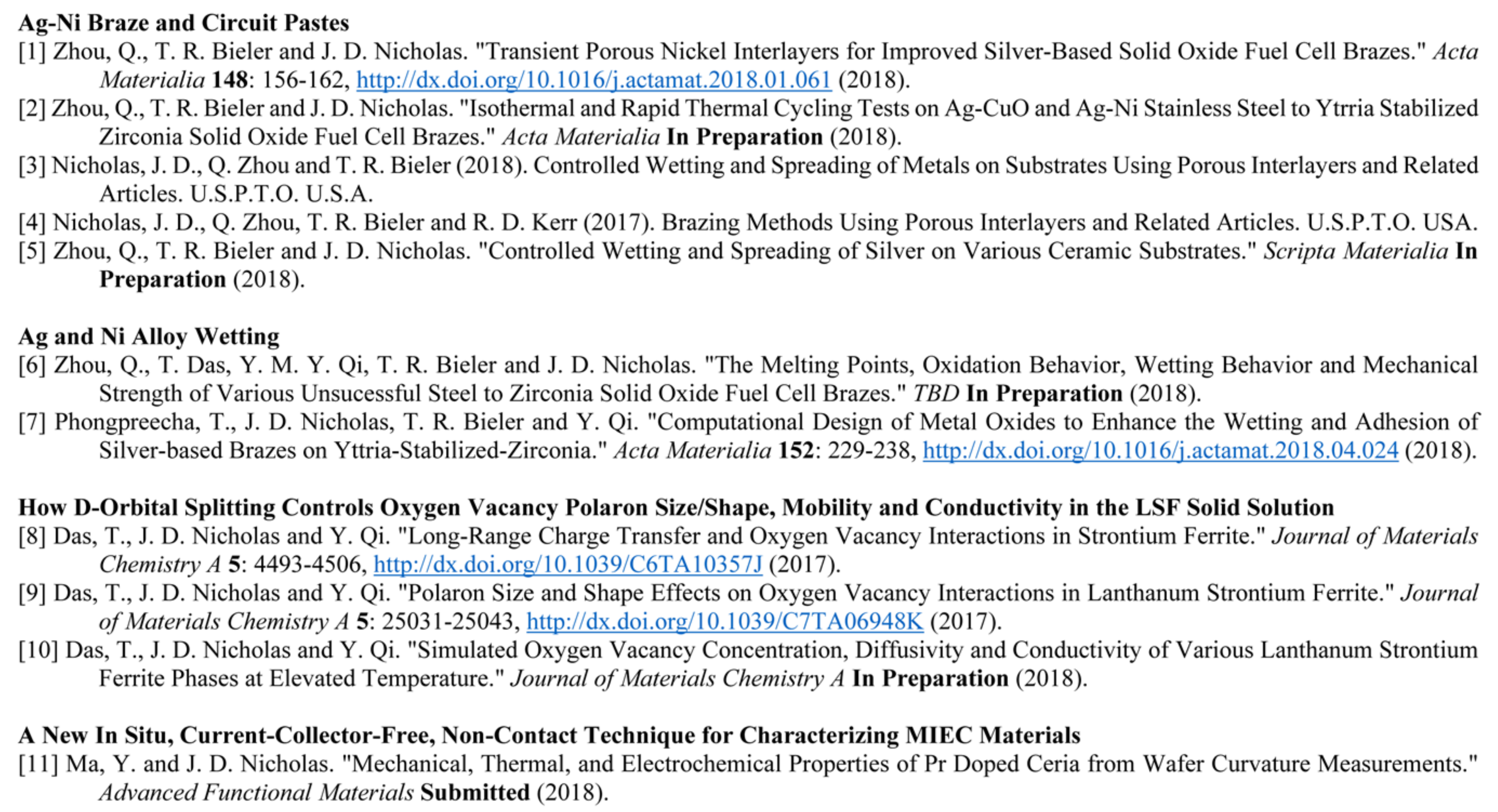
- **MSU:**

Jason D. Nicholas	PI, now tenured
Yue Qi	PI
Thomas R. Bieler	PI
Quan Zhou	PhD student, now at Hitachi Metals
Tridip Das	PhD student, now at Intel
Yuxi Ma	PhD student
Thanaphong Phongprecha	PhD student
Riley O’Shea	Undergraduate student, now at Nexteer Automotive
Young Kim	Undergraduate student, now at Fraunhofer USA

- **Delphi:**
    - Rick Kerr (and his team …)
    - Stephanie Surface
    - Bryan A. Gillispie

- **NETL**
    - Joseph Stoffa

Products Resulting From This Work



Ag-Ni Braze and Circuit Pastes

[1] 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).

[2] Zhou, Q., T. R. Bieler and J. D. Nicholas. "Isothermal and Rapid Thermal Cycling Tests on Ag-CuO and Ag-Ni Stainless Steel to Ytrria Stabilized Zirconia Solid Oxide Fuel Cell Brazes." *Acta Materialia* **In Preparation** (2018).

[3] Nicholas, J. D., Q. Zhou and T. R. Bieler (2018). Controlled Wetting and Spreading of Metals on Substrates Using Porous Interlayers and Related Articles. U.S.P.T.O. U.S.A.

[4] Nicholas, J. D., Q. Zhou, T. R. Bieler and R. D. Kerr (2017). Brazing Methods Using Porous Interlayers and Related Articles. U.S.P.T.O. USA.

[5] Zhou, Q., T. R. Bieler and J. D. Nicholas. "Controlled Wetting and Spreading of Silver on Various Ceramic Substrates." *Scripta Materialia* **In Preparation** (2018).

Ag and Ni Alloy Wetting

[6] Zhou, Q., T. Das, Y. M. Y. Qi, T. R. Bieler and J. D. Nicholas. "The Melting Points, Oxidation Behavior, Wetting Behavior and Mechanical Strength of Various Unsucessful Steel to Zirconia Solid Oxide Fuel Cell Brazes." *TBD* **In Preparation** (2018).

[7] Phongpreecha, T., J. D. Nicholas, T. R. Bieler and Y. Qi. "Computational Design of Metal Oxides to Enhance the Wetting and Adhesion of Silver-based Brazes on Yttria-Stabilized-Zirconia." *Acta Materialia* **152**: 229-238, http://dx.doi.org/10.1016/j.actamat.2018.04.024 (2018).

How D-Orbital Splitting Controls Oxygen Vacancy Polaron Size/Shape, Mobility and Conductivity in the LSF Solid Solution

[8] Das, T., J. D. Nicholas and Y. Qi. "Long-Range Charge Transfer and Oxygen Vacancy Interactions in Strontium Ferrite." *Journal of Materials Chemistry A* **5**: 4493-4506, http://dx.doi.org/10.1039/C6TA10357J (2017).

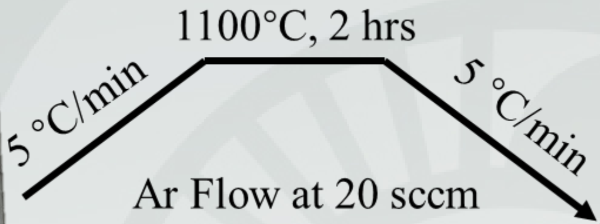
[9] Das, T., J. D. Nicholas and Y. Qi. "Polaron Size and Shape Effects on Oxygen Vacancy Interactions in Lanthanum Strontium Ferrite." *Journal of Materials Chemistry A* **5**: 25031-25043, http://dx.doi.org/10.1039/C7TA06948K (2017).

[10] Das, T., J. D. Nicholas and Y. Qi. "Simulated Oxygen Vacancy Concentration, Diffusivity and Conductivity of Various Lanthanum Strontium Ferrite Phases at Elevated Temperature." *Journal of Materials Chemistry A* **In Preparation** (2018).

A New In Situ, Current-Collector-Free, Non-Contact Technique for Characterizing MIEC Materials

[11] Ma, Y. and J. D. Nicholas. "Mechanical, Thermal, and Electrochemical Properties of Pr Doped Ceria from Wafer Curvature Measurements." *Advanced Functional Materials* **Submitted** (2018).

Ag Melt Infiltrate the Porous Ni Interlayer and Spread Accordingly

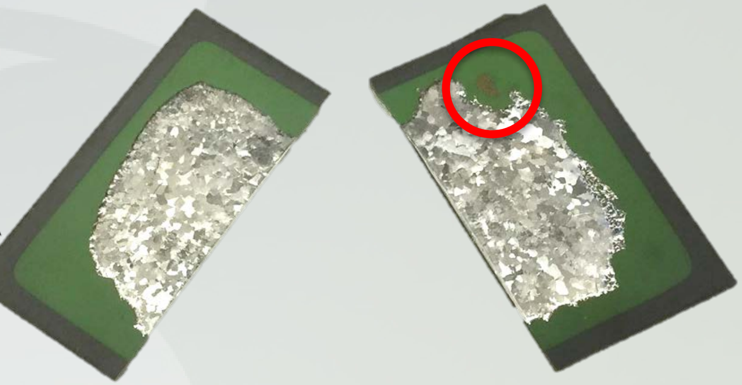


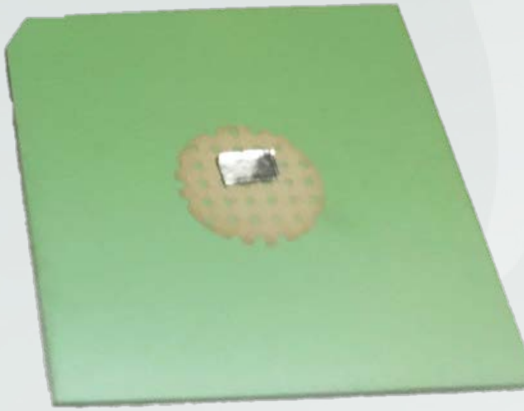
1100°C, 2 hrs

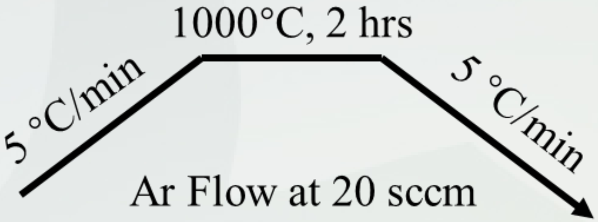
5 °C/min

5 °C/min

Ar Flow at 20 sccm







1000°C, 2 hrs

5 °C/min

5 °C/min

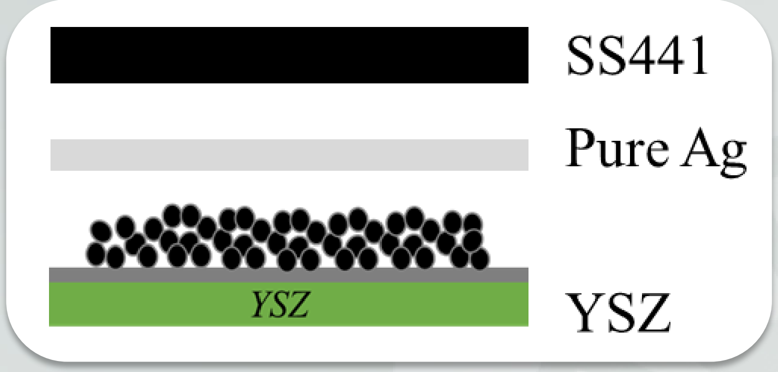
Ar Flow at 20 sccm

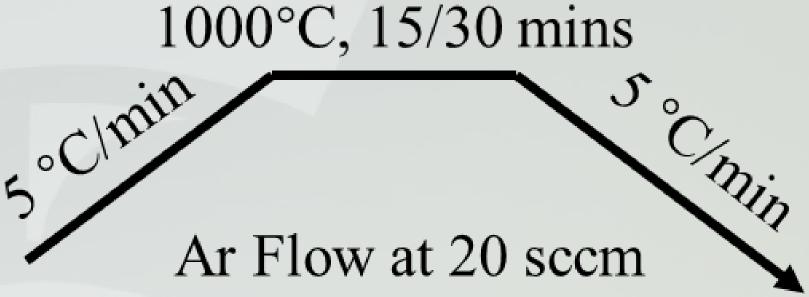
Before

After

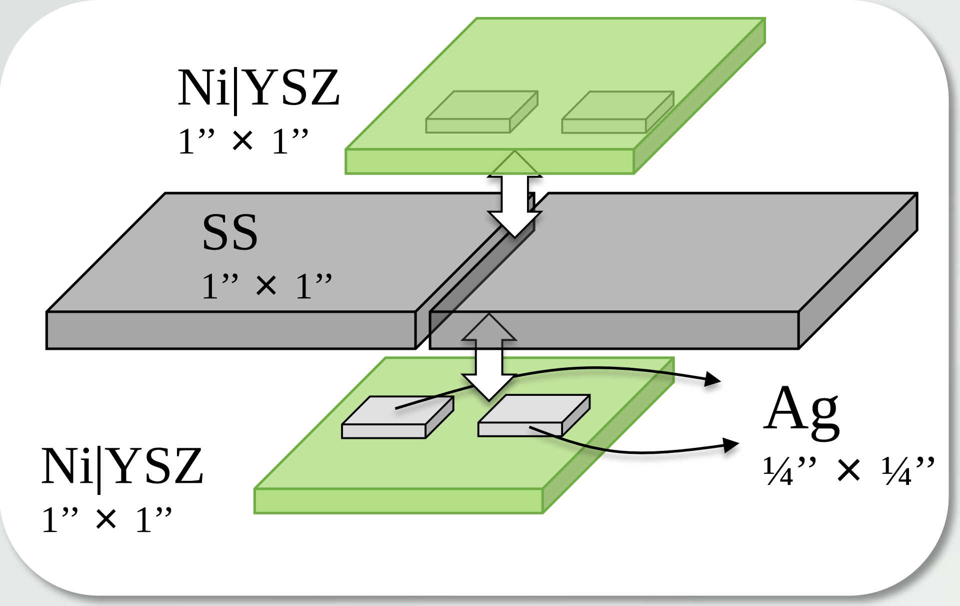
Brazing Set-up

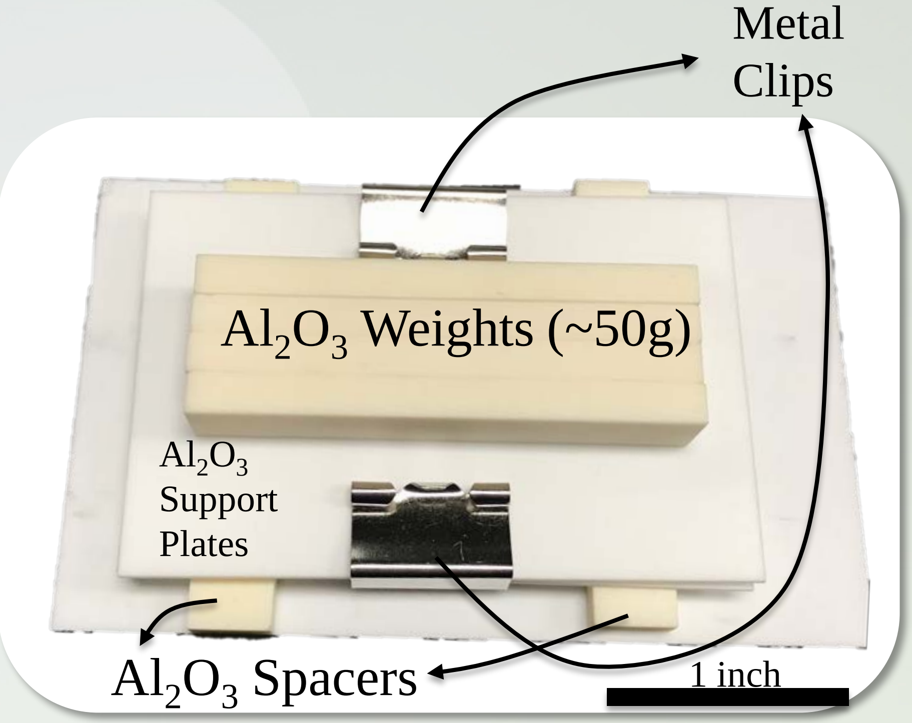
Brazing for 30 or 15 mins





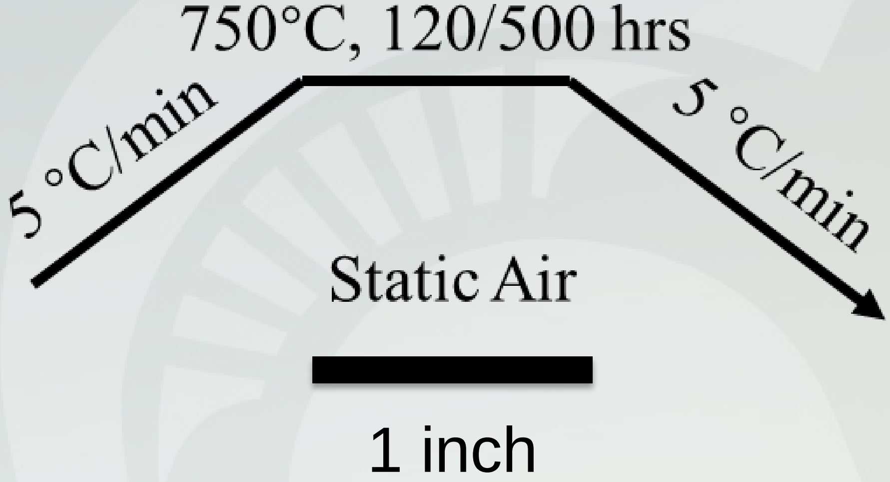
Symmetric Double Shear Lap





750°C Isothermal Test in Air for Oxidation

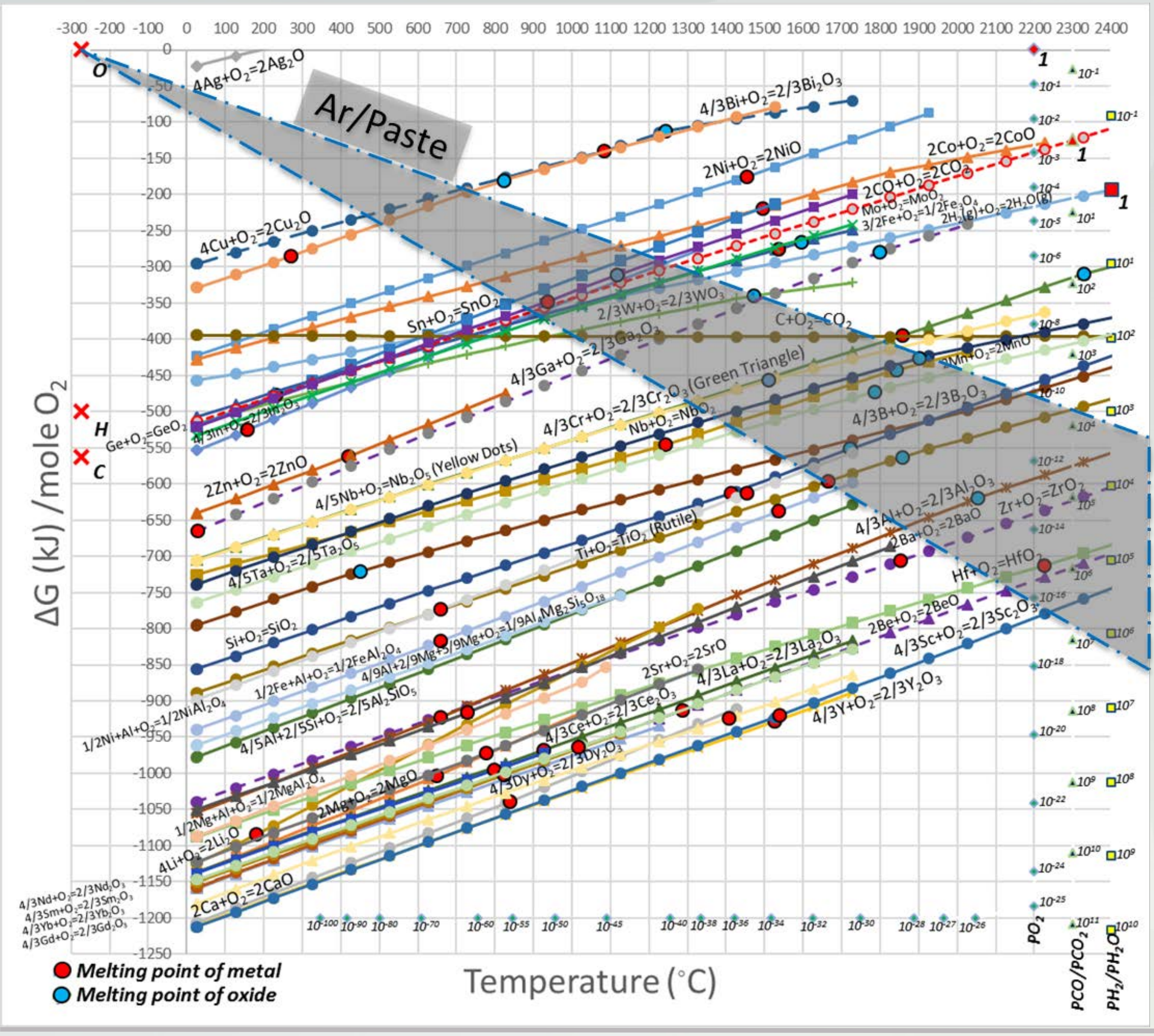
As-Brazed



Post Oxidation

Samples were cross-sectioned, polished and examined with scanning electron microscope (SEM) as well as energy dispersive X-ray spectroscopy (EDS).

Inert Atmospheres should be Used as the Brazing Atmosphere



1. Ni won’t oxidize in inert gas (with paste)
2. Inert atmosphere is cost-effective and easy to apply in industrial production
3. Vacuum brazing is not compatible with high-throughput SOFC manufacturing

Nagesh, V.K. and J.A. Pask, Journal of Materials Science, 1983. ***18*** *(9): p. 2665-2670.*
Hula, R.C., et al., Applied Surface Science, 2010. ***256*** *(14): p. 4697-4701.*

Potential Problems with the Ag-Ni Brazing System

1. The ***volume change*** associated with Nickel particle oxidation near the air side of the joint could cause mechanical stress that degrades the joint.
    - This may be OK if a ***small amount of Ni*** is used in the joint, or if the Ni is transient.
    - Compared to Ag-CuO brazes, compressive stress in the braze (due to the volume expansion accompanying Ni oxidation) is better than Type II porosity (caused by the volume shrinkage accompanying CuO reduction).

2. The ***interfacial strength*** between Ag/Ni composite and YSZ may be low.

3. The ***Oxidation layer*** on the stainless steel may reduce wettability.

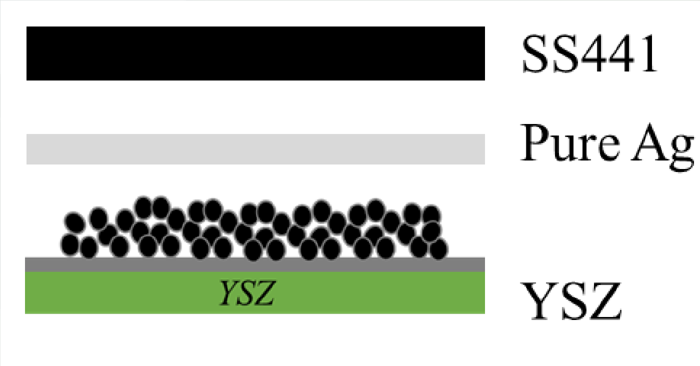
Project Objective

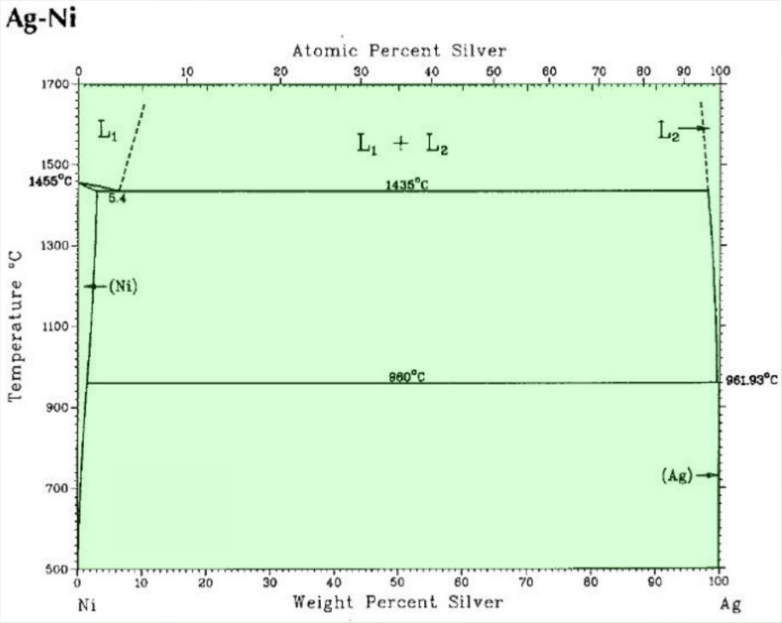
- **Project Duration: October 2014 to October 2018**
- **2014 Proposal Executive Summary:**

The objective of the proposed work is to **design and test new, SOFC-compatible, silver-free brazes forming durable, oxygen and hydrogen impermeable protective surface scales**. This will be accomplished using a combined computational-experimental approach to develop new braze compositions with the combination of liquidus temperature, coefficient of thermal expansion (CTE), wetting angle, bond strength, ductility, oxygen conductivity, hydrogen conductivity, and chemical stability necessary to produce SOFCs that can withstand 40,000 hours of 750^{o}C operation and thermal cycling. In addition to 1) instituting a new paradigm for braze development, and 2) generating a wealth of important, fundamental materials property data, the proposed work will provide aspiring DOE SECA Industrial Participant Delphi Inc. with new brazes specifically designed to withstand the extremes in temperature, time, atmosphere and thermal cycling encountered during SOFC operation. These new, self-passivating, non-precious-metal brazes will result in extended SOFC lifetimes and reduced SOFC stack costs.

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

1. Two step approach by
   - Deposit and partially-sinter porous ***Ni layers*** onto YSZ in Argon
   - Melt silver piece atop the porous nickel layer
2. Ni ***will not melt*** during brazing (MP_{Ni}=1455°C, MP_{Ag}=961.8°C)
3. The Ni interlayer ***will not dissolve*** into molten silver.
4. Ag can wet Ni in inert atmospheres, so that molten silver can ***melt infiltrate*** the Ni interlayer (spontaneous infiltration at wetting angle <50.7°).
   - θ =~ 9° in Zr-gettered helium
   - θ = ~30° in inert atmosphere
   - θ = ~90° in air





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. Applied Surface Science, 2010. ***256*** *(14): p. 4697-4701.*

Trumble, K.P., Spontaneous infiltration of non-cylindrical porosity: Close-packed spheres. Acta Materialia, 1998. 46 (7): p. 2363-2367.

The Ag-Ni Braze Has Several Key Benefits

Pore Type	Reactive Air Brazing	Ag-Ni Brazing
Type I (wetting) Pore Formation	• ***θ = 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].	• θ = 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.

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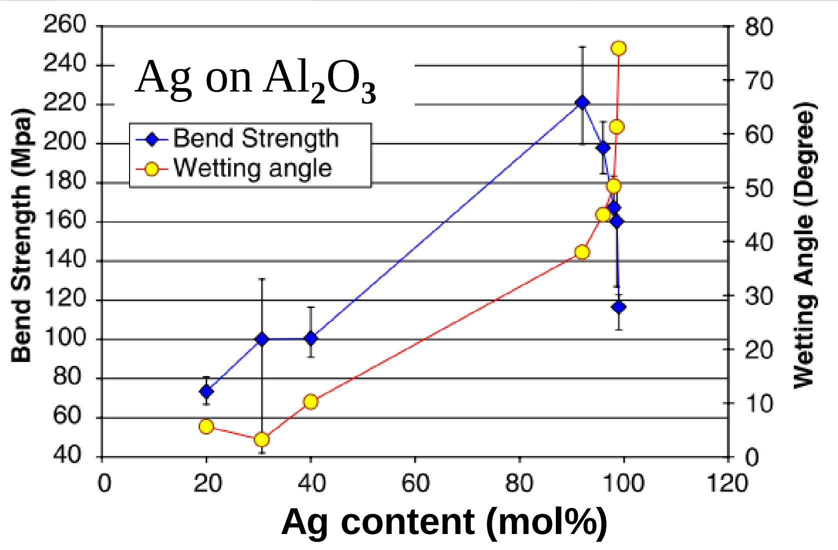
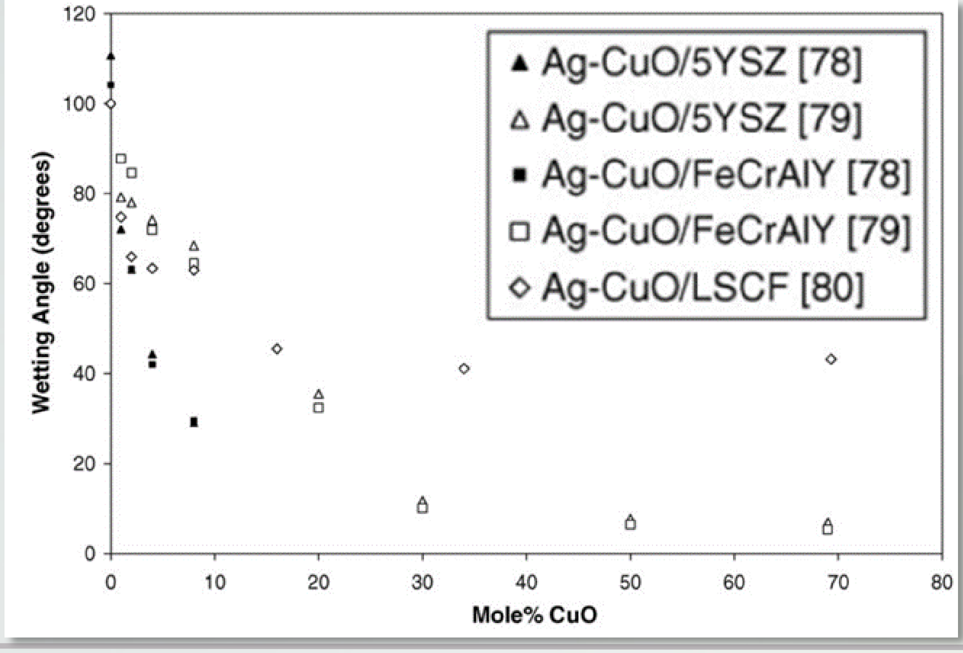
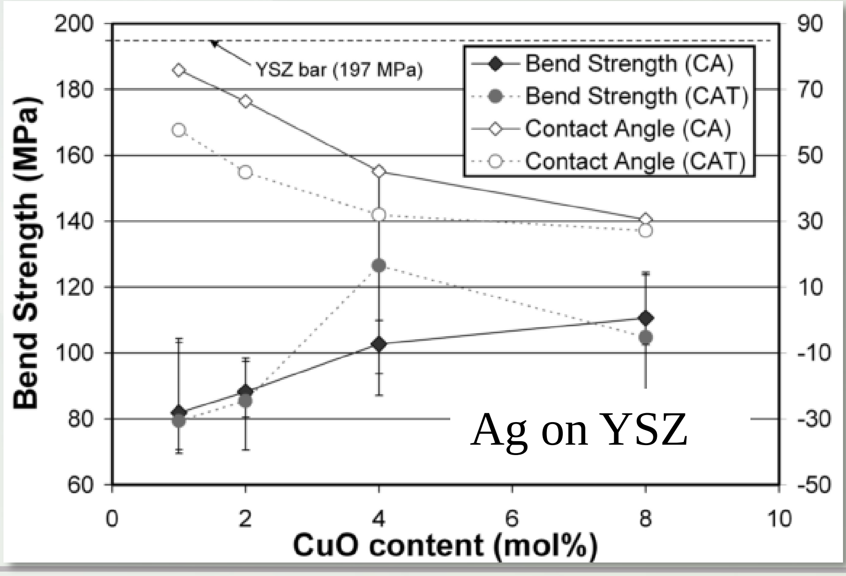
[1] Kim, J.Y. et. al, Journal of the American Ceramic Society, 2005.
[2] Kim, J.Y. et. al, Journal of Materials Research, 2005.
[3] Bobzin, K. et. al, Advanced Engineering Materials, 2014.
[4] Bause, T., et al., Fuel Cells, 2013.
[5] Trumble, K.P., Acta Materialia, 1998.
[6] Kim, J.Y. et. al, International Journal of Hydrogen Energy, 2007.

Ag-Based Reactive Air Brazes (RAB) Seem Promising at First Glance

1. Reactive air braze additions improve silver on yttrium-stabilized-zirconia (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***.

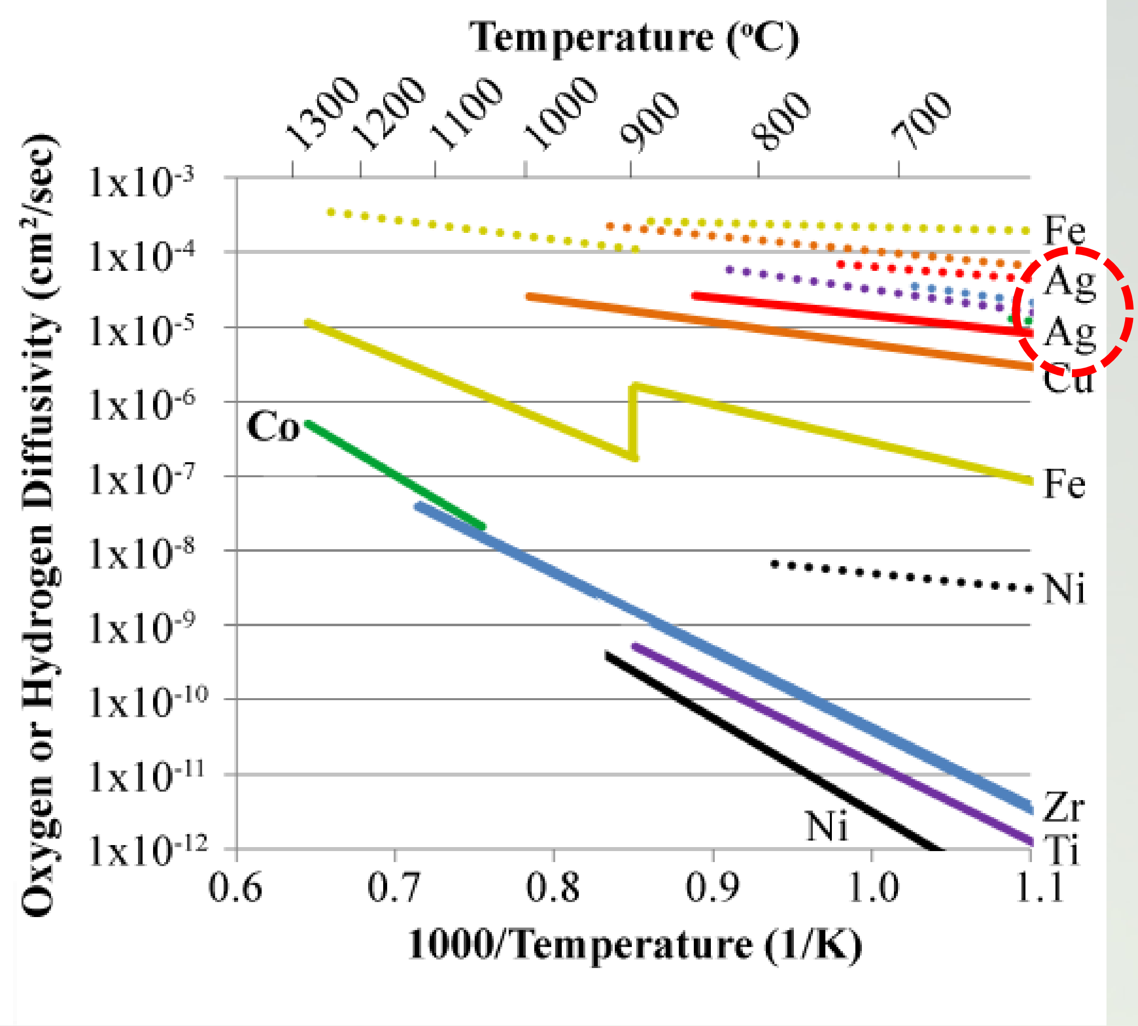






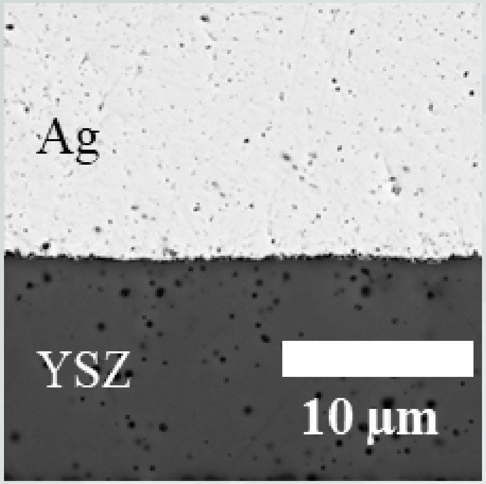
Kim, J.Y., J.S. Hardy, and K.S. Weil, Journal of the American Ceramic Society, 2005. 88 (9): p. 2521-2527.
Kim, J.Y., J.S. Hardy, and K.S. Weil, Journal of Materials Research, 2005. 20 (3): p. 636-643.
Fergus, J.W., Materials Science and Engineering A, 2005. 397 (1-2): p. 271-283.

Oxygen Diffusivities (Solid Lines) and Hydrogen Diffusivity (Dotted Lines) for Several Common Metals

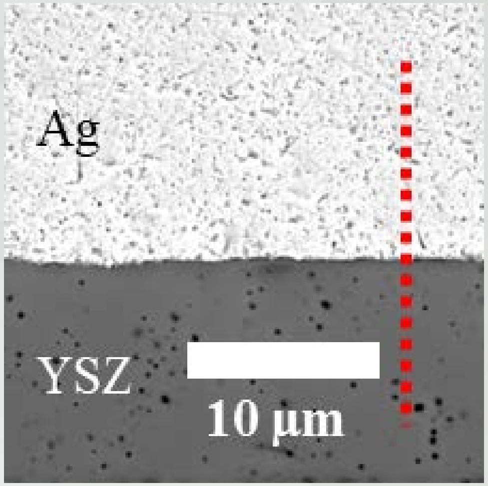


C. Smithells, W. Gale, T. Totemeier. Smithells Metals Reference Book. 8th ed.

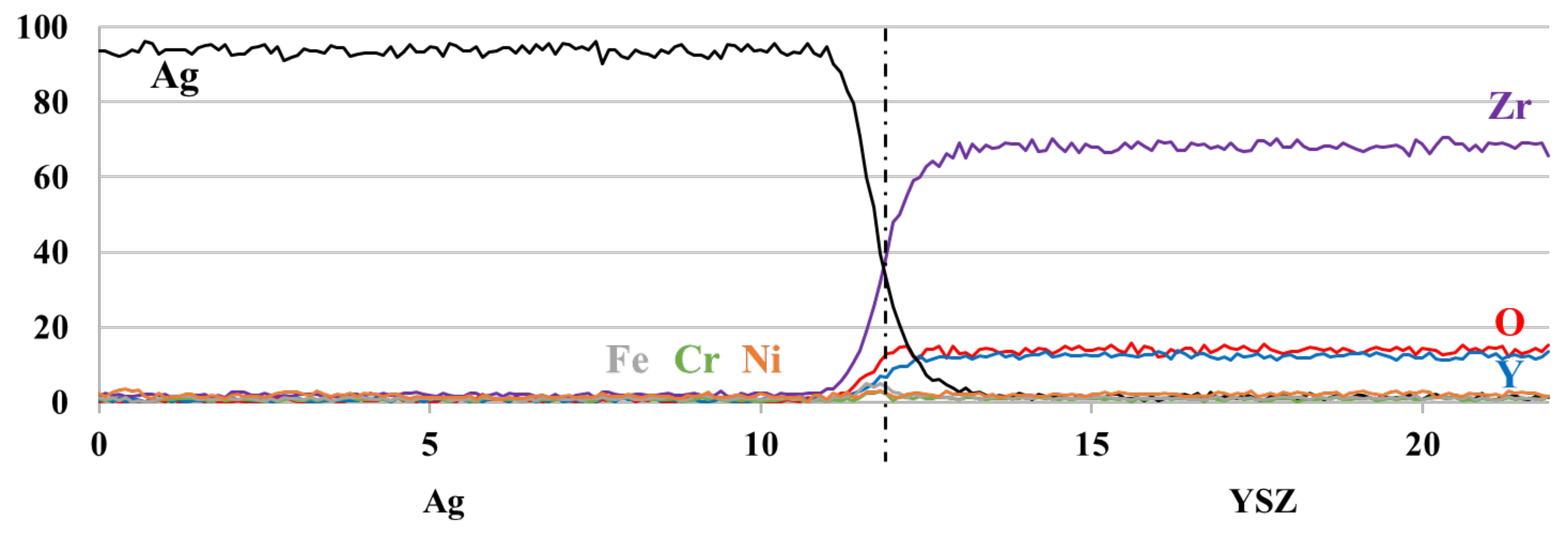
Ag and YSZ Form a Good Bond with the Assistance of the Ni Interlayer



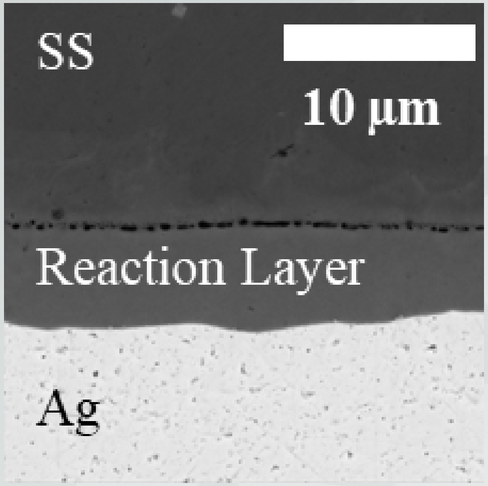
15 Mins Brazed



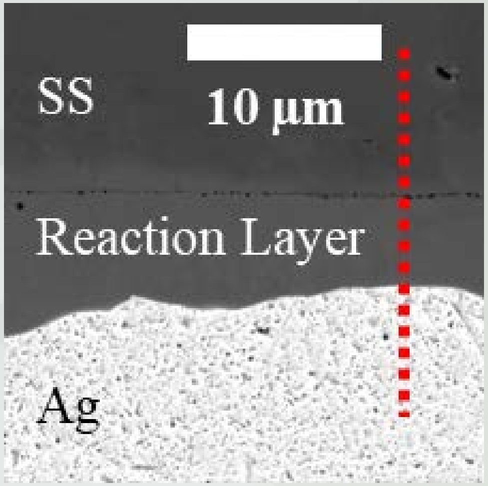
30 Mins Brazed



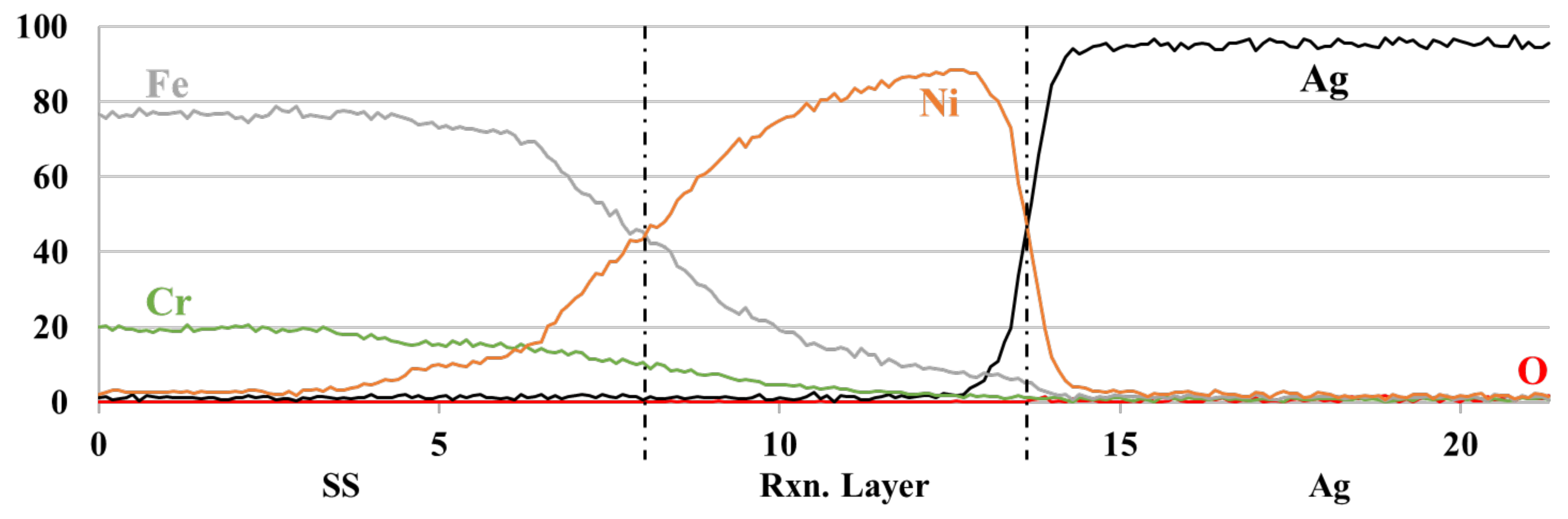
Inter-Diffusion Occurs at the Stainless Steel Interface



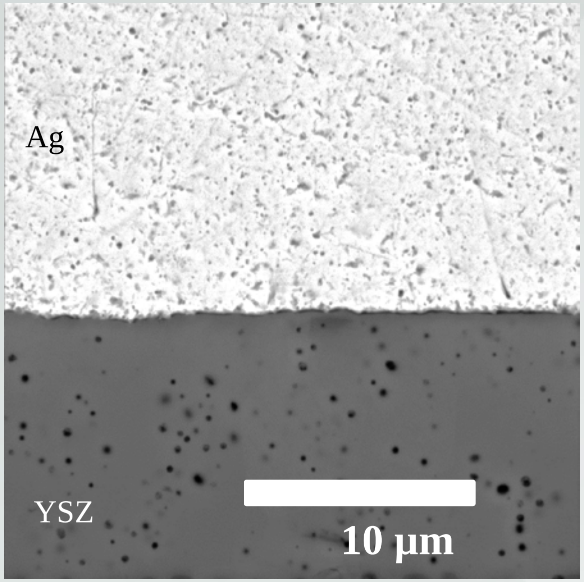
15 Mins Brazed



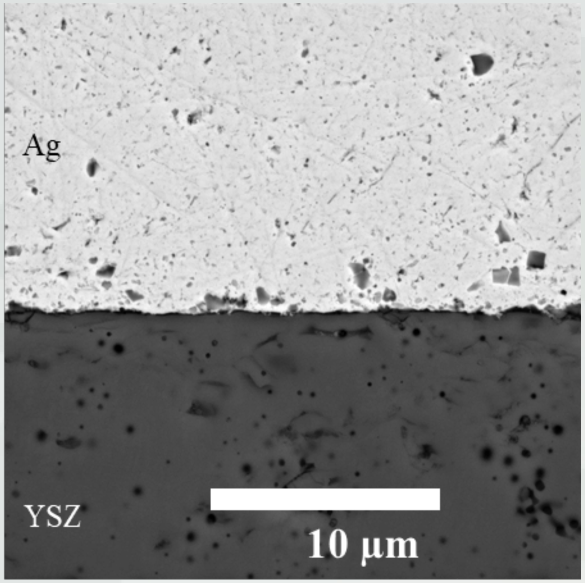
30 Mins Brazed



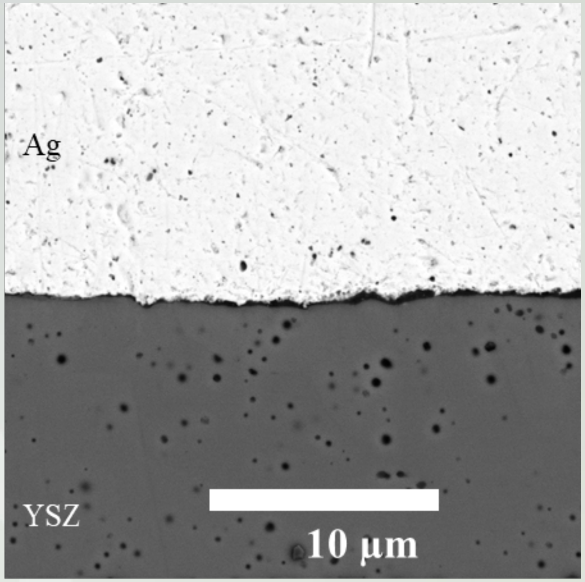
Minimal Changes at the Ag-YSZ Interface



30 Mins Brazed Sample (As-Brazed, Before Oxidation)

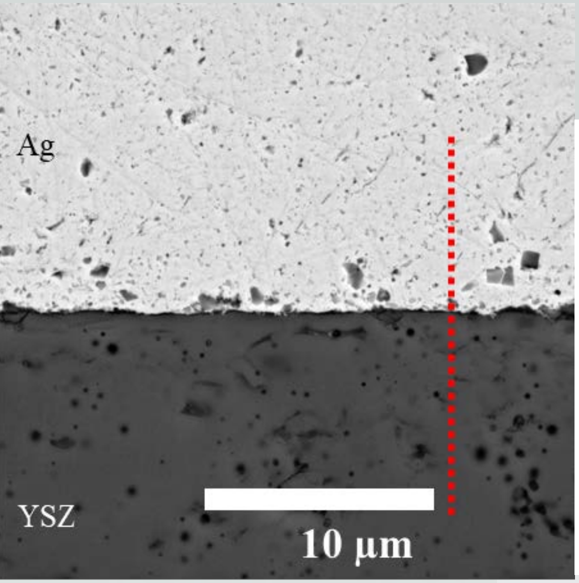


30 Mins Brazed Sample (After 120 Hour Oxidation)

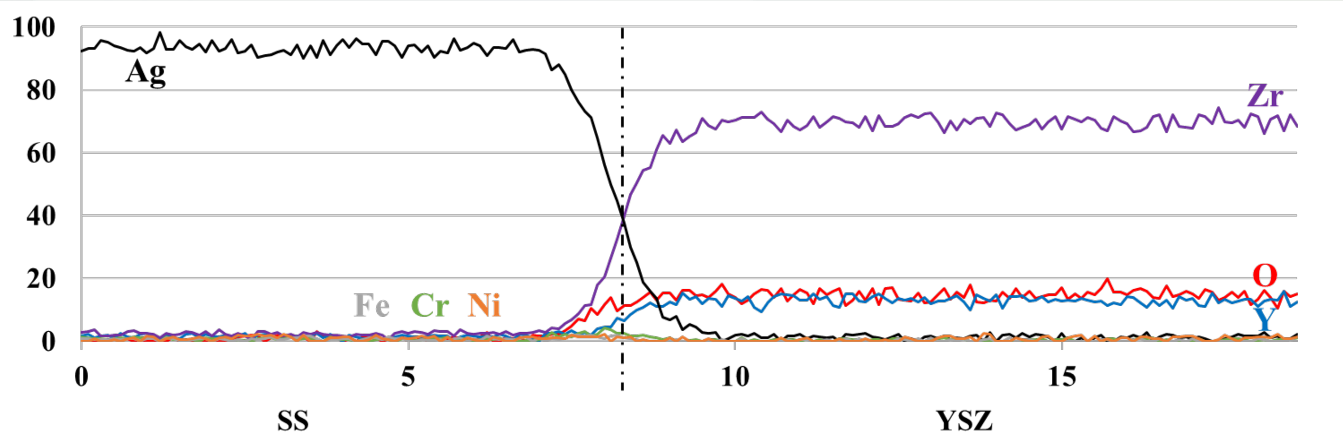


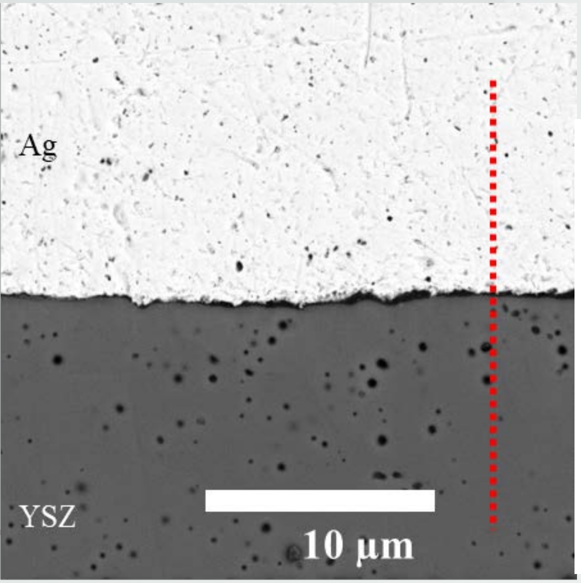
30 Mins Brazed Sample (After 500 Hour Oxidation)

There is a Thin Oxide Layer Developing at the YSZ Interface

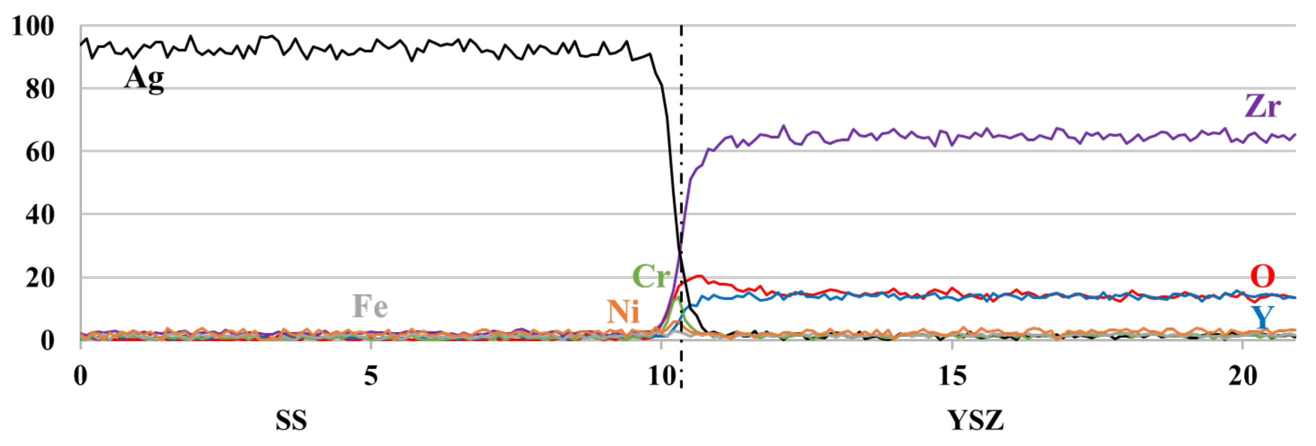


120 Hours of Oxidation

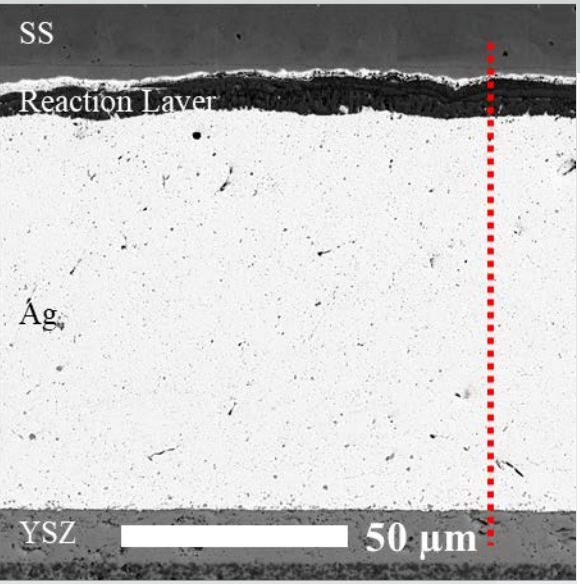




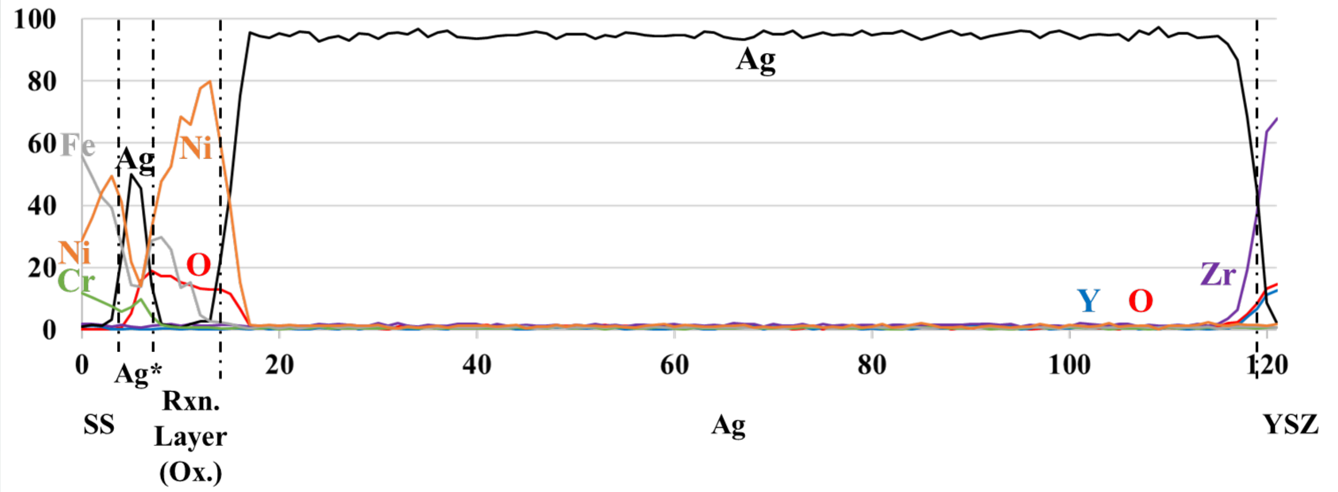
500 Hours of Oxidation

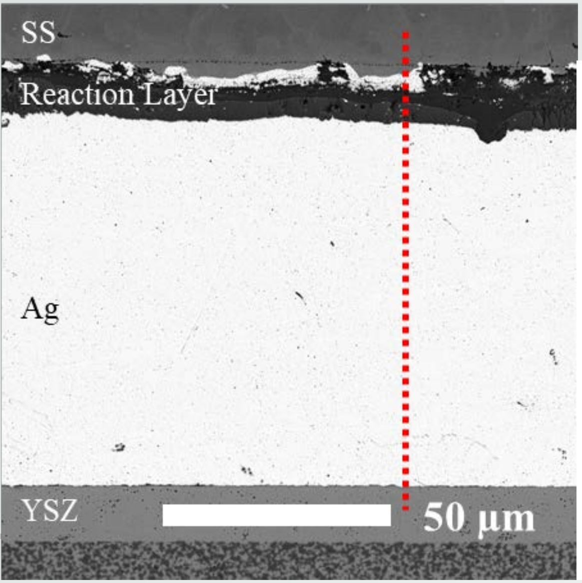


No Compositional Changes Occur within the Ag Upon Oxidation

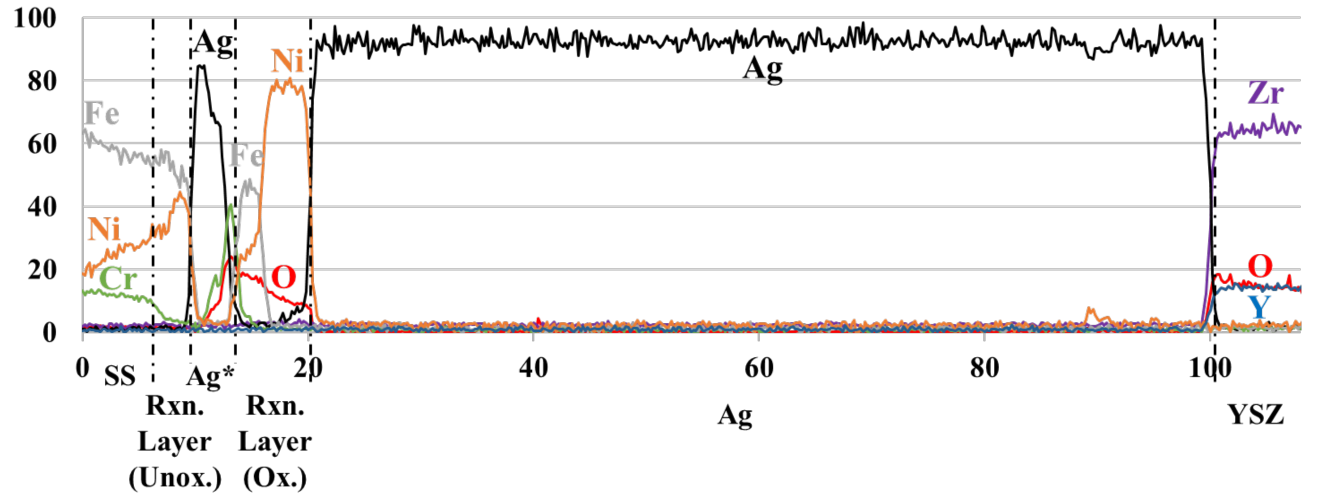


120 Hours of Oxidation

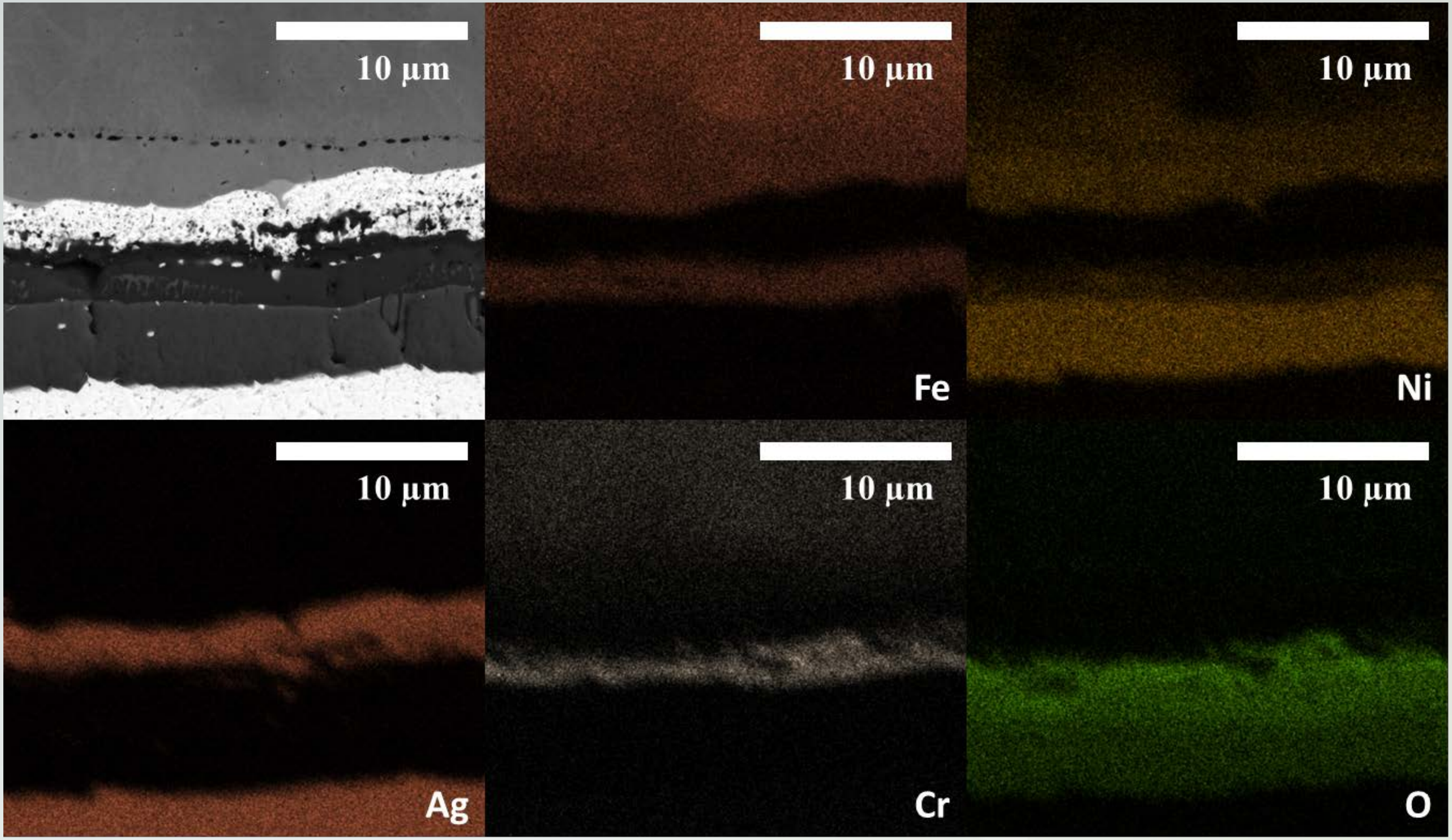




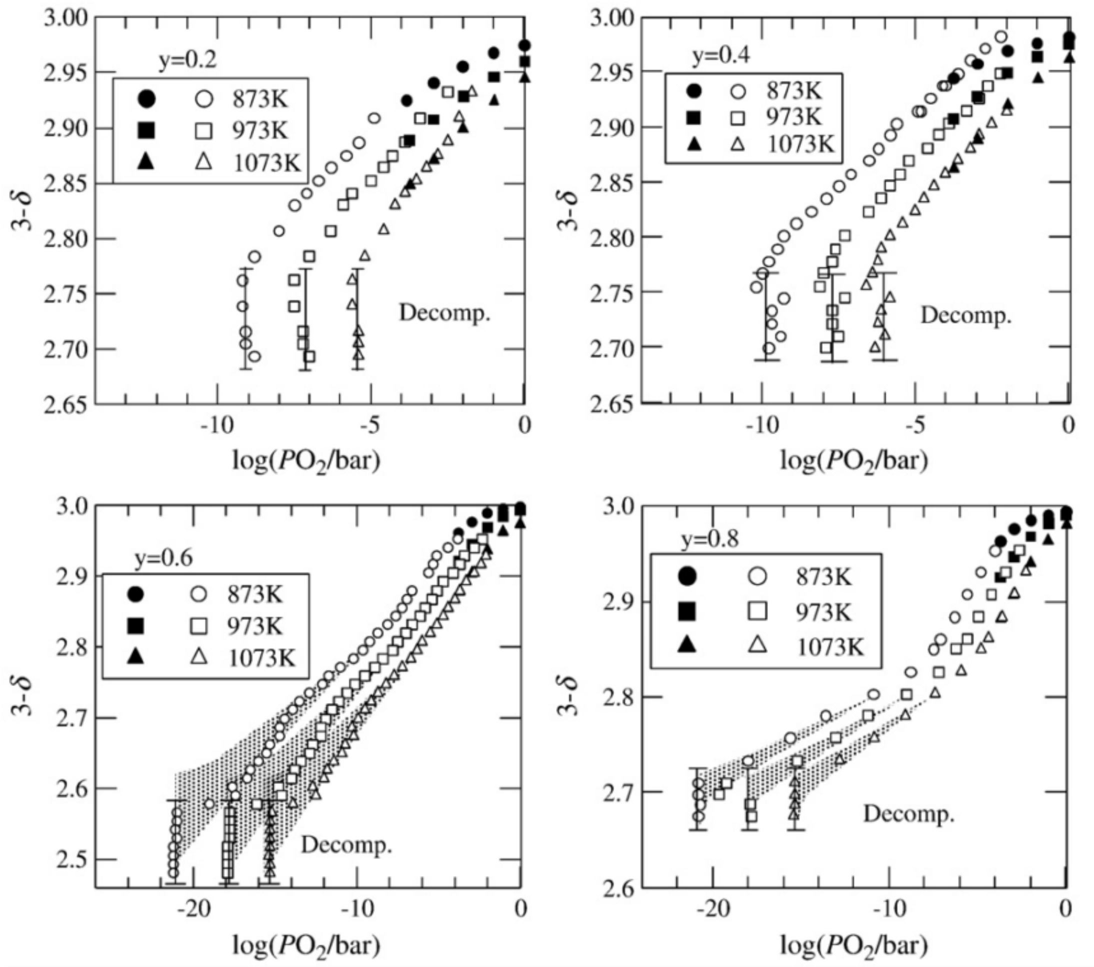
500 Hours of Oxidation



A Protective Chromia Scale Forms on the Stainless Steel after Oxidation



Vacuum Brazing is Incompatible with SOFC Electrode Materials

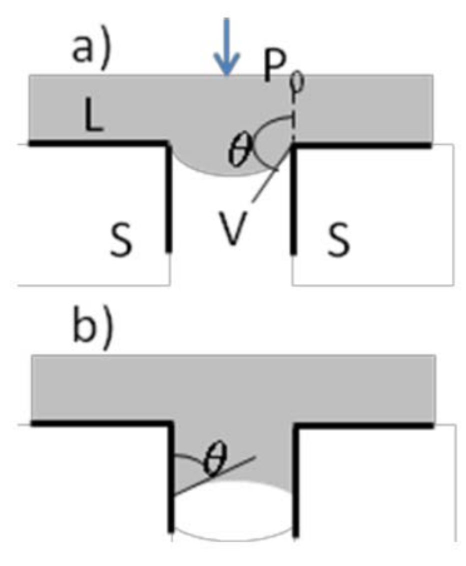


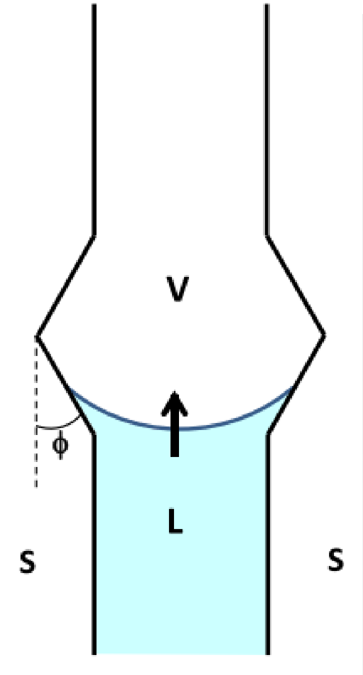
Oxygen nonstoichiometry of $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-\delta}$ *(y= 0.2, 0.4, 0.6, 0.8) as a function of* P_{O2}*. Closed symbols from high temperature gravimetry; open symbols from coulometric titration.*

- For the ***Co rich*** compounds, decomposition occurs at a P_{O2}=***10^{-6} bar*** at 800°C.
- For the ***Fe rich*** compounds, decomposition was observed at lower P_{O2} =***10^{-15} bar*** at 800°C.
- To be safe, brazing should be performed in ***inert/air or moderately reducing*** atmospheres.

Hashimoto, S., et al., *Oxygen nonstoichiometry and thermo-chemical stability of La0.6Sr0.4Co1-yFeyO3-delta (y=0.2, 0.4, 0.6, 0.8).* Solid State Ionics, 2010. **181** (37-38): p. 1713-1719.

Ni has good wettability to be infiltrated by Ag





$$P_C = -(2\sigma_{LV}/r_{eff})\cos\theta$$

$$h^2 = r_{eff}^2 \frac{\Delta P}{4\eta} t$$ (Washburn)

$$h^2 = r_{eff} \frac{\sigma_{LV}\cos\theta}{2\eta} t$$

h: Penetration depth;
θ: Contact angle;
r_{eff}: Effective pore radius;
P_C: Capillary pressure;
σ_{LV}: Surface tension;
ΔP: P_0-P_C, excess pressure;
η: Dynamic viscosity;
t: Time.

➔ *In equilibrium, infiltration happens when* $\theta < 90°$.

When there's increase in pore area

$$\boldsymbol{h^2 = r_{eff} \frac{\sigma_{Lv} \cdot \cos(\theta + \varphi)}{2\eta} \cdot t}$$

➔ *In equilibrium, infiltration happens when* $\theta + \varphi < 90°$.

Eustathopoulos, N., Metals, 2015. ***5*** *(1): p. 350-370.*
Washburn, E.W., Physical Review, 1921. ***17*** *(3): p. 273-283.*

Ni has good wettability to be infiltrated by Ag

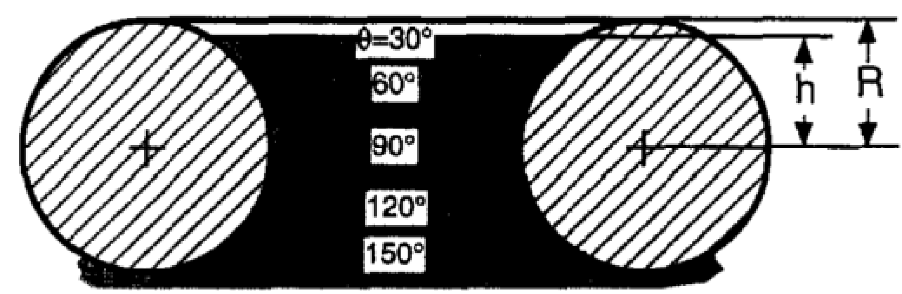
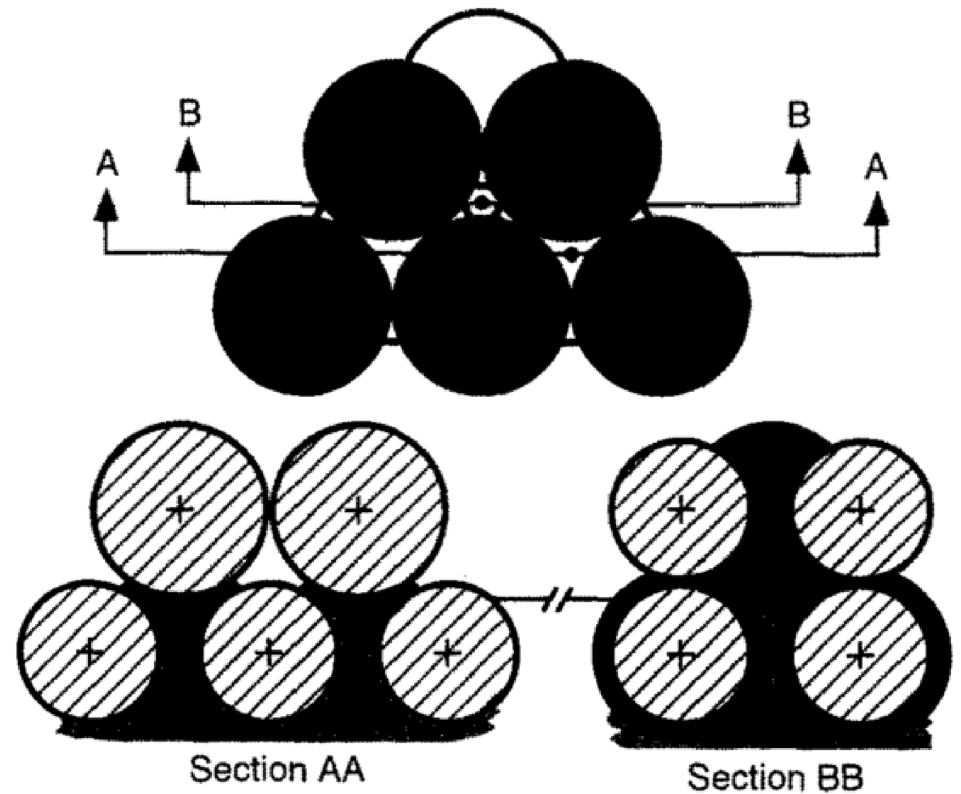
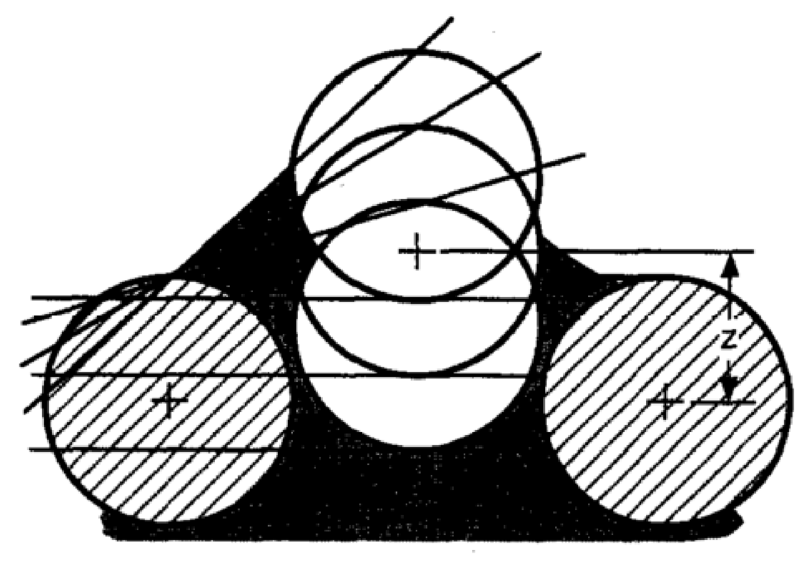


Fig. 4. Cross section of a toroid pore ($R/r = 1$) showing static liquid surface position as a function of contact angle for $\Delta P = 0$ (spontaneous infiltration).

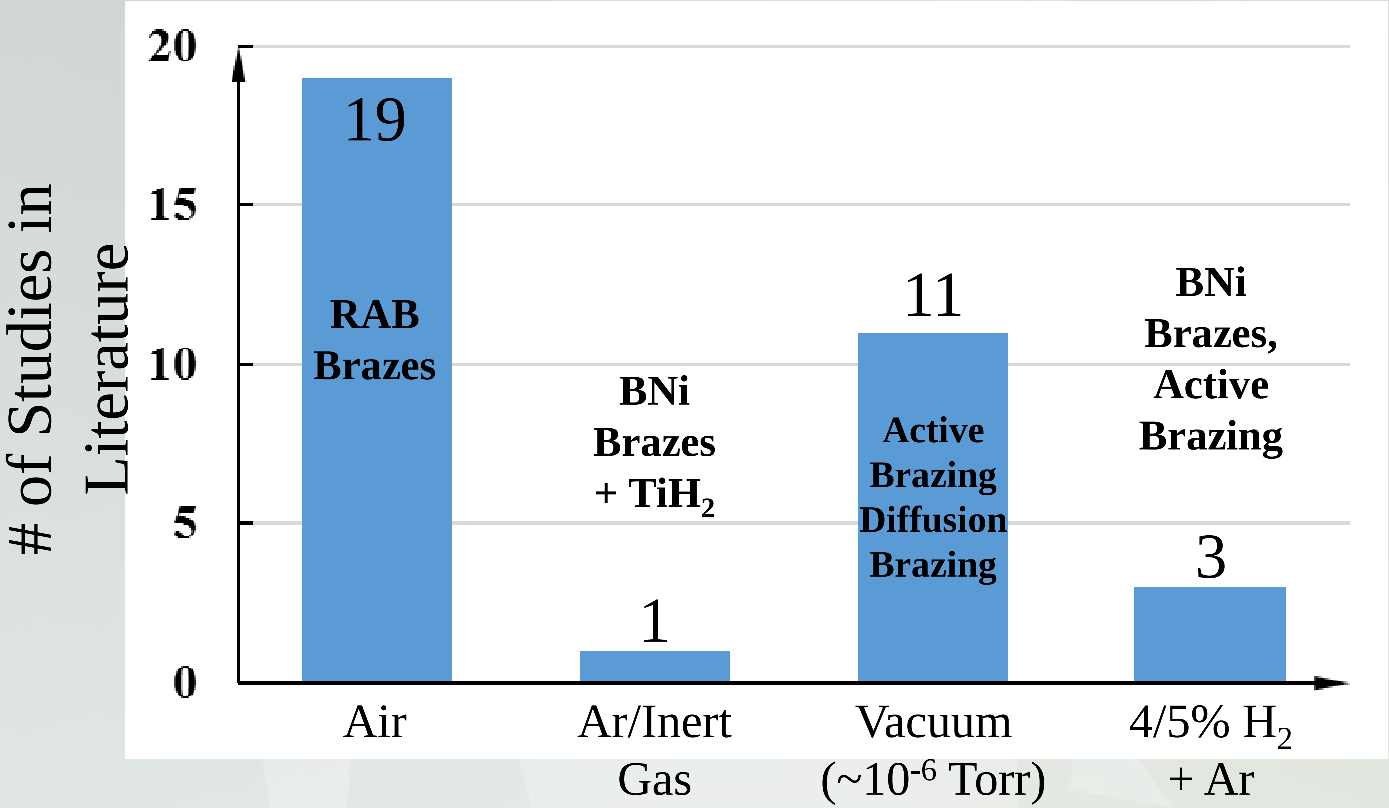




- Through calculation of the ratio between h and R critical wetting angles can be estimated based on packing geometry.
- Smallest critical wetting angle is **50.7°** for perfect penetration.

Trumble, K.P., Spontaneous infiltration of non-cylindrical porosity: Close-packed spheres. Acta Materialia, 1998. ***46*** *(7): p. 2363-2367.*

Brazing SOFC in Inert Gases is a Lightly Studied Topic



[1] Weil, K.S., Journal of Power Sources, 2005.
[2] Kuhn, B., Advanced Engineering Materials, 2014.
[3] Kim, J.Y., Journal of the Electrochemical Society, 2005.
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[23] Singh, M., Journal of Materials Science, 2008.
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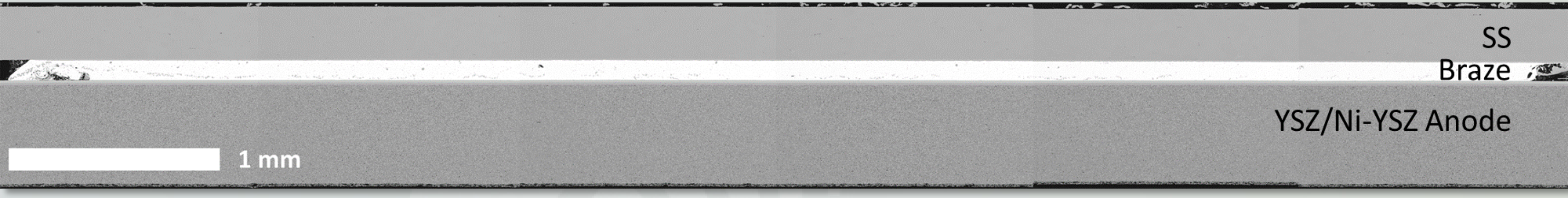
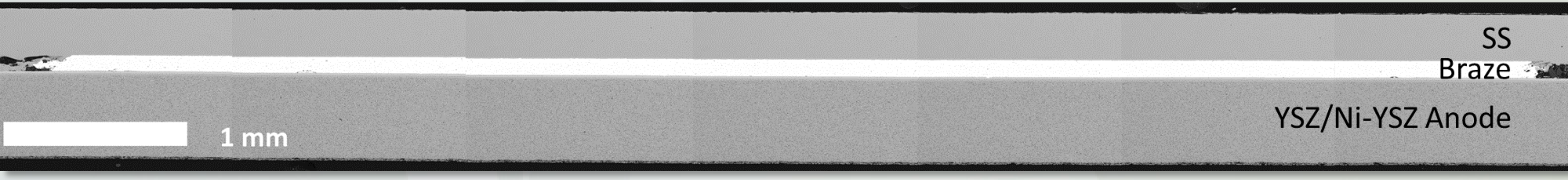
[26] Lin, K.L., Ceramics International, 2012.
[27] Lin, K.-L., Ceramics International, 2014.
[28] Wei, S.H., Journal of Materials Research, 2014.
[29] Lin, K.-L., Journal of the European Ceramic Society, 2014.
[30] Indacochea, J.E., Designing of Interfacial Structures in Advanced Materials and their Joints, 2007.
[31] Cao, J., Materials Characterization, 2013.
[32] Kobsiriphat, W., Journal of Fuel Cell Science and Technology, 2008.
[33] Kim, J.-H., Journal of Fuel Cell Science and Technology, 2009.
[34] Lee, S., Journal of Alloys and Compounds, 2009.

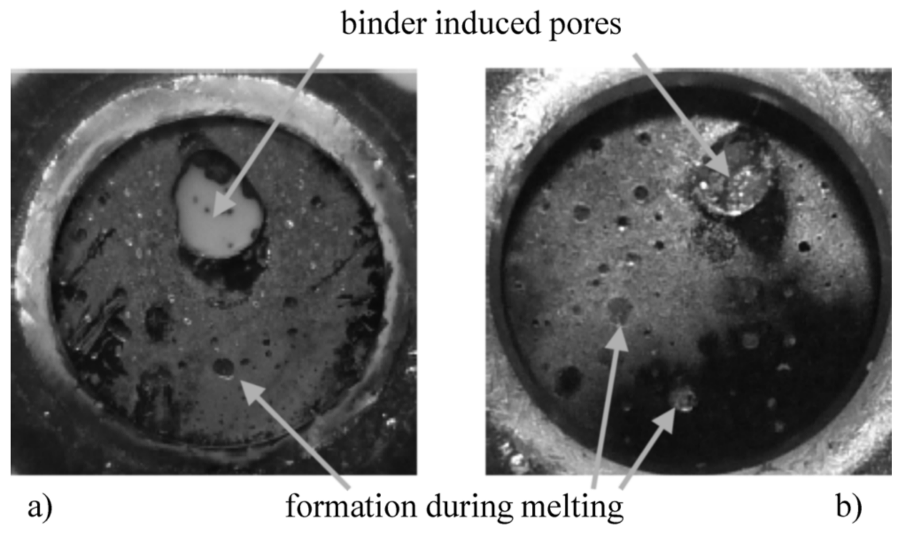
No Formation of Big Type I Pores with Ag Melt Impregnation

15 Mins Brazed Sample



30 Mins Brazed Sample

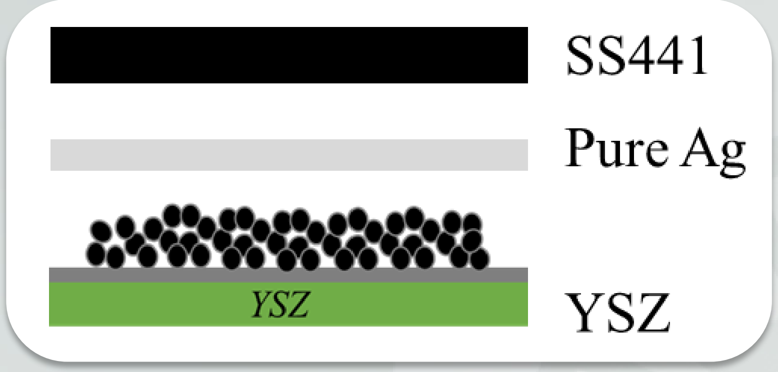


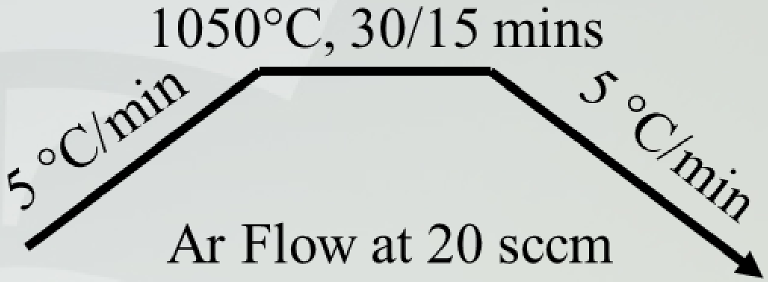


- Solid, dense joints were achieved with the Ag/Ni method using Ag foils.
- Whereas organics (binder) used in the paste form of braze filler materials often lead to big pores.

Bobzin, K., N. Kopp, and S. Wiesner, Influence of Filler and Base Material on the Pore Development during Reactive Air Brazing. Advanced Engineering Materials, 2014. ***16*** *(12): p. 1456-1461.*

Thickness of the Joints





Porous Ni interlayer: ~20 µms

+

Ag foil of 75 µms

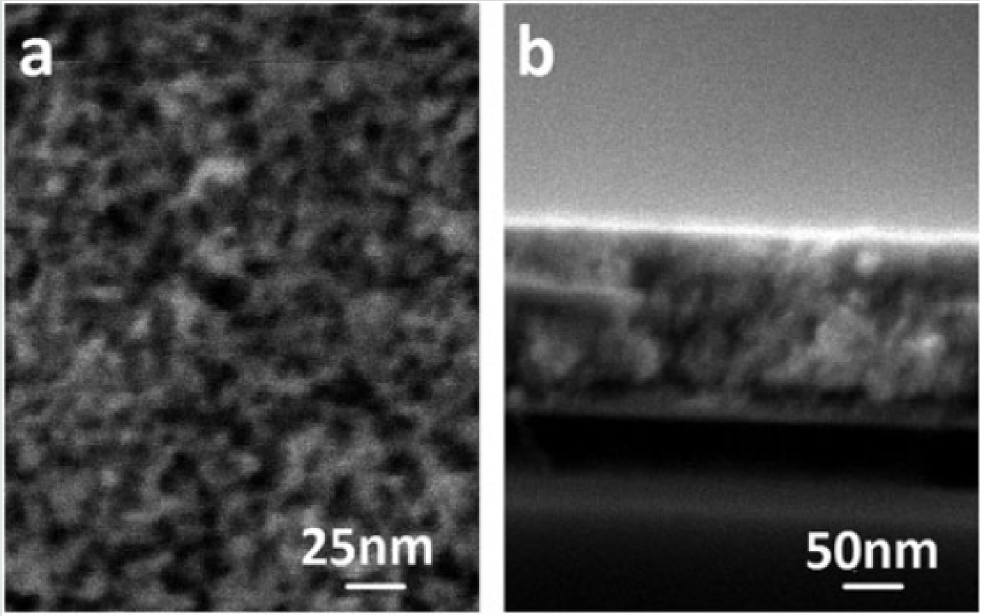
+

Some of the SS elements diffused into the braze

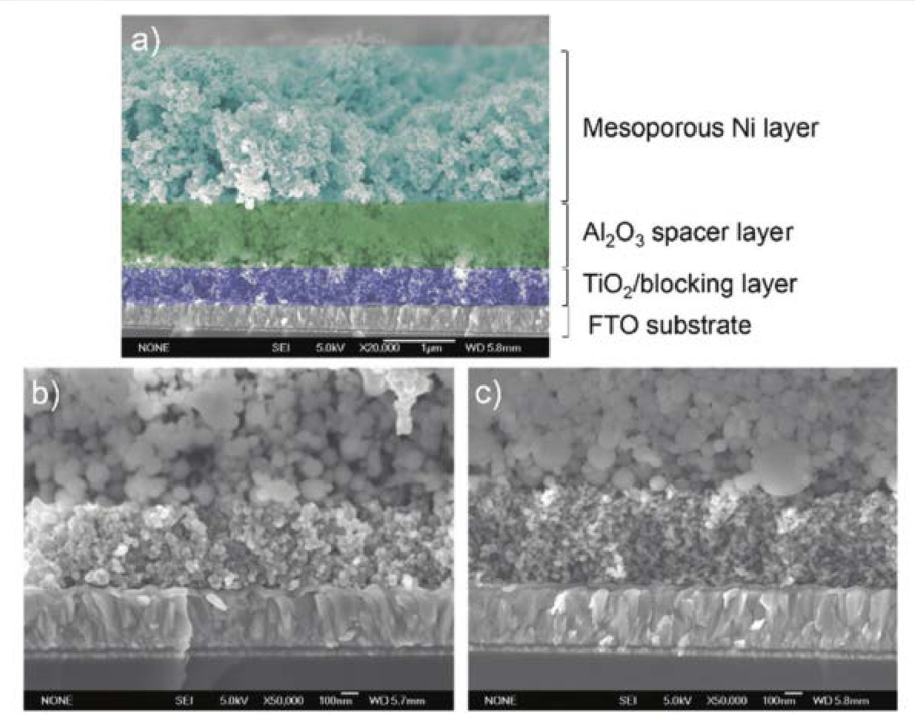
Joint thickness of ~100 µms

Several Strategies for Improving the Air-Tolerance of Ag-Ni Brazes Exist

3. Application of a nano-/meso-porous Ni/Ni-alloy layer (thin film) on the YSZ or SS surface. This can be achieved though chemical dealloying or simple reduction.



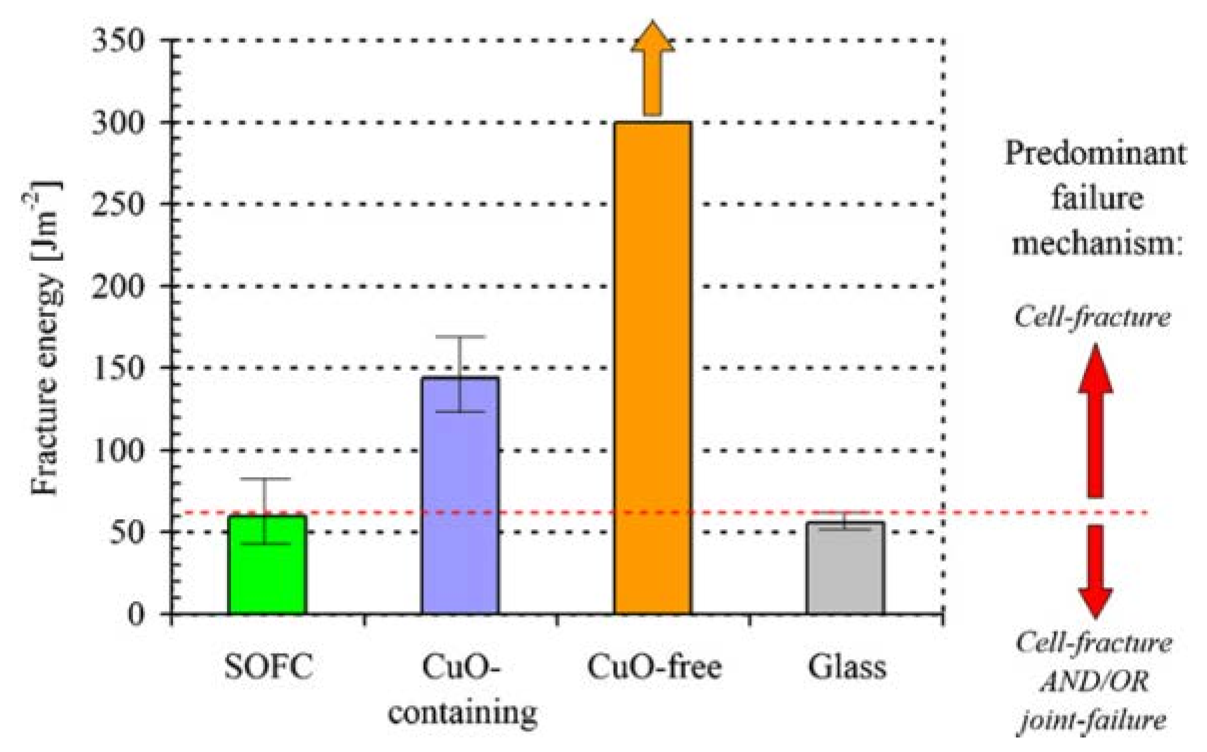
Chemically dealloyed $Ni_{33}Mg_{67}$ thin film (pure Ni)



Wang, L. and T.J. Balk, Synthesis of nanoporous nickel thin films from various precursors. Philosophical Magazine Letters, 2014. 94 (9): p. 573-581.

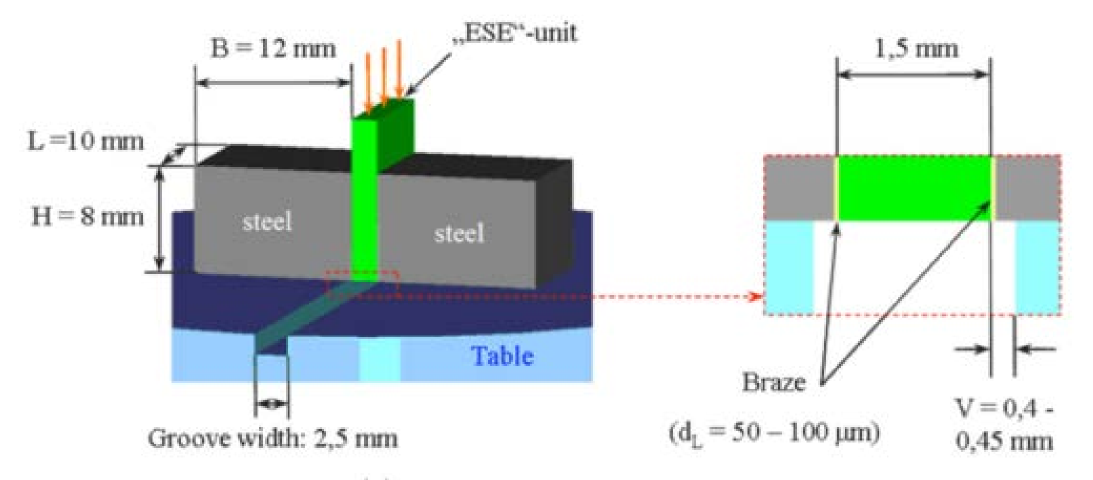
Ku, Z.L., et al., A mesoporous nickel counter electrode for printable and reusable perovskite solar cells. Nanoscale, 2015. 7 (32): p. 13363-13368.

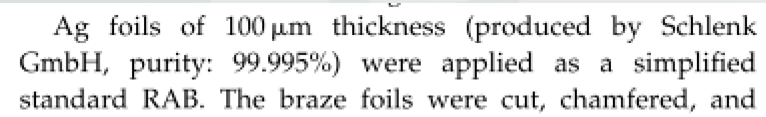
On Ag joint strength

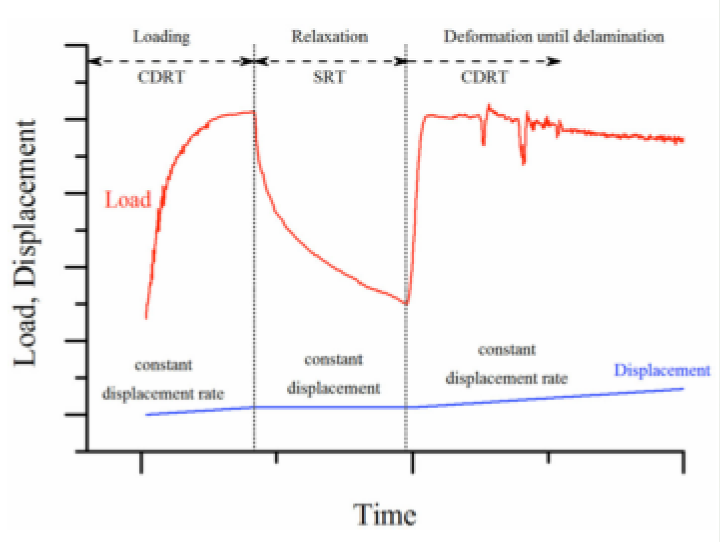


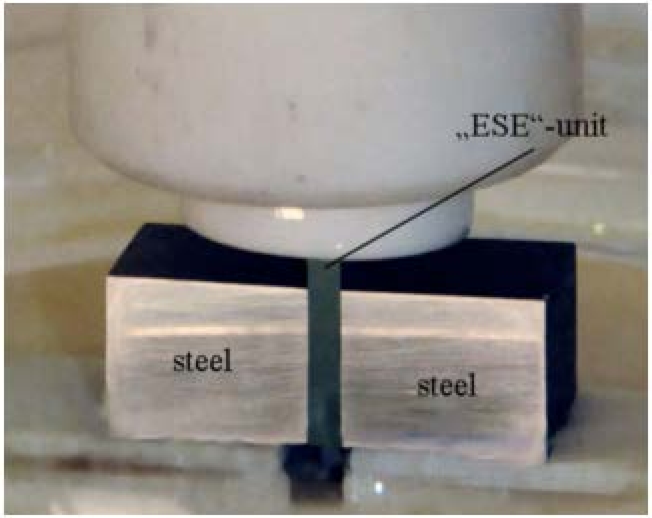
Ku, Z.L., et al., *A mesoporous nickel counter electrode for printable and reusable perovskite solar cells.* Nanoscale, 2015. **7** (32): p. 13363-13368.

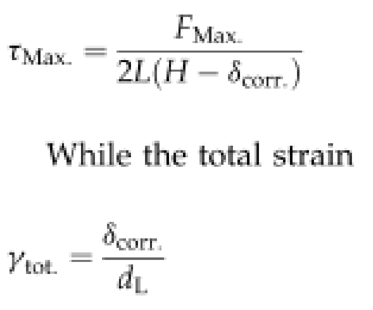
Kuhn, 2014




Ag foils of 100 µm thickness (produced by Schlenk GmbH, purity: 99.995%) were applied as a simplified standard RAB. The braze foils were cut, chamfered, and






$$\tau_{\text{Max.}} = \frac{F_{\text{Max.}}}{2L(H - \delta_{\text{corr.}})}$$

While the total strain

$$\gamma_{\text{tot.}} = \frac{\delta_{\text{corr.}}}{d_L}$$

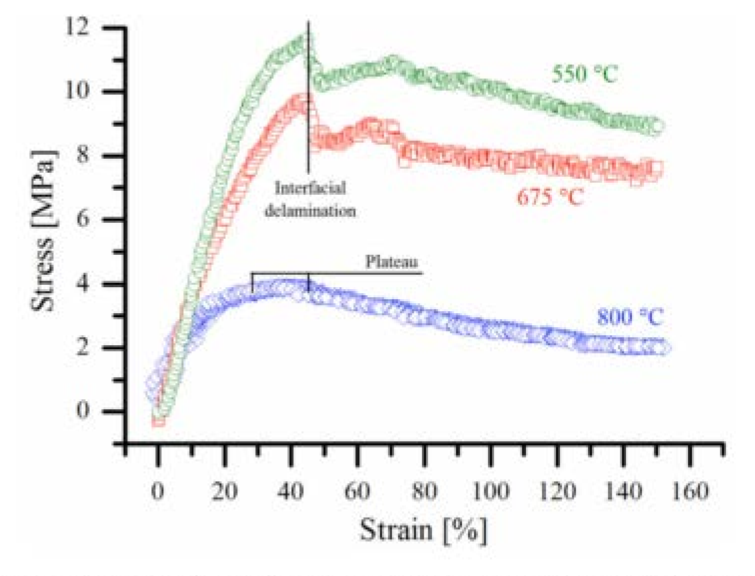
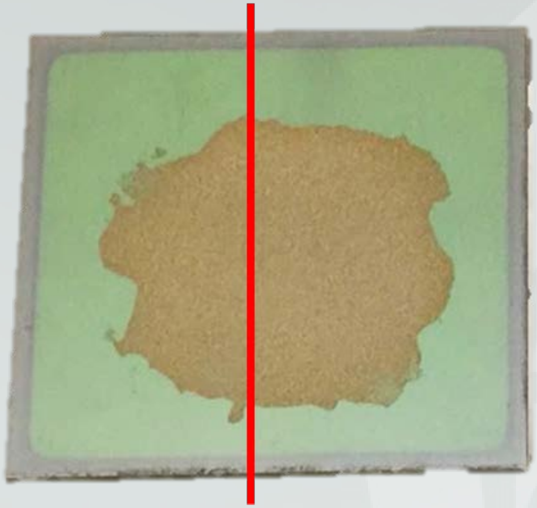


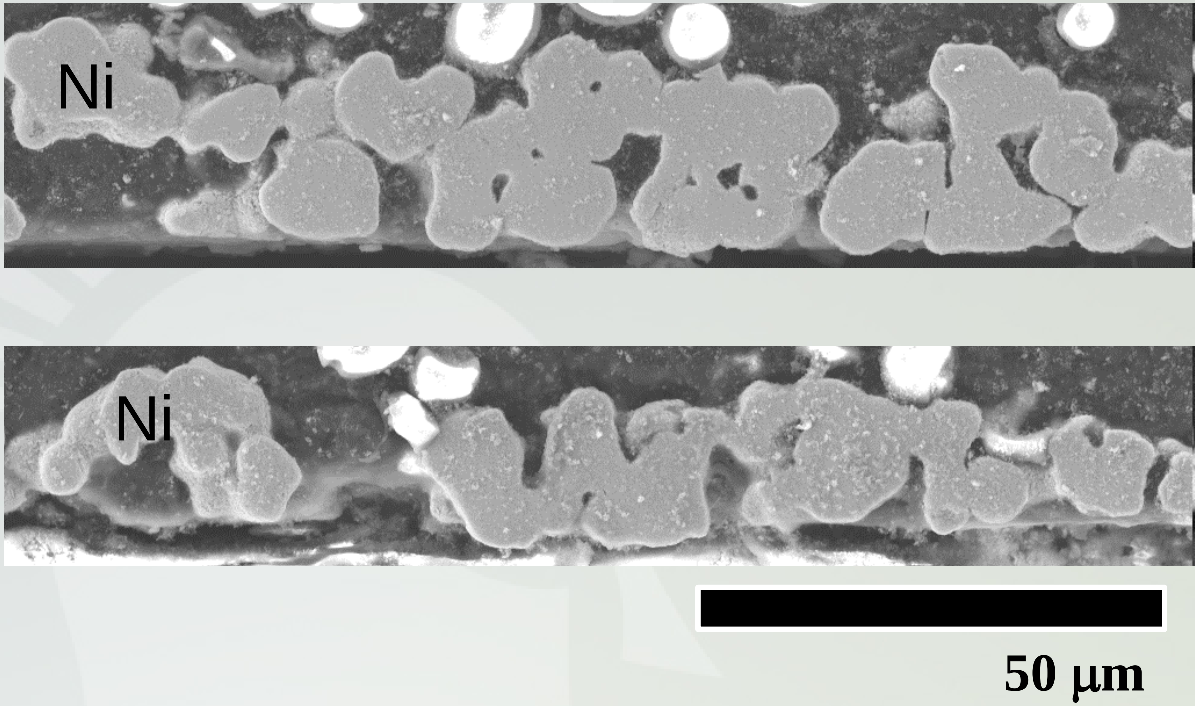
Fig. 5. Stress-Strain curves of as-brazed pure Ag-joints at 550, 675, and 800 °C in air.

Porous Interlayer of Ni Layer was Achieved on the YSZ



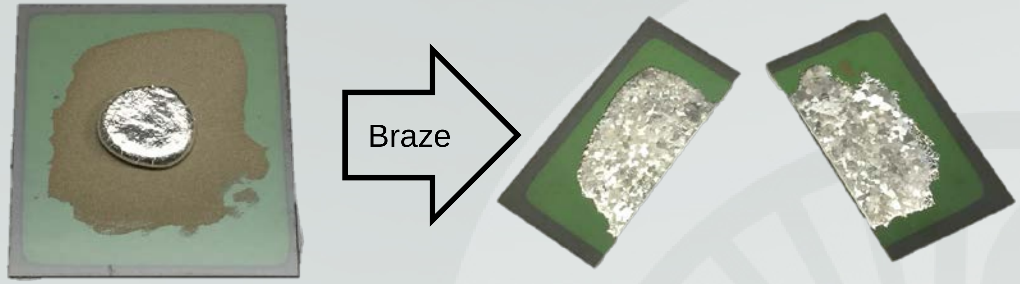
- Sample cross-sectioned to examine the as-sintered microstructure.

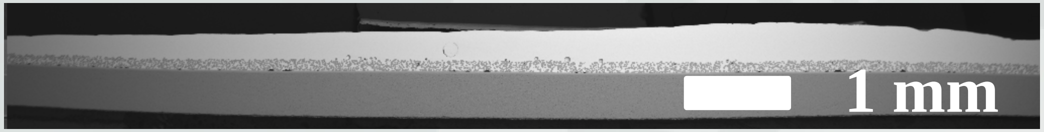
- Hot mounted @ ~30kN, ~190° C

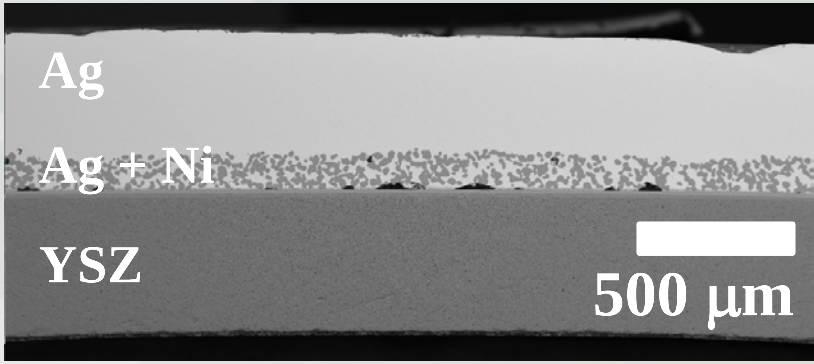


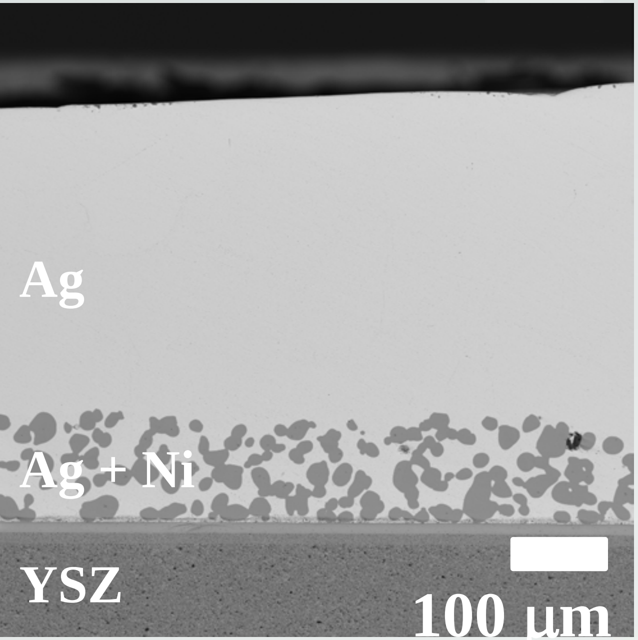
A partially sintered Ni particle interlayer has formed on the YSZ surface.

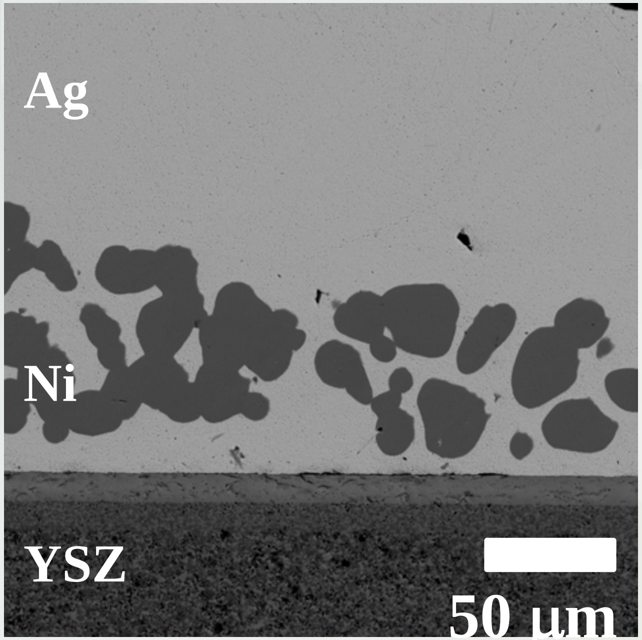
No formation of big Type I pores with Ag infiltration

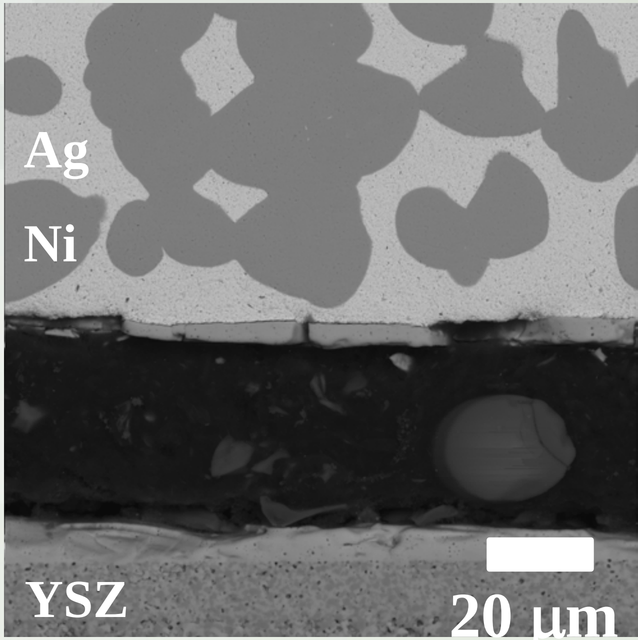












Ag-Ni Braze Optimization

1. Different Ni particle sizes
   - The smallest particle size that can still provide good “wetting” of the Ag on YSZ;
2. Layer thickness of the pre-sintered Ni network
   - The thinnest layer of Ni to achieve similar wetting characteristics;
   - Other technique to apply the Ni layer;
   - Relationship to the formation of the reaction layer at the SS interface.
3. Brazing time and temperature
   - Control of the distribution of Ni (particles/layer);
   - The resulting mechanical properties after oxidation (with different as-brazed microstructures).

Ag-Ni Braze Joint Quality Control

1. Joint Radiography at Delphi ➔ to check for ***Type I pores***
   - With no organics used in the actual brazing step, there should be no Type I pores

2. Test braze ***joint strengths*** (tensile tests done here at MSU)
   - Systematic tests to obtain statistically meaningful strength;
   - Bend tests to assess the bonding strength.

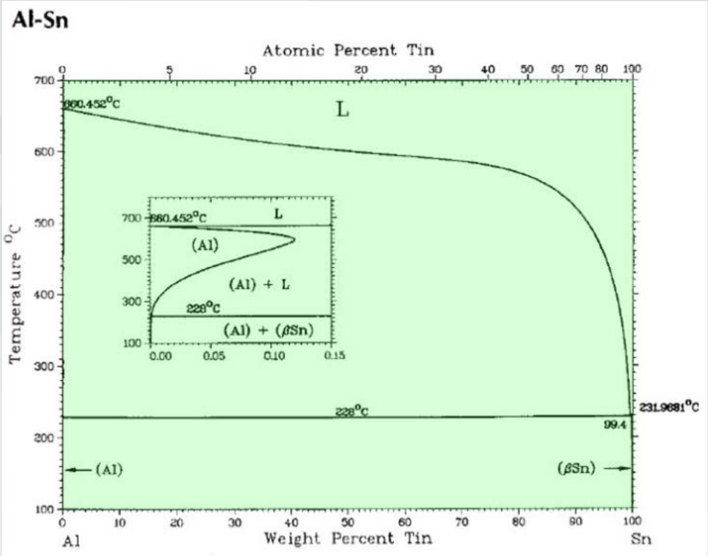
3. Test braze joint resistance to rapid ***thermal cycling*** at Delphi
   - Again the TMC performance should be similar to Ag-CuO since the matrix is still ductile Ag

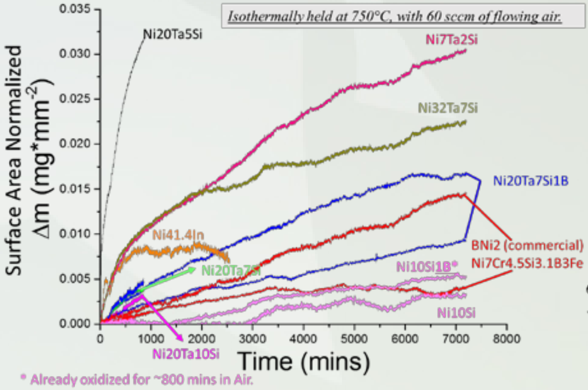
4. Test braze joint ***permeability*** (at MSU)
   - According the previous literature study, the metallic/braze seal are much better in gas permeability in TMC tests.
   - Also, consider the Type II pores to be suppressed in the long run, gas tightness in operation should be better.

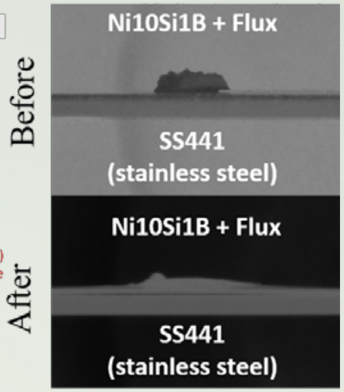
Porous Metal Interlayers for Other Brazing Systems

1. Other two-metal systems
    - Lower temperature systems (like Sn/Al) for lower brazing temperature applications.

2. Incorporate with previous investigated Ni-base brazing systems
    - In the previous work, a Ni-based brazing system with good melting range, excellent oxidation resistance was developed for SOFC applications;
    - The only problem with this Ni-based system is poor wetting on the YSZ, which could be solved with the new porous metal interlayer technique.

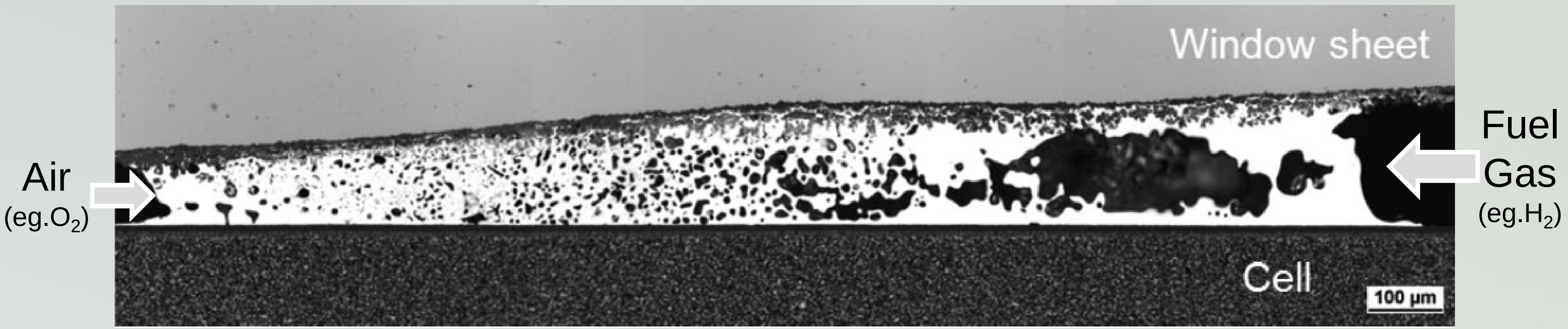






ASM handbook Volume 03

Standard Ag-CuO Brazes Have Durability Problems

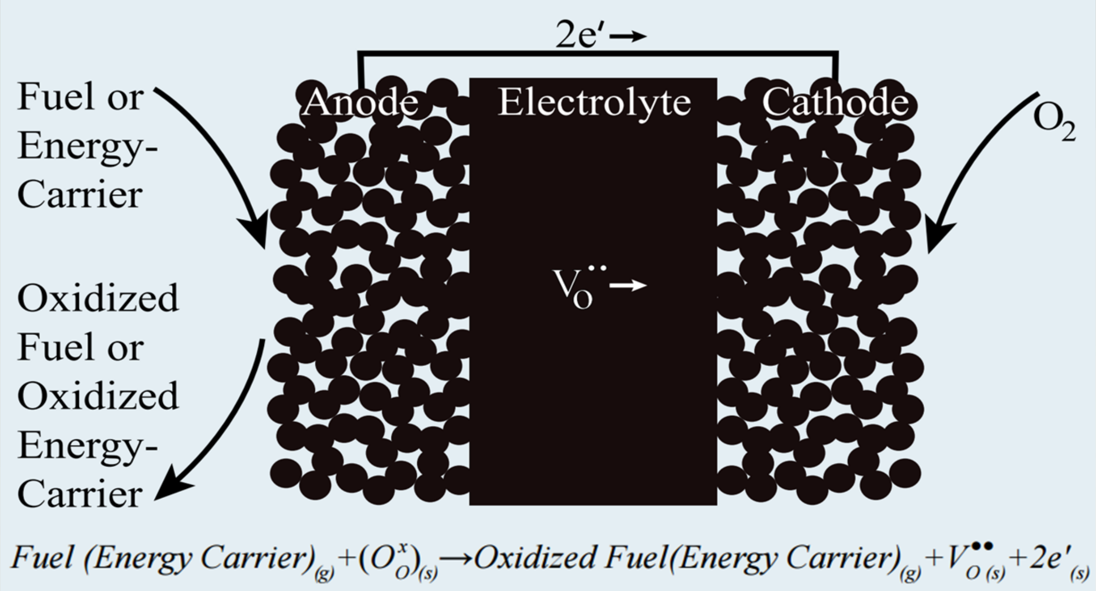


Cross-section of the brazed section
(an extreme case)

- The extremely high <u>hydrogen and oxygen diffusivities</u> in silver (8×10^{-5} and 2×10^{-5} cm^2/sec at 750° C, respectively), which in long-term operations will lead to:
    - ➢ Reduction of copper oxide within the braze ➔ **Pores** along the interface
    - ➢ Formation of steam pockets within the braze ➔ **Pores** in the matrix, sponge-like structure
- These pores can lead to <u>mechanical failure and hermetic seal failure.</u>

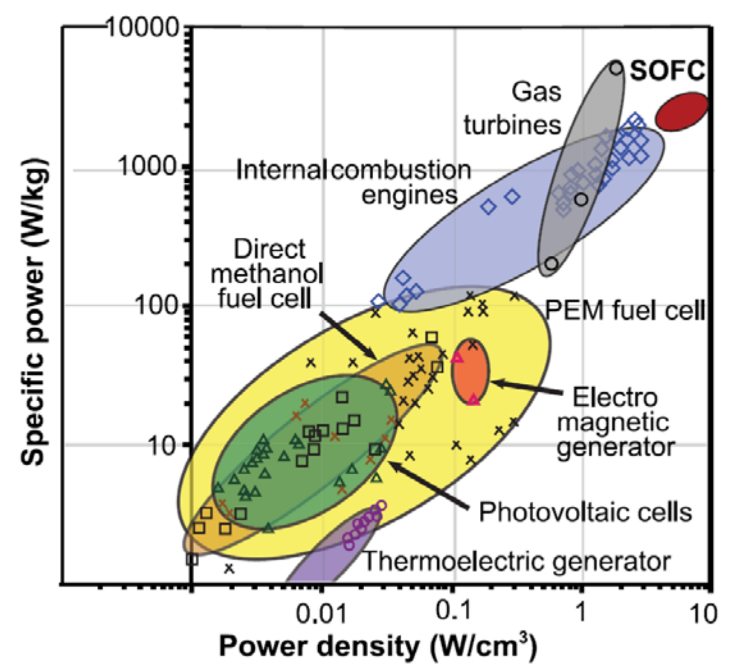
T. Bause, J. Malzbender et. al., Damage and Failure of Silver Based Ceramic/Metal Joints for SOFC Stacks,2013

Solid Oxide Fuel Cell (SOFC) is a Promising Alternative Energy Technology



$$Fuel\ (Energy\ Carrier)_{(g)} + (O_O^x)_{(s)} \rightarrow Oxidized\ Fuel(Energy\ Carrier)_{(g)} + V_{O\,(s)}^{\bullet\bullet} + 2e'_{(s)}$$

Components and operation of a typical SOFC



Gravimetric and volumetric power densities for various electricity generation technologies.

J. D. Nicholas, "Highlights from the 2013 National Science Foundation Solid Oxide Fuel Cell Promise, Progress, and Priorities (SOFC-PPP) Workshop"
E. D. Wachsman, K. Lee, "Lowering the Temperature of Solid Oxide Fuel Cells", Science, 2011

Research Team

- **MSU:**
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  - Yue Qi PI, Computational Materials Science
  - Thomas R. Bieler PI, Metallurgy
  - Quan Zhou Graduate Student (Ni-based Brazes)
  - Yuxi Ma Graduate Student (Cu and Co-based Brazes)
  - Tridip Das Graduate Student (Simulations)
  - Joe Phongpreecha Graduate Student (Simulations)

- **Delphi:**
  - Rick Kerr (and his team …)
  - Stephanie Surface
  - Bryan A. Gillispie