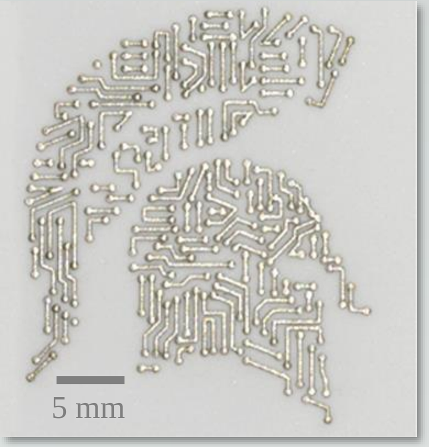

High Performance Circuit Pastes for Solid Oxide Fuel Cell Applications

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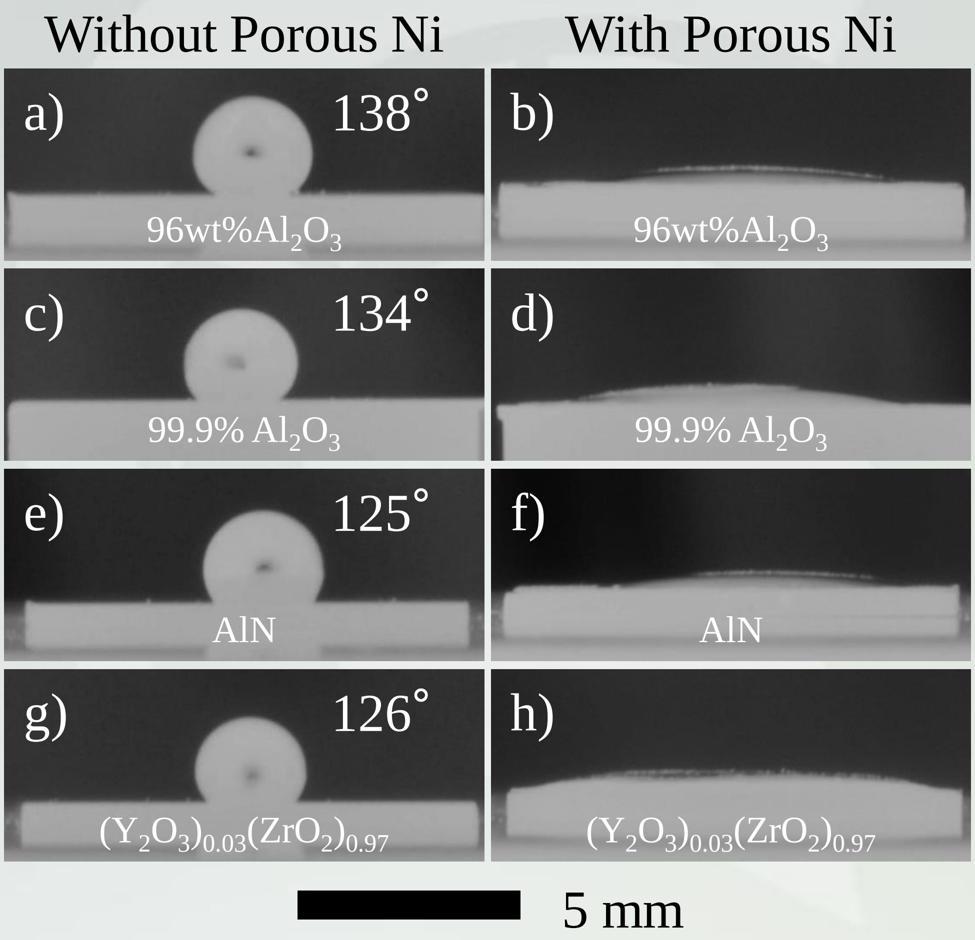
Funded by the Department of Energy Solid Oxide Fuel Cell Core Technology Program through Agreement Number DE-FE-0031672

November 2021

Outline

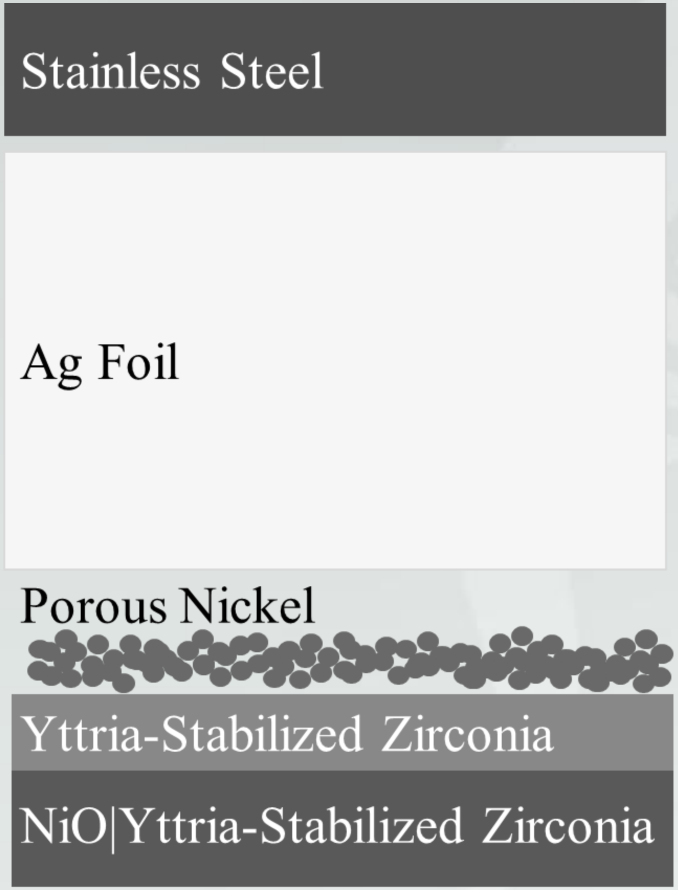
- **Background and Motivation**
  - Porous Ni Can Promote Ag Wetting on Different Substrates
- **Sample Fabrication**
- **Results and Discussion**
  - Ag-Ni Electrical Performance
  - Ag-Ni Mechanical Performance
  - Ag-Ni Wetting Molecular Dynamics Simulation and Optimal Pattern Determination
  - Nickel Phase-Field Sintering Simulations
- **Conclusions**

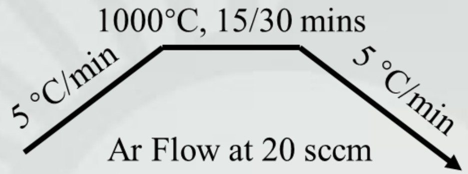
Porous Ni Interlayers Can Be Used to Direct the Wetting and Spreading of Ag on a Variety of Ceramic Substrates

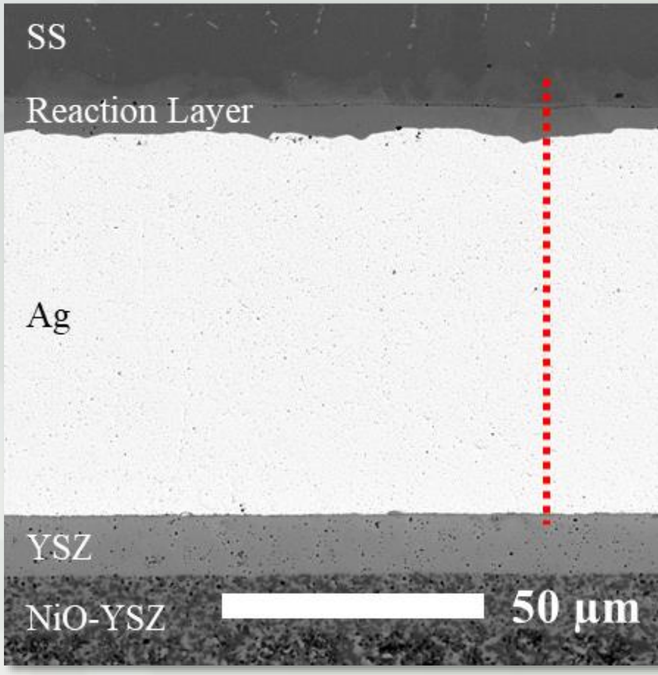


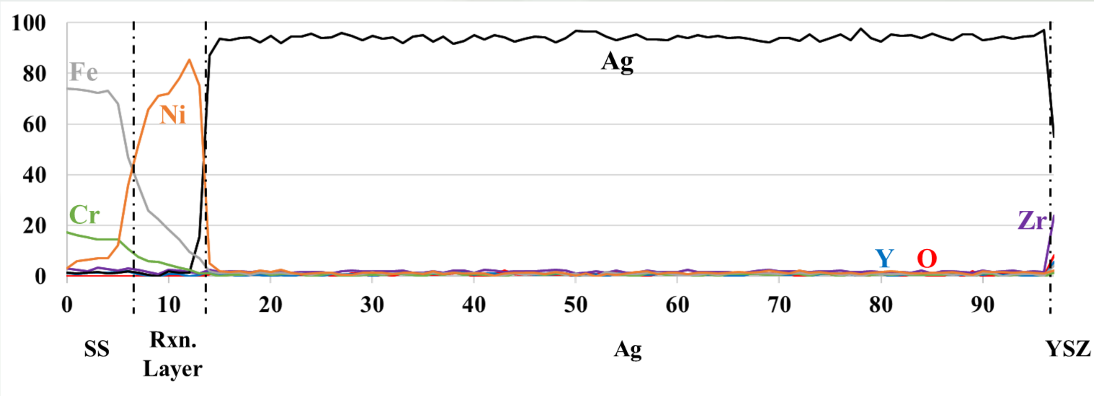
Hu, Genzhi, et al. "Patterned nickel interlayers for enhanced silver wetting, spreading and adhesion on ceramic substrates." *Scripta Materialia* 196 (2021): 113767.

Results From Our Previous DOE SOFC Project: Ag-Ni Works Great As a YSZ to Stainless Steel Braze!









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 (2018).

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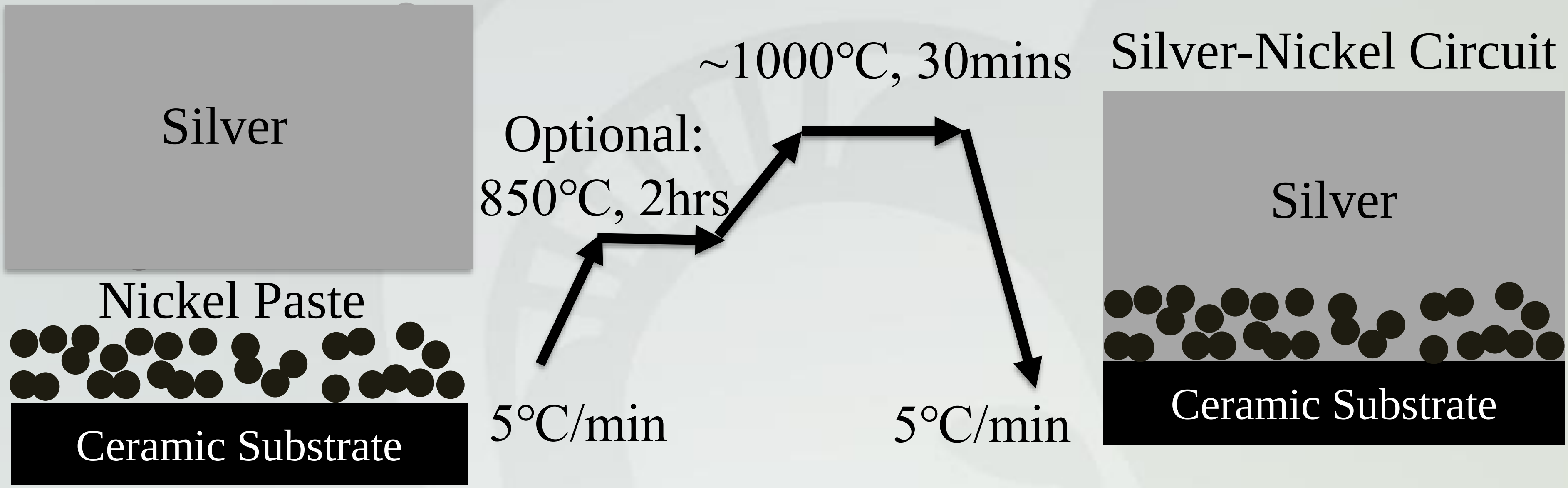
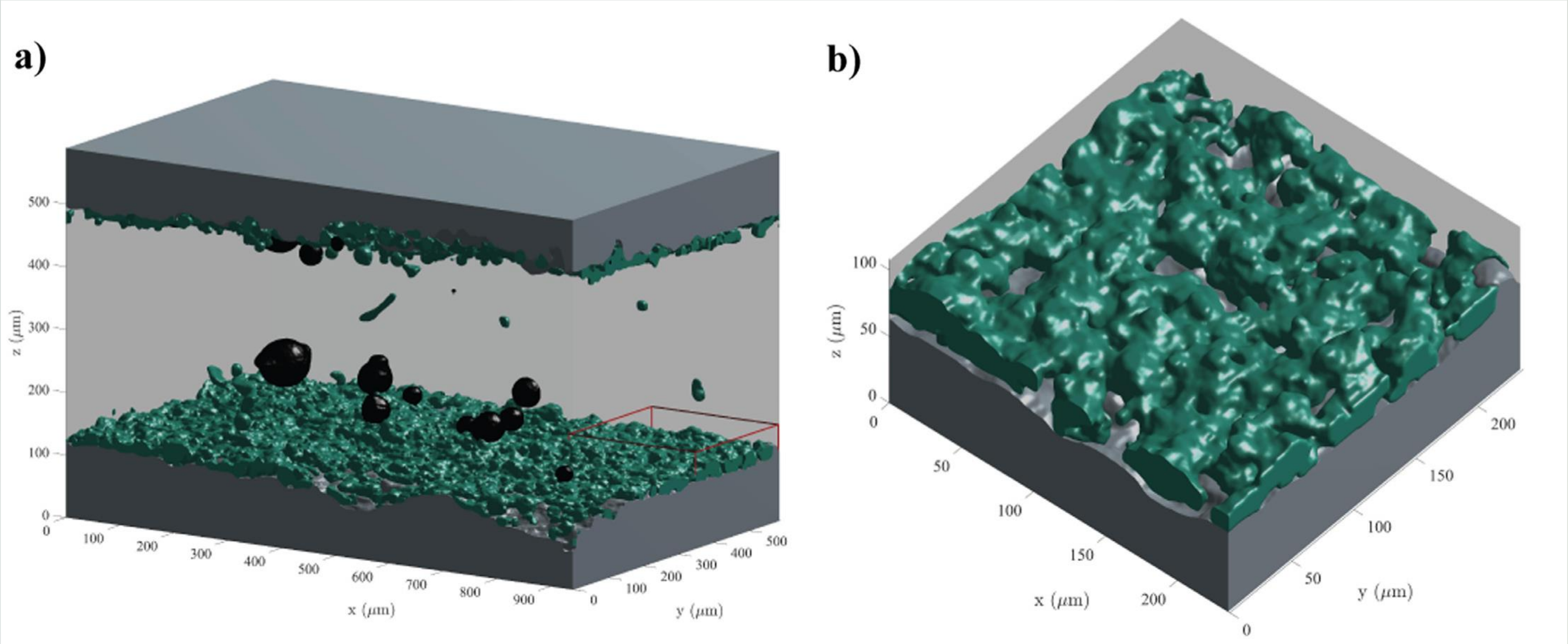
Ag-Ni Circuit Paste Fabrication



Ar Flow at 20 sccm

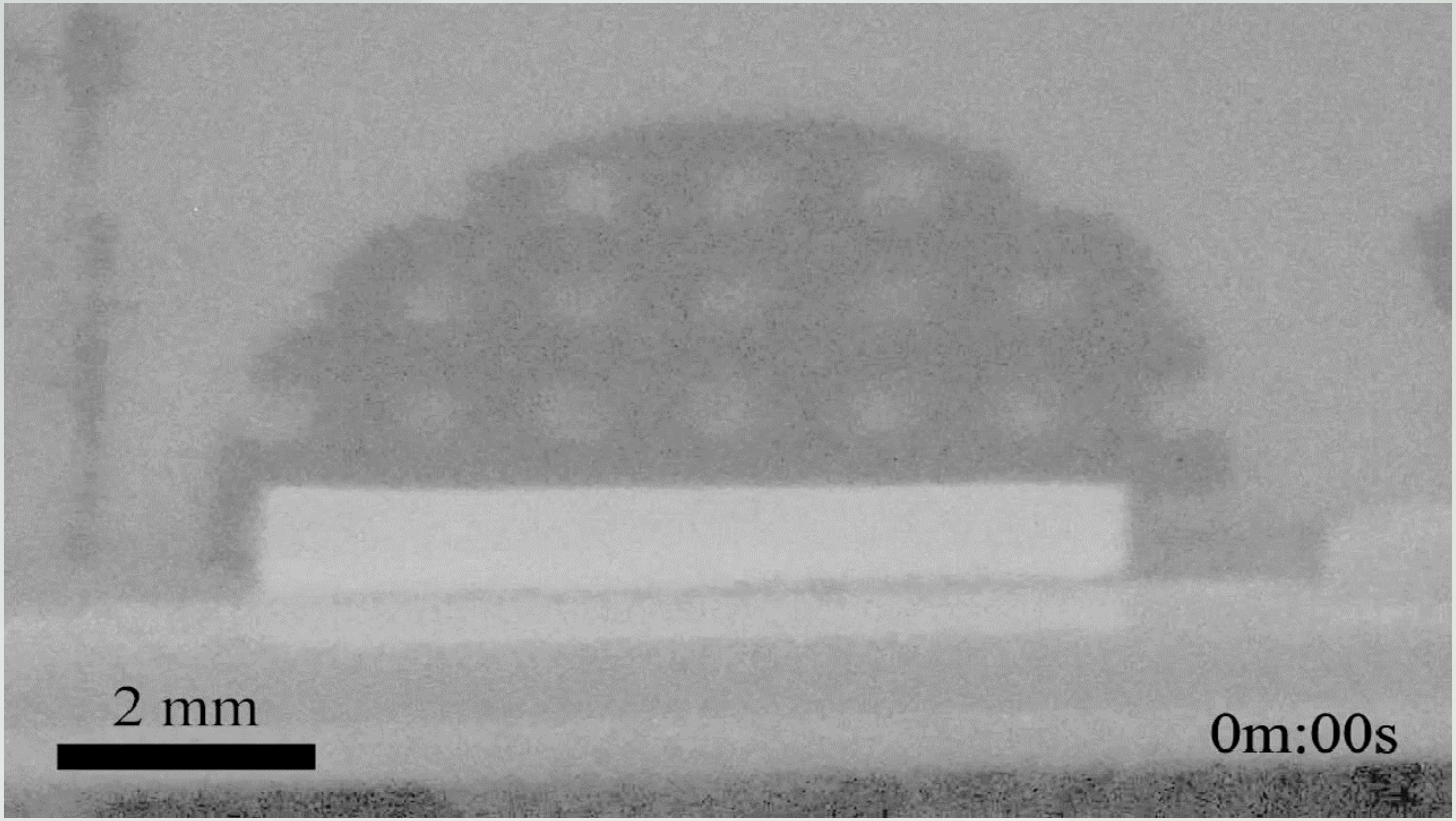
Ag-Ni Circuits >97% Dense Can Be Produced With this Technique



3D X-ray Tomography on Sapphire|Ni|Ag|Ni|Sapphire Samples Performed at Argonne National Laboratory

Hu, et al. "Patterned nickel interlayers for enhanced silver wetting, spreading and adhesion on ceramic substrates." *Scripta Materialia* 196 (2021): 113767.

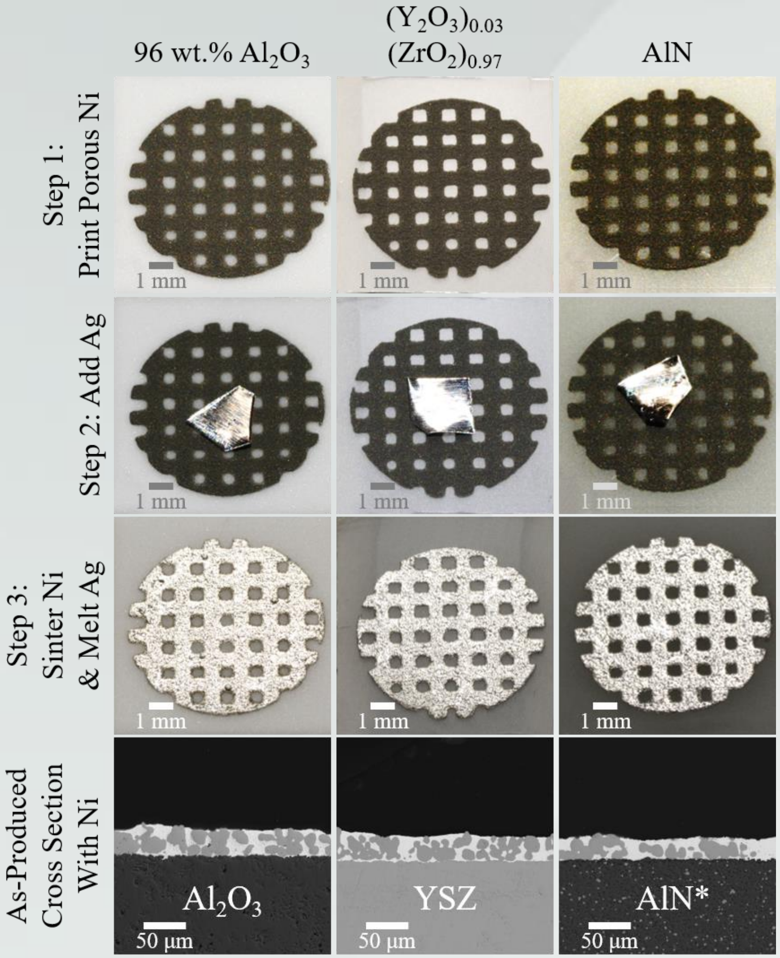
Silver Can Wet Nickel and Move Upwards against Gravity on a Non-wetting Ceramic Substrate!



In-Situ molten silver wetting on a sapphire-supported nickel interlayer at ~1000°C

Hu, et al. "Patterned nickel interlayers for enhanced silver wetting, spreading and adhesion on ceramic substrates." *Scripta Materialia* 196 (2021): 113767.

This Nickel-Patterned Ag Wetting Can Be Achieved on A Variety of Substrates

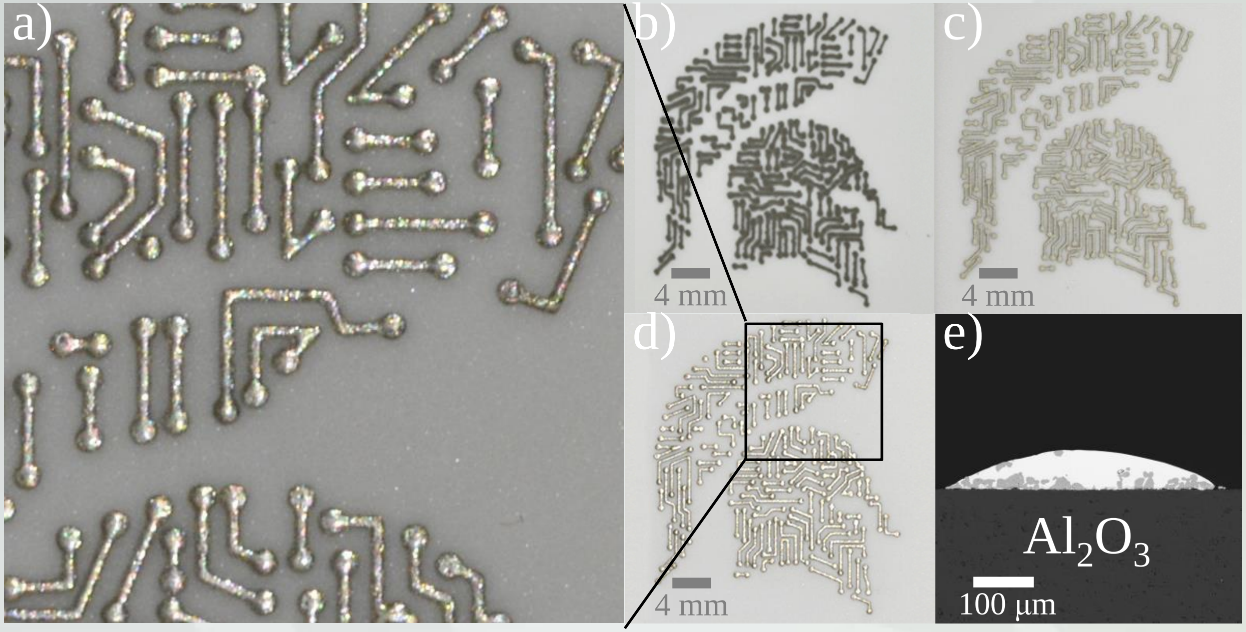


Plan and cross-sectional views of Ag-Ni circuits produced using a 3-step process:

1. Print nickel pastes on the substrate
2. Add a piece of Ag foil
3. Optionally hold to 850 °C for 2 hours in Ar with carbon as an oxygen getter to sinter the Ni and then hold at ~1000 °C for 5-30 minutes to melt the Ag.

Hu, et al. "Patterned nickel interlayers for enhanced silver wetting, spreading and adhesion on ceramic substrates." *Scripta Materialia* 196 (2021): 113767.

Intricate Ag-Ni Circuit Patterns Can Also Be Produced by Printing and Melting Ag Ink on Porous Ni Ink



Intricate circuit pattern Figure (a) produced by:

Step 1: Figure (b): Print Ni paste on the substrate

Step 2: Figure (c): Print Ag paste on top of the Ni pattern

Step 3: Figure (d): Optionally heat to 850 °C for 2 hours in Ar with carbon as an oxygen getter to sinter the Ni and then ramp and hold at ~1000°C for 5-30 min to melt Ag to produce the X-Section in Figure 1(e).

Hu, et al. "Patterned nickel interlayers for enhanced silver wetting, spreading and adhesion on ceramic substrates." *Scripta Materialia* 196 (2021): 113767.

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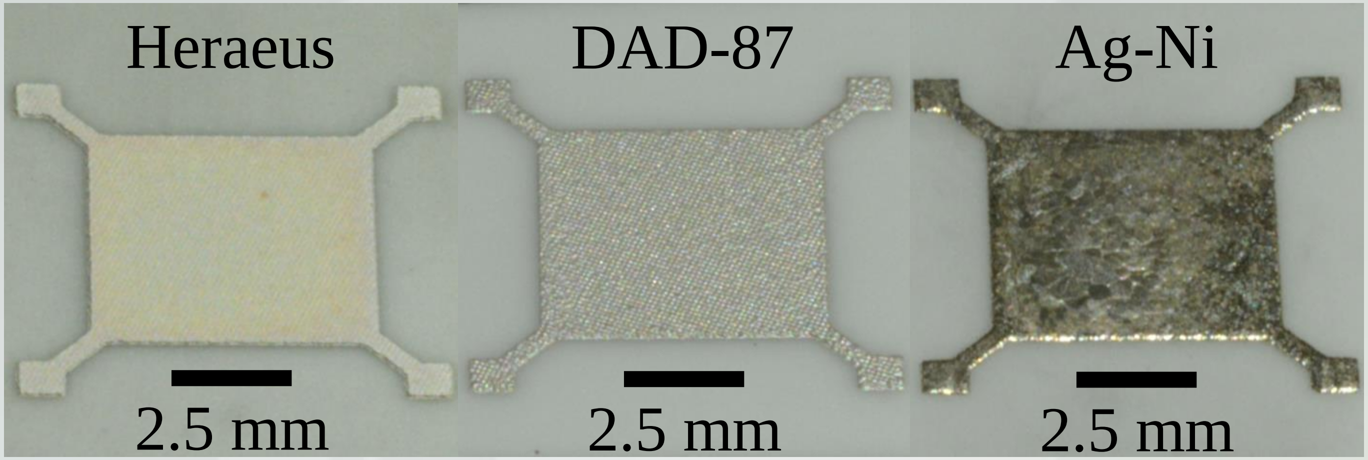
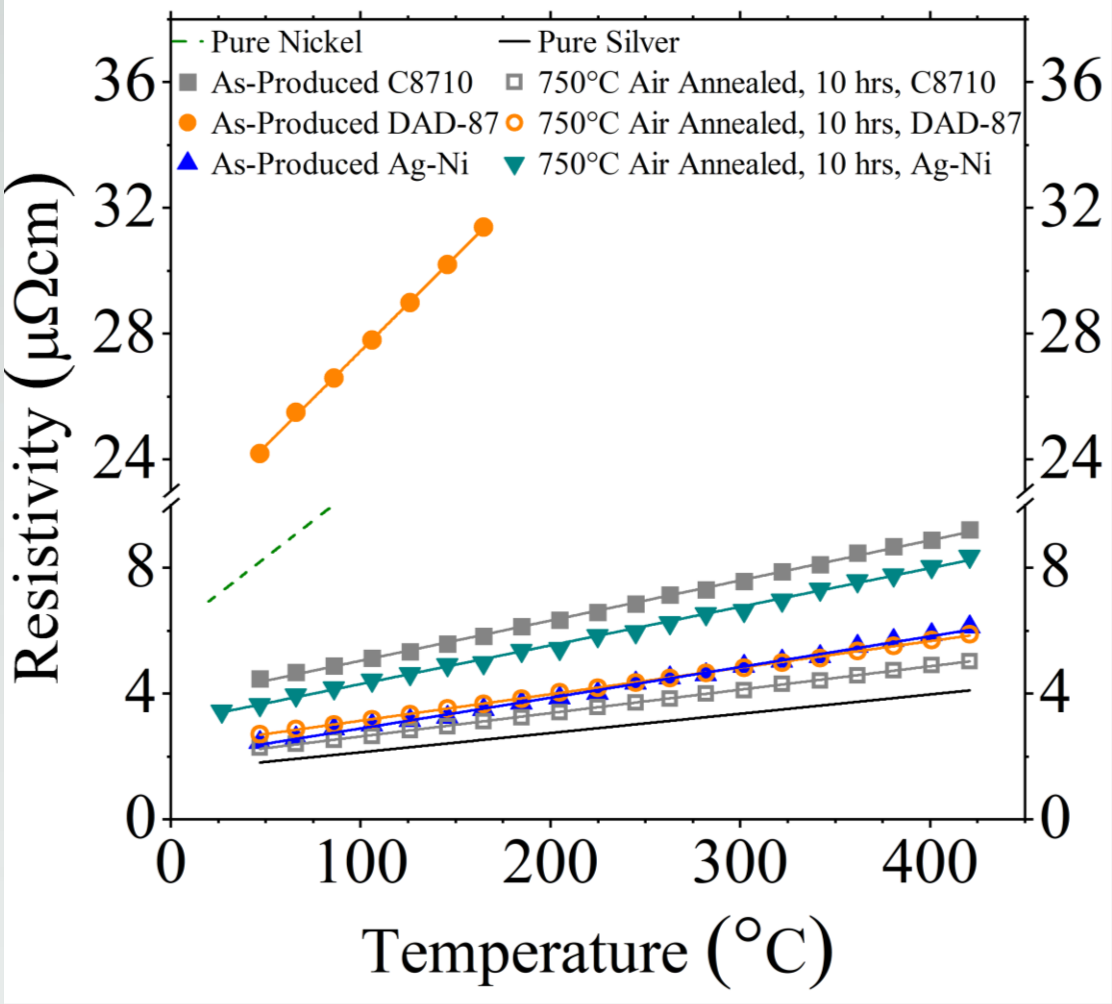
The Sheet Resistivity of Commercial Ag vs Ag-Ni Circuits Was Measured in a Van der Pauw Configuration



Plan view of as-produced sheet resistivity measurement samples produced using Heraeus C8710, DAD-87 and Ag-Ni

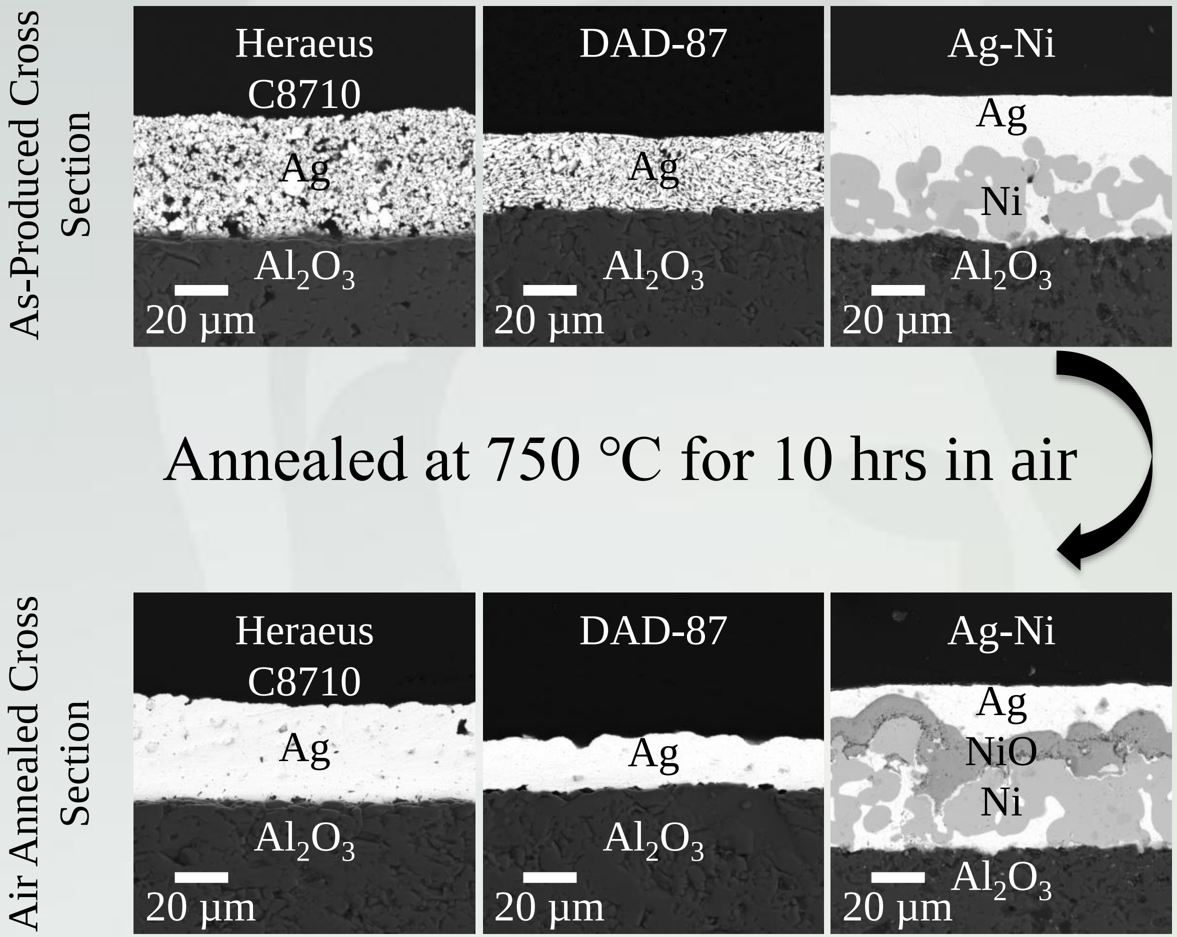
Hu, et al. "Patterned nickel interlayers for enhanced silver wetting, spreading and adhesion on ceramic substrates." *Scripta Materialia* 196 (2021): 113767.

The As-Produced Ag-Ni Circuits Had Lower Sheet Resistivity than Some Commercial Ag Pastes. After Annealing in Air, the Ag-Ni Sheet Resistivity Only Increased Slightly



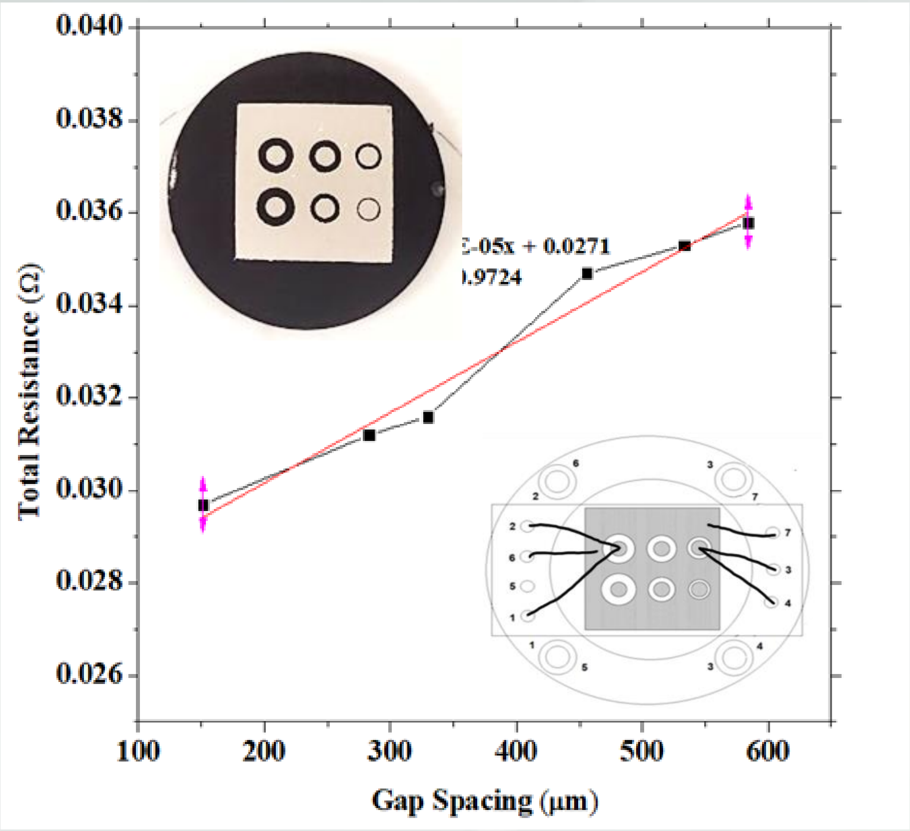
Hu, et al. "Patterned nickel interlayers for enhanced silver wetting, spreading and adhesion on ceramic substrates." *Scripta Materialia* 196 (2021): 113767.

The High Density of the Ag-Ni Circuits Promoted the Low In-Plane Sheet Resistivity



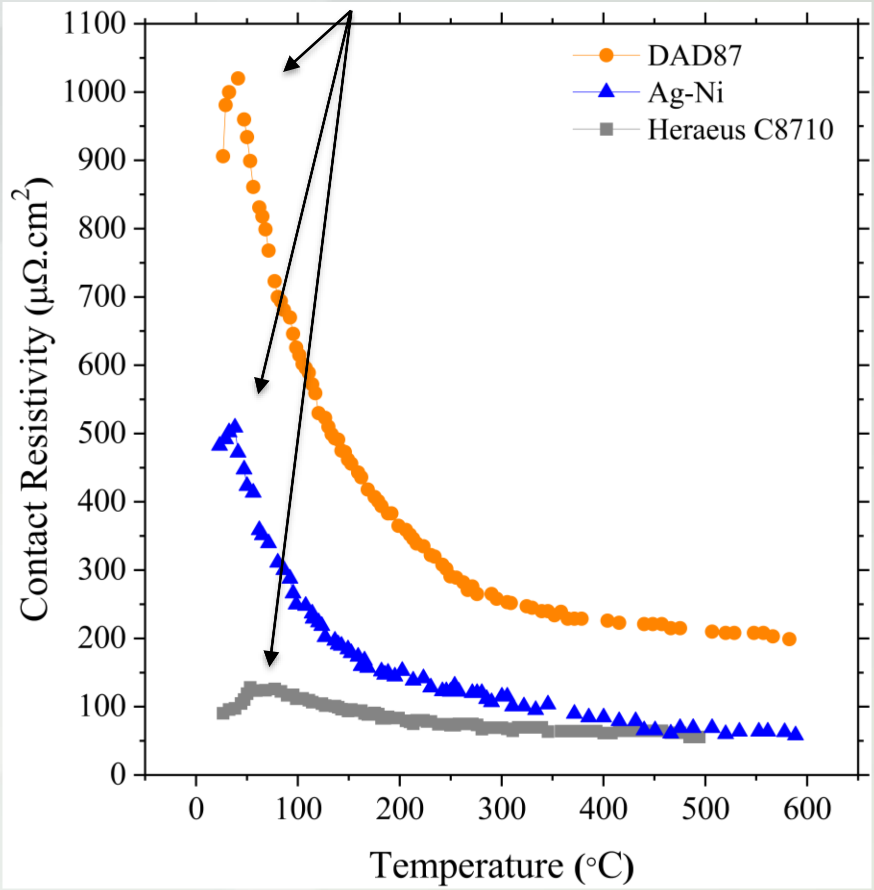
Hu, et al. "Patterned nickel interlayers for enhanced silver wetting, spreading and adhesion on ceramic substrates." *Scripta Materialia* 196 (2021): 113767.

The Ag-Ni Circuits Had a Low Contact Resistivity on Lanthanum Strontium Manganite



The total resistance versus gap spacing for Heraeus C8710. The contact resistance is 2x the y-axis intercept

LSM ferromagnetic-paramagnetic transitions



The contact resistivity of 750 °C air annealed Ag circuits at different temperatures

Bhatlawande, Aishwarya, et al. "High Temperature Contact and Bulk Resistivity of Several Silver-Based Circuit Pastes in Air." *Journal of Electronic Materials* (In preparation) 2022.

Outline

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- **Experiments**
- **Results and Discussion**
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  - Ag-Ni Mechanical Performance
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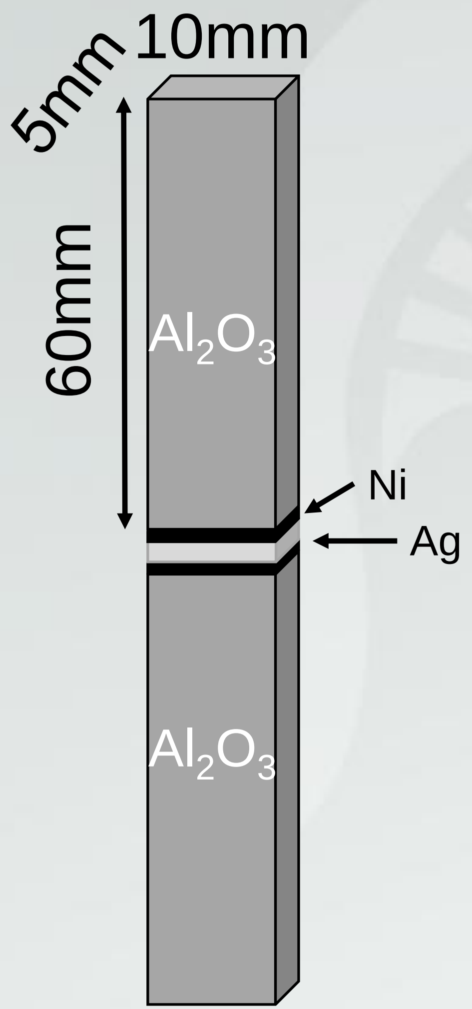
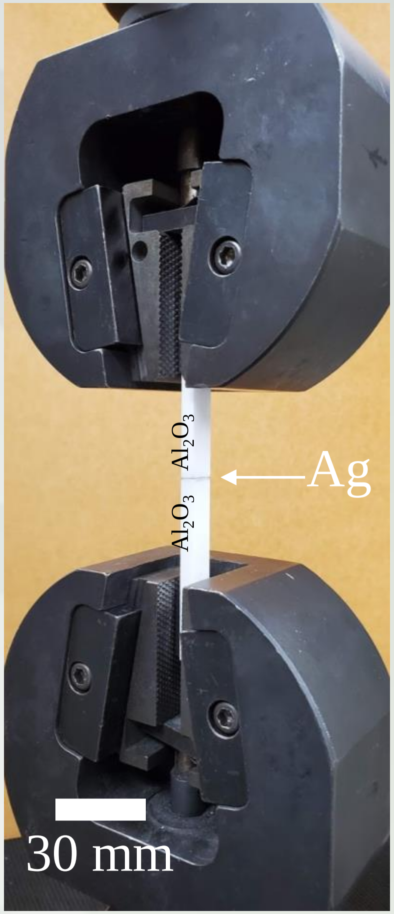
  - Nickel Phase-Field Sintering Simulations
- **Conclusions**

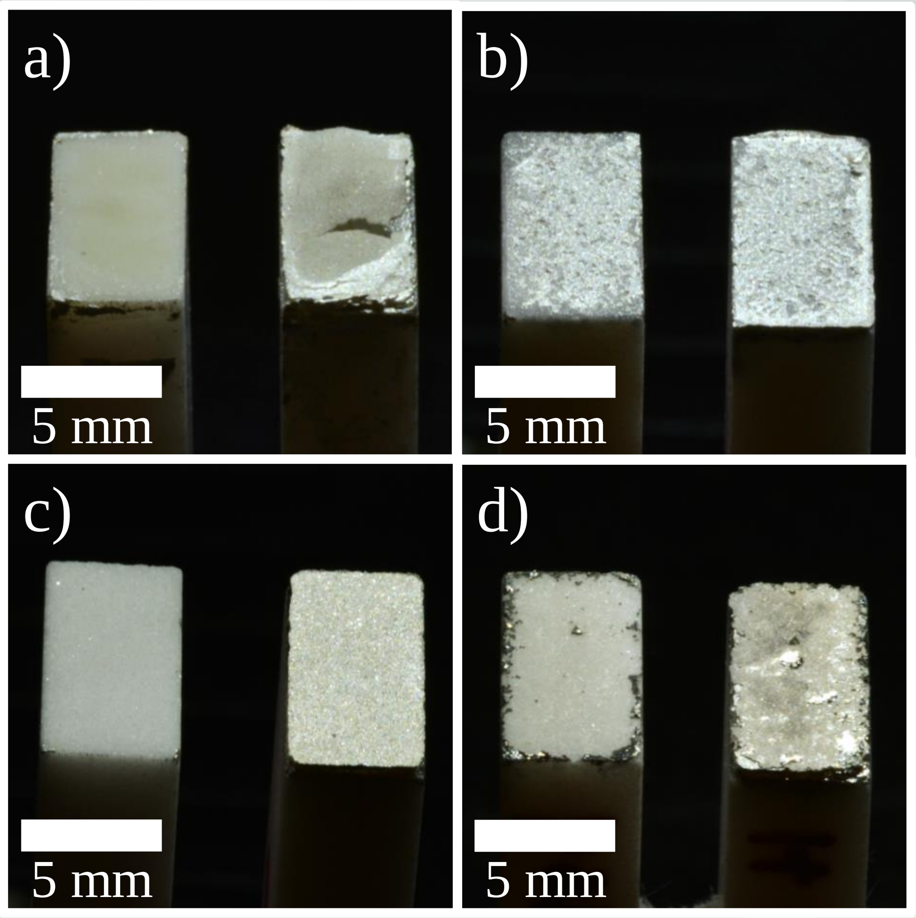
The Bonding Strength between Ag Pastes and Sapphire Was Measured via Tensile Testing





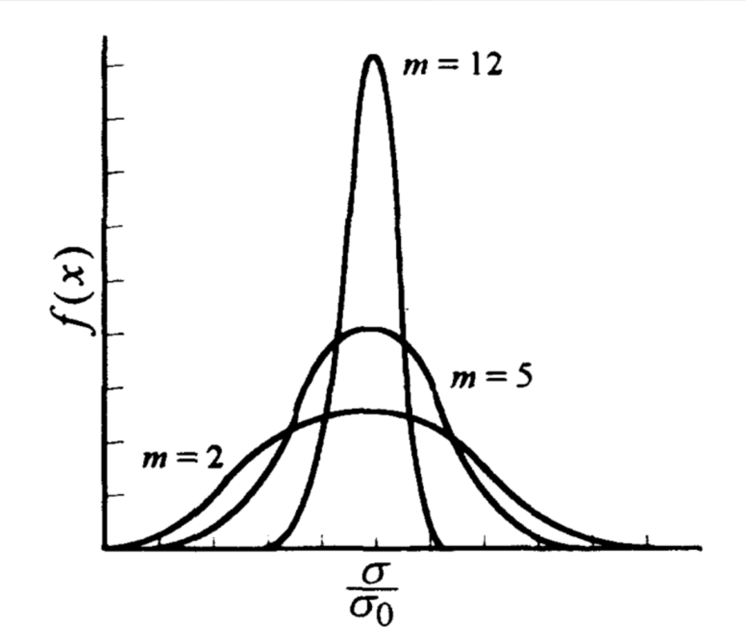
The tensile test sample and experiment set up

Both the Ag and Ag-Ni Samples Fractured Along the Metal-Sapphire Interface After 10 hrs of 750°C Air Annealing



The fracture of (a) air annealed Heraeus C8710, (b) as-produced Ag-Continuous Ni, (c) air annealed Ag-Continuous Ni, (d) air annealed DAD-87

Weibull Plots Are a Statistical Approach to Describe Processing-Inconsistency-Induced Strength Distributions



If the survival probability S is assumed to take the form

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

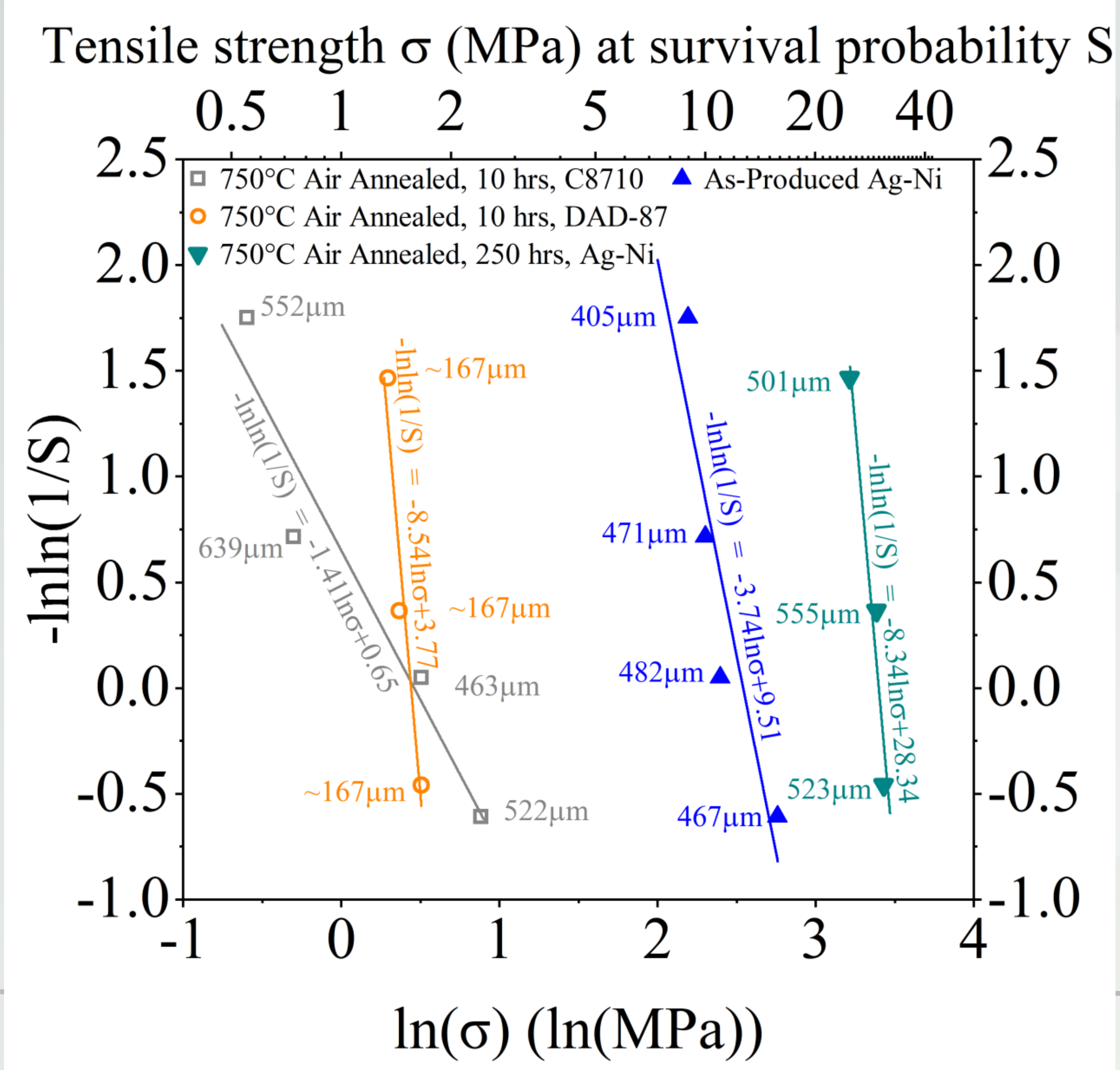
then,

$$\text{-ln ln}\frac{1}{S} = -m ln\sigma + m ln\sigma_0$$

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.

Weibull, W. A Statistical Distribution Function of Wide Applications. **1951,** *103* (730), 293-297.
Barsoum, M. W. *Fundamentals of Ceramics*, Institute of Physics Publishing: Bristol and Philadelphia, 2003.

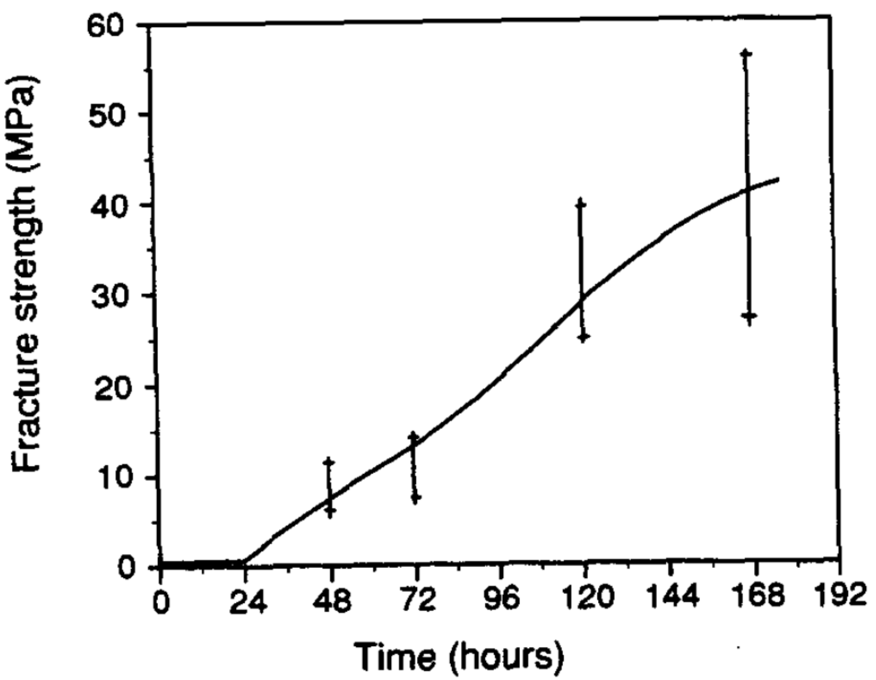
The Sapphire|Ag-Ni Interface Actually Gets Stronger After Oxidation (Even though Brittle NiO Is Forming)



Paste	C8710	DAD-87	As-Produced Ag-Ni	Air Annealed Ag-Ni
Stress (MPa)	6.0×10^{-2}	0.91	3.7	17

Design stress ensuring a survival probability of 99%

Stronger Bonding after Air Annealing Has Been Observed Both Experimentally and Computationally in the Literature



Fracture strength of Ag/Al_2O_3 bonds annealed at 900°C for 24 h in vacuum vs. reoxidation time at 900°C in air

Work of adhesion (J/m^2)	
Ag(l)/YSZ(1 1 1)	(Ag(l)+2O)/YSZ(1 1 1)
0.11±0.01	0.43±0.01

The work of adhesion change between Ag/YSZ substrate with and without oxygen.

Air annealing increased the oxygen concentration in Ag circuits, which increased the work of adhesion and the bonding tensile strength.

Treheux, *et al*. *Scripta Metallurgica et Materialia;(United States)*(1994)
Phongpreecha, T., *et al.* Acta Materialia(2018)

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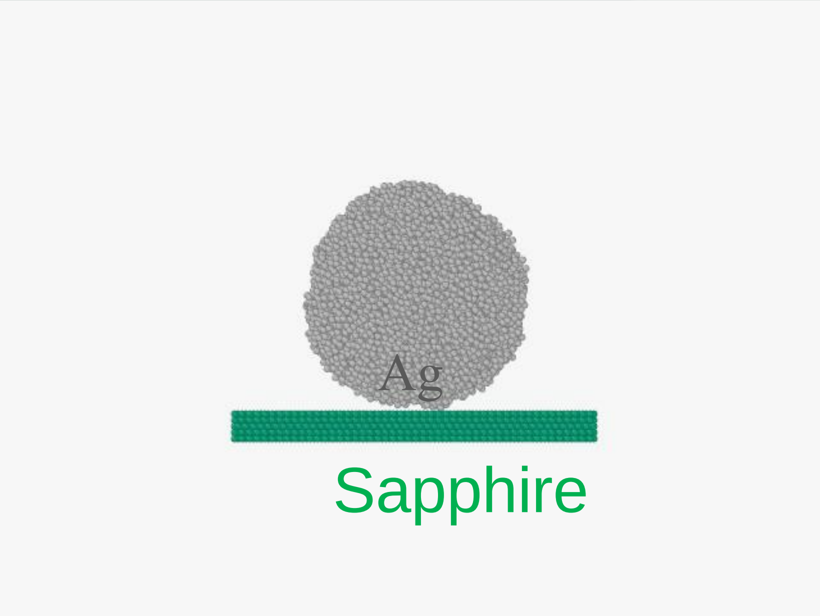
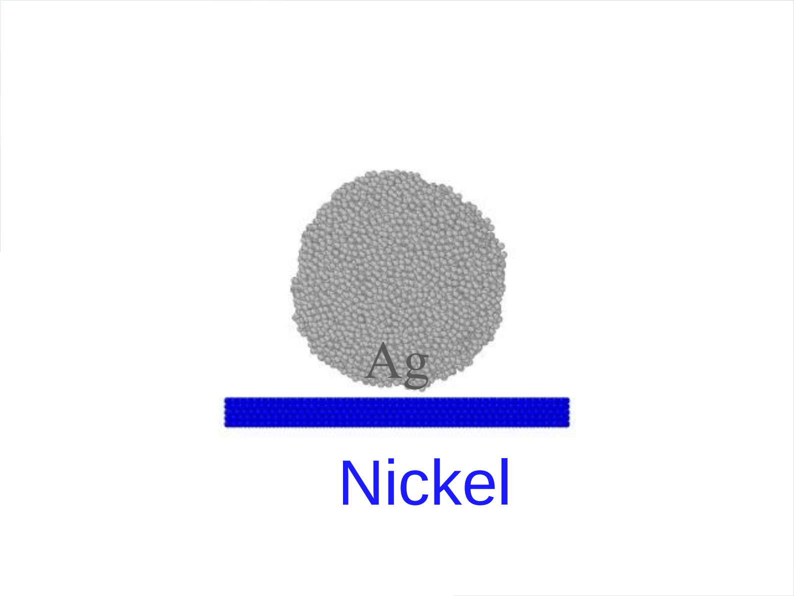
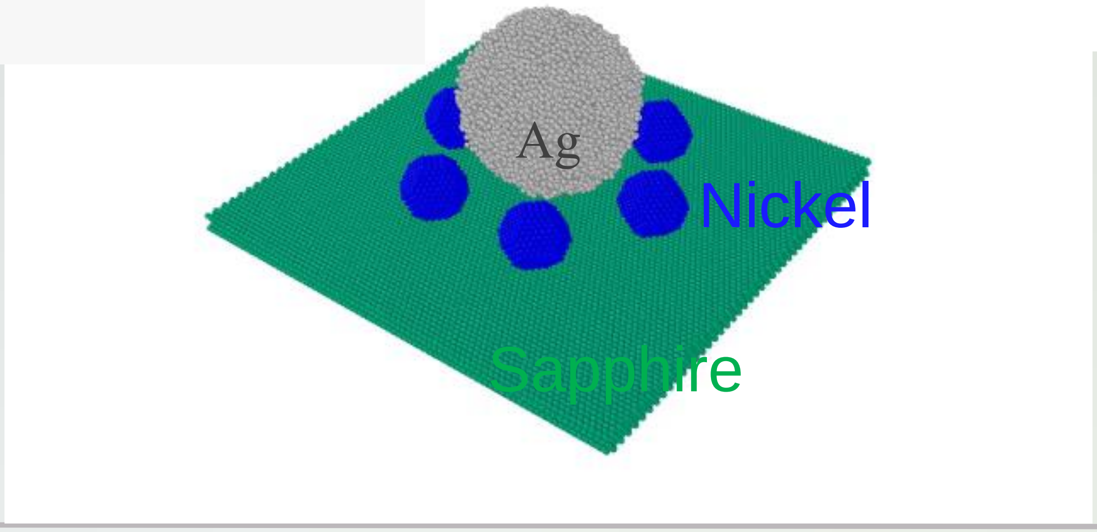
DFT-Informed Molecular Dynamics Modeling Was Performed

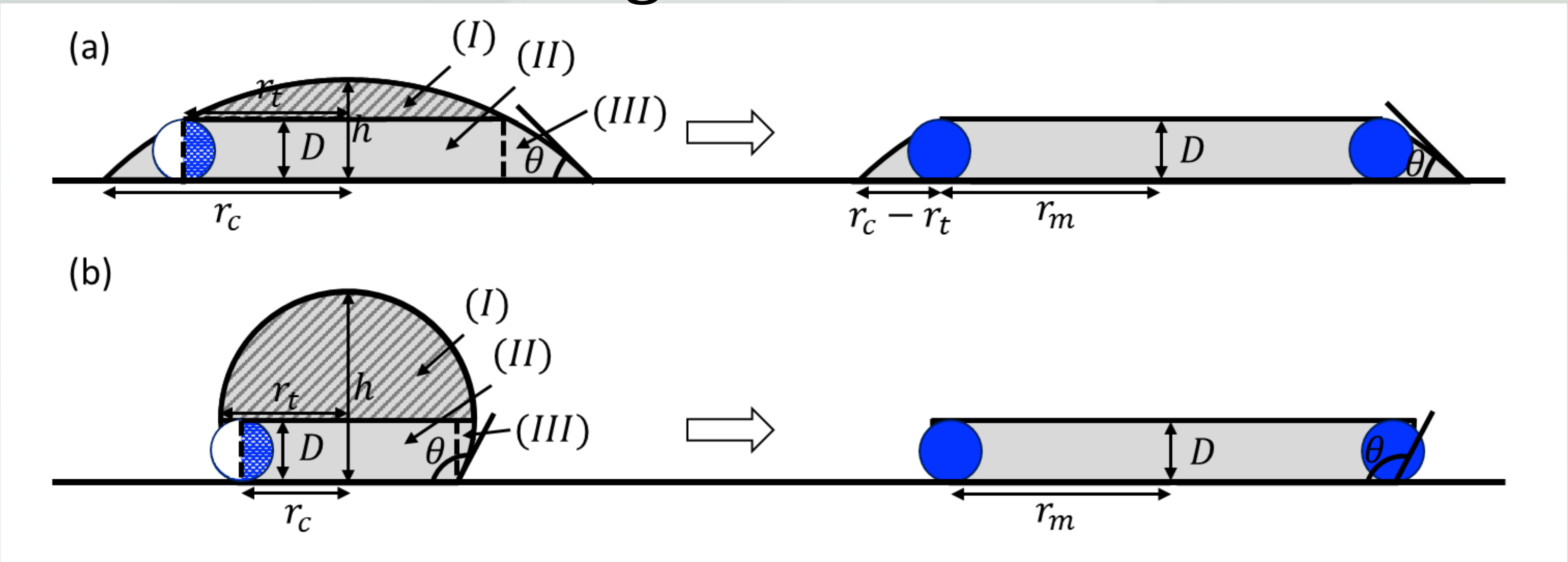






Park, Jiyun, et al. "Enhanced liquid metal wetting on oxide surfaces via patterned particles." *Acta Materialia* 199 (2020): 551-560.

An Analytical Model Was Established to Analyze the Wetting Enhancement



Schematic of the cross-section of a droplet on the substrate, where the shaded gray region represents a Ag liquid droplet on a bare substrate (left), and the cross-section of a transformed droplet when Ni particles (blue circles) are placed on the substrate (right): On the left, the circle refers to a Ni particle to visualize where the Ni particles will be placed for better understanding. The volume of the dotted blue region in the circle was considered to calculate rm. (a) $r_t < r_c$ and (b) $r_t > r_c$.

$$\frac{A_{patterned}}{A_{bare}} = \begin{cases} \frac{(r_m + r_c - r_t)^2}{r_c^2} \; for\; r_t < r_c \\ \frac{r_m^2}{r_c^2} \; for\; r_t > r_c \end{cases}$$

Park, Jiyun, et al. "Enhanced liquid metal wetting on oxide surfaces via patterned particles." *Acta Materialia* 199 (2020): 551-560.

Hexagonal Ni Particle Patterns Were Identified as the Optimal Ni Arrangement, Creating a Maximum Wetting Area Enhancement of 224%

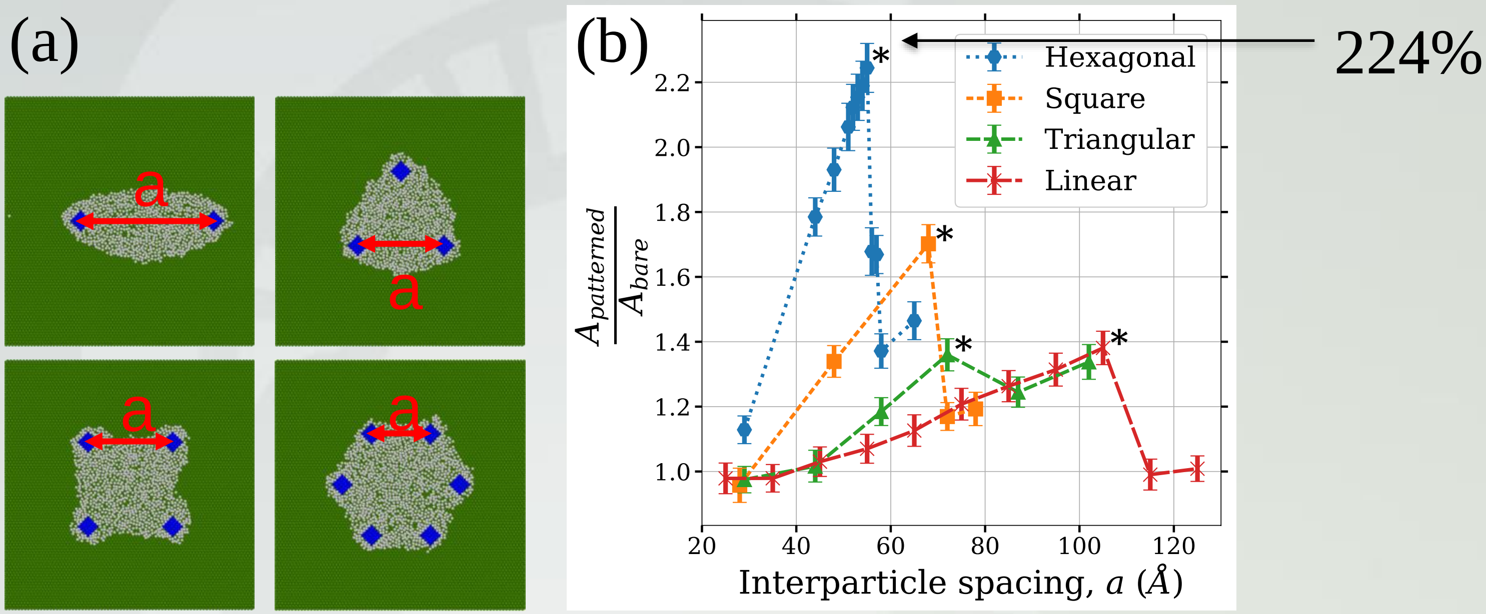
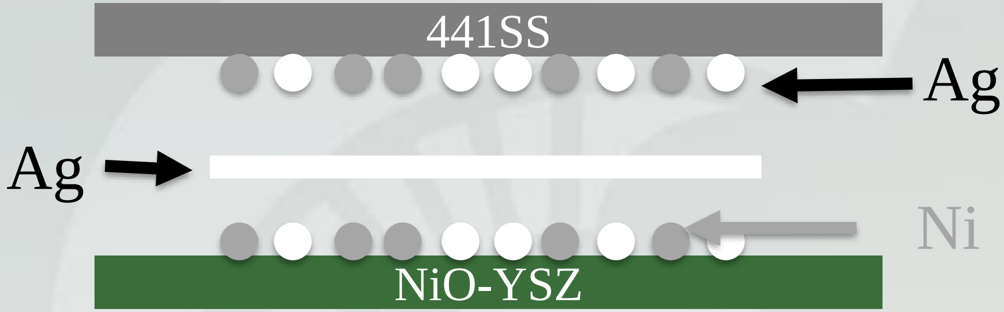


Figure (a): the four different nickel particle configurations on YSZ surface and the wetting area by liquid silver.
Figure (b) the wetting area enhancement by varying the interparticle spacing at each configuration.
Error bars denote the standard deviation of the area enhancement values.

Park, Jiyun, et al. "Enhanced liquid metal wetting on oxide surfaces via patterned particles." *Acta Materialia* 199 (2020): 551-560.

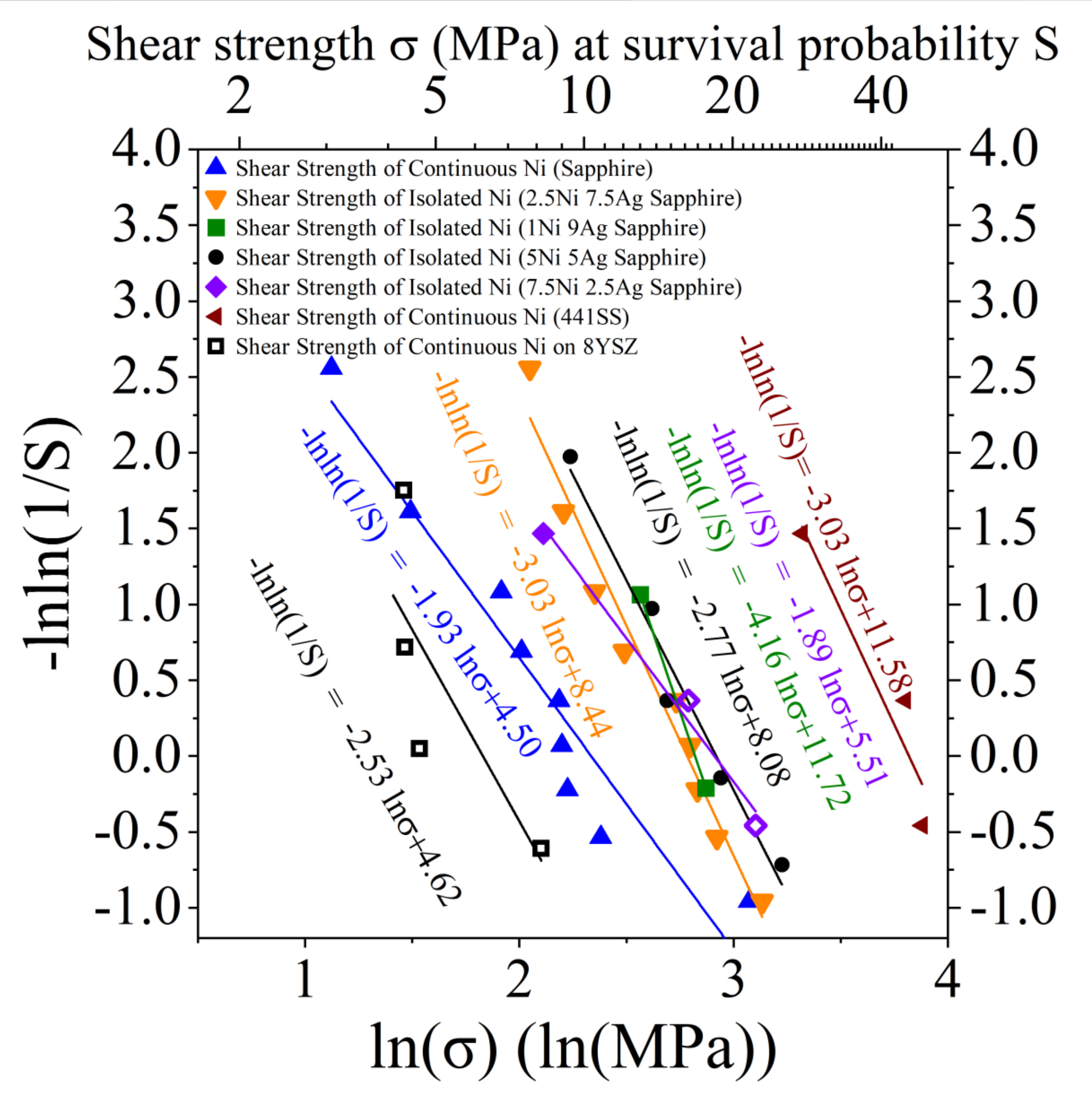
Diluting Nickel with Silver Powder Can Also Result in Dense Ag-Ni Brazes/Circuit Pastes

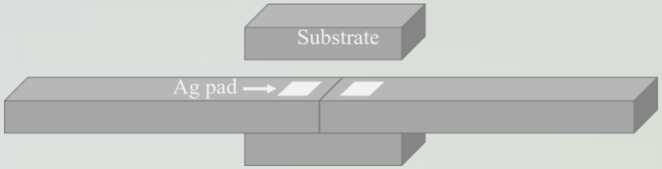


Isolated Ni Particles Can Be Produced by Printing an Interlayer Ink that is a Mixture of Ni and Ag

Back-scattered SEM cross-sectional image of NiO-YSZ|25%Ni|Ag|25%Ni|441SS braze as-produced sample

"Isolated" Nickel Ag-Ni Exhibits Shear Strengths Similar to "Continuous" Nickel Ag-Ni





Double shear lap sample design

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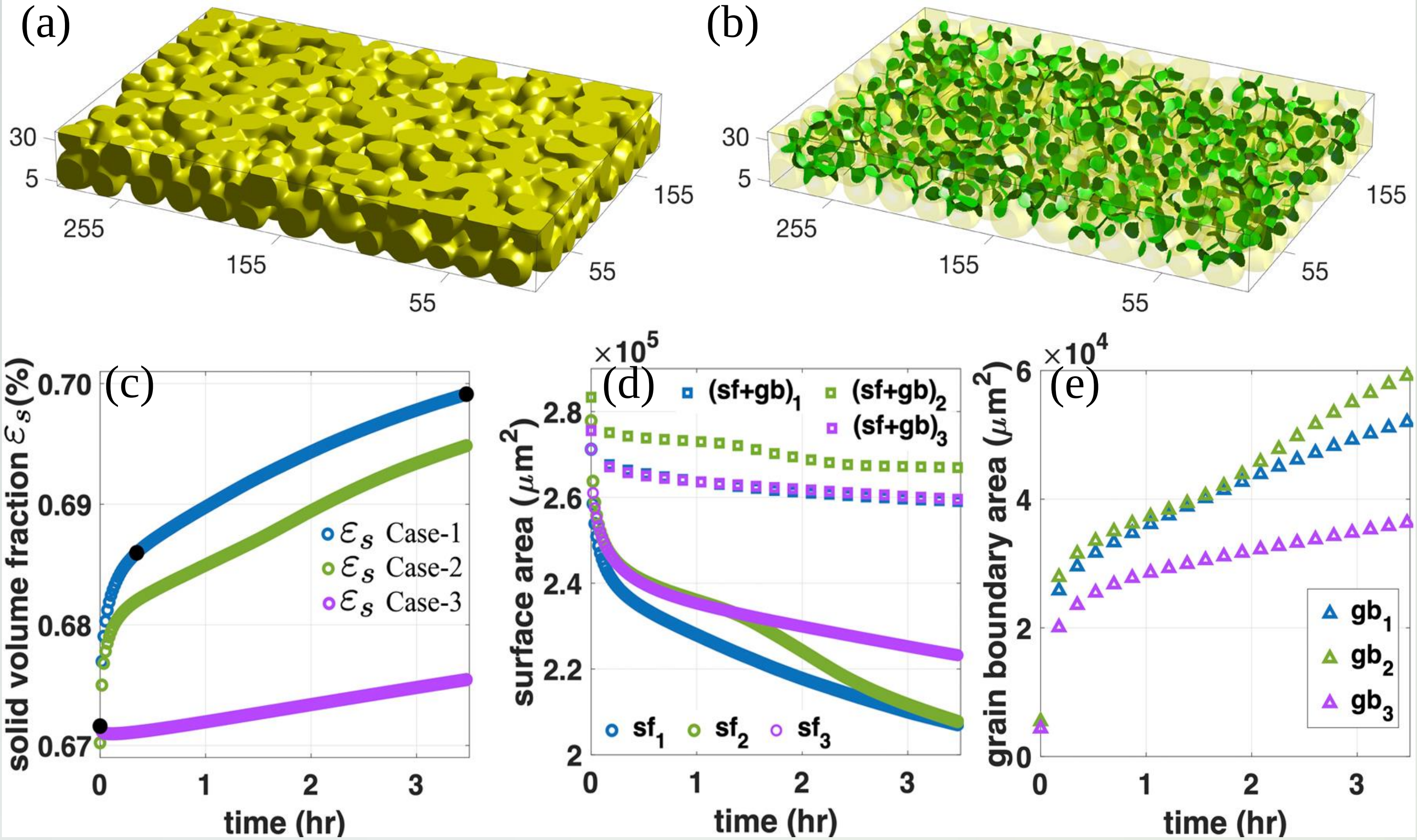
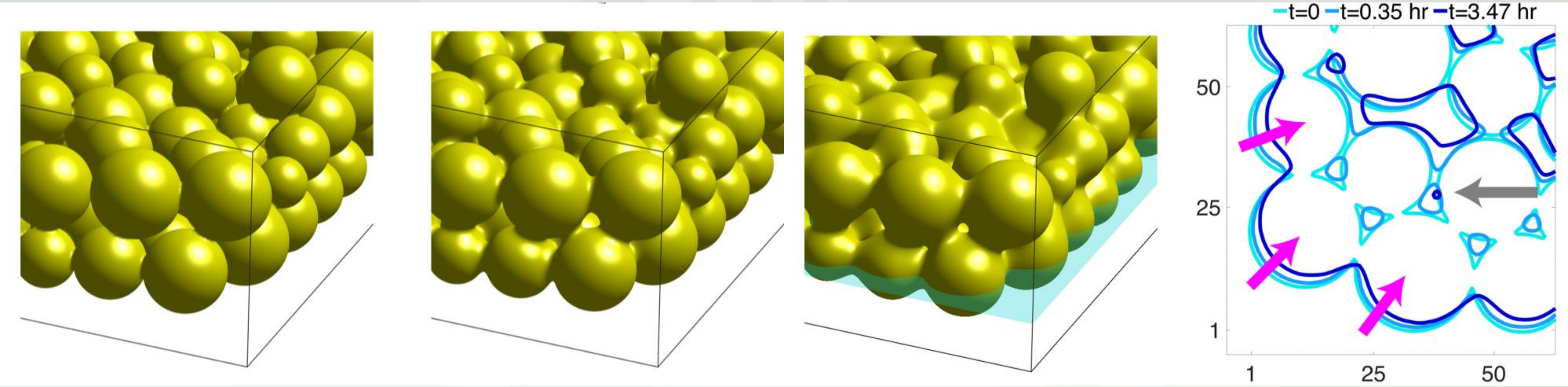
The Solid Volume Fraction, Surface Area and Grain Boundary Area Were Calculated during the Sintering Simulation Process



Termuhlen, Robert, et al. "Three-dimensional phase field sintering simulations accounting for the rigid-body motion of individual grains." *Computational Materials Science* 186 (2021): 109963.

See the Citation Below for a New Computational Trick to Incorporate the Rigid Body Motion of Individual Particles into Phase-field Sintering Models, While Keeping Memory Requirements Low.

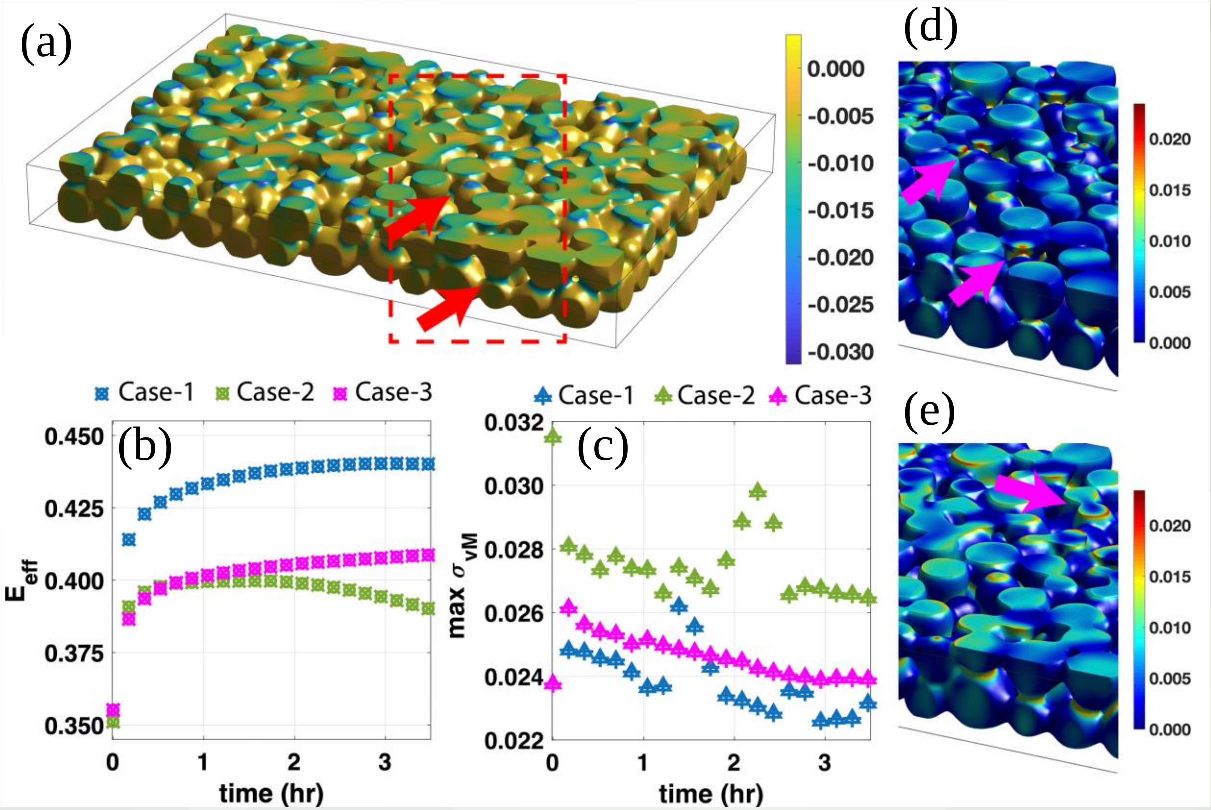


t=0 t=0.35 h t=3.47 h

Ni particles following Gaussian distribution at *t*=0, 0.35h and 3.47h. The contour lines on the z=10 μm plane. Different lines correspond to different times.

Termuhlen, Robert, et al. "Three-dimensional phase field sintering simulations accounting for the rigid-body motion of individual grains." *Computational Materials Science* 186 (2021): 109963.

The Maximum von Mises Stresses Were Calculated for Each Configuration



These calculations showed that the nickel interlayer particles must be at least a few microns in size to ensure they are not delaminated from the substrate by the capillary forces accompanying molten Ag infiltration.

Termuhlen, Robert, et al. "Three-dimensional phase field sintering simulations accounting for the rigid-body motion of individual grains." *Computational Materials Science* 186 (2021): 109963.

Conclusions

1. Porous Ni interlayers dramatically improve the wetting, spreading, and adhesion of molten Ag on otherwise non-wetting substrates.
2. Even with the nickel oxidation that occurs after 10 hours in 750^{o}C air, Ag-Ni circuits have a sheet resistance that is only double that of pure, dense Ag and have SOFC operating temperature contact resistances on LSM that are as good as the best commercial Ag pastes.
3. On ceramic substrates Ag-Ni circuits adhere 20x better than those made from commercial Ag pastes.
4. Make sure to use nickel particles >1 micron in size when making Ag-Ni circuits/brazes.
5. Lower nickel particle loadings, perhaps produced via the optimal hexagonal Ni particle pattern predicted here, may improve the electrical and mechanical properties even further.

This work was generously supported by U.S. Department of Energy
Solid Oxide Fuel Cell Award Number DE-FE-0031672
Project Managers: Drew O’Connell & Venkat Venkataraman

Project Publications to Date

1. Park, Jiyun, et al. "Enhanced liquid metal wetting on oxide surfaces via patterned particles." *Acta Materialia* 199 (2020): 551-560.

2. Hu, Genzhi, et al. "Patterned nickel interlayers for enhanced silver wetting, spreading and adhesion on ceramic substrates." *Scripta Materialia* 196 (2021): 113767.

3. Termuhlen, Robert, et al. "Three-dimensional phase field sintering simulations accounting for the rigid-body motion of individual grains." *Computational Materials Science* 186 (2021): 109963.

4. Termuhlen, Robert, et al. "Smoothed Boundary Method for Simulating Incompressible Flow in Complex Geometries." *Computer Methods in Applied Mechanics and Engineering* (Submitted)

5. Bhatlawande, Aishwarya, et al. “High Temperature Contact and Bulk Resistivity of Several Silver-Based Circuit Pastes in Air.” *Journal of Electronic Materials* (In preparation)