High Performance Circuit Pastes for Solid Oxide Fuel Cell Applications

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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

Without Porous Ni | With Porous Ni
---|---
![Image](image1.png) 138° | ![Image](image2.png) 138°
96wt%Al₂O₃ | 96wt%Al₂O₃
![Image](image3.png) 134° | ![Image](image4.png) 134°
99.9% Al₂O₃ | 99.9% Al₂O₃
![Image](image5.png) 125° | ![Image](image6.png) 125°
AlN | AlN
![Image](image7.png) 126° | ![Image](image8.png) 126°
(Y₂O₃)₀.₀₃(ZrO₂)₀.₉₇ | (Y₂O₃)₀.₀₃(ZrO₂)₀.₉₇

5 mm

Hu et al., Patterned Porous Nickel Interlayers for Enhanced Silver Wetting, Spreading and Adhesion on Ceramic Substrates, In Preparation, 2020
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Nickel Interlayers Can Also Be Used to Direct the Wetting and Spreading of Silver on a Variety of Ceramic 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.

Hu et al., Patterned Porous Nickel Interlayers for Enhanced Silver Wetting, Spreading and Adhesion on Ceramic Substrates, In Preparation, 2020
Ag-Ni Circuit Fabrication

Silver Paste

Nickel Paste

Sapphire

Silver-Nickel Circuit

850°C, 2hrs

5°C/min

~1000°C, 30mins

5°C/min

Ar Flow at 20 sccm

Sapphire
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).

Hu et al., Patterned Porous Nickel Interlayers for Enhanced Silver Wetting, Spreading and Adhesion on Ceramic Substrates, In Preparation, 2020
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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

Kim et al., Microelectron. Eng(2014)
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

Annealed at 750 °C for 10 hrs in air
The Contact Resistivity Was Measured by 4-Wire Measurement Technique

Heraeus  DAD-87  Ag-Ni

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

The wire connection illustration

Marlow et al., Solid-State Electrons(1982)
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.

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

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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

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

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 $\sigma_0$ 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 Al$_2$O$_3$ Is Stronger than Those of Commercial Ag Pastes

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)

Design stress ensuring a survival probability of 99%
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

<table>
<thead>
<tr>
<th>Work of adhesion (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(l)/YSZ(1 1 1)</td>
</tr>
<tr>
<td>(Ag(l)+2O)/YSZ(1 1 1)</td>
</tr>
<tr>
<td>0.11±0.01</td>
</tr>
<tr>
<td>0.43±0.01</td>
</tr>
</tbody>
</table>

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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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

<table>
<thead>
<tr>
<th>Surface</th>
<th>Wetting area enhancement</th>
<th>MD</th>
<th>Analytical model</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>2.24 ± 0.076</td>
<td>2.20</td>
<td></td>
</tr>
<tr>
<td>Non-Wetting</td>
<td>3.66 ± 0.227</td>
<td>3.76</td>
<td></td>
</tr>
<tr>
<td>Large contact angle (&lt;90°)</td>
<td>1.61 ± 0.042</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>Small contact angle (&lt;90°)</td>
<td>1.40 ± 0.033</td>
<td>1.32</td>
<td></td>
</tr>
</tbody>
</table>
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• Conclusions
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

Ni particles following Gaussian distribution at $t=0$, 0.35h and 3.47h. The contour lines on the $z=10 \, \mu m$ 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.

Termuhlen et al. Three-Dimensional Phase Field Sintering Simulations Accounting for the Rigid-Body Motion of Individual Grains. In Preparation. 2020
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 $\text{Al}_2\text{O}_3$ 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

<table>
<thead>
<tr>
<th>Alternative Names / Flavors of this Technique</th>
<th>Constrained Sintering</th>
<th>Pressure Assisted Sintering</th>
<th>Reaction Assisted Sintering</th>
<th>Stress-Migration Bonding</th>
<th>Current Assisted Sintering</th>
<th>Light Assisted Sintering</th>
<th>Pressure Joining</th>
<th>Transient Liquid Brazing</th>
<th>Silver Alloy Brazing</th>
<th>Porous Templated Wetting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Local curvature differences between particles in a porous Ag sample</td>
<td>the application of an external stress to a porous Ag sample</td>
<td>a chemical of physical reaction (such as the reduction of Ag₂O or solvent evaporation to form Ag nano-particles)</td>
<td>Thin film deposition, CTE mismatch, or other internal compressional film stresses</td>
<td>Joule heating, electro-migration etc. caused by passing electric current through a porous Ag sample</td>
<td>Joule heating, electro-migration etc. caused by focusing light on a porous Ag sample</td>
<td>Dense Ag foils are deformed and brought into intimate contact with a substrate through the application of an external force</td>
<td>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</td>
<td>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</td>
<td>Bulk melting and subsequent wetting and spreading of Ag foils or porous films directed by the placement of Ag-wettable particles on a substrate</td>
</tr>
<tr>
<td>Fabrication Atmosphere</td>
<td>Any</td>
<td>Any</td>
<td>Reaction Dependent</td>
<td>Any</td>
<td>Any</td>
<td>Any</td>
<td>Additive Dependent</td>
<td>Additive Dependent</td>
<td>Additive Dependent</td>
<td></td>
</tr>
<tr>
<td>External Fabrication Pressure</td>
<td>0 MPa</td>
<td>1-50 MPa [5, 6, 21] 0 MPa [7], 5-15 MPa [8, 9]</td>
<td>0 MPa</td>
<td>0 MPa</td>
<td>0 MPa</td>
<td>6-7 MPa [14, 15]</td>
<td>0 MPa</td>
<td>0 MPa</td>
<td>0 MPa</td>
<td></td>
</tr>
<tr>
<td>Final Ag Relative Density</td>
<td>&lt; 68% [5] 73% here</td>
<td>87% [5]</td>
<td>~85% [7], ~95% [8, 9]</td>
<td>~100% [10, 11]</td>
<td>No results for Ag on sapphire</td>
<td>~70% [12]</td>
<td>~100% [14, 15]</td>
<td>~100% [17]</td>
<td>~100% here</td>
<td></td>
</tr>
<tr>
<td>Maximum Joint Tensile Strength</td>
<td>&lt; 3 MPa here</td>
<td>No results for Ag on sapphire</td>
<td>70 MPa [8]</td>
<td>No results for Ag on sapphire</td>
<td>No results for Ag on sapphire</td>
<td>70 MPa [15, 16, 22]</td>
<td>No results for Ag on sapphire</td>
<td>22 MPa with Cu [23] 72 MPa with Cu on Ti [24]</td>
<td>18-35 MPa depending on atmosphere, Likely higher with less Ni</td>
<td></td>
</tr>
</tbody>
</table>

### Fabrication Atmosphere
- **Any**
- **Additive Dependent**

### External Fabrication Pressure
- **0 MPa**
- **1-50 MPa** [5, 6, 21]
- **0 MPa** [7], **5-15 MPa** [8, 9]
- **6-7 MPa** [14, 15]
- **0 MPa**

### Final Ag Relative Density
- **< 68%** [5]
- **73% here**
- **87%** [5]
- **~85%** [7], **~95%** [8, 9]
- **~100%** [10, 11]
- **~70%** [12]
- **~100%** [14, 15]
- **~100%** [17]
- **~100%** here

### Maximum Joint Tensile Strength
- **< 3 MPa here**
- **No results for Ag on sapphire**
- **70 MPa** [8]
- **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]

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### 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]
- **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]

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**THIS WORK**
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<tr>
<td><strong>Maximum Joint Shear Strength</strong></td>
<td>12 MPa [25]</td>
<td>40 MPa [5]</td>
<td>36 MPa [9]</td>
<td>No results for Ag on sapphire</td>
<td>No results for Ag on sapphire</td>
<td>68-75 MPa [22, 26]</td>
<td>No results for Ag on sapphire</td>
<td>90 MPa with Cu [23]</td>
<td>No results for Ag on sapphire</td>
<td></td>
</tr>
<tr>
<td><strong>Ag 25°C Sheet Resistivity</strong></td>
<td>2.2 μΩcm here, 5 μΩcm on glass [2]</td>
<td>2.4 μΩcm [6]</td>
<td>1.6 μΩcm [7]</td>
<td>No results for Ag on sapphire</td>
<td>No results for Ag on sapphire</td>
<td>1.6 μΩcm by virtue of starting with pure, dense, Ag foil</td>
<td>1.6 μΩcm by virtue of having most of the Ag layer be pure, dense, Ag foil</td>
<td>1.9 μΩcm with Cu on lead zionate titanate [27]</td>
<td>2.2-3.6 μΩcm here, depending on atmosphere.</td>
<td></td>
</tr>
<tr>
<td><strong>Maximum Final Ag Use Temperature</strong></td>
<td>Up to ~950°C in air</td>
<td>Up to ~950°C in air</td>
<td>Up to ~950°C in air</td>
<td>Up to ~950°C in air</td>
<td>Up to ~950°C in air</td>
<td>Depends on the Additive</td>
<td>Depends on the Additive</td>
<td>Up to ~950°C in air, Up to ~1400°C in pO₂ &lt; 1x10⁻⁵</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Most Compelling Features for Circuit Production</strong></td>
<td>Easy</td>
<td>Conductive Ag layers produced at low temperature</td>
<td>Conductive Ag layers produced at very low temperature</td>
<td>High adhesion strength</td>
<td>Somewhat reduced sintering temperature</td>
<td>Ability to define circuits with fine line widths</td>
<td>Dense conductive circuits are guaranteed</td>
<td>Adhesion strength can be greater than that of pure Ag</td>
<td>Adhesion strength can be greater than that of pure Ag</td>
<td>Easily made dense, well-adhered thick or thin film Ag circuits</td>
</tr>
<tr>
<td><strong>Most Serious Drawbacks for Circuit Production</strong></td>
<td>Low density, poor adhesion, high resistivity</td>
<td>Pressing during fabrication introduces complexity, raises cost, &amp; can crack substrates</td>
<td>Poor adhesion strength is often a problem</td>
<td>Cannot produce thick Ag films on substrates with an arbitrary CTE</td>
<td>Current focusing can cause Ag layer density variations</td>
<td>Poor adhesion. Cannot produce thick film Ag circuits due to laser adsorption</td>
<td>Cannot be used for thin films due to the mechanical fragility of the original Ag foils</td>
<td>Cannot be used for thin films due to the mechanical fragility of the original Ag foils</td>
<td>Better wetting results in less Ag circuit flaws but more chance of molten Ag runout.</td>
<td>High fabrication temperatures and potential atmosphere control raises cost &amp; limits compatible materials</td>
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Reference


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