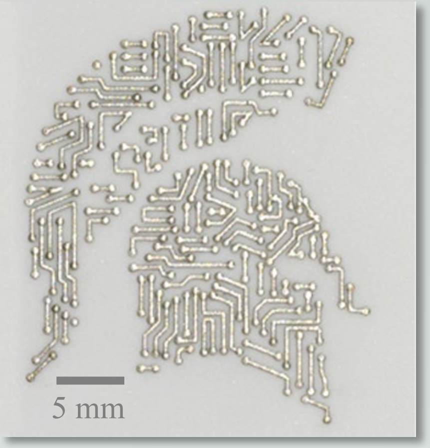

A Combined "Final" Summary: High-Performance Ag:Ni Brazes and Circuit Pastes for SOFC/SOEC Applications

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4 Computational Mathematics, Science & Eng. Department, Michigan State University

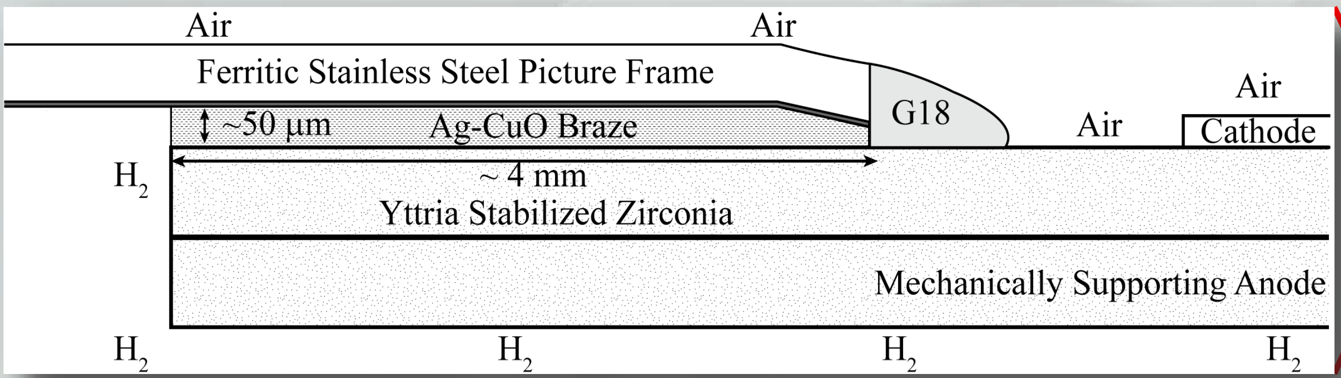
DE-FE-0023315 Braze Project Dates: 10/1/2014 to 9/30/2018
DE-FE-0031672 Circuit Project Dates: 8/17/2018 to 8/16/2022
Program Managers: Joe Stoffa, Venkat Venkataraman, Drew O'Connell
Industrial Partner: Delphi Automotive
Please Send Technical Inquiries to jdn@msu.edu

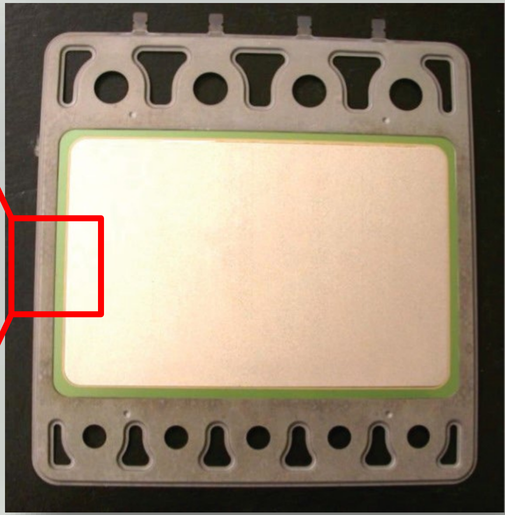
October 27, 2022

TALK Outline

1. Ag:Ni Brazes
2. Ag:Ni Circuit Pastes/Current Collectors/Electrical Contacts

Conventional Ag-CuO Reactive Air Brazes Have Many Benefits

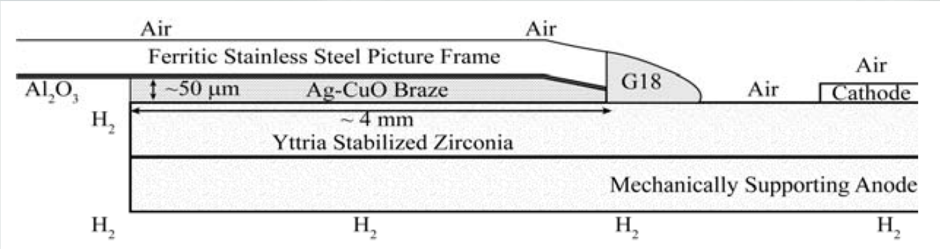




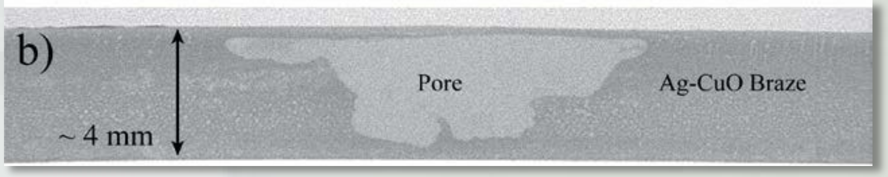
Delphi Technologies Inc, U.S. Patent No US7855030B2

- Ag-4CuO brazes are very ductile, so CTE mismatch is no concern
- Ag-4CuO brazing can be performed in air
- No flux is needed to utilize Ag-4CuO brazes
- The enhanced wetting provided by CuO allows Ag-4CuO brazes to be used to bond to a variety of ceramics

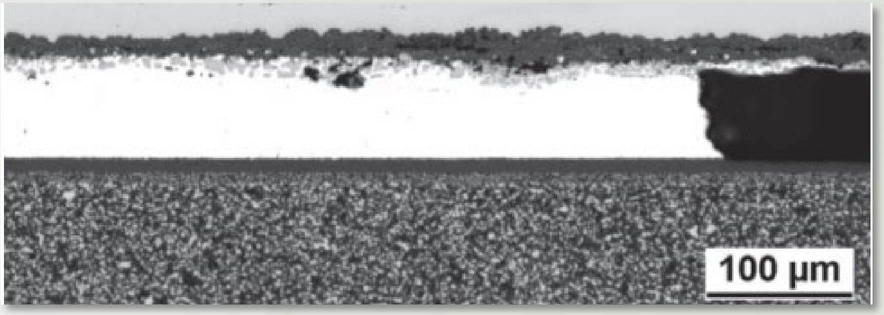
Reactive Air Brazes Have Several Fatal Flaws



1. Ag-CuO brazes only partially wet ceramics ($\theta = 45^o$) resulting in manufacturing defects (**Type I Pores**);



2. CuO volume reductions by hydrogen during SOFC operation can result in **Type II Pores;**



3. <u>After ~10,000 hours</u>, severe **Type III pores** form when dissolved hydrogen and oxygen in the Ag react to form water pockets/pores.

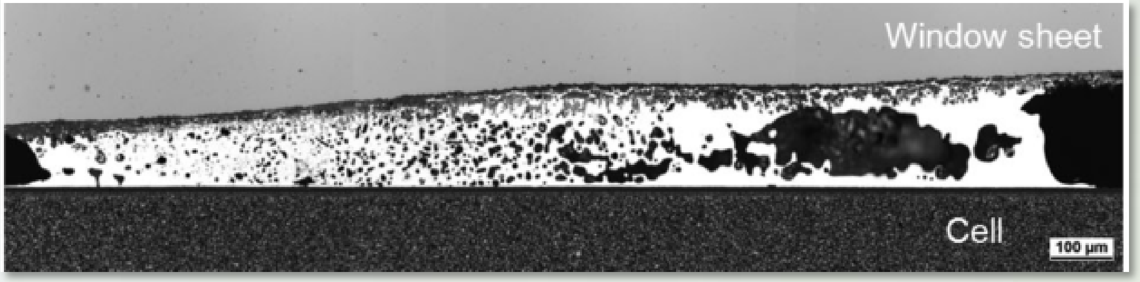
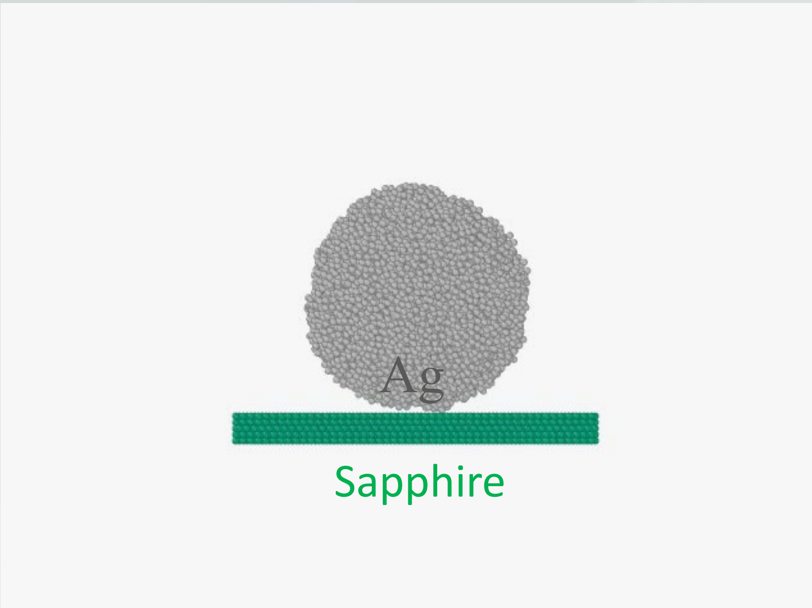
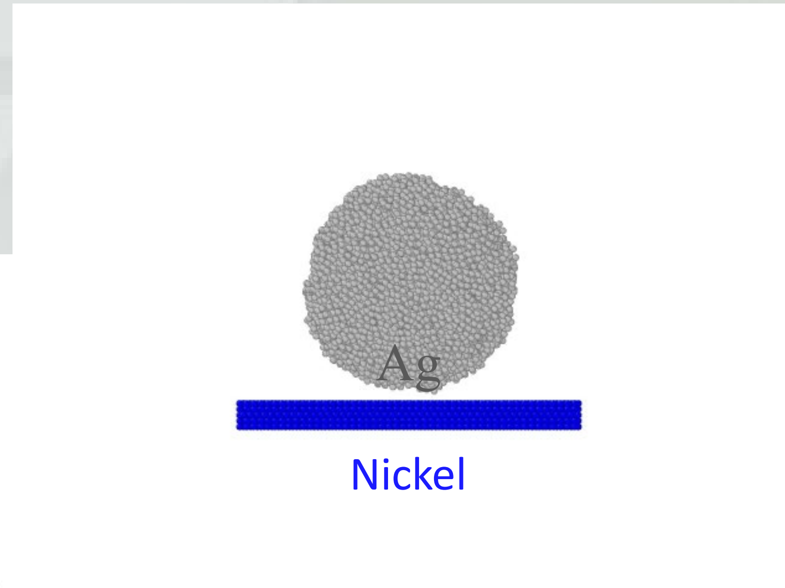


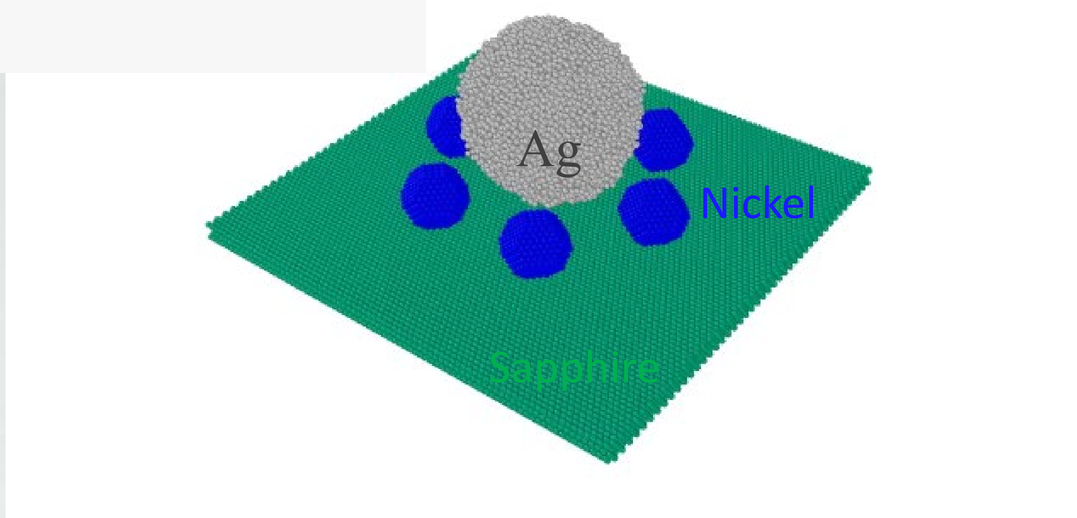
Image b) courtesy of Delphi Automotive. The bottom two images are from Bause *et al*., *Fuel Cells*, v13 p578 (2013).

Simulations Suggest Porous Ni Interlayers Can Be Used To Promote Ag Wetting and Spreading on Ceramics



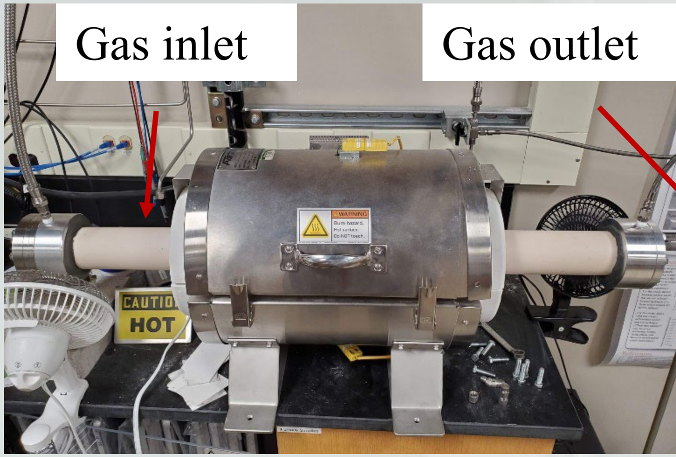


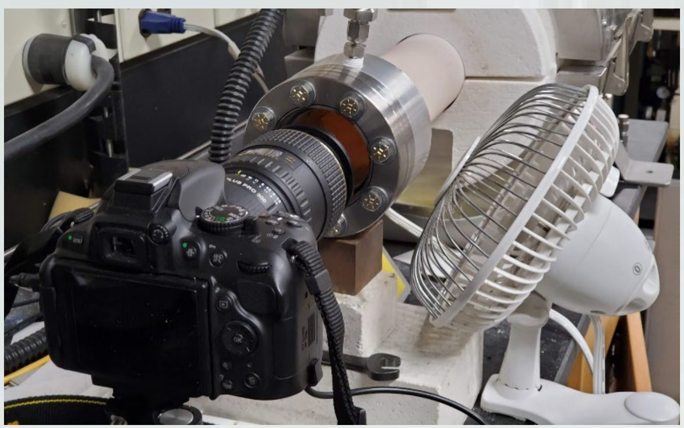
* Note, this modeling suggests that Ag:Ni circuits can be produced with either "isolated" Ni particles, or "continuous", porous Ni layers.



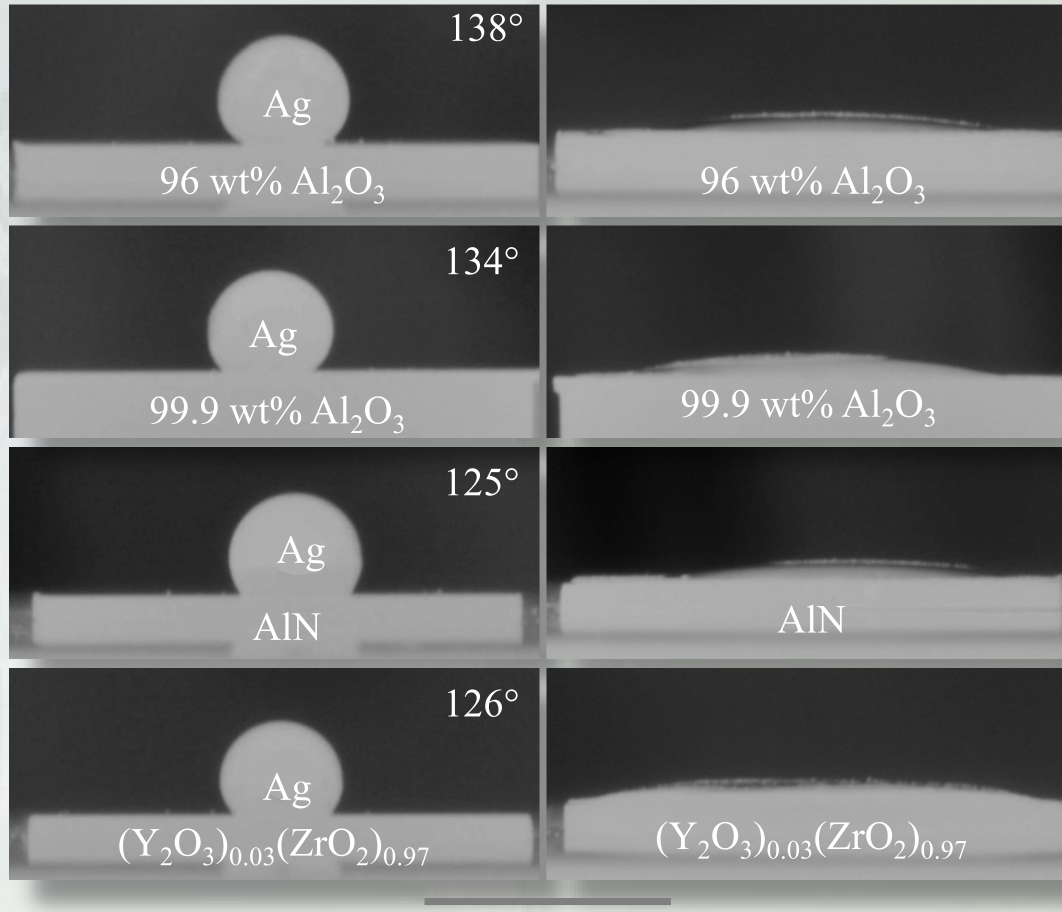
Park *et al.*, *Acta Materialia*, v199 p551 (2020).

Experiments Confirm Porous Ni Interlayers Can Be Used To Promote Ag Wetting and Spreading on a Variety of Ceramics





Without Porous Ni | **With Porous Ni**



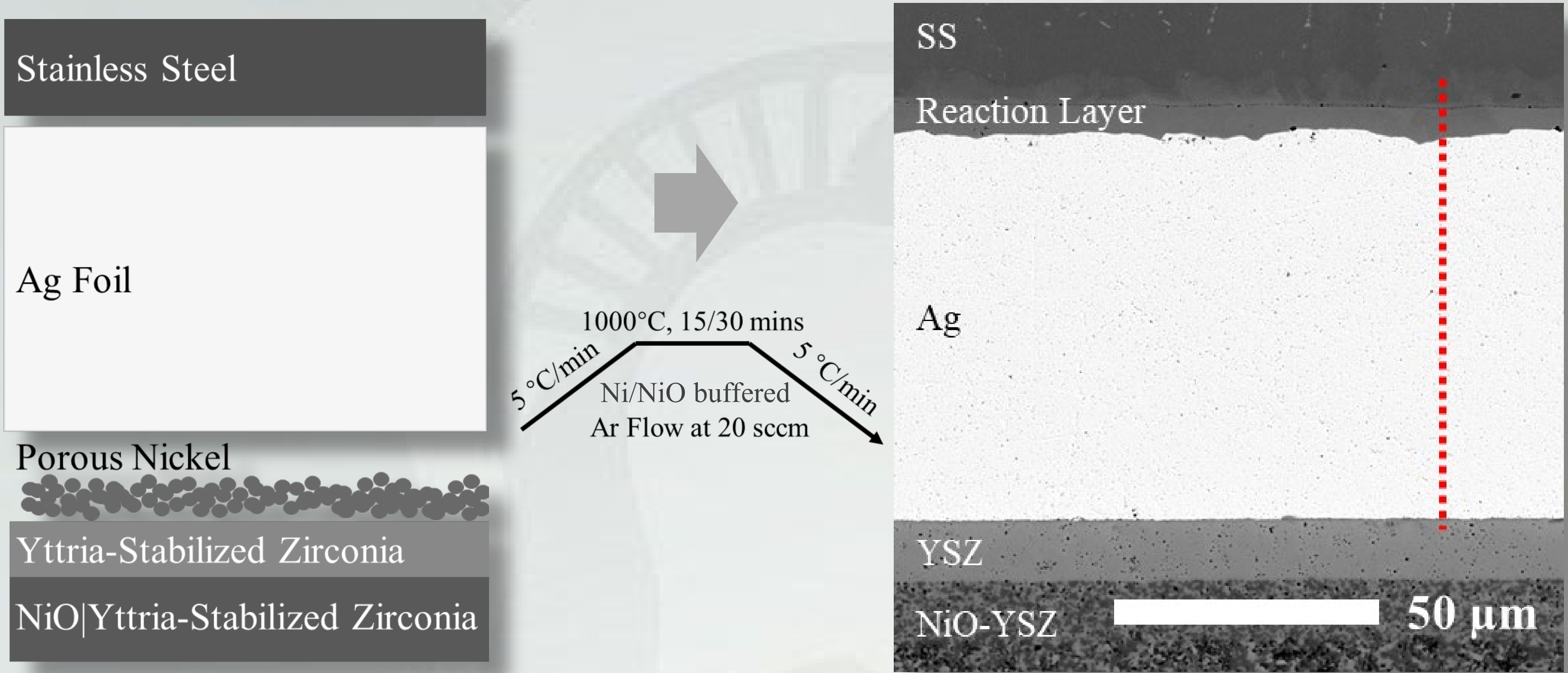
5 mm

* Note, all wetting images were taken in 20 sccm of 1025°C Ni/NiO buffered Ar.

** Continuous, screen-printed, porous Ni layers were used in all the work in this talk, unless noted otherwise

Hu *et al.*, *Scripta Materialia*, v196 p113767 (2021).

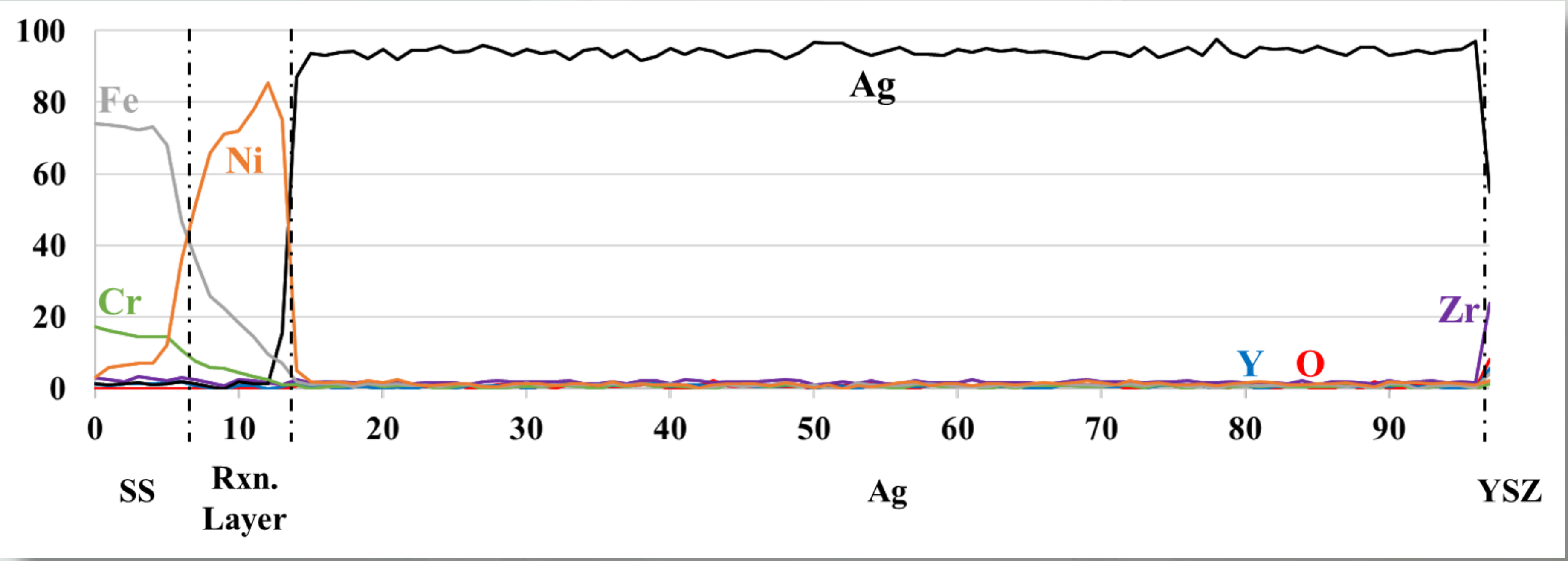
Ag:Ni Can Be Used Instead of Reactive-Air Brazes to Bond Metals to Ceramics Without Type I Pores Forming



* Note, a Ni/NiO buffered atmosphere provides enough oxygen to remove residual carbon in the fired Ni paste, but not enough oxygen to oxide Ni during joint manufacture.

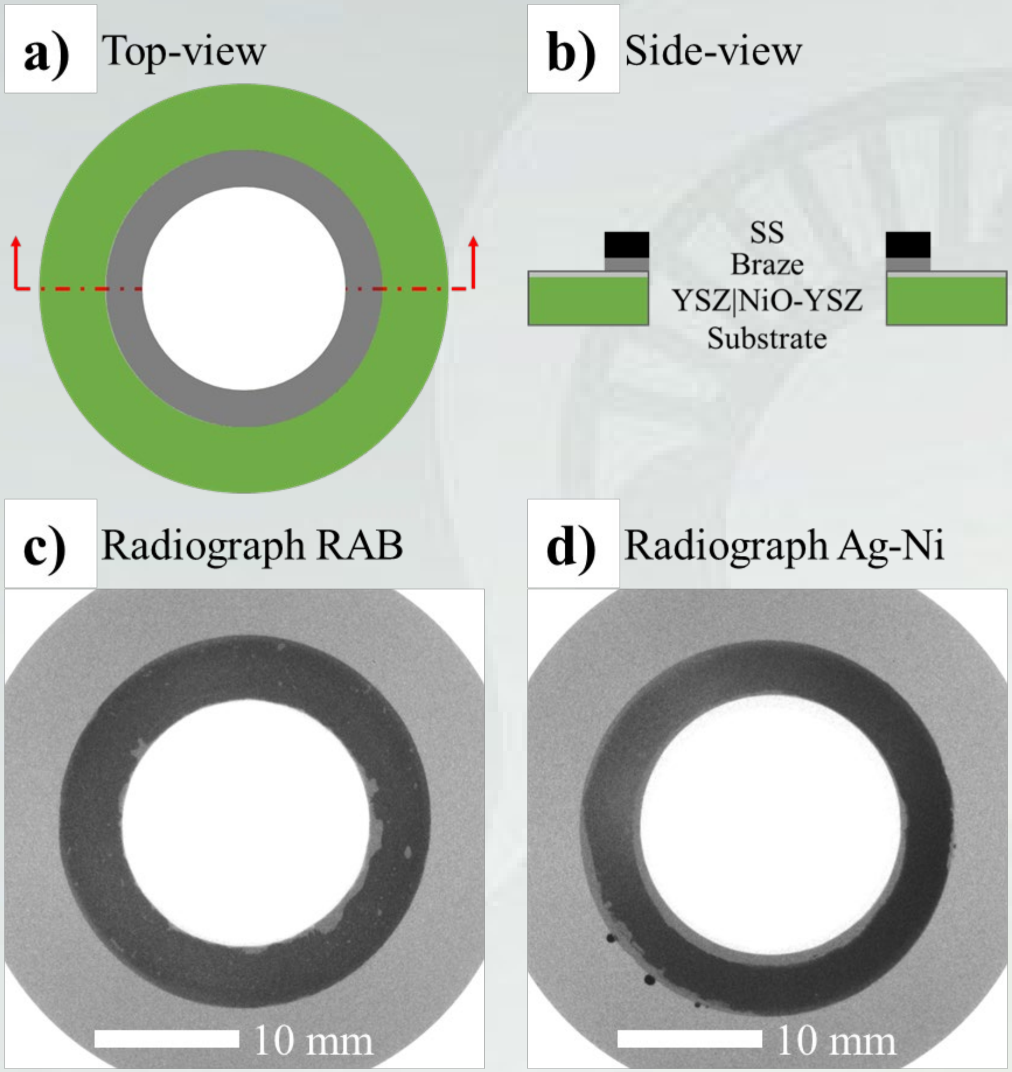
Zhou *et al.*, *Acta Materialia*, v148 p156 (2018).

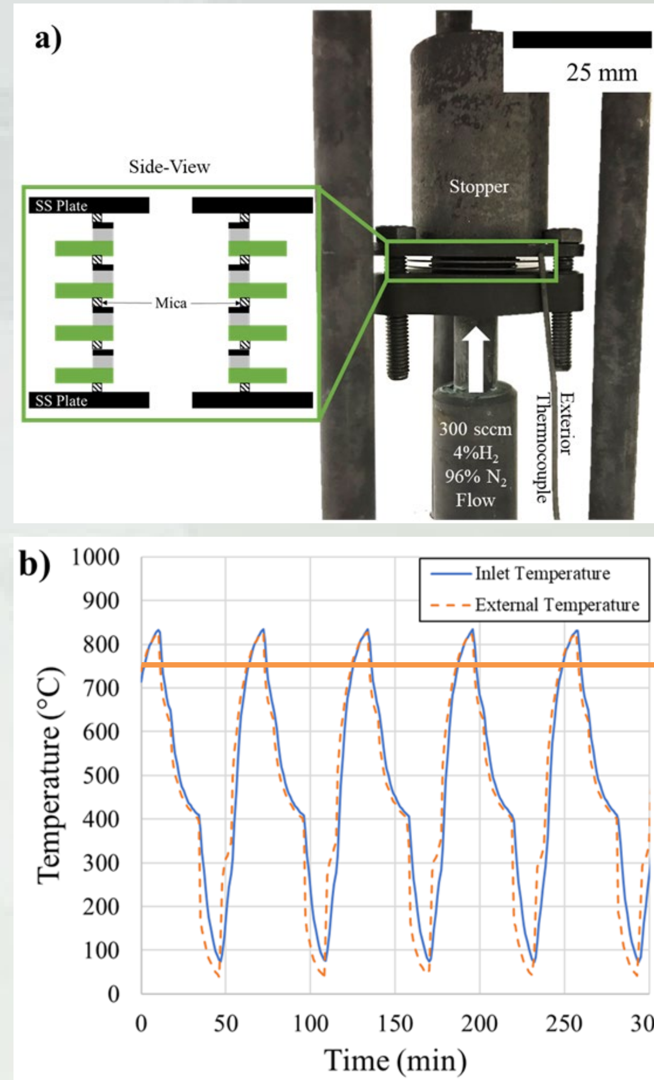
The Ni That Promotes Ag Wetting is Transient When Used to Bond to 441 Stainless Steel



Zhou *et al.*, *Acta Materialia*, v148 p156 (2018).

The Type II Pores That Form Under Dual Atmosphere Conditions in Ag-CuO Brazes Do Not Form in Ag:Ni



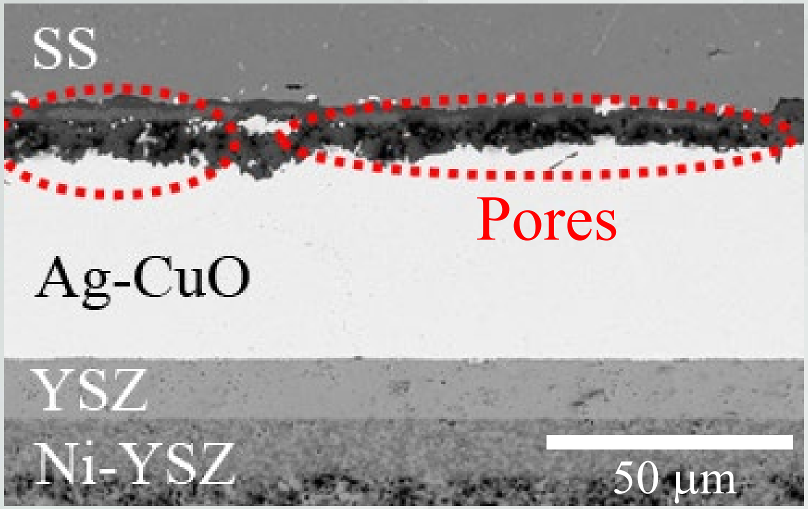


Special thanks to Rick Kerr and Bryan Gillespie of Delphi Automotive for assistance with these measurements

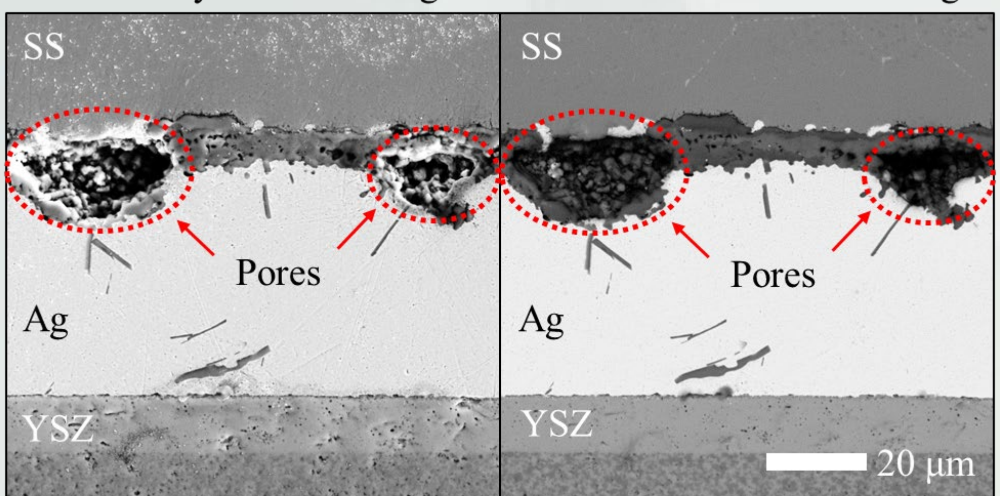
Zhou *et al.*, *J. Electrochem. Soc., v166* pF494 (2019).

The Type II Pores That Form Under Dual Atmosphere Conditions in Ag-CuO Brazes Do Not Form in Ag:Ni

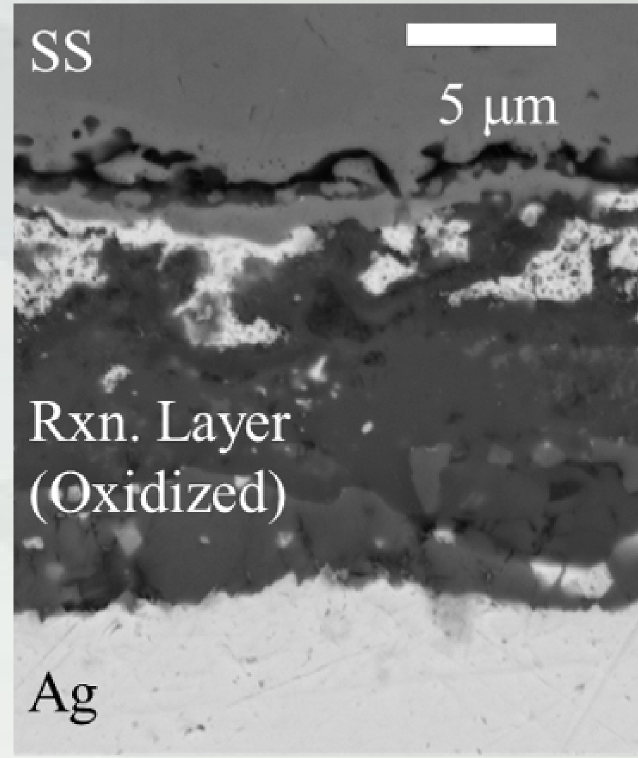
H_2 Side of An Ag-4CuO Seal



Secondary Electron Image   Backscattered Electron Image



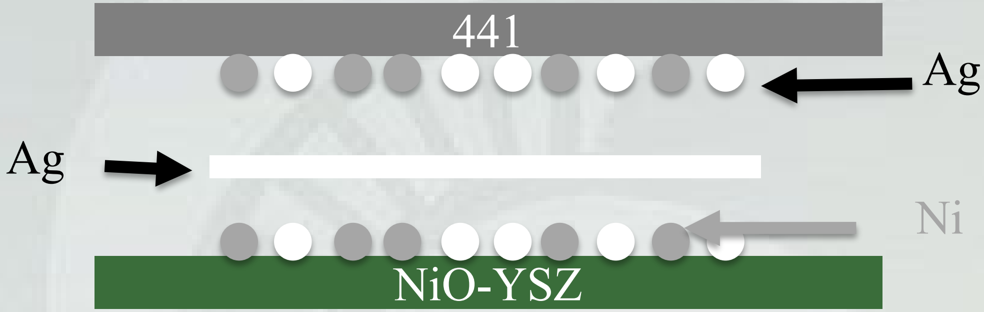
H_2 Side of An Ag:Ni Seal

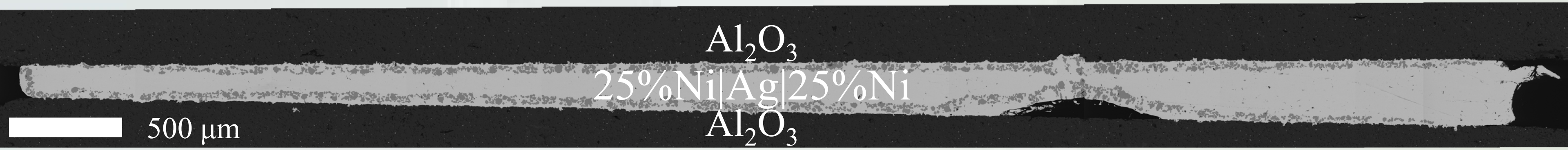


* Note, similar microstructures are seen in dual atmosphere joints rapid thermally cycled from 35 to 830^{o}C at ~25^{o}C/min. See the reference below for details.

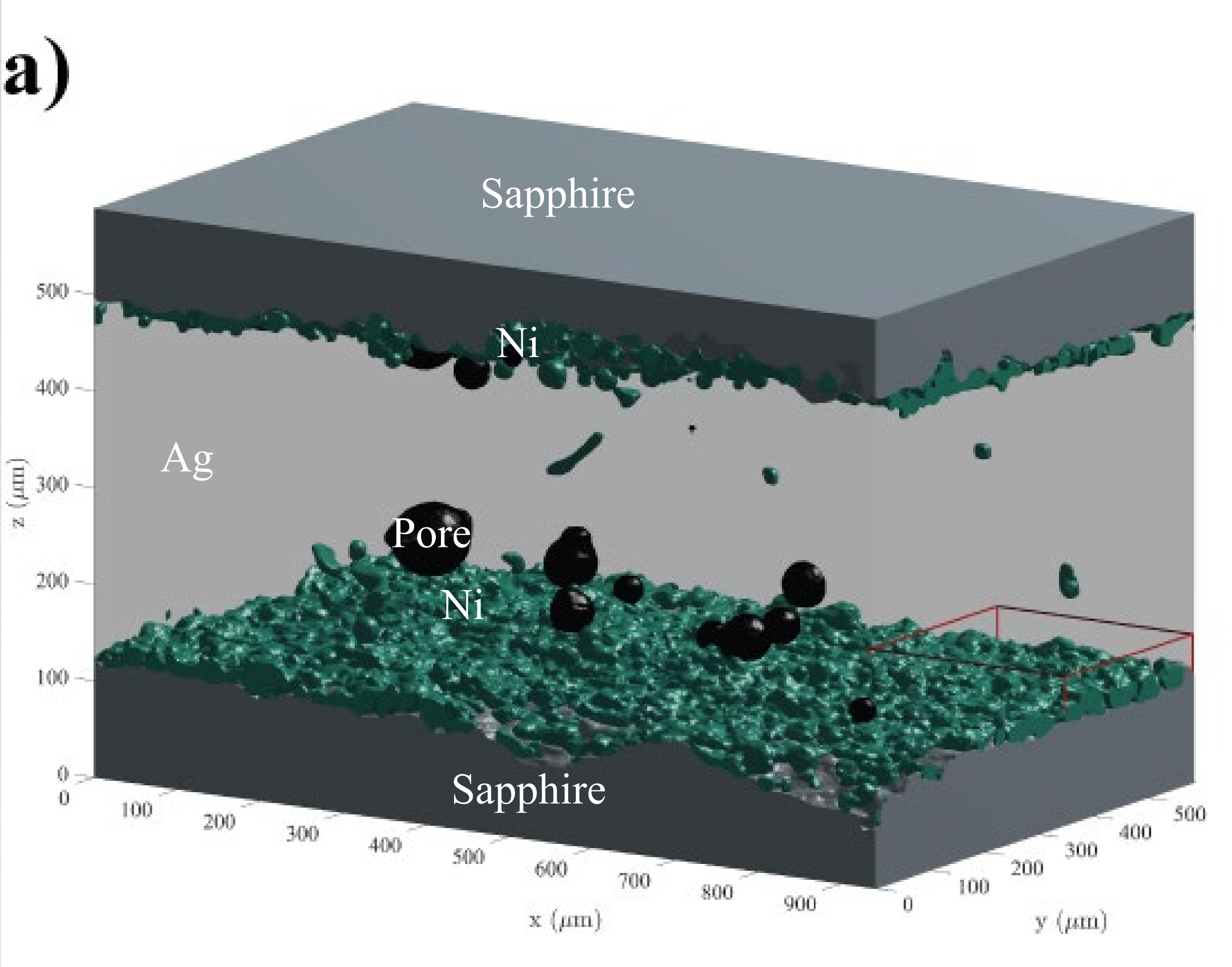
Zhou *et al.*, *J. Electrochem. Soc., v166* pF494 (2019).

The Ni Interlayer Microstructure and the Surface Roughness Doesn't Matter Much: Even "Isolated" Ni Particles Work



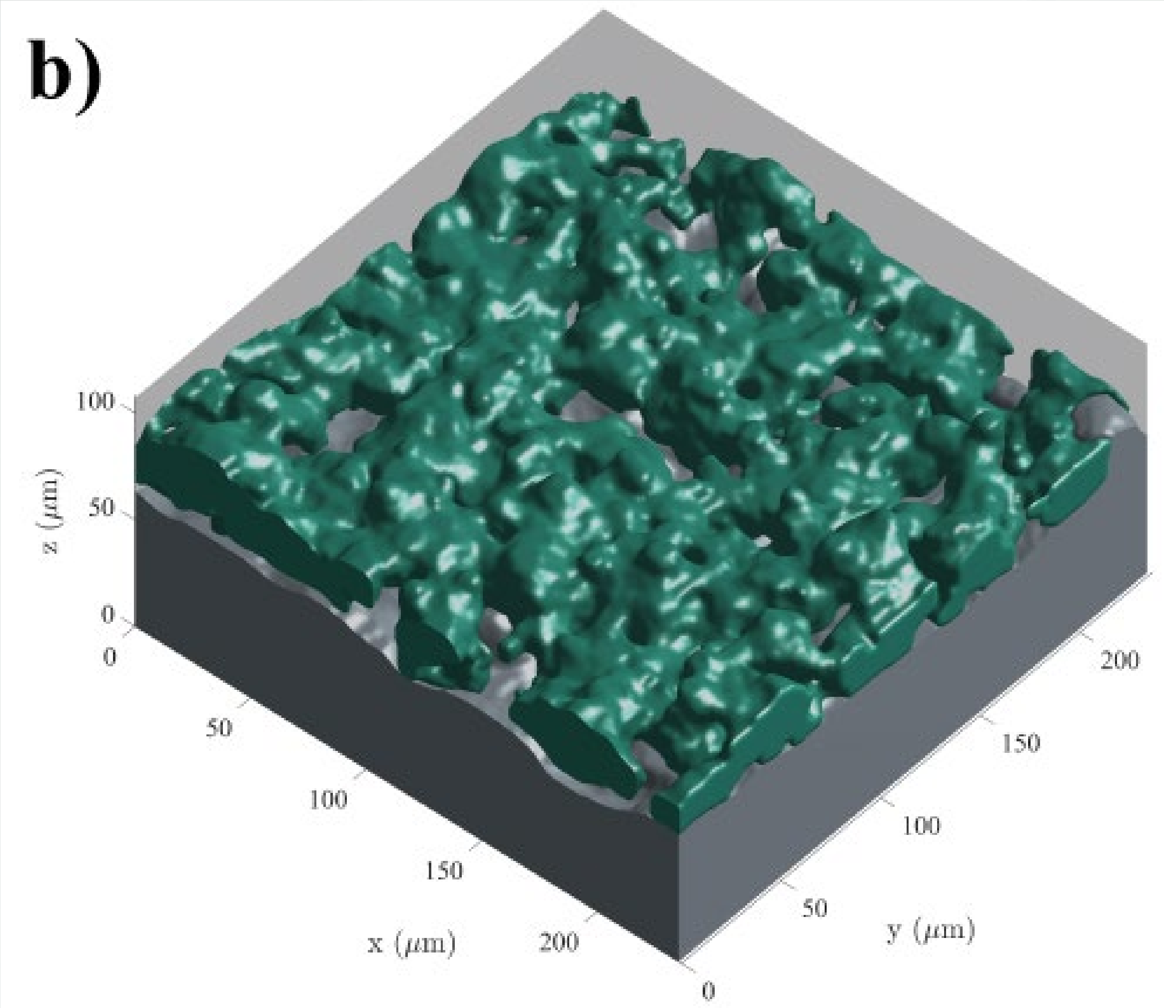


Ag:Ni Can Also Be Used For Ceramic-Ceramic Bonding



The data for this 3D X-Ray tomography reconstruction was obtained at Argonne National Laboratory
Hu *et al*., *Scripta Materialia.*, v196 p113767 (2021).

Ag:Ni Can Also Be Used For Ceramic-Ceramic Bonding

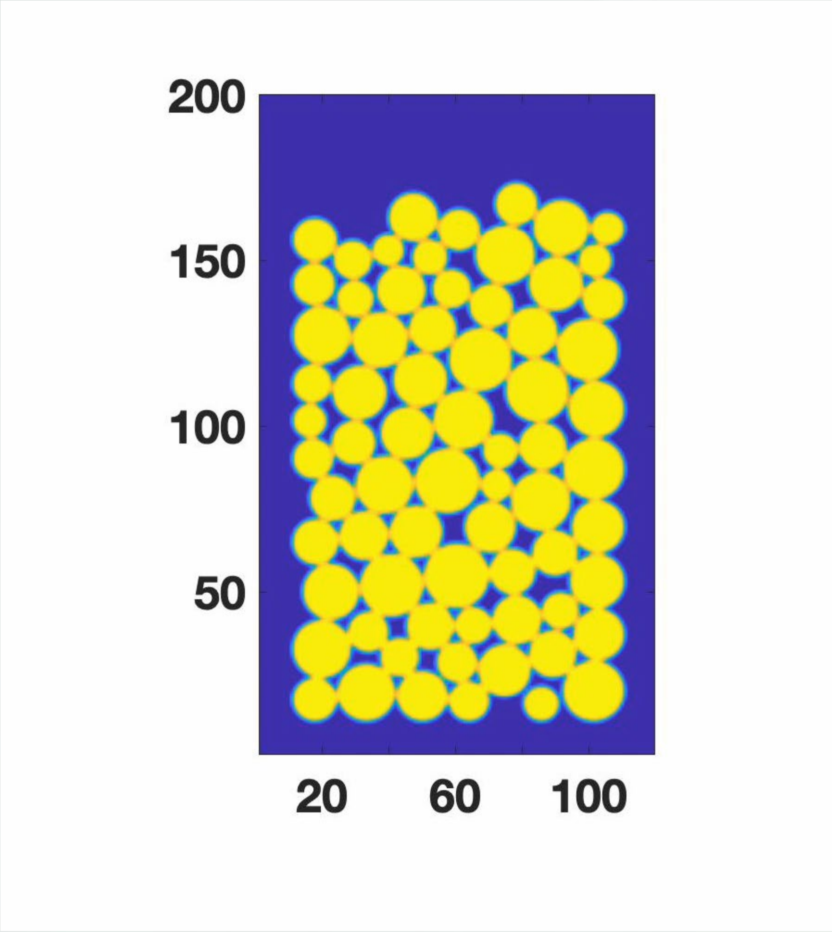


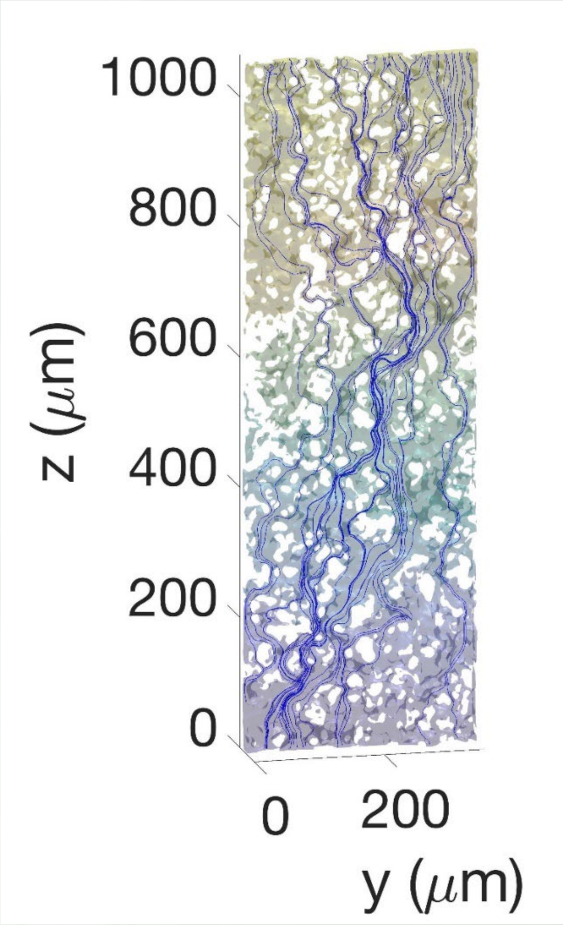
Ni is Green, Pores are Black, Sapphire is Gray, and Silver is Transparent

The data for this 3D X-Ray tomography reconstruction was obtained at Argonne National Laboratory

Hu *et al*., *Scripta Materialia.,* v196 p113767 (2021).

New 2D and 3D Computational Simulations Can Be Used to Predict and Optimize Ni Sintering and Molten Ag Intrusion

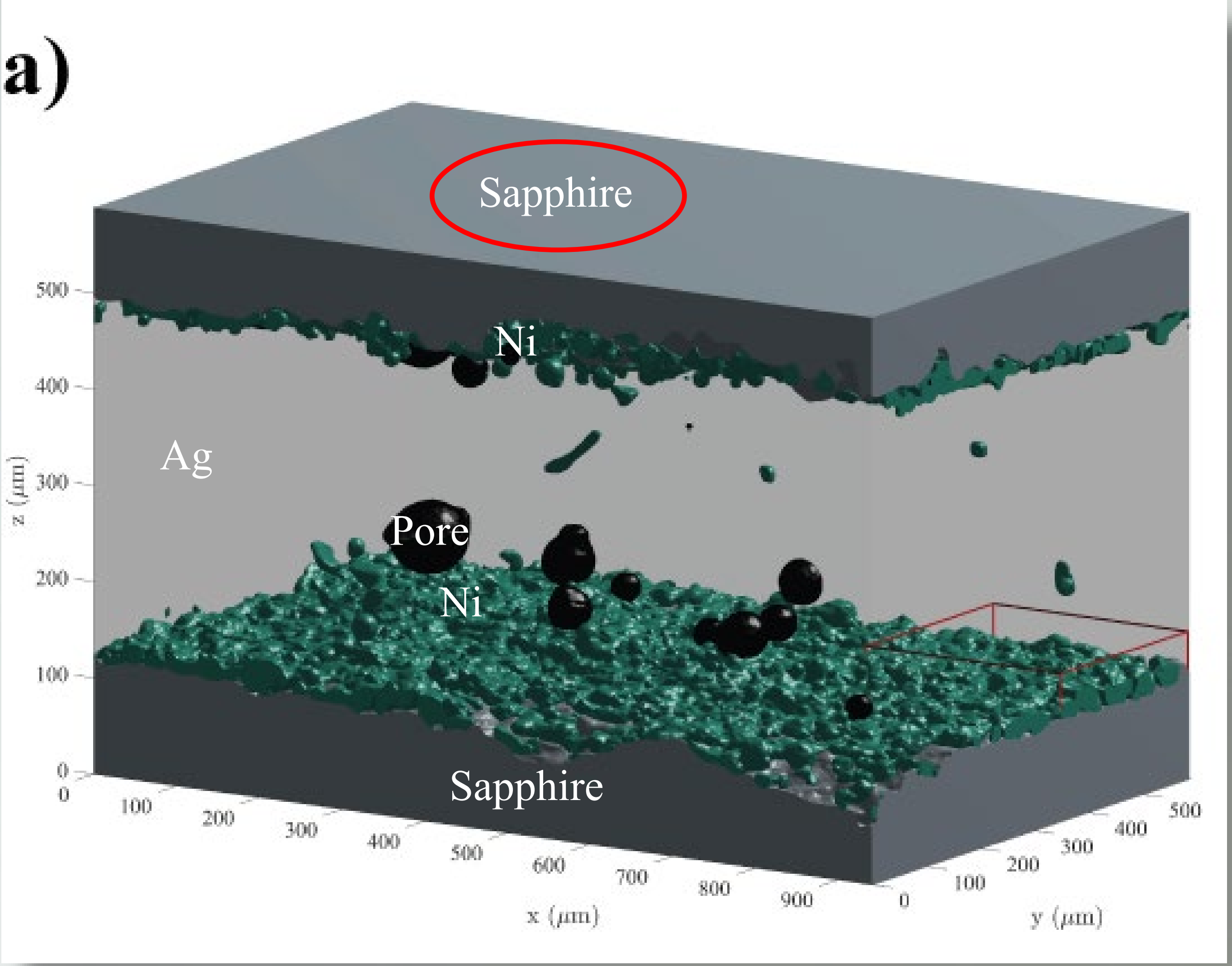




* This modeling indicates that 2 minutes at 1025^{o}C should be enough time to form a braze/circuit, and that lateral Ag spreading is limited to less than 1 centimeter.

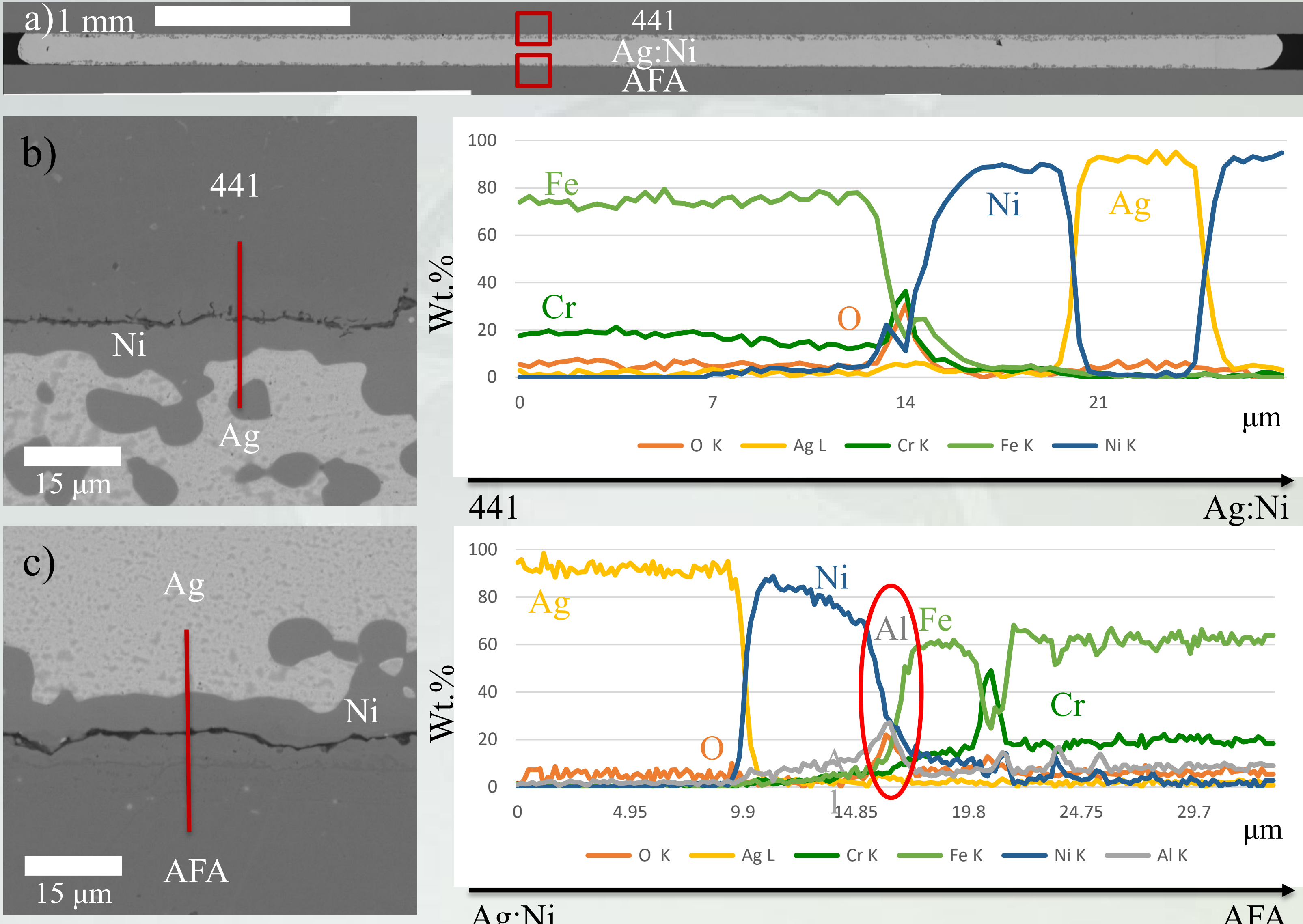
Termuhlen *et al.*, *Computational Materials Science,* v186 p109963 (2021).
Termuhlen *et al.*, *Computer Methods in Applied Mechanics and Engineering,* v339 p115312 (2022).
Termuhlen *et al.* In Preparation (2023).

Ag:Ni Can Also Be Used For Ceramic-Ceramic Bonding



The data for this 3D X-Ray tomography reconstruction was obtained at Argonne National Laboratory
Hu *et al*., *Scripta Materialia.*, v196 p113767 (2021).

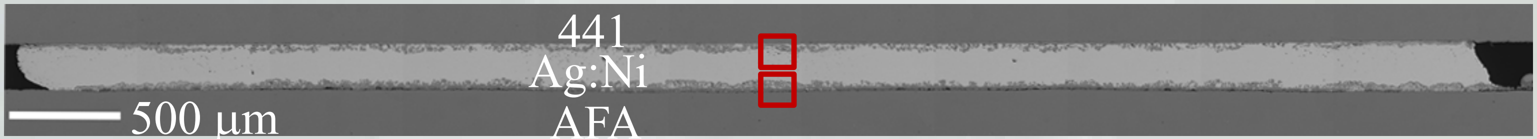
Ag:Ni Can Also Be Used to Braze Stainless Steels that Form Protective Al_2O_3 Surface Scales, $(Ni,Fe)Al_2O_{4-x}$ Likely Forms

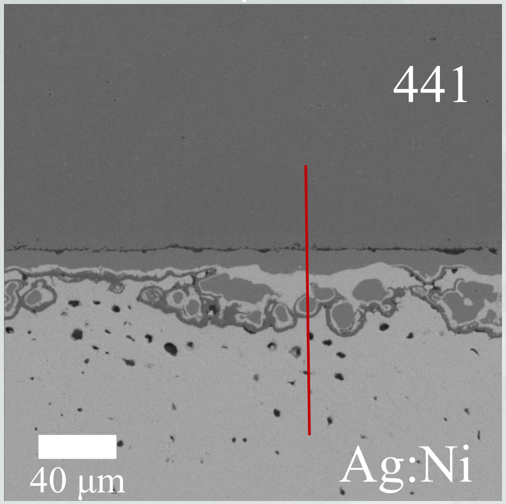


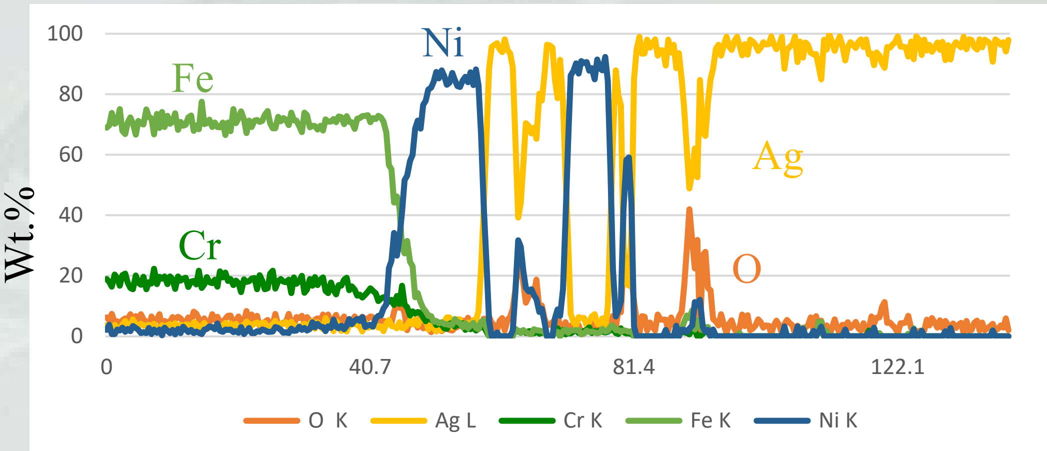
* Please See Our DOE SOFC Program Review Meeting Poster for Detailed Information on This Topic

Ag:Ni Brazes Tolerate RedOx Cycling Well

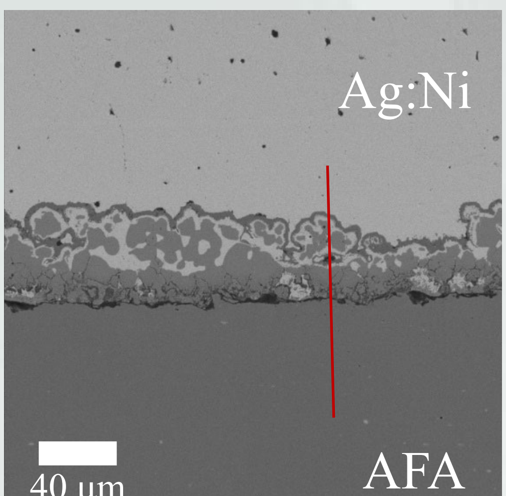
Ag:Ni braze after twenty-five 12-hr-in-4%H_2 | 12-hr-in-air RedOx cycles at 650°C.

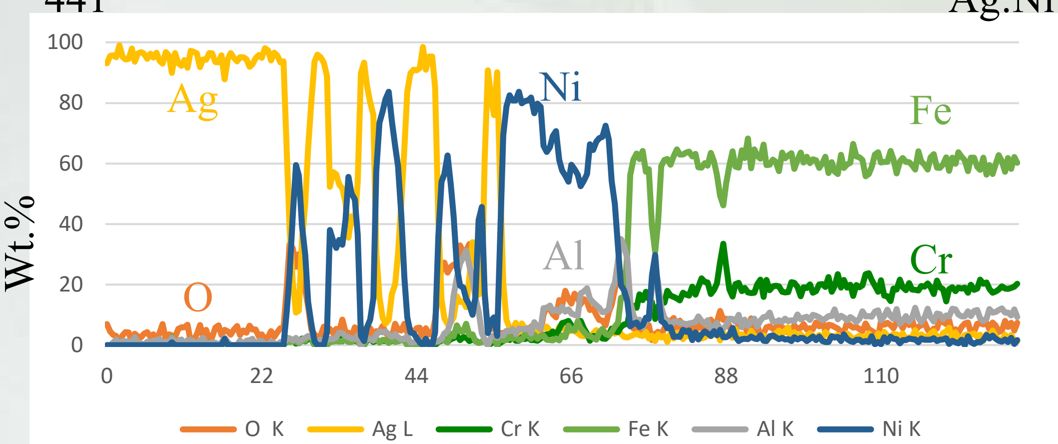






441 → Ag:Ni

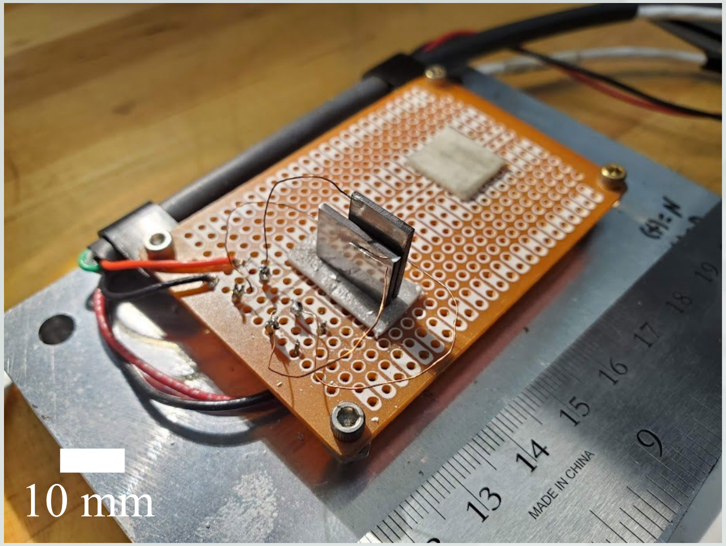




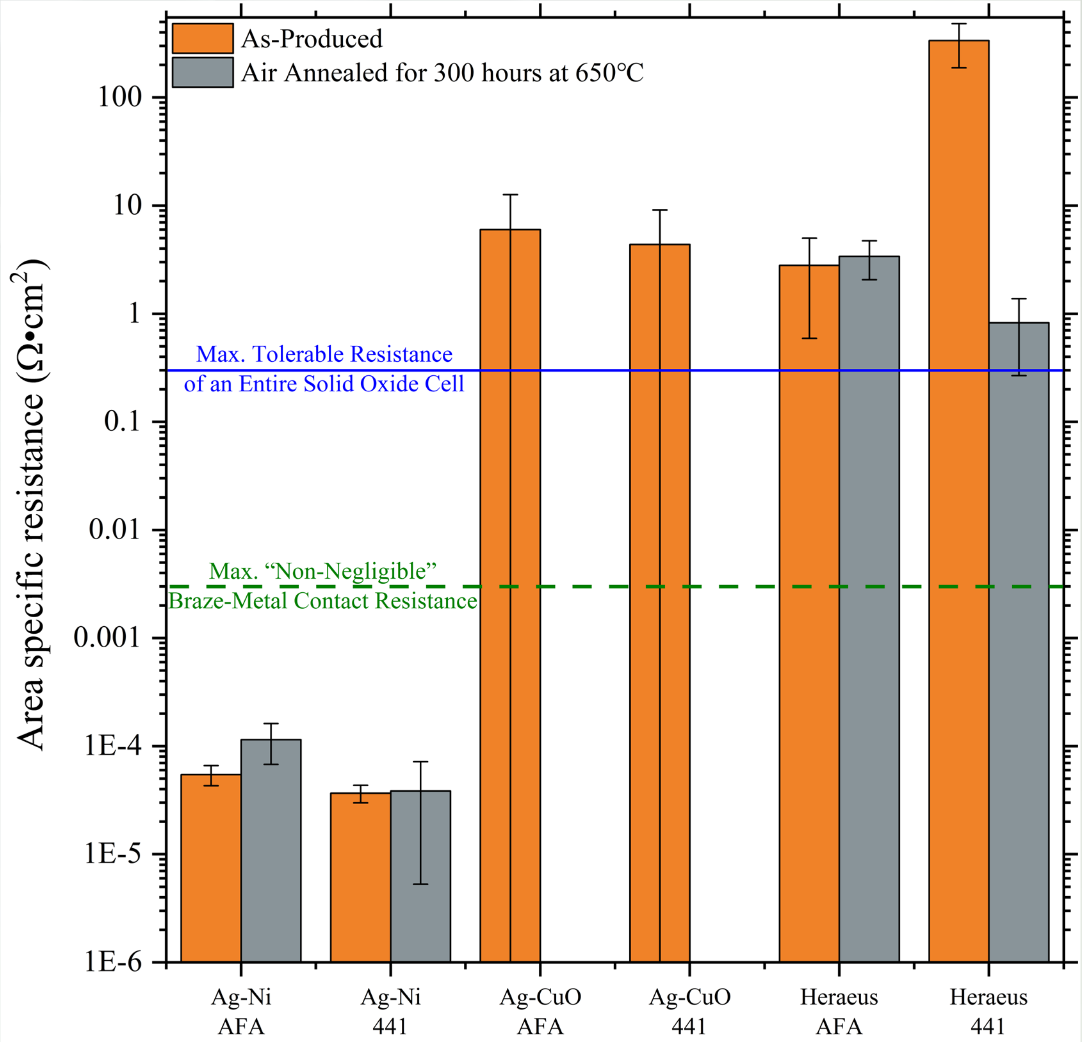
Ag:Ni → AFA

* Good braze survivability with RedOx cycling is also seen on 441|Ag:Ni|YSZ joints.

Ag:Ni to Stainless Steel Electrical Contacts Have a Much Lower Contact Resistance than Ag-CuO or Commercial Ag Pastes



Steele and Heinzel, Nature p345 (2001) says the ideal ASR for all SOFC components < 0.3 Ω•cm^2

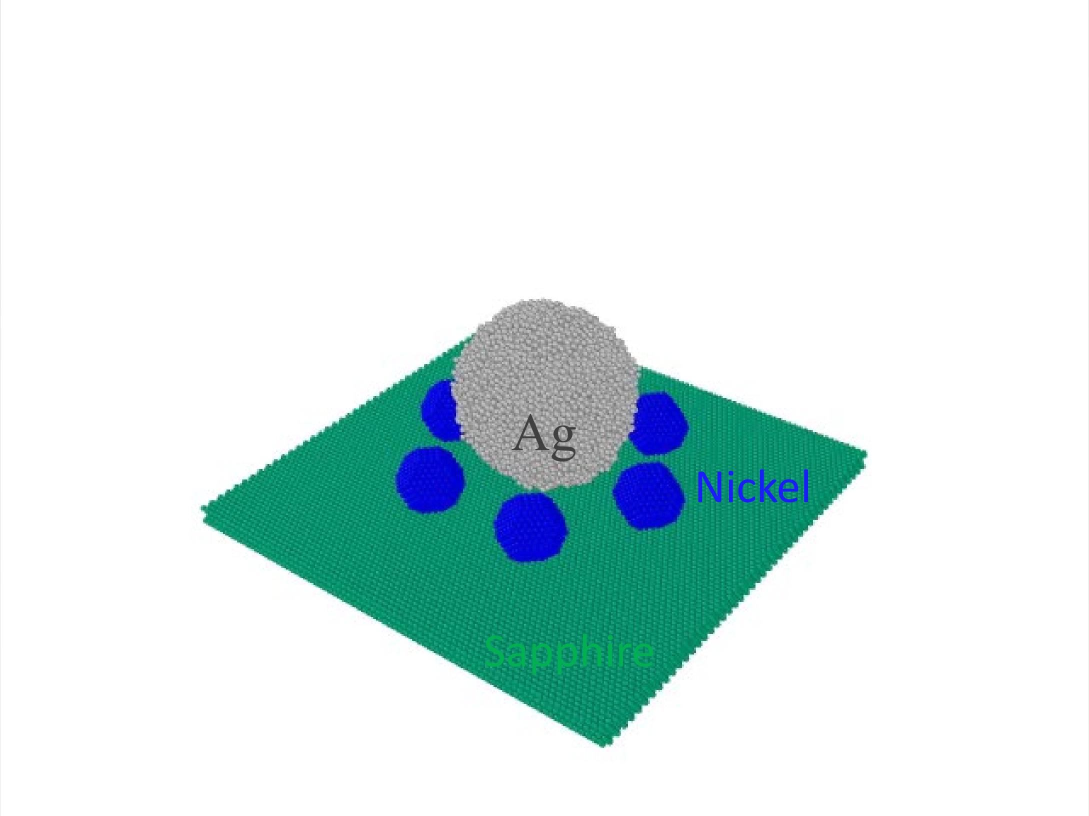


* Please See Our DOE SOFC Program Review Meeting Poster for Detailed Information on This Topic

TALK Outline

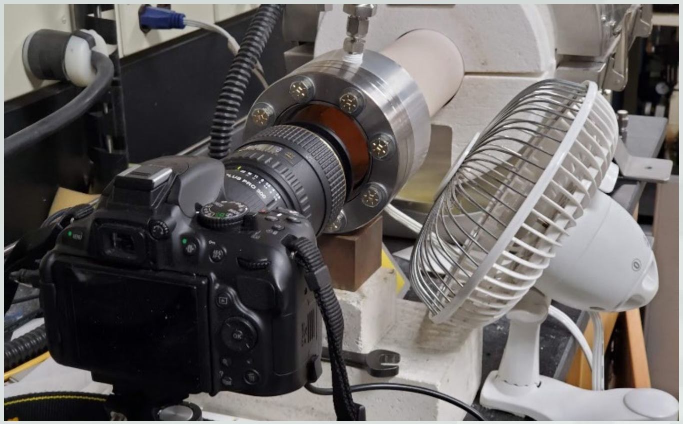
1. Ag:Ni Brazes
2. Ag:Ni Circuit Pastes/Current Collectors/Electrical Contacts

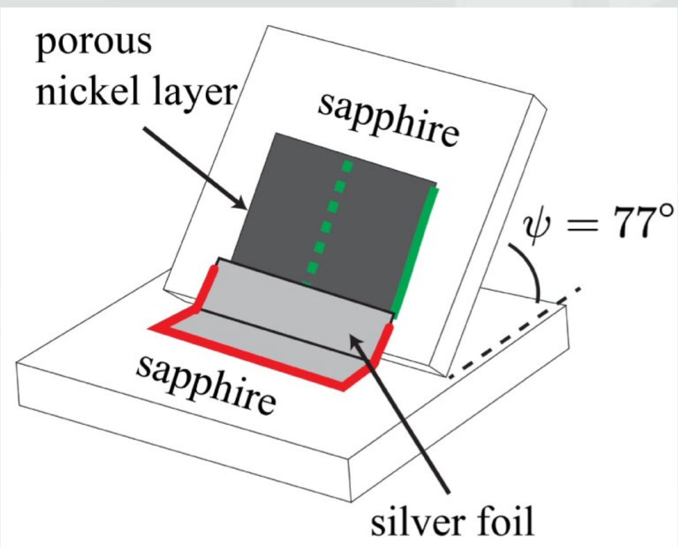
Ag:Ni Can Be Used to Produce Patterned Current Collectors. Unfortunately, Wetting Problems Prevent That in Ag-CuO.

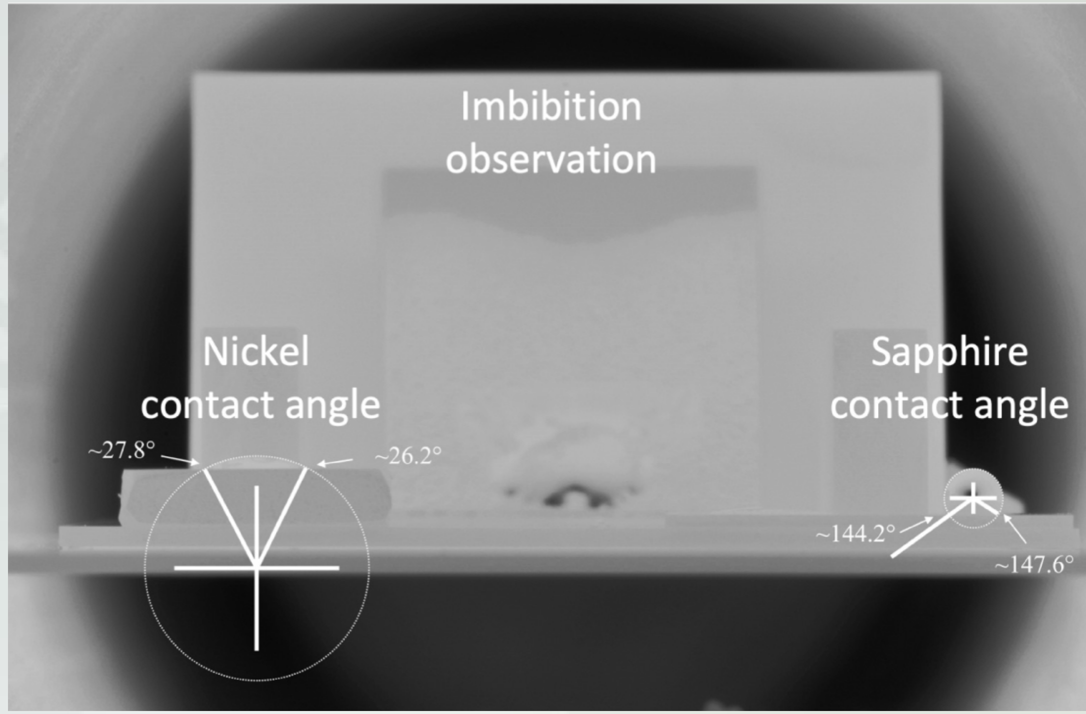


Park *et al.*, *Acta Materialia*, v199 p551 (2020).

Molten Silver Can Defy Gravity As it Intrudes Into a Pre-Patterned Nickel Network on Sapphire



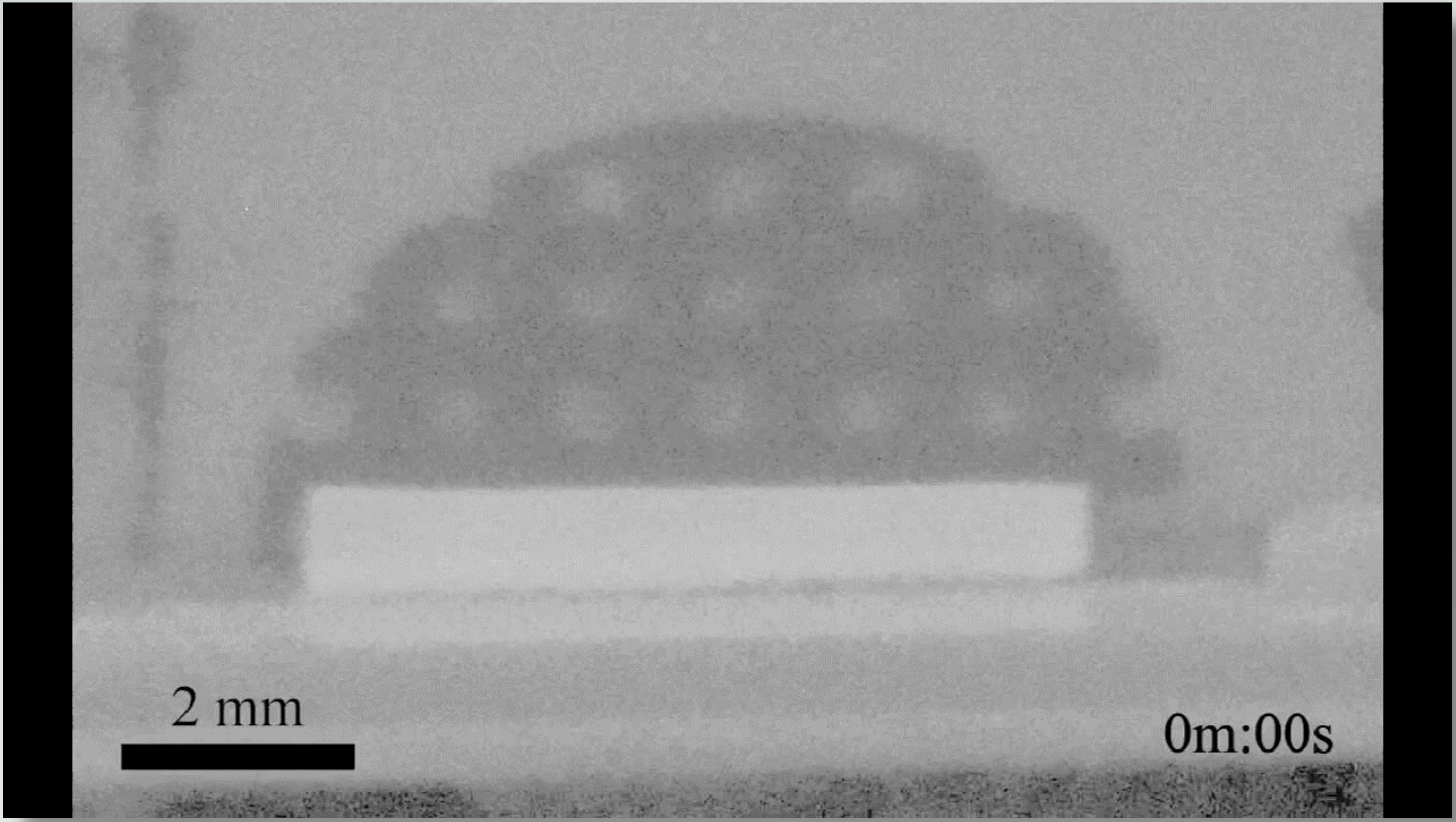




Temperature: 1025°C
Atmosphere: Ni/NiO Buffered Argon

Termmuhlen *et al,* In Preparation (2023).

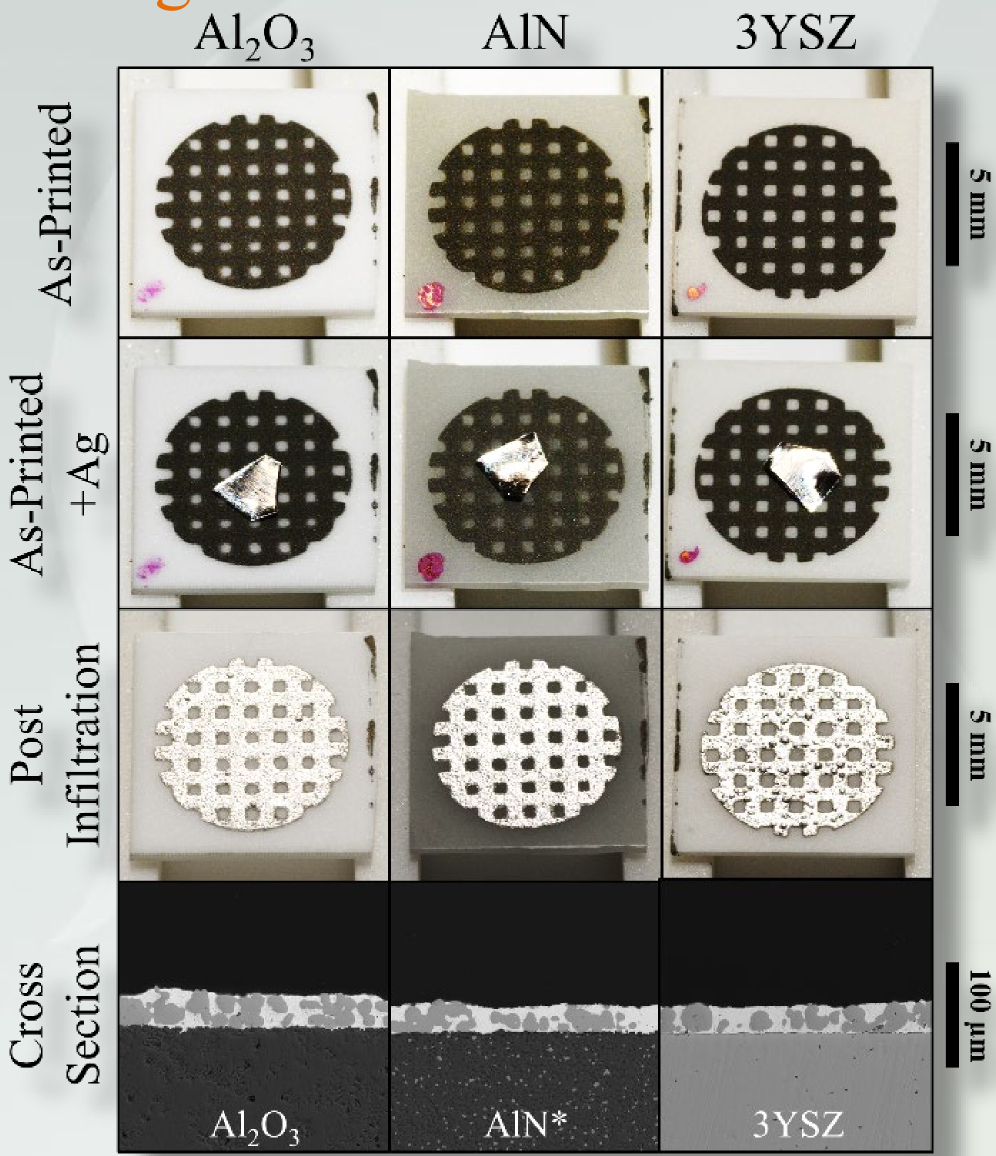
A Self-Assembled Ag:Ni Circuit Made by Molten Ag Defying Gravity As it Intrudes Into a Pre-Patterned Ni Network on Al_2O_3



Temperature: ~1025^{o}C Atmosphere: Ni/NiO Buffered Argon

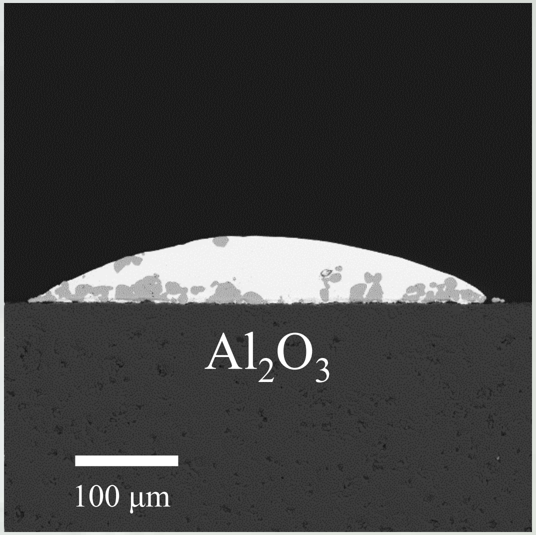
Hu *et al*., *Scripta Materialia.*, v196 p113767 (2021).

Dense Patterned Ag Circuits Can Also Be Made by Intruding Molten Ag Into a Pre-Patterned Ni Network



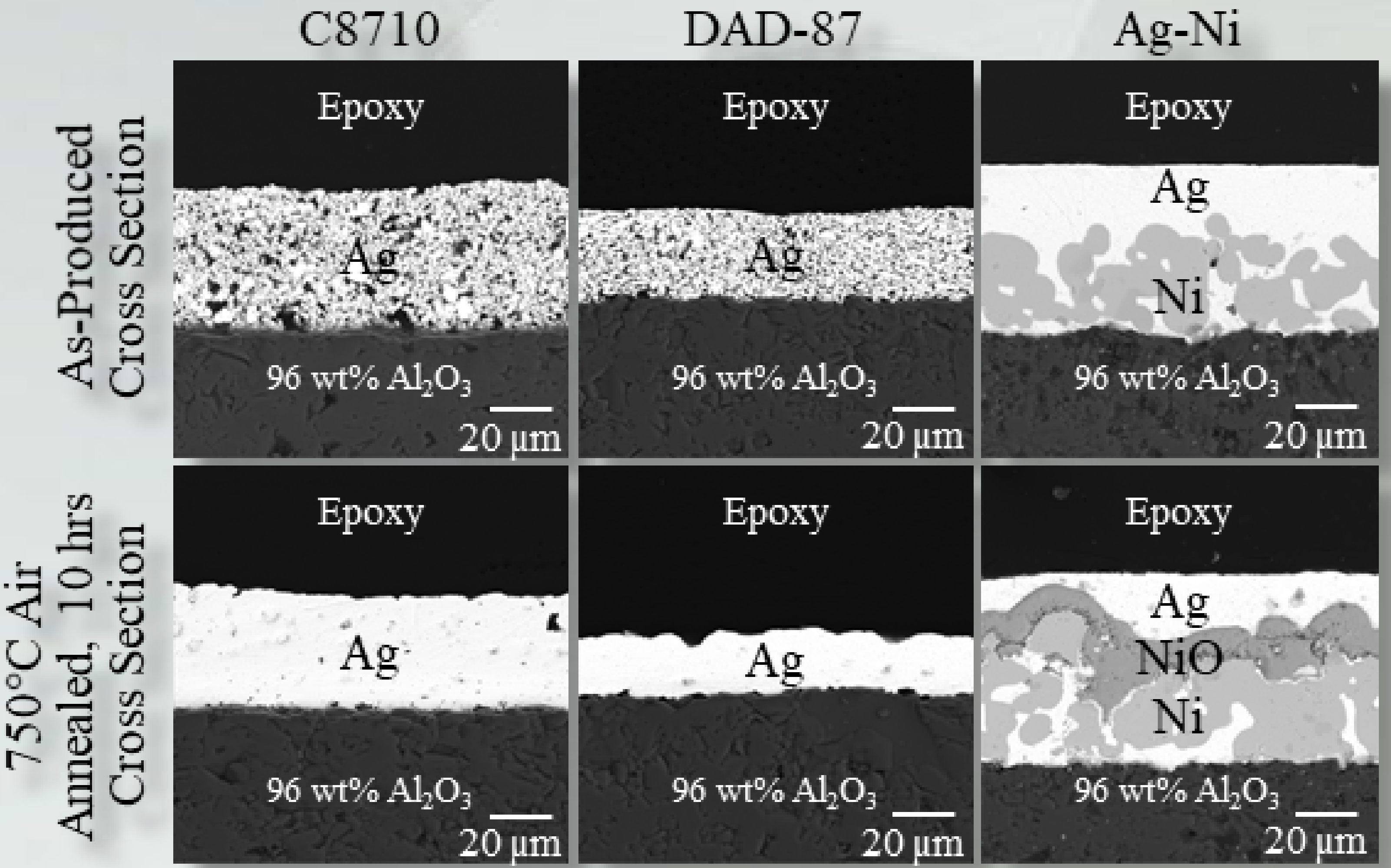
Hu *et al*., *Scripta Materialia.*, v196 p113767 (2021).

Dense Patterned Ag Circuits Can Also be Made by Screen Printing Ag Ink Over Ni Ink and Firing at 1025^{o}C in Ni/NiO Buffered Ar



Hu *et al.*, *Scripta Materialia.*, v196 p113767 (2021).

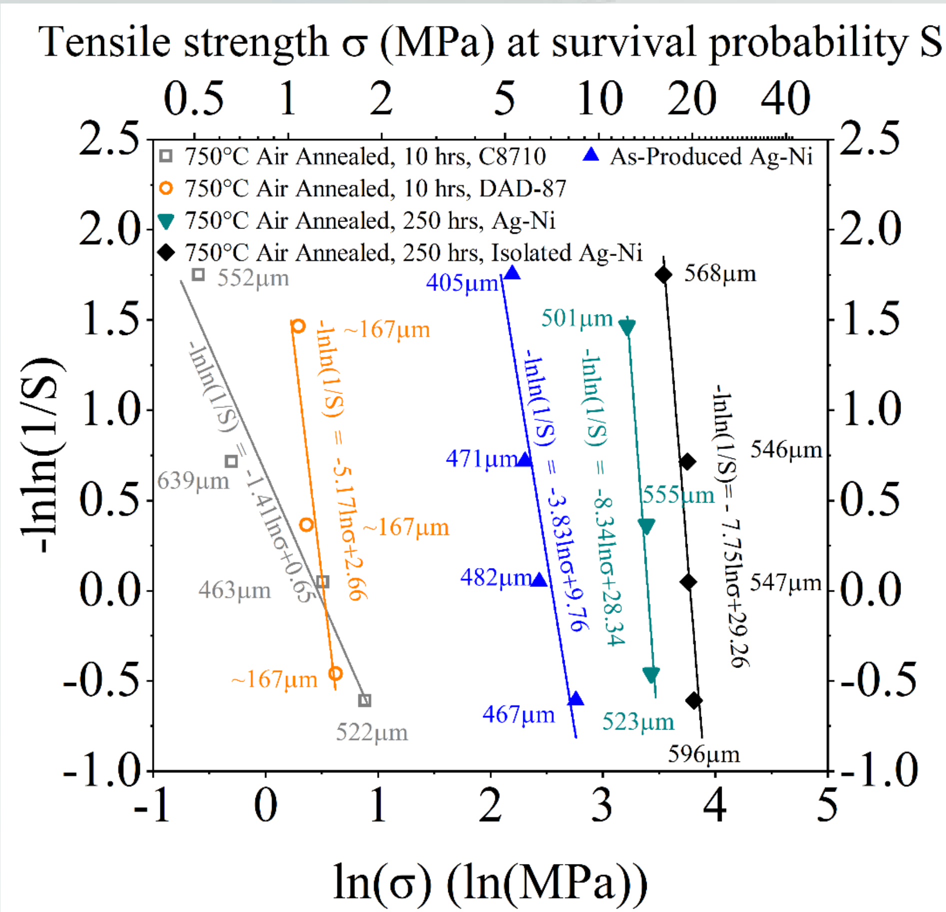
Unlike Commercial Ag Pastes, Ag:Ni Current Collectors Are Dense Immediately After Manufacturing

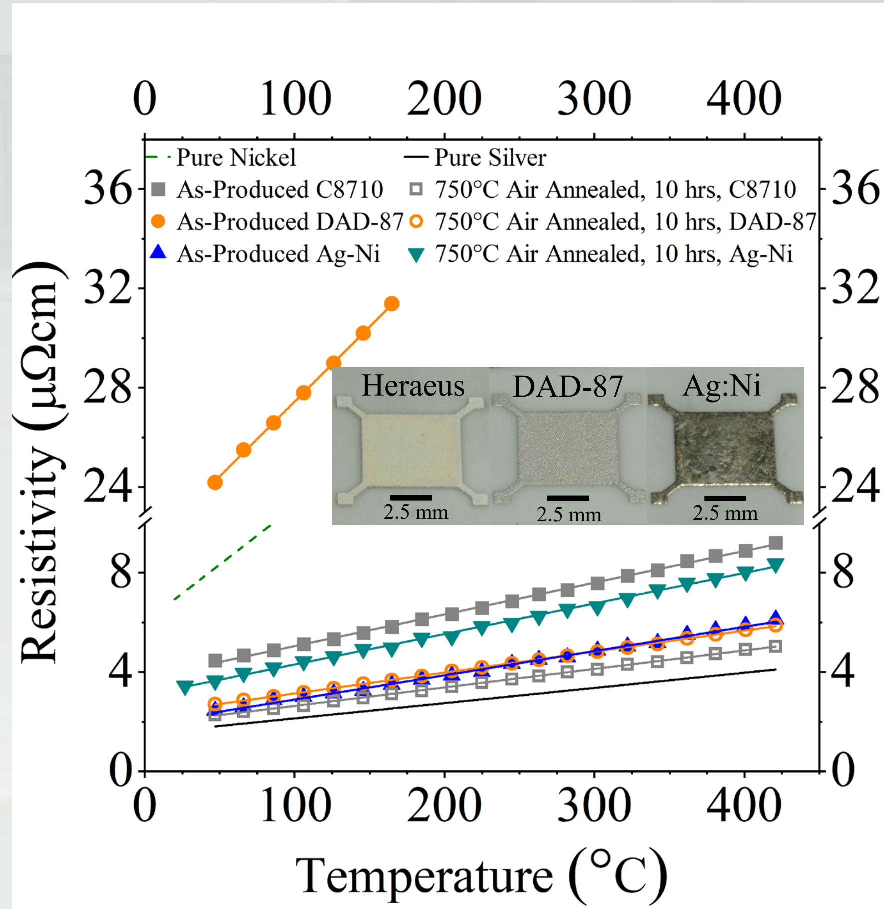


* Less Ni will result in less NiO

Hu *et al.*, *Scripta Materialia.*, v196 p113767 (2021).

On Sapphire, Ag:Ni Has a 10x Higher Adhesion Strength and < 2x Higher In-Plane Resistivity than Commercial Ag Pastes



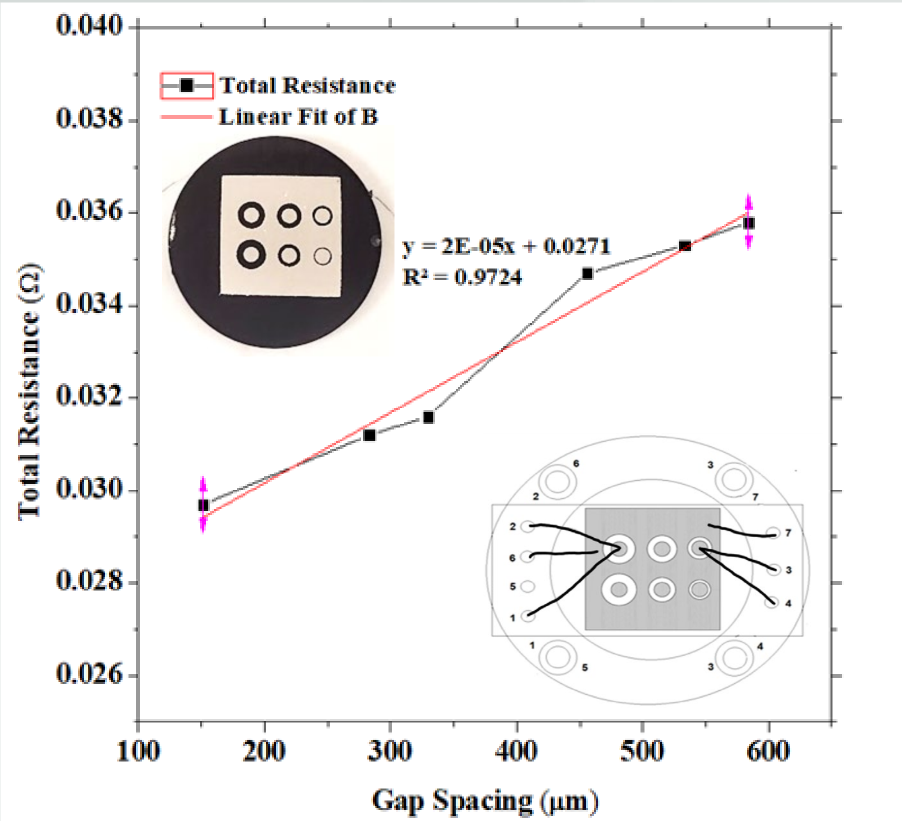


* Note, Ag:Ni circuits with “isolated” (25 vol%) Ni particles, instead of the “continuous” porous nickel layers used here, would likely result in lower in-plane resistance.

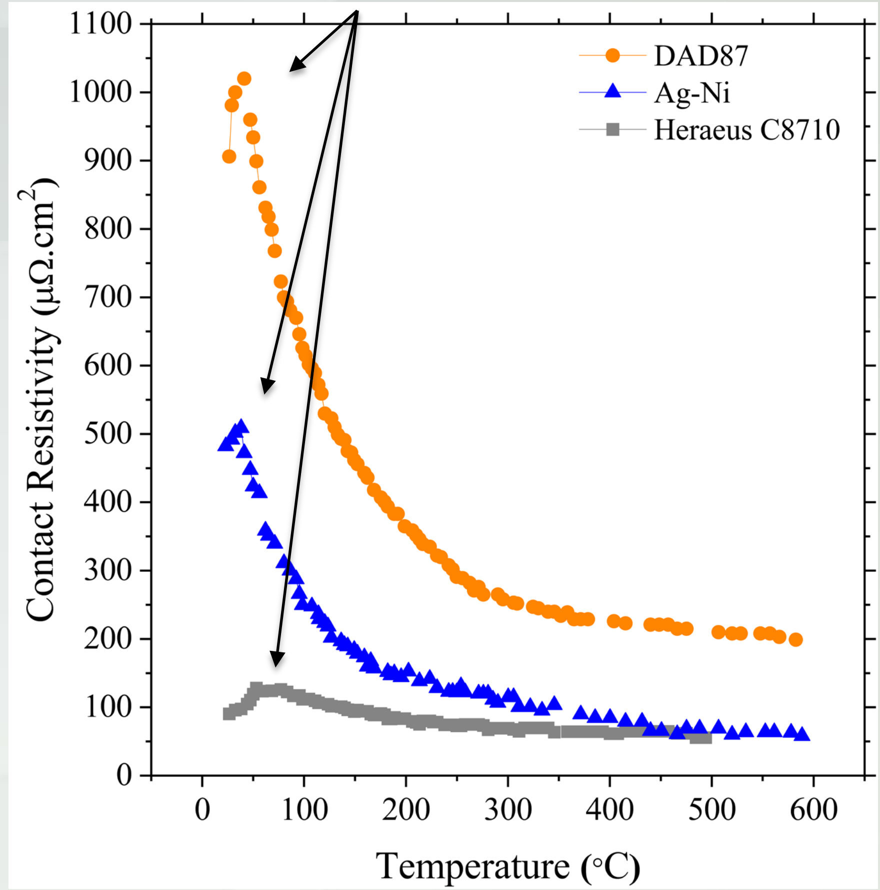
Hu *et al*., *Scripta Materialia.*, v196 p113767 (2021).

Ag:Ni Current Collectors Have High-Temperature Contact Resistances Equal to the Best Commercial Ag Pastes

LSM ferromagnetic-paramagnetic transitions



The total resistance versus gap spacing for Heraeus C8710. The contact resistance is the y-axis intercept



The contact resistivity of 750 °C air annealed Ag circuits on LSM vs. temperature

Hammouche, *et al.*, Solid State Ionics(1988)
Hassini, *et al.*, Solid State Sci(2002)

DE-FE-0023315 Braze Project Products

1. Ma, Y., Zhou, Q. & Nicholas, J. "High Temperature Thermo-Mechanical Properties of Praseodymium Doped Ceria Thin Films Measured Two Ways" *Materials Advances* **3**, 1574-1580, https://doi.org/10.1039/D1MA00842K (2022).
2. Ma, Y. & Nicholas, J. D. "Silicon Contamination of the Praseodymium Doped Ceria Oxygen Surface Exchange Coefficient" *Journal of the Electrochemical Society* **168**, 104518, https://doi.org/10.1149/1945-7111/ac2e1d (2021).
3. Das, T., Nicholas, J. D. & Qi, Y. "Composition, Crystallography, and Oxygen Vacancy Ordering Impacts on the Oxygen Ion Conductivity of Lanthanum Strontium Ferrite" *Phys. Chem. Chem. Phys.* **22**, 9723-9733, https://dx.doi.org/10.1039/D0CP00206B (2020).
4. Zhou, Q., Bieler, T. R. & Nicholas, J. D. "Dual Atmosphere Isothermal Aging and Rapid Thermal Cycling of Ag-Ni and Ag-CuO Stainless Steel to Zirconia Braze Joints" *Journal of the Electrochemical Society* **166**, F594-F603, https://doi.org/10.1149/2.0911910jes (2019).
5. Nicholas, J. D., Zhou, Q. & Bieler, T. R. "Controlled Wetting and Spreading of Metals on Substrates Using Porous Interlayers and Related Articles" *U.S.P.T.O. Patent Number 0320528 A1* (2019).
6. Zhou, Q., Bieler, T. R. & Nicholas, J. D. "Transient Porous Nickel Interlayers for Improved Silver-Based Solid Oxide Fuel Cell Brazes" *Acta Materialia* **148**, 156-162, https://doi.org/10.1016/j.actamat.2018.01.061 (2018).
7. Phongpreecha, T., Nicholas, J. D., Bieler, T. R. & Qi, Y. "Computational Design of Metal Oxides to Enhance the Wetting and Adhesion of Silver-Based Brazes on Yttria-Stabilized-Zirconia" *Acta Materialia* **152**, 229-238, https://doi.org/10.1016/j.actamat.2018.04.024 (2018).
8. Nicholas, J. D., Zhou, Q., Bieler, T. R. & Kerr, R. D. "Brazing Methods Using Porous Interlayers and Related Articles" *Patent Number: US11167363B2* (2018).
9. Ma, Y. & Nicholas, J. D. "Mechanical, Thermal, and Electrochemical Properties of Pr Doped Ceria from Wafer Curvature Measurements" *Phys. Chem. Chem. Phys.* **20**, 27350-27360, https://doi.org/10.1039/c8cp04802a (2018).
10. Das, T., Nicholas, J. D. & Qi, Y. "Long-Range Charge Transfer and Oxygen Vacancy Interactions in Strontium Ferrite" *Journal of Materials Chemistry A* **5**, 4493-4506, https://doi.org/10.1039/C6TA10357J (2017).
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DE-FE-0031672 Circuit Project Products

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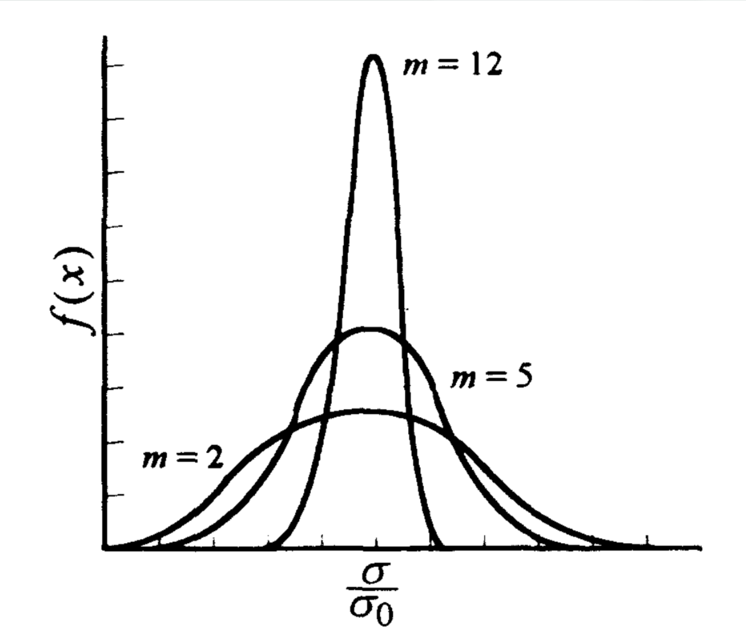
Conclusions

	PRO	CON
Commercial Ag Pastes	• Produced in air • Current collectors possible • Brazes possible • Produced at 25°C • No external pressure required	• High initial porosity • Poor Shear Strength: < 2 MPa for Al_2O_3, even after densification at 750°C
Ag-CuO	• Brazes Possible • Produced in air • Excellent shear strength: >100 MPa for Al_2O_3 • No external pressure required	• Braze runout during joining common • Current collectors not possible • Type I pores • Type II pores • Type III pores • ~1000°C fabrication temp.
Ag:Ni	• Brazes and Current Collectors Possible • No braze run out during joining • Self-assembled circuits and joints possible • No Type I pores • No Type II pores • Delayed Type III pores (since no Type I/II pores) • Good shear strength: ~ 30 MPa for Al_2O_3 • Better dual atmosphere, rapid thermal cycling, and RedOx mechanical stability than Ag-CuO • 10,000x lower contact resistance with Al_2O_3-protected or Cr_2O3-protected stainless steel, compared to Ag-CuO or commercial Ag pastes. • No external pressure required	• Fabrication done in Ni/NiO buffered inert gas • Eventual Type III pores • ~1025°C fabrication temp.

Backup Slides

Weibull Plots Are a Statistical Approach to Describe Strength Distribution



If the survival probability S is assumed to take the form

$$S = \exp[-\left(\frac{\sigma}{\sigma_0}\right)^m]$$

then,

$$\ln\ln\frac{1}{S} = mln\sigma - mln\sigma_0$$

where m is a shape factor, referred to as the *Weibull modulus* and σ_0 is the stress where the survival probability is 37%. This last equation indicates that fracture strength data plotted in lnln1/S vs ln σ yields a straight line.

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Ag:Ni Joints with Different Amounts/Morphologies of Ni in the Interlayer Have Similar As-Produced Shear Strength