



High Performance Circuit Pastes for Solid Oxide Fuel Cell Applications

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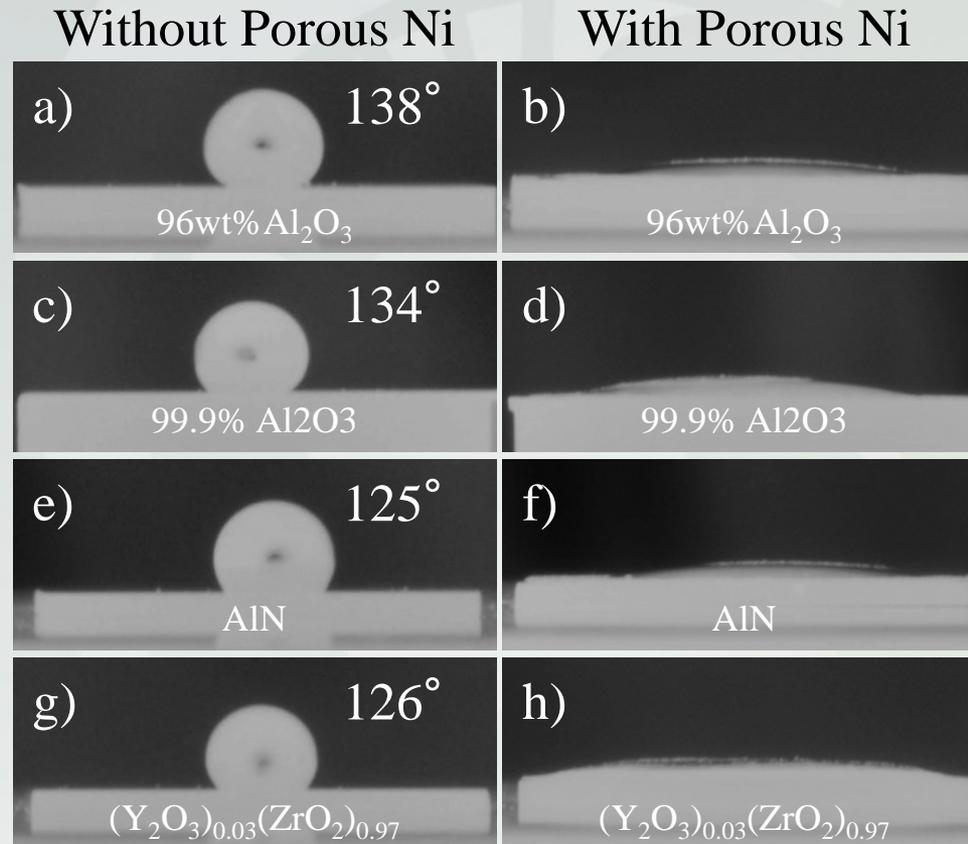
Funded by the Department of Energy Solid Oxide Fuel Cell Core Technology Program through Agreement Number DE-FE-0031672

July 2020

Outline

- **Background and Motivation**
 - Porous Ni Can Promote Ag Wetting on Different Substrates
- **Experiments**
- **Results and Discussion**
 - The Electrical Performance
 - The Mechanical Performance
 - Ag Wetting Molecular Dynamics Simulation and Optimal Pattern Calculation
 - Nickel Phase Sintering Simulation
- **Conclusions**

Nickel Interlayers Can Be Used to Improve the Wetting and Spreading of Silver on a Variety of Ceramic Substrates



5 mm

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Nickel Interlayers Can Also Be Used to Direct the Wetting and Spreading of Silver on a Variety of Ceramic Substrates

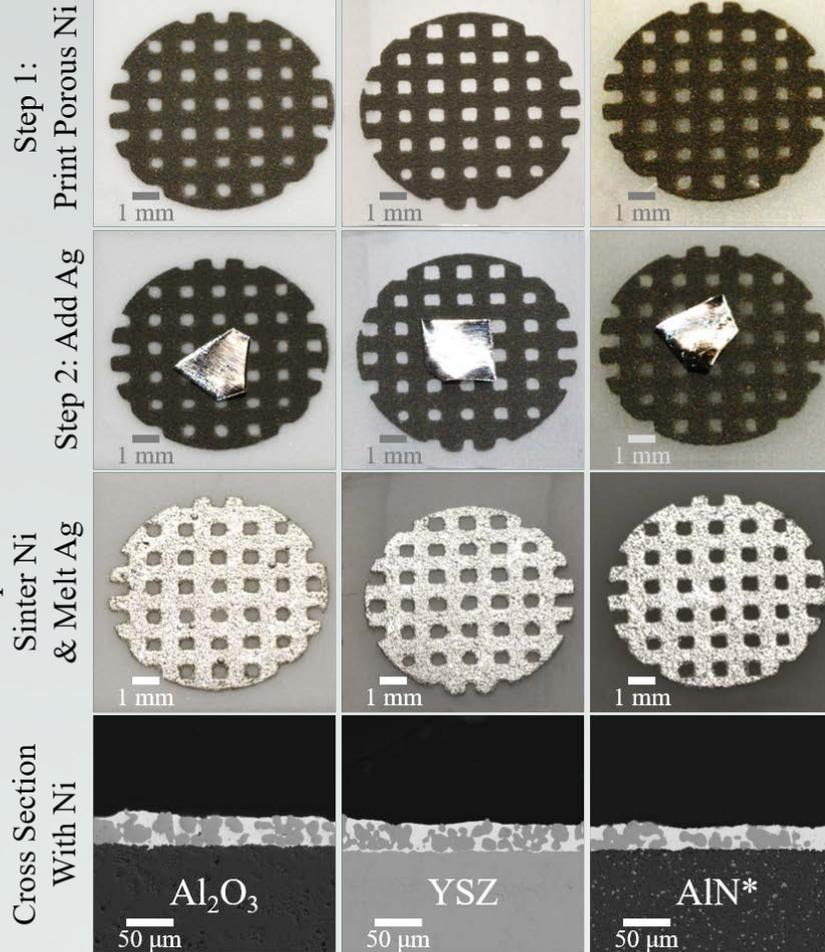
(Y₂O₃)_{0.03}
(ZrO₂)_{0.97} AlN Substrates

96 wt.% Al₂O₃

(Y₂O₃)_{0.03}
(ZrO₂)_{0.97}

AlN

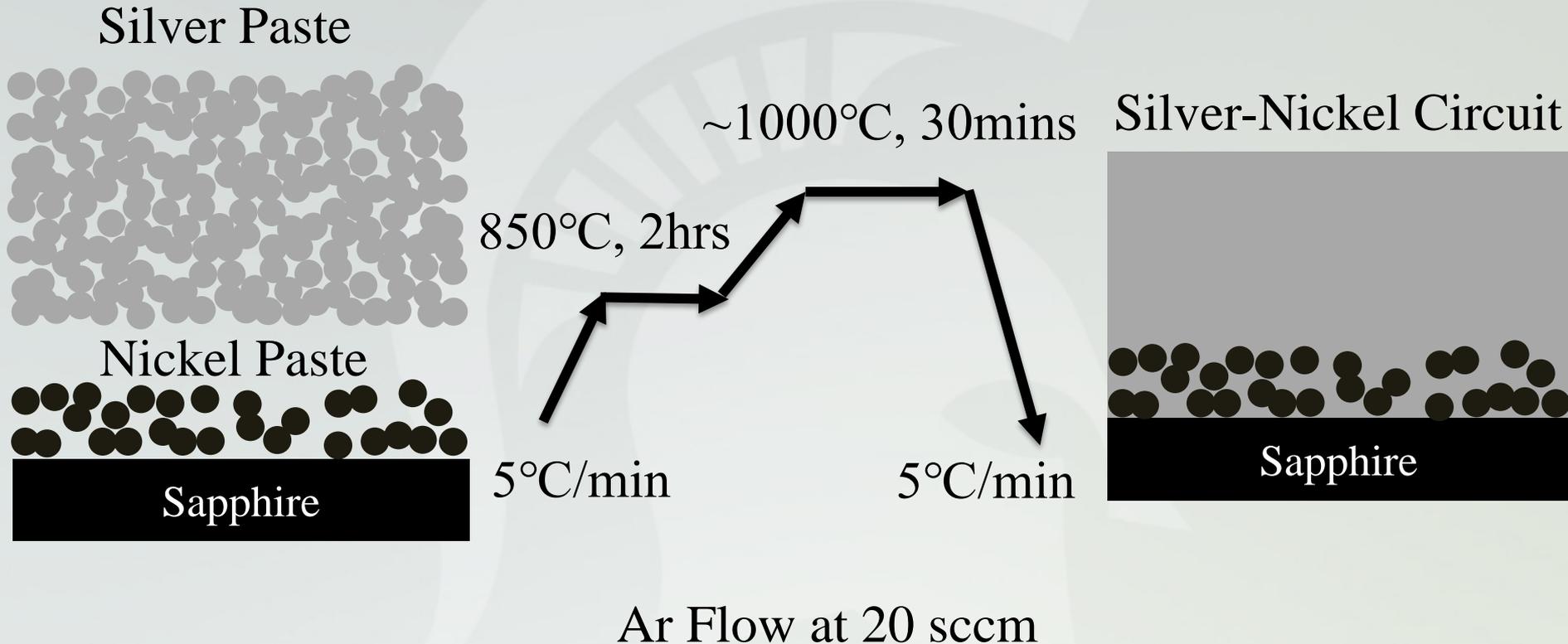
Substrates



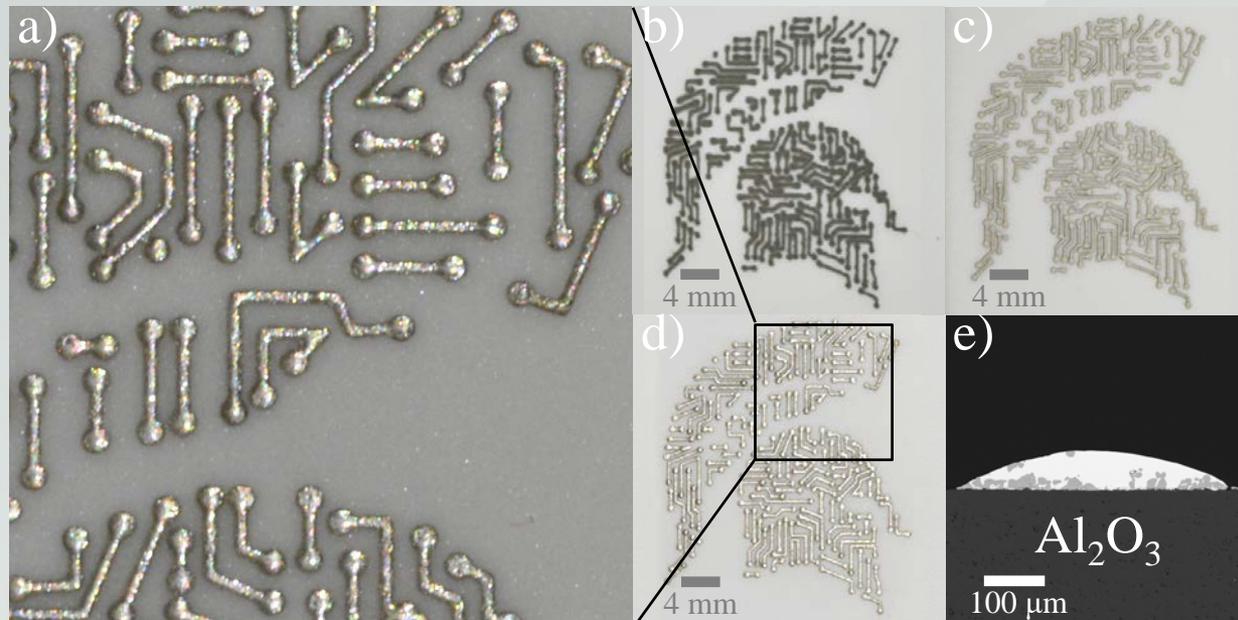
Plan and cross-sectional views of Ag-Ni circuits produced using a 3 step process:

1. Print nickel pastes on the substrate
2. Add a piece of Ag foil
3. Heat 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 30 minutes to melt the Ag.

Ag-Ni Circuit Fabrication



Intricate Ag-Ni Circuit Patterns Can Be Produced by Printing and Melting Ag on Screen Printed Ni Inks



Intricate circuit pattern Figure (a) produced by:

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

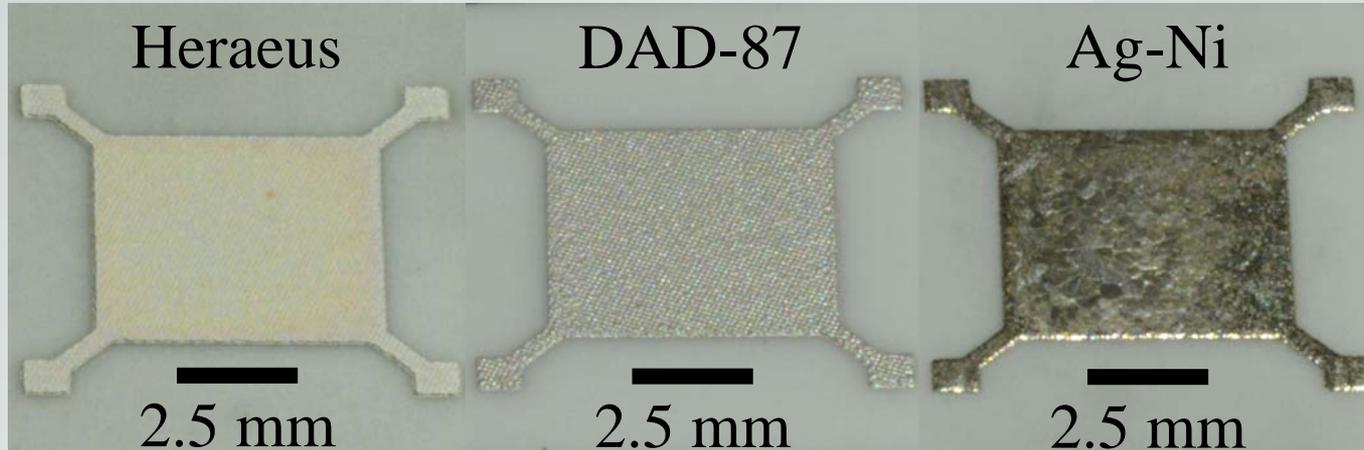
Step 2, Figure (c): Print Ag paste overtop the Ni paste pattern

Step 3, Figure (d): Heat 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 30 minutes to melt Ag to produce the X-Section in Figure 1(e).

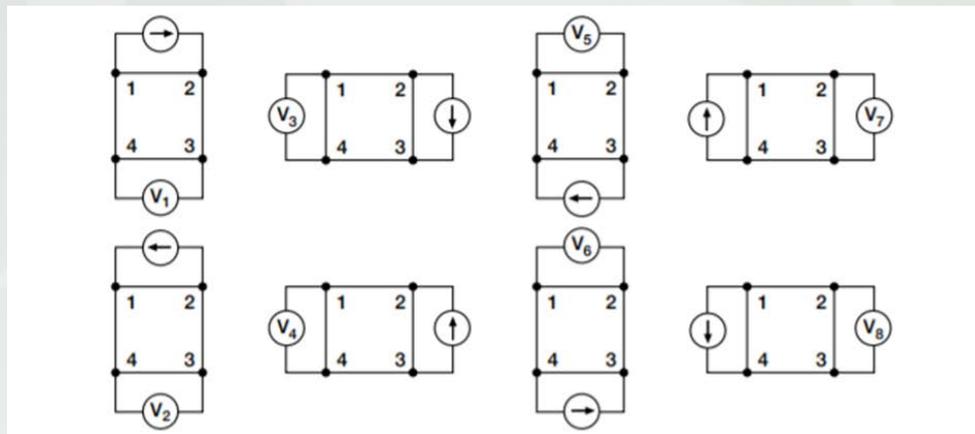
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The Sheet Resistivity Was Measured in a Van der Pauw Configuration

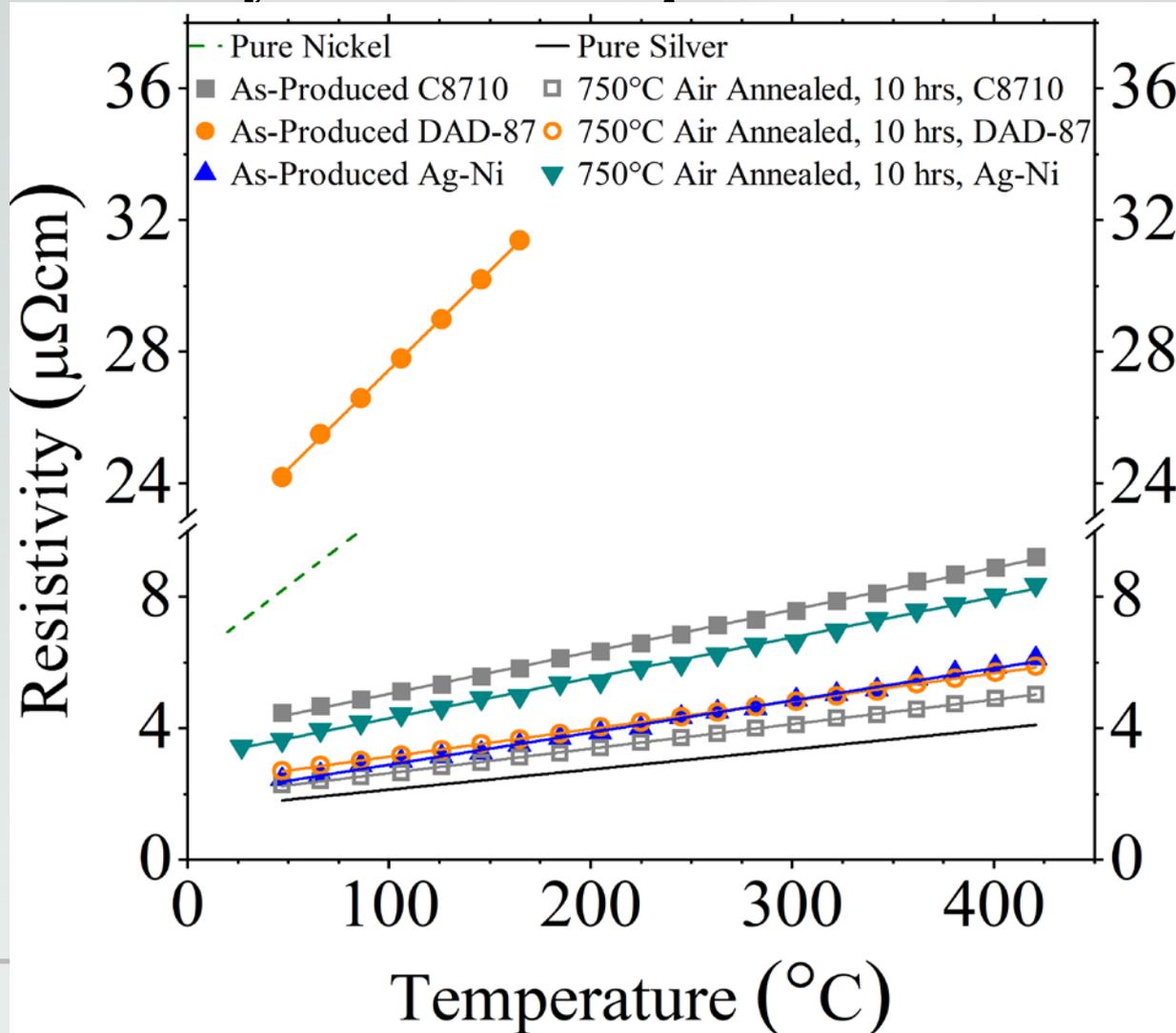


The plan view of as-produced sheet resistivity measurement samples produced by Heraeus C8710, DAD-87 and Ag-Ni

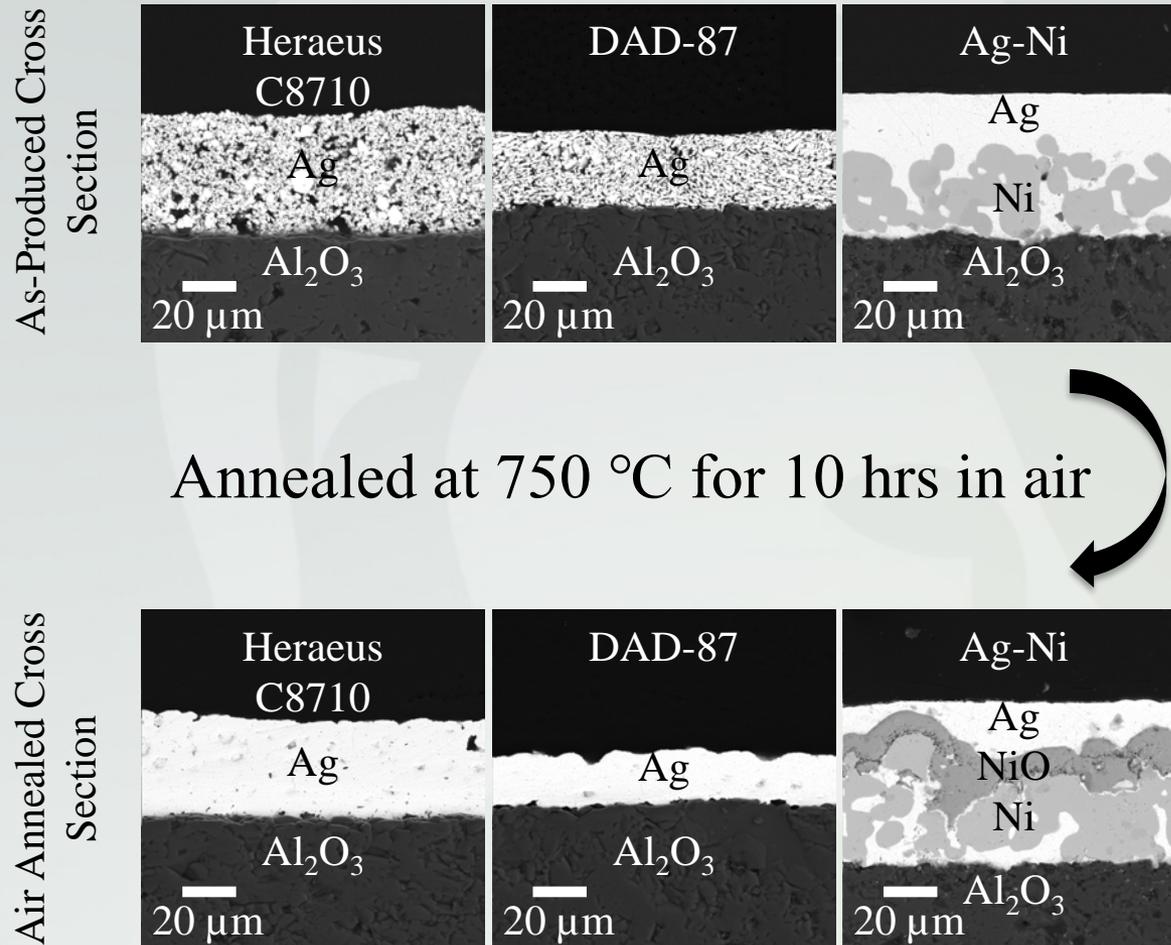


Van der Pauw resistivity measurement configurations

The As-Produced Ag-Ni Circuit Has Lower Resistivity than Commercial Ag Pastes. After Annealing in Air, the Resistivity Is Still Comparable to Pure Ag



The Lower Resistivity of Ag-Ni than Commercial Ag Pastes Results from the Dense Microstructure

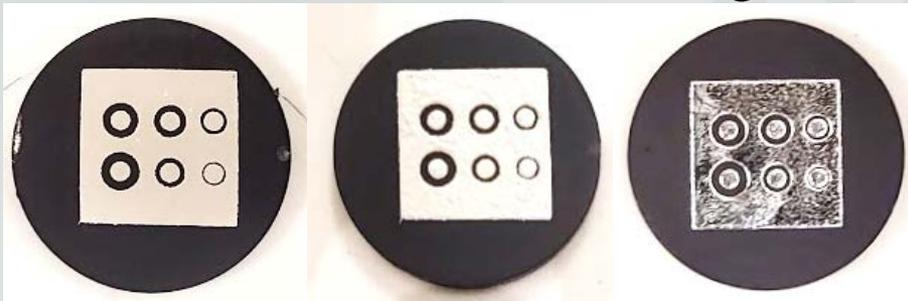


The Contact Resistivity Was Measured by 4-Wire Measurement Technique

Heraeus

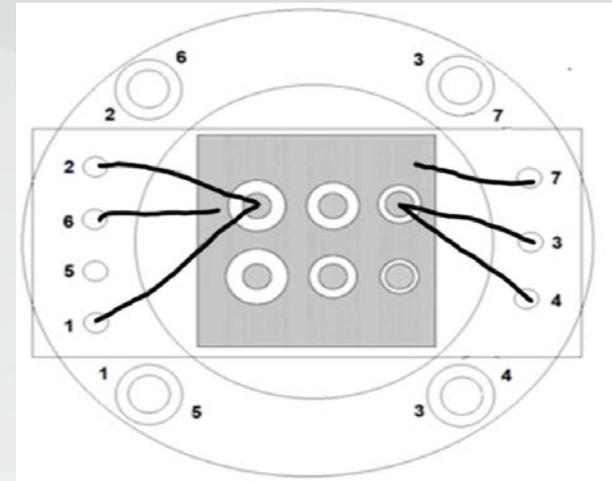
DAD-87

Ag-Ni



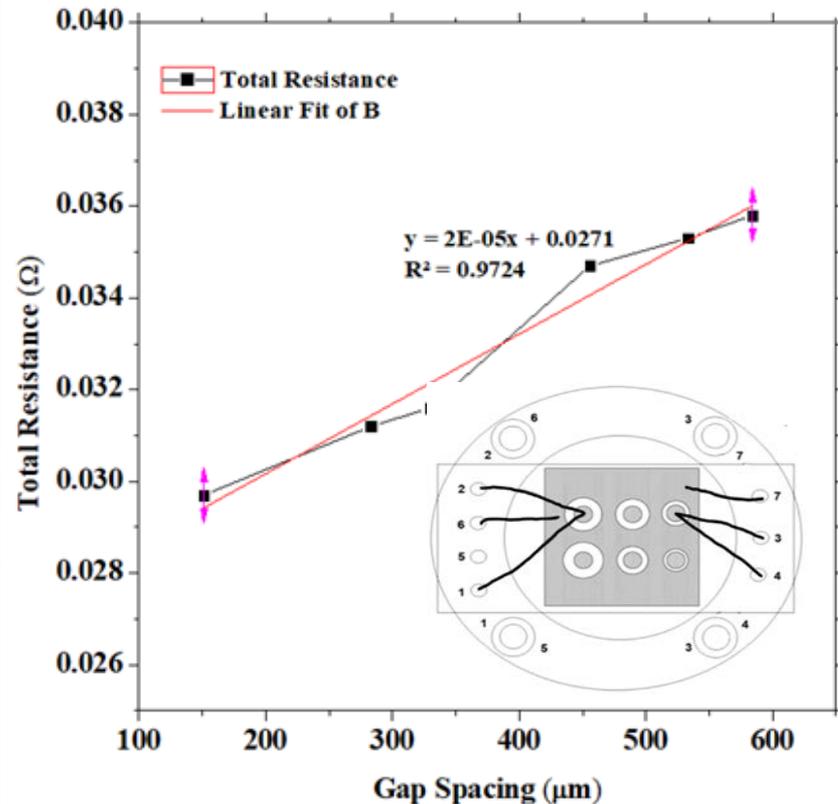
2.5 mm

The plan view of as-produced contact resistivity measurement samples produced by Heraeus C8710, DAD-87 and Ag-Ni on $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$



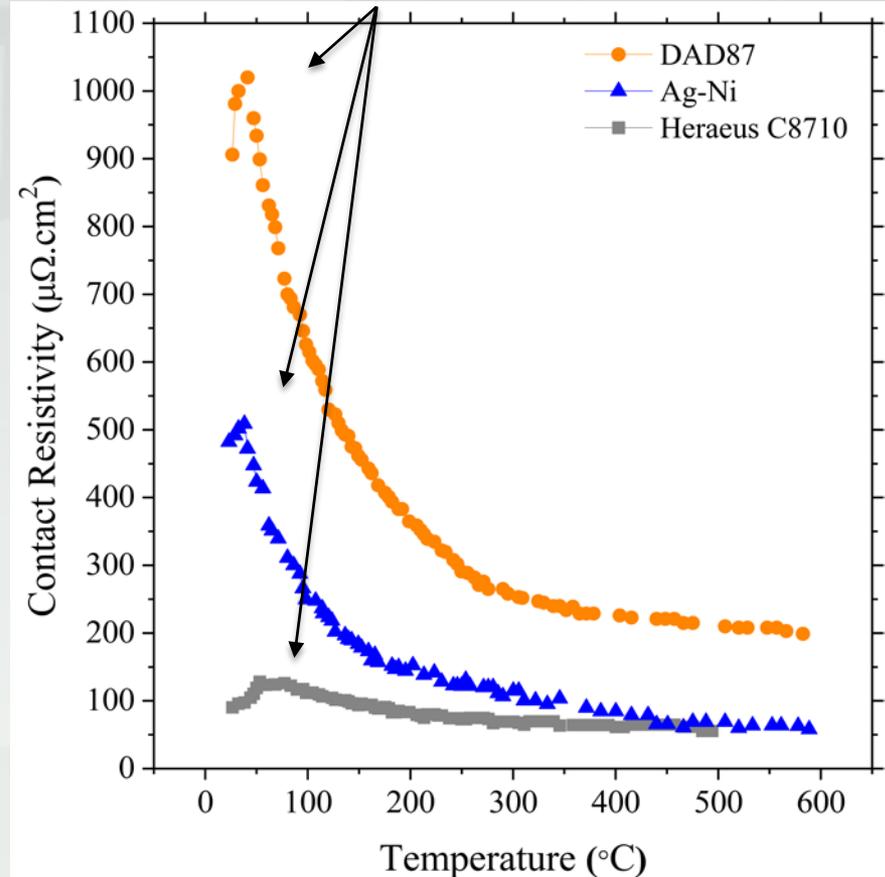
The wire connection illustration

The Ag-Ni Circuit Has Low Contact Resistivity on Lanthanum Strontium Manganite Substrates



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

LSM ferromagnetic-paramagnetic transitions

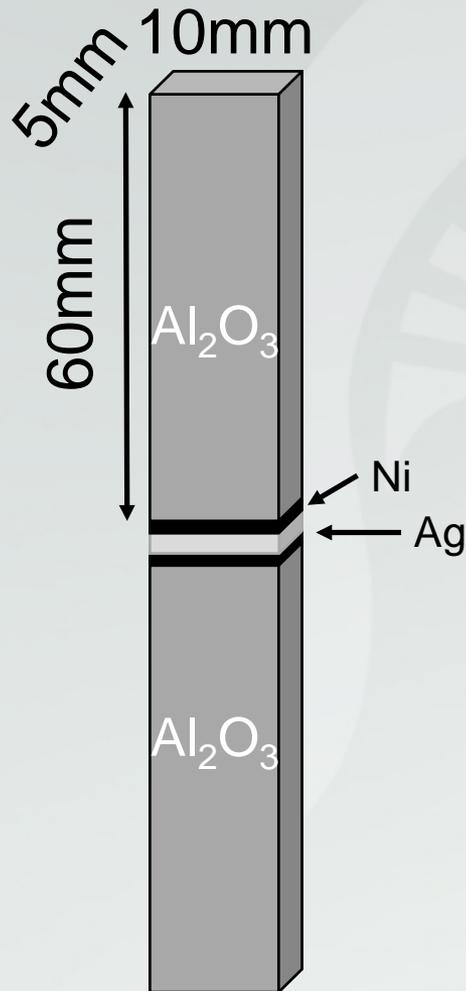


The contact resistivity of 750 °C air annealed Ag circuits at different temperatures

Outline

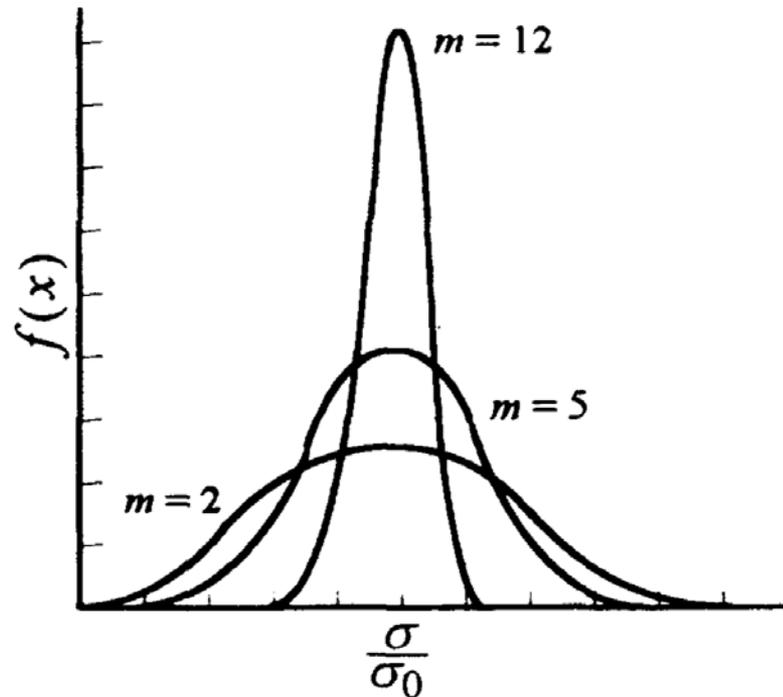
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The Bonding Strength between Ag Pastes and Alumina Was Measured by Tensile Tests



The tensile test sample and experiment set up

Weibull Plots Are a Statistical Approach to Describe Strength Distributions



If the survival probability S is assumed to take the form

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

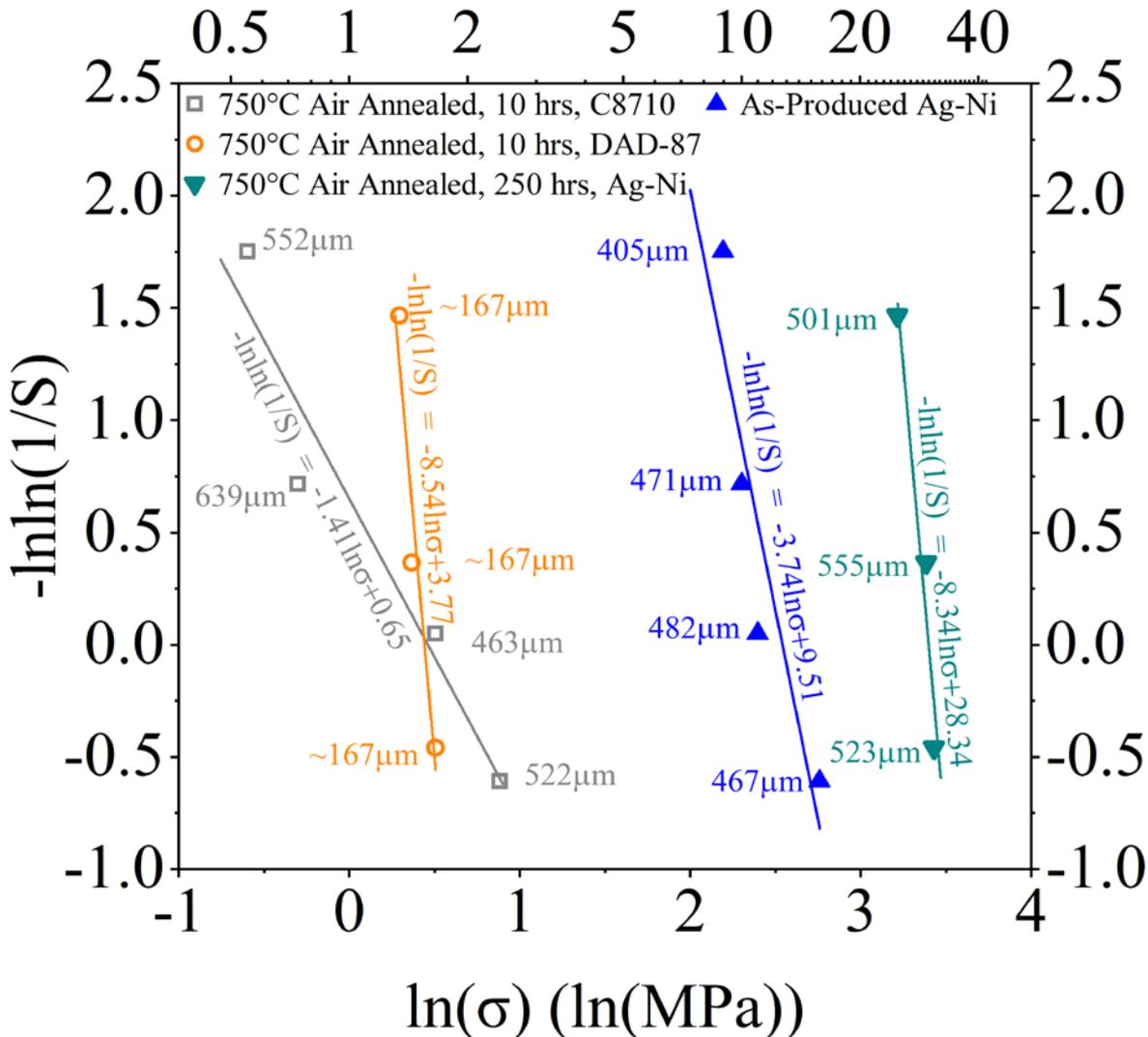
then,

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

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 $\ln \ln 1/S$ vs $\ln \sigma$ yields a straight line.

The Tensile Strength between Ag-Ni and Al₂O₃ Is Stronger than Those of Commercial Ag Pastes

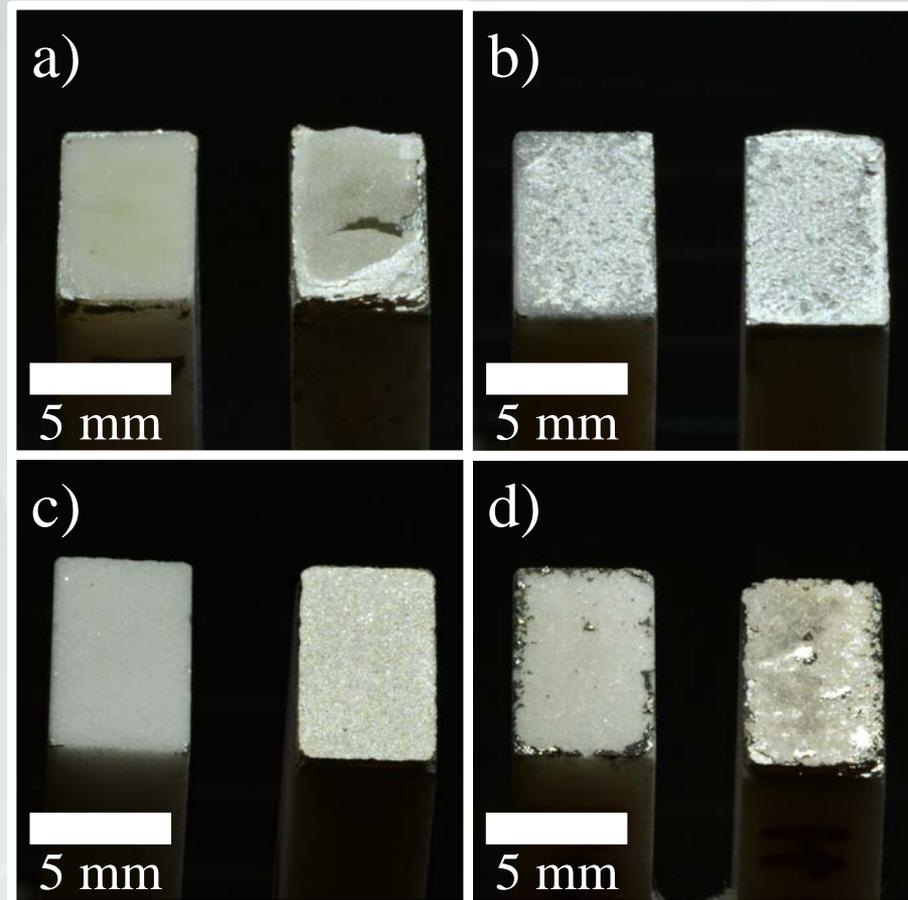
Tensile strength σ (MPa) at survival probability S



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

Design stress ensuring a survival probability of 99%

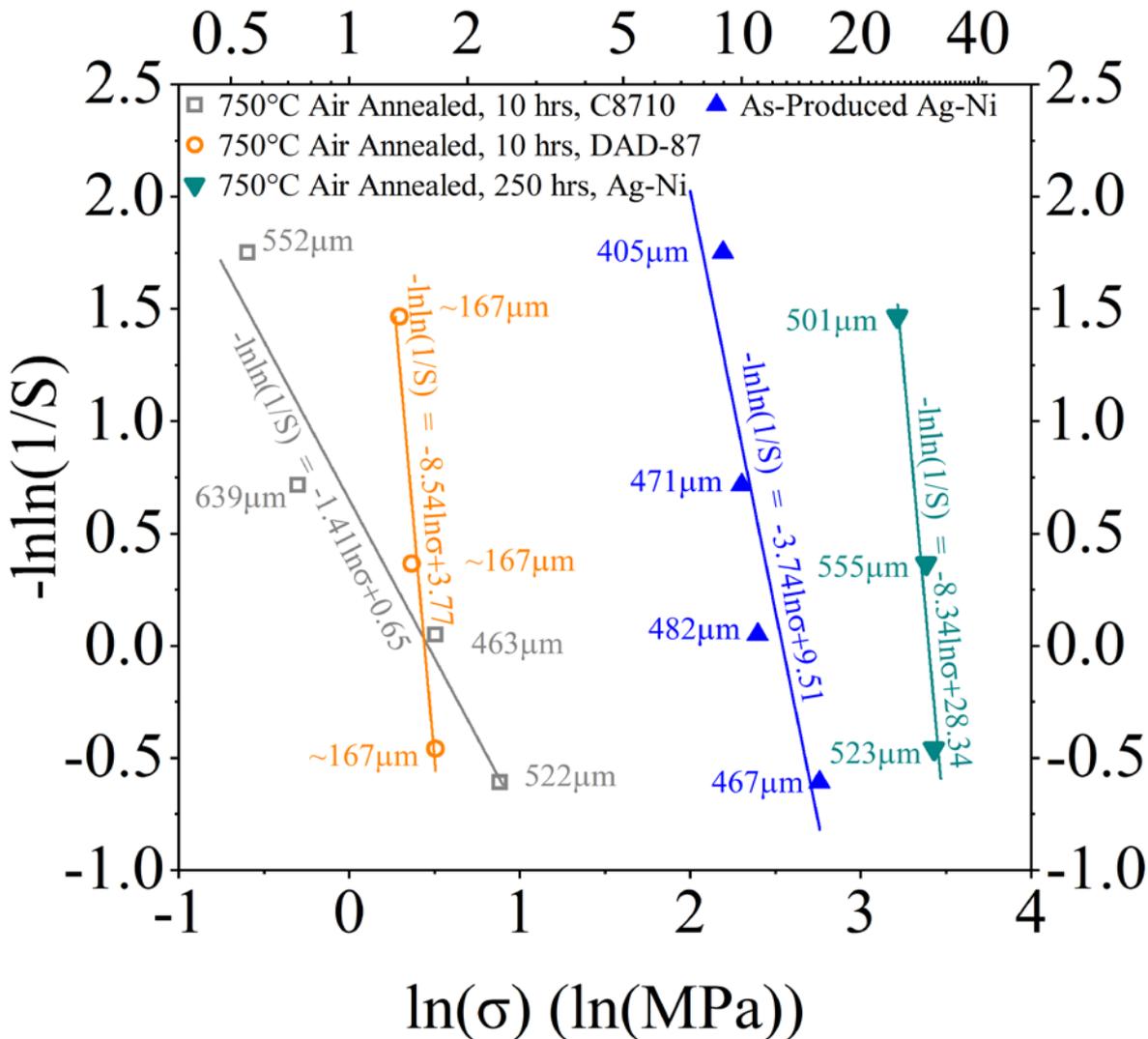
Both Ag and Ag-Ni Samples Fractured Along the Metal-Sapphire Interface



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

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

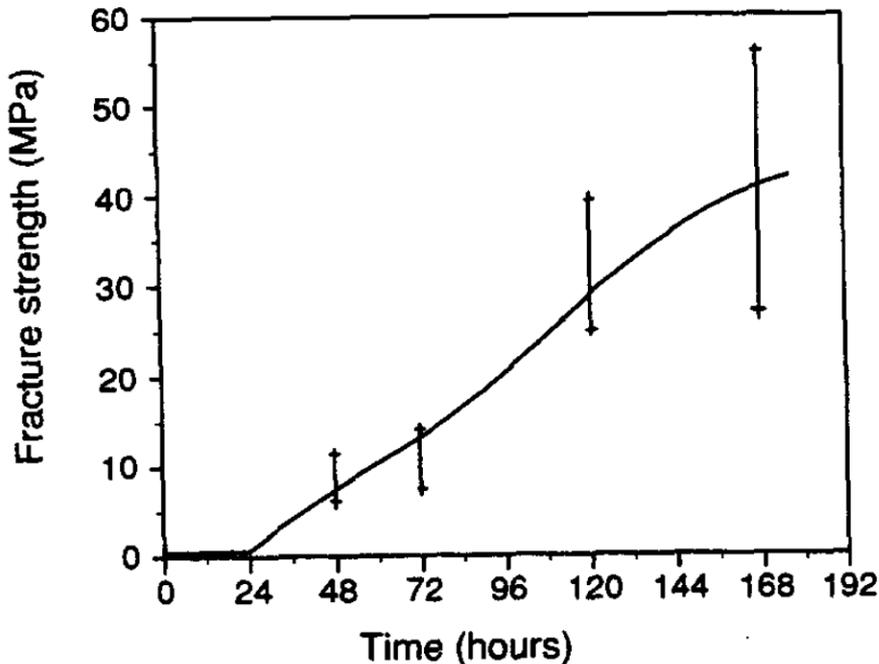
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More Dissolved Oxygen in the Ag Makes Oxidized Ag-Ni Joints Stronger



Fracture strength of Ag/Al₂O₃ 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

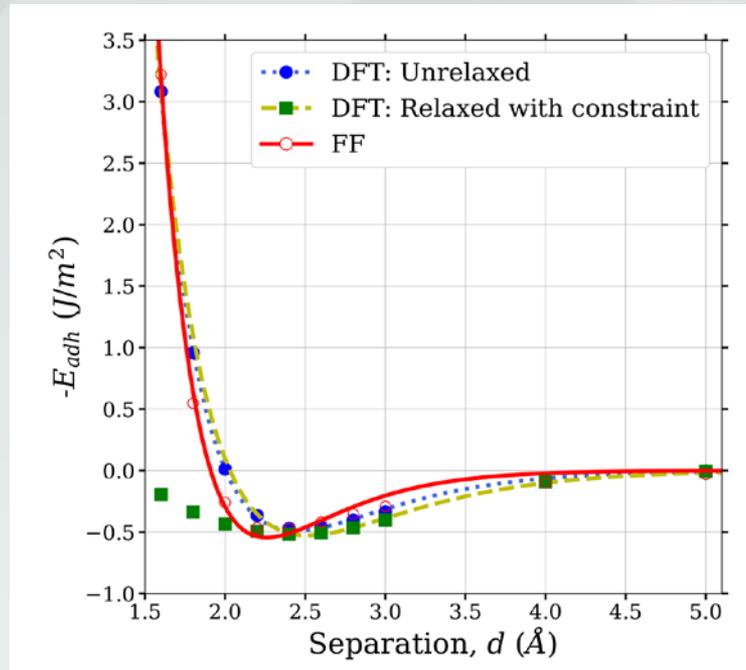
The work of adhesion change between Ag/YSZ substrate with and without oxygen.

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

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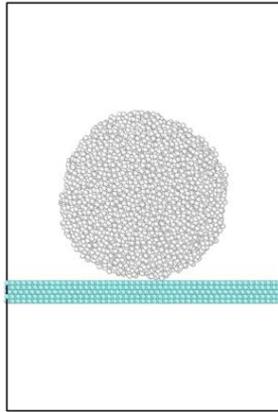
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Silver-Sapphire, and Silver-Nickel Force Field (FF) Parameters Were Determined by Fitting the Interfacial Binding Energy to Density-Functional Theory (DFT)

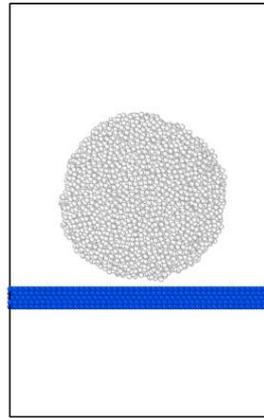


A comparison between the optimized FF and DFT calculations for the interfacial binding energy at various separation distance, d . For the DFT calculations, the unrelaxed interface and relaxed interface with constraint were used. The dotted and solid lines represent fitted UBER curves for each case.

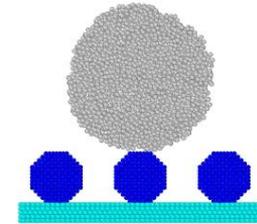
Molecular Dynamics Simulations Shows that Nickel Promotes the Wetting and Spreading of Silver on Ceramics



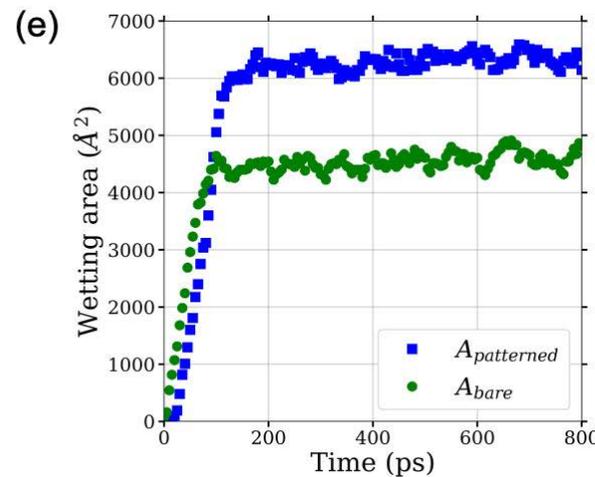
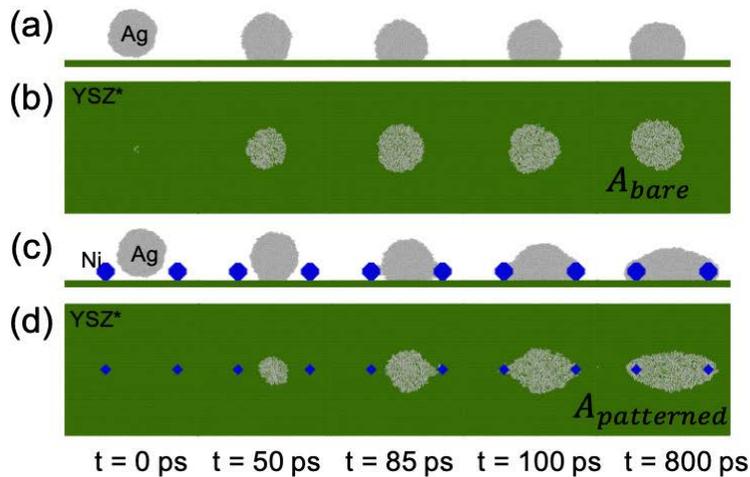
Ag on bare YSZ



Ag on bare Ni



Ag on YSZ with Ni particles



The YSZ area wet by liquid Ag on bare surface from (a) side view and (b) top view; and on Ni patterned surface from (c) side view and (d) top view.

Figure (e) shows the wetting area evolution on two surfaces.

Hexagonal Ni Particles Patterns Create a Maximum Silver Wetting Area Enhancement of 224%

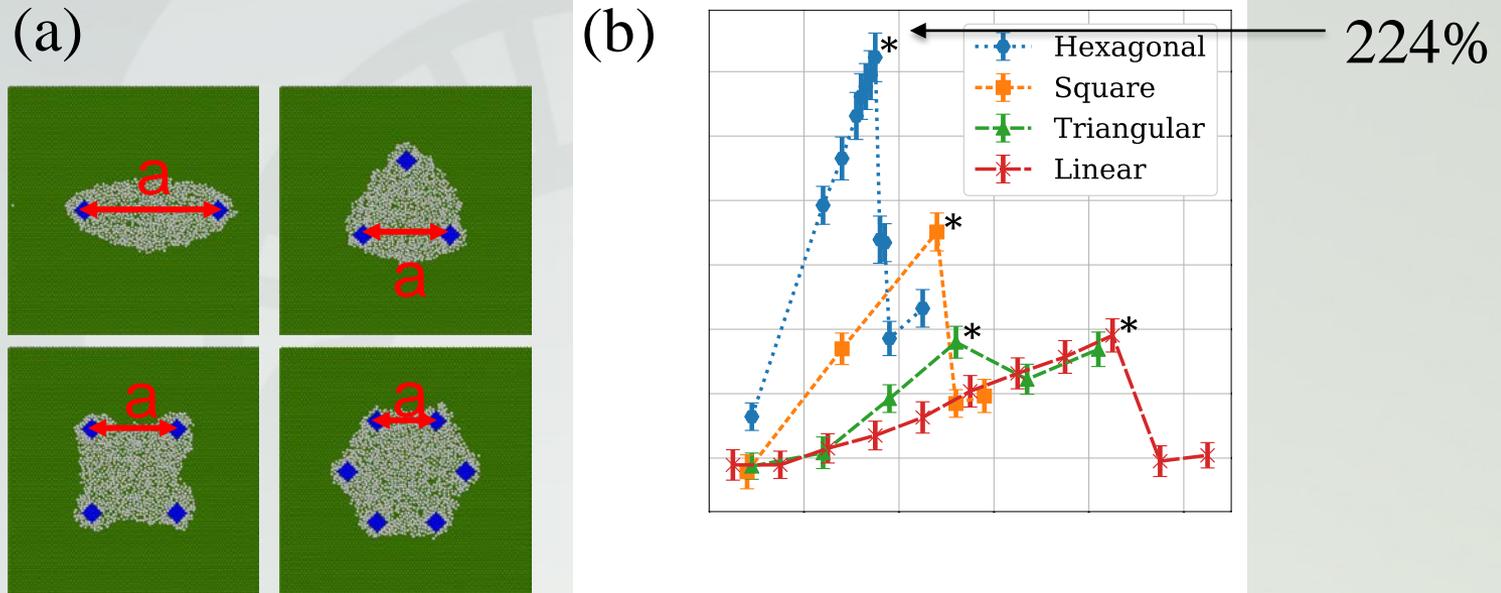
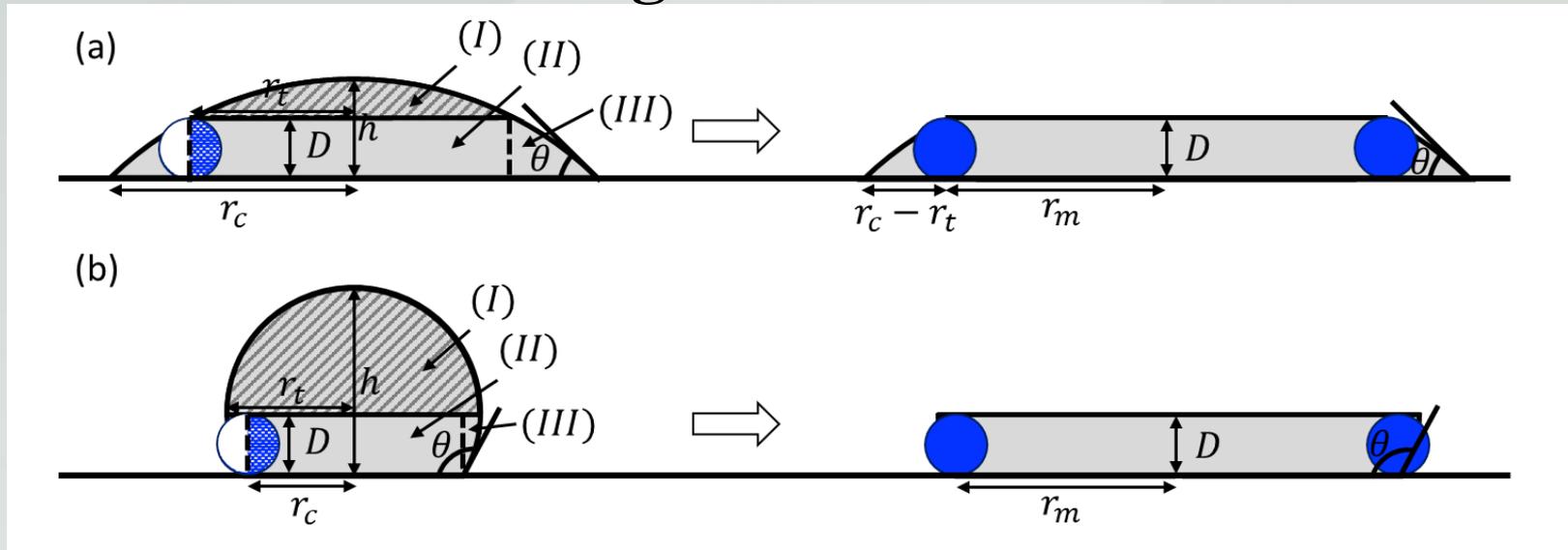


Figure (a): the four different nickel particle configurations on YSZ surface and the wetting area by liquid silver.

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.

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 r_m . (a) $r_t < r_c$ and (b) $r_t > r_c$.

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

The Analytical Model Was Validated by Molecular Dynamics Simulations

Surface	Wetting area enhancement	
	MD	Analytical model
YSZ	2.24 ± 0.076	2.20
Non-Wetting	3.66 ± 0.227	3.76
Large contact angle (<math><90^\circ</math>)	1.61 ± 0.042	1.49
Small contact angle (<math><90^\circ</math>)	1.40 ± 0.033	1.32

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A Three-Dimensional Phase Sintering Model Was Established Based on the Sintered Ni Particle Size Distribution

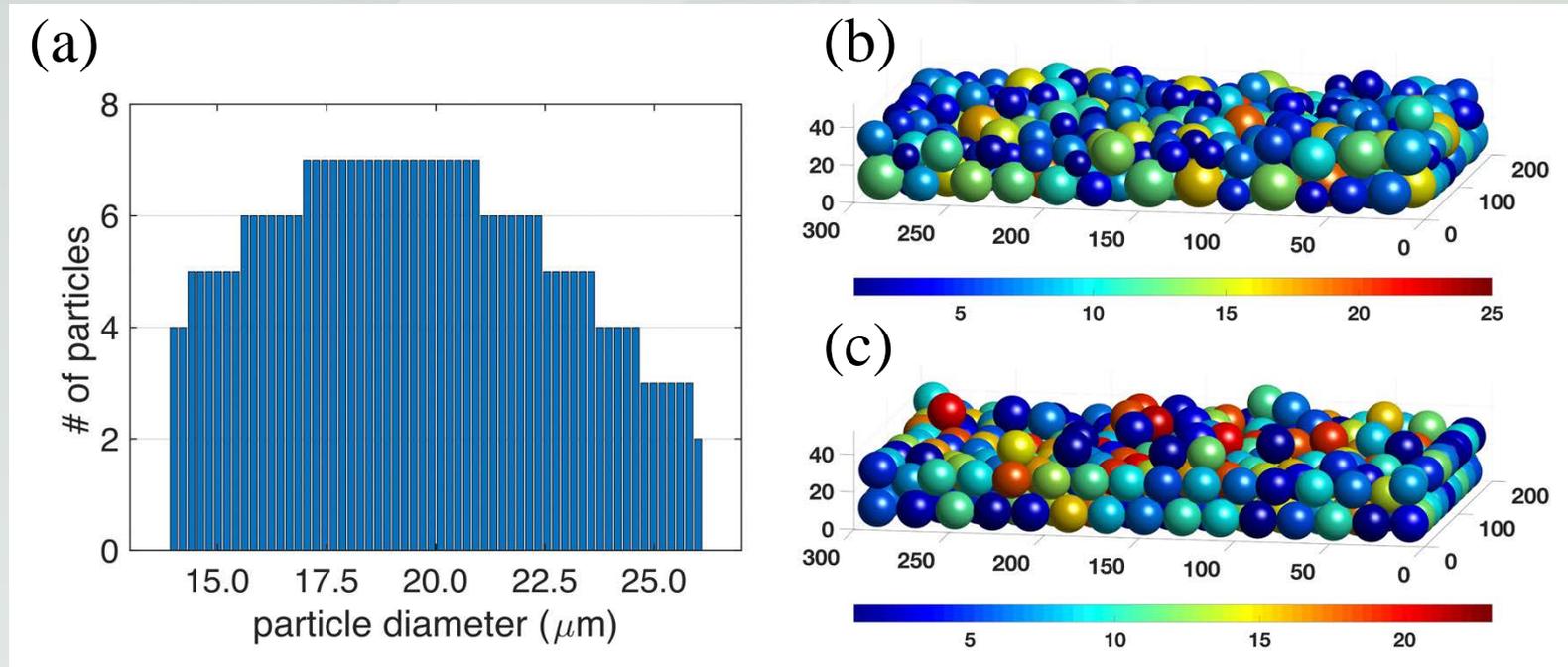
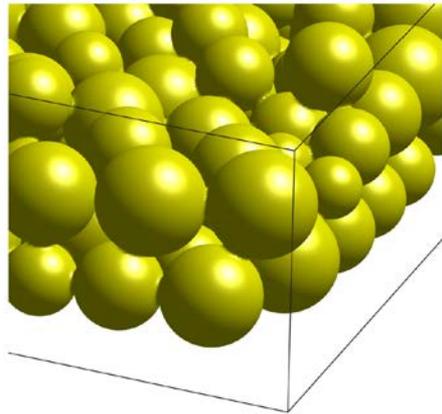
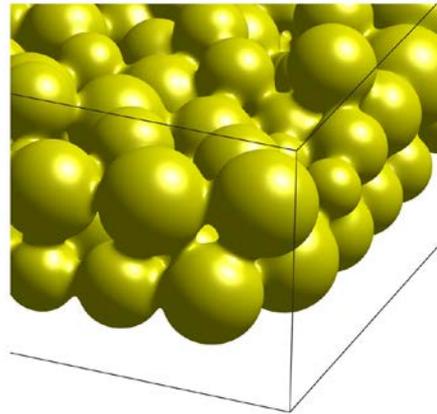


Figure (a): Particle size distribution from sintered nickel scanning electron microscope images. Figure (b): Case 1, Ni particle configuration based on the particle size distribution, which follows a Gaussian curve with lower bound of 14 μm , upper bound of 26 μm and mean at 19 μm . Figure (c): Case 2, Ni particle configuration with a uniform diameter of 20 μm .

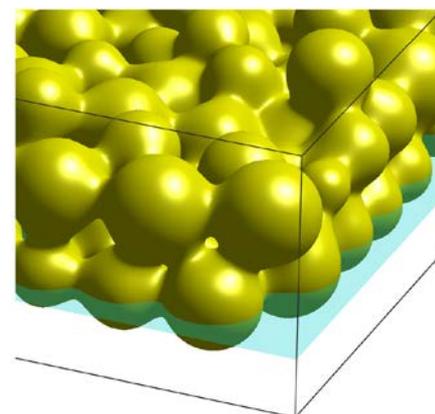
Voids Shrinkage and Volume Densification Were Observed during the Sintering Simulation Process



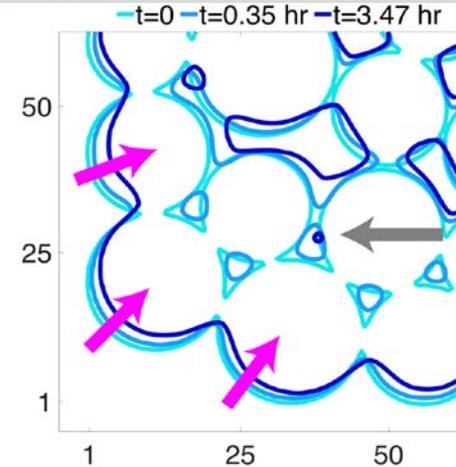
$t=0$



$t=0.35$ 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 time.



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

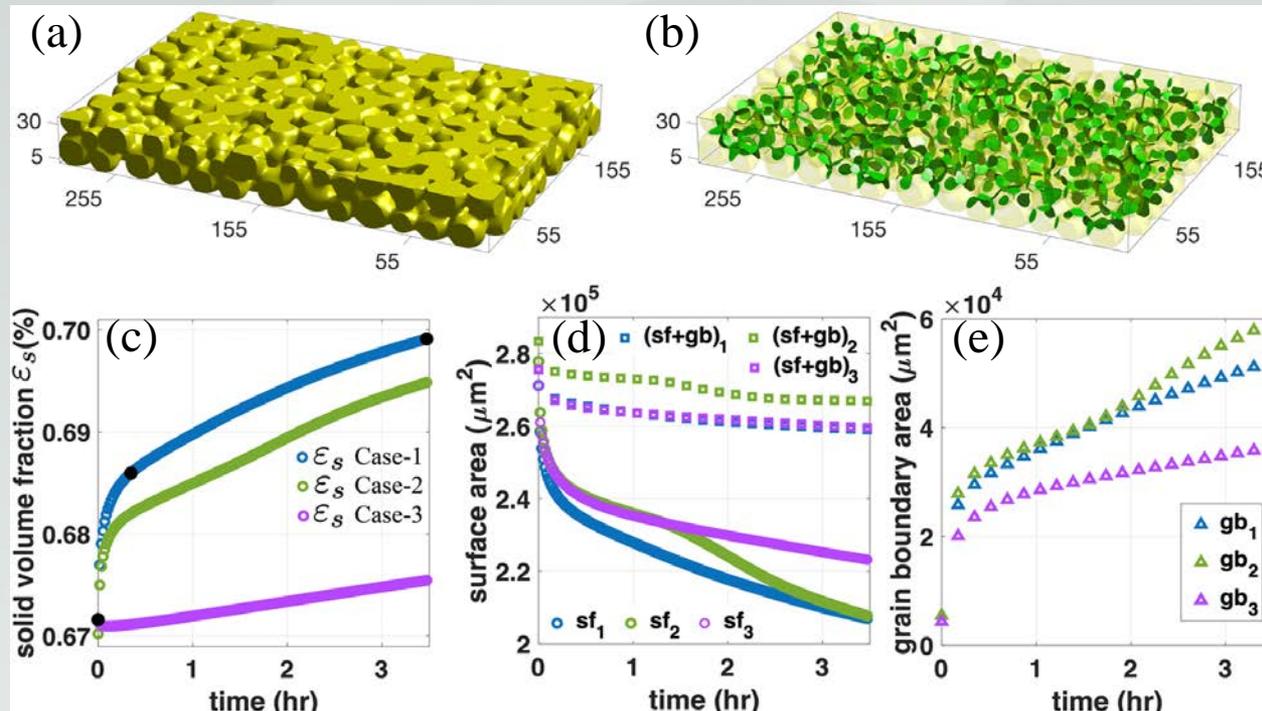


Figure (a): the solid structure at $t=3.47$ h with Ni particles following Gaussian distribution. (b) the grain boundary in the solid structure shown by green color. (c) the solid volume fraction (Case 3 has identical particle configuration except that rigid-body motion was ignored). (d) the surface area evolution and the sum of surface area and grain boundary (e) the grain boundary area evolution.

The Maximum von Mises Stresses Were Calculated for Each Configuration

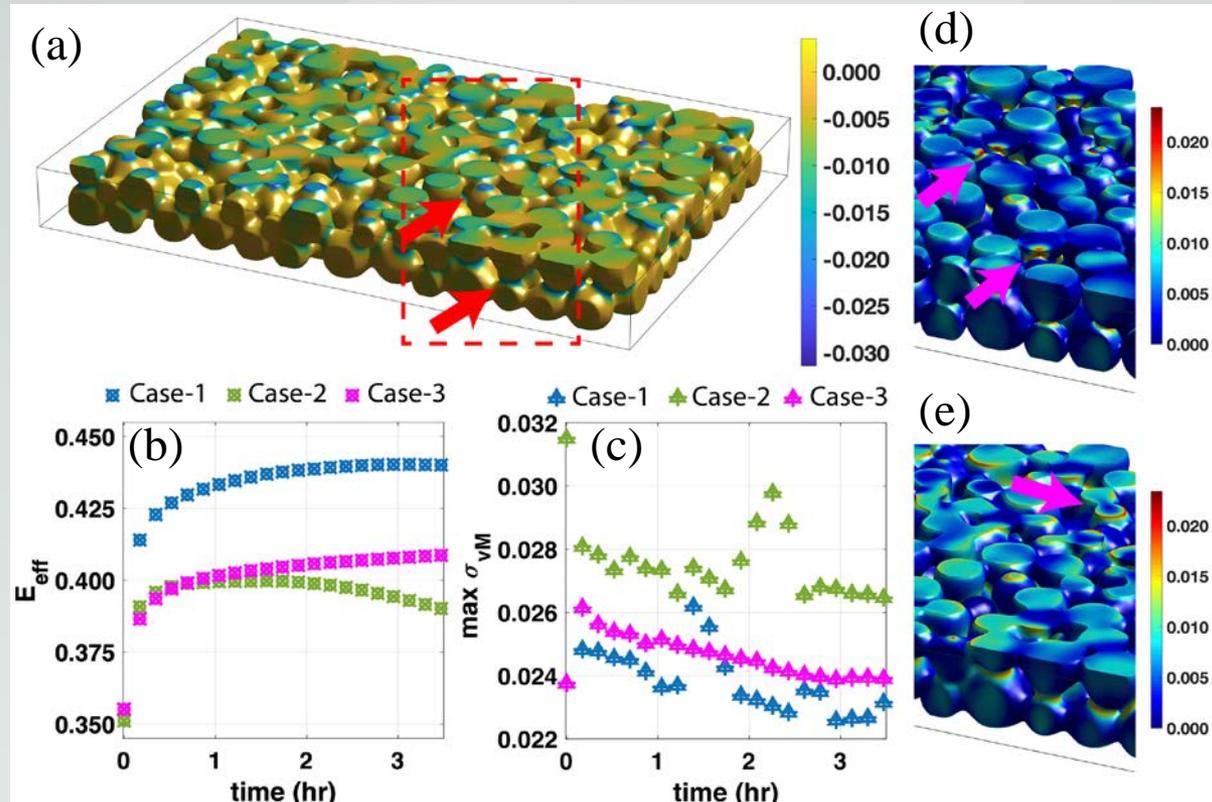


Figure (a): the solid structure at $t=3.47$ h with Ni particles following Gaussian distribution under the loading of $\bar{\epsilon}_{zz} = -0.01$. (b) The effective Young's modulus of the microstructure at different times. (c) The calculated maximum von Mises stress in the microstructures, where the markers ' Δ ' and '+' are for the compression and tension loadings, respectively. The von Mises stress in Case-1 microstructure at (d) $t=0$ and (e) $t=3.47$ hr, which corresponds to the red box in (a)

Conclusions

1. Here a new Particle Interlayer Directed Wetting and Spreading (PIDWAS) technique was used to produce Ag-Ni circuits on a variety of ceramic substrates that Ag alone would not wet.
2. Ag-Ni circuits have low sheet resistivity.
3. Ag-Ni circuits have a low contact resistivity on LSM.
4. Ag-Ni circuits bond to Al_2O_3 much stronger than commercial Ag pastes. Air annealing enhances their adhesion strength.
5. The optimal hexagonal Ni particle pattern was predicted by molecular dynamics simulation.
6. A porous Phase Field Nickel Sintering model enabling the rigid body motion of individual particles for was established for the first time, allowing an examination in how sintering affects structure-property relations.
7. The PIDWAS technique developed here is one of the few pressureless silver-sapphire joining techniques with a demonstrated capacity for producing dense, intricate, thick film silver patterns on ceramic substrates for circuit, current collector, sealing, joining and other applications.

The Most Common Silver-Sapphire Joining Techniques Comparison

	Constrained Sintering	Pressure Assisted Sintering	Reaction Assisted Sintering	Stress-Migration Bonding	Current Assisted Sintering	Light Assisted Sintering	Pressure Joining	Transient Liquid Brazing	Silver Alloy Brazing	Porous Templated Wetting
Alternative Names / Flavors of this Technique	Pressureless Sintering	Hot Isostatic Pressing, Sintering Forging	In-situ Formation, Reaction Bonding	Silver Direct Bonding	Spark Plasma Sintering, Microwave Sintering	Laser Sintering, Infrared Sintering	Solid State Bonding	Solid Liquid Interdiffusion Bonding, Direct Silver Bonding	Reactive Air Brazing, Active Metal Brazing	THIS WORK
Description	Solid state densification, creep and/or plastic flow induced or assisted by:						Dense Ag foils are deformed and brought into intimate contact with a substrate through the application of an external force	Local melting of a low T_m layer (such as an impurity-induced local eutectic) that is subsequently consumed by reaction with the solid substrate or solid Ag foil	Bulk melting of Ag alloy foils or porous samples with impurities that migrate to the Ag surface to react with the substrate and promote wetting	Bulk melting and subsequent wetting and spreading of Ag foils or porous films directed by the placement of Ag-wettable particles on a substrate
	local curvature differences between particles in a porous Ag sample	the application of an external stress to a porous Ag sample	a chemical of physical reaction (such as the reduction of Ag_2O or solvent evaporation to form Ag nano-particles)	Thin film deposition, CTE mismatch, or other internal compressional film stresses	Joule heating, electro-migration etc. caused by passing electric current through a porous Ag sample	Joule heating, electro-migration etc. caused by focusing light on a porous Ag sample				
Part Fabrication Temperature	200-550°C [1-4] 750°C-850°C here	250-275°C [5, 6]	90°C [7], 200-400°C [8, 9]	200-300°C [10, 11]	No results for Ag on sapphire	290°C [12] 850°C [13]	260°C with Au TiW [14], 500-900°C [15, 16]	Additive Dependent , 946°C with Cu [17]	Additive Dependent , 980-1000°C with Cu [18-20]	> 962°C (Ag T_m), 1050°C here
Fabrication Atmosphere	Any	Any	Reaction Dependent	Any	Any	Any	Any	Additive Dependent	Additive Dependent	Additive Dependent
External Fabrication Pressure	0 MPa	1-50 MPa [5, 6, 21]	0 MPa [7], 5-15 MPa [8, 9]	0 MPa	0 MPa	0 MPa	6-7 MPa [14, 15]	0 MPa	0 MPa	0 MPa
Final Ag Relative Density	< 68% [5] 73% here	87% [5]	~85% [7], ~95% [8, 9]	~100% [10, 11]	No results for Ag on sapphire	~70% [12]	~100% [14, 15]	~100% [17]	~100% [18-20]	~100% here
Maximum Joint Tensile Strength	< 3 MPa here	No results for Ag on sapphire	70 MPa [8]	No results for Ag on sapphire	No results for Ag on sapphire	No results for Ag on sapphire	70 MPa [15, 16, 22]	No results for Ag on sapphire	22 MPa with Cu [23] 72 MPa with Cu on Ti [24]	18-35 MPa depending on atmosphere. Likely higher with less Ni

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Maximum Joint Shear Strength	12 MPa [25] 18 MPa [1]	40 MPa [5] 50 MPa [6]	36 MPa [9]	120 MPa [10]	No results for Ag on sapphire	No results for Ag on sapphire	68-75 MPa [22, 26]	No results for Ag on sapphire	90 MPa with Cu [23]	No results for Ag on sapphire
Ag 25°C Sheet Resistivity	2.2 $\mu\Omega\text{cm}$ here, 5 $\mu\Omega\text{cm}$ on glass [2] >50 $\mu\Omega\text{cm}$ on Si [4]	2.4 $\mu\Omega\text{cm}$ [6]	1.6 $\mu\Omega\text{cm}$ [7]	No results for Ag on sapphire	No results for Ag on sapphire	2.4 $\mu\Omega\text{cm}$ [13], >8 $\mu\Omega\text{cm}$ [12]	1.6 $\mu\Omega\text{cm}$ by virtue of starting with pure, dense, Ag foil	1.6 $\mu\Omega\text{cm}$ by virtue of having most of the Ag layer be pure, dense, Ag foil	1.9 $\mu\Omega\text{cm}$ with Cu on lead ziconate titanate [27]	2.2-3.6 $\mu\Omega\text{cm}$ here, depending on atmosphere.
Maximum Final Ag Use Temperature	Up to ~950°C in air	Up to ~950°C in air	Up to ~950°C in air	Up to ~950°C in air	Up to ~950°C in air	Up to ~950°C in air	Up to ~950°C in air	Depends on the Additive	Depends on the Additive	Up to ~950°C in air, Up to ~1400°C in pO ₂ < 1x10 ⁻⁵
Most Compelling Features for Circuit Production	Easy	Conductive Ag layers produced at low temperature	Conductive Ag layers produced at very low temperature	High adhesion strength	Somewhat reduced sintering temperature	Ability to define circuits with fine line widths	Dense conductive circuits are guaranteed	Adhesion strength can be greater than that of pure Ag	Adhesion strength can be greater than that of pure Ag	Easily made dense, well-adhered thick or thin film Ag circuits
Most Serious Drawbacks for Circuit Production	Low density, poor adhesion, high resistivity	Pressing during fabrication introduces complexity, raises cost, & can crack substrates	Poor adhesion strength is often a problem	Cannot produce thick Ag films on substrates with an arbitrary CTE	Current focusing can cause Ag layer density variations	Poor adhesion. Cannot produce thick film Ag circuits due to laser adsorption	Cannot be used for thin films due to the mechanical fragility of the original Ag foils	Cannot be used for thin films due to the mechanical fragility of the original Ag foils	Better wetting results in less Ag circuit flaws but more chance of molten Ag runoff.	High fabrication temperatures and potential atmosphere control raises cost & limits compatible materials

Reference

1. Wang, T., et al., *Low-temperature sintering with nano-silver paste in die-attached interconnection*. Journal of Electronic Materials, 2007. **36**(10): p. 1333-1340.
2. Sukanuma, K., et al., *Low-temperature low-pressure die attach with hybrid silver particle paste*. Microelectronics Reliability, 2012. **52**(2): p. 375-380.
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