Comparison of Several Silver-Based Braze Formulations for Use in Solid Oxide Cell Environments

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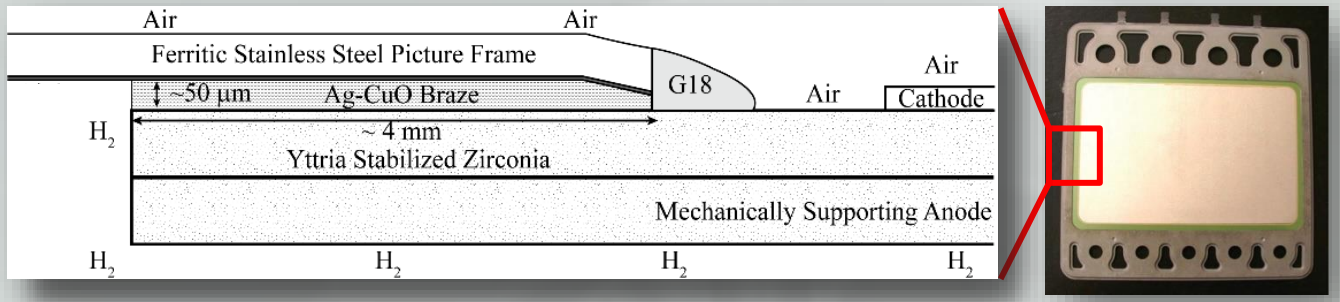
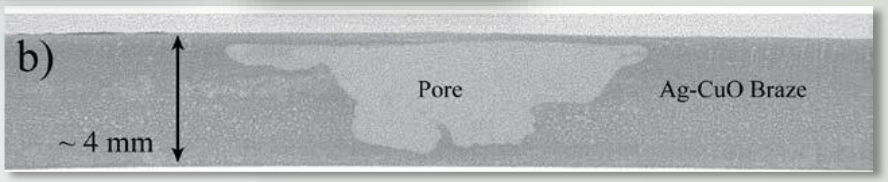
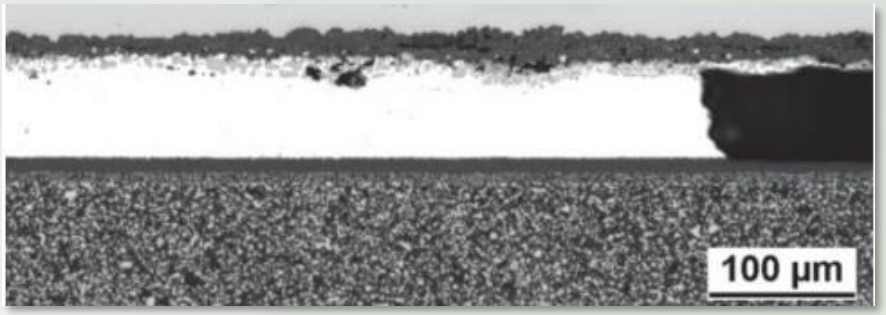
Reactive Air Brazes Can Be Made in Air w/o Flux, But Have Issues



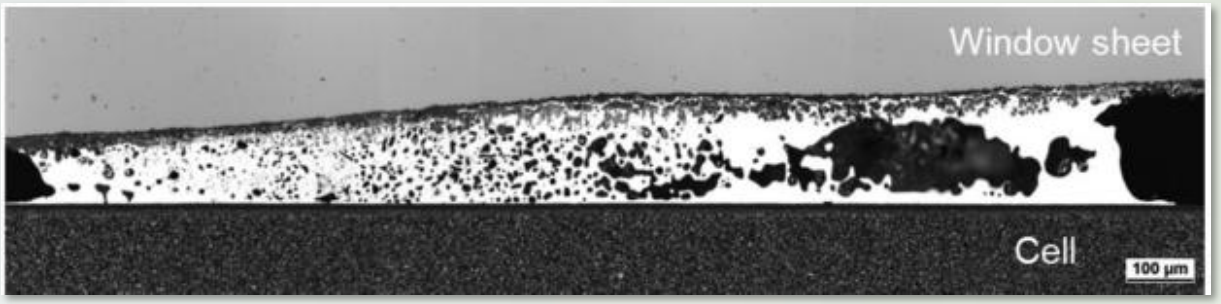
1. Reactive air silver brazes are only partially wetting ($\theta > 40^{o}$), resulting in occasional manufacturing defects (**Type I Pores**);



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

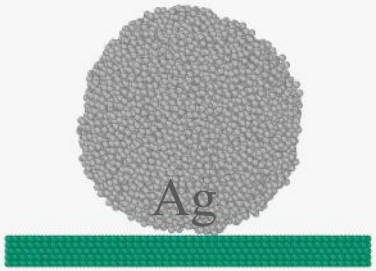


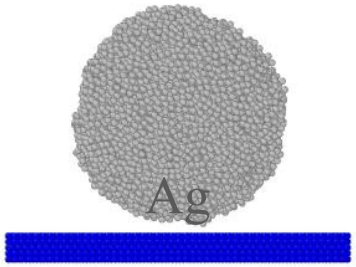
3. After ~ 10,000 hours, **Type III pores** form when dissolved hydrogen and oxygen in the Ag react to form water pockets/pores.

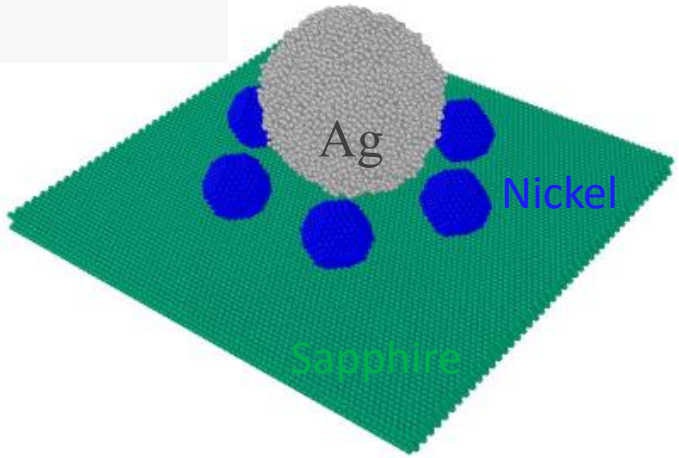


Delphi Technologies Inc, U.S. Patent No US7855030B2; Bause *et al.*, *Fuel Cells*, v13 p578 (2013).

Porous Nickel Layers Can Be Used To Promote Silver Wetting and Spreading on Ceramics

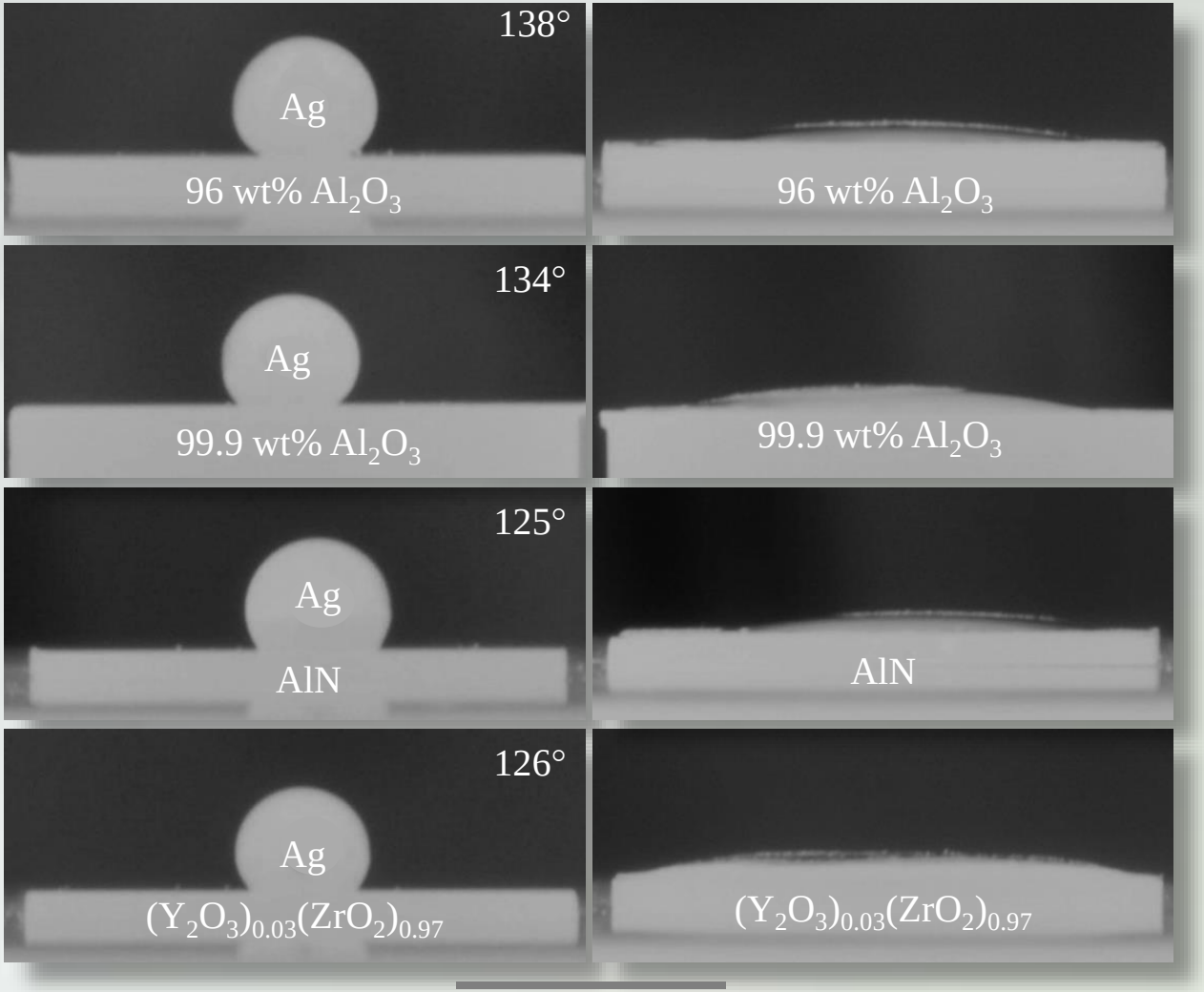






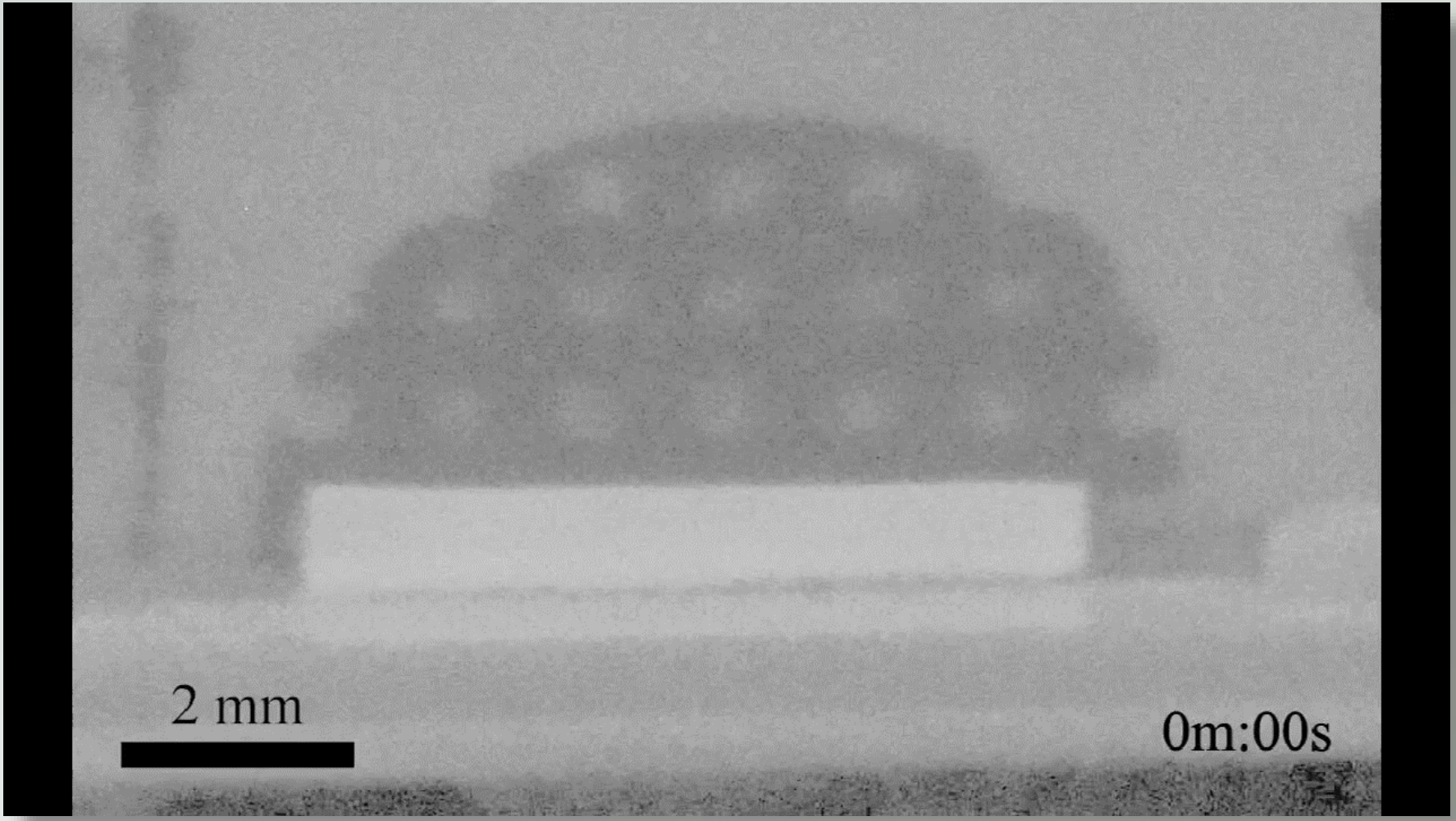
Park *et al.*, *Acta Materialia*, v199 p551 (2020).

Porous Nickel Layers Can Be Used To Promote Silver Wetting and Spreading on a Variety of Ceramic Substrates



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

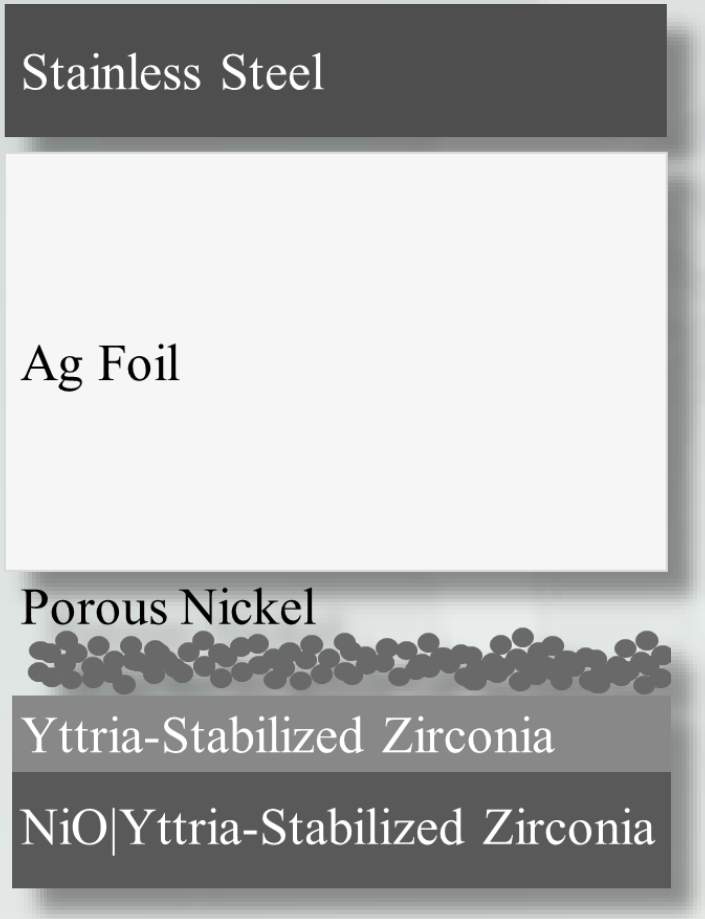
MOVIE: Molten Silver Defying Gravity as it Infiltrates Into a Pre-Patterned Nickel Network

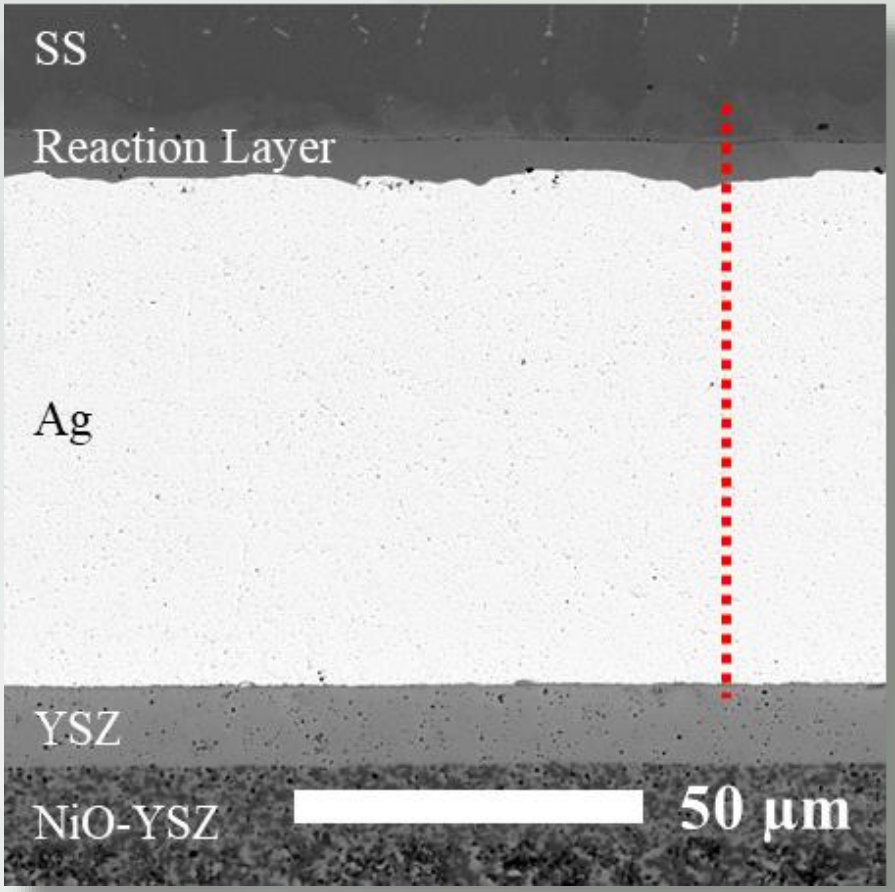


Temperature: ~1000°C Atmosphere: Carbon and Nickel Oxide Buffered Argon

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

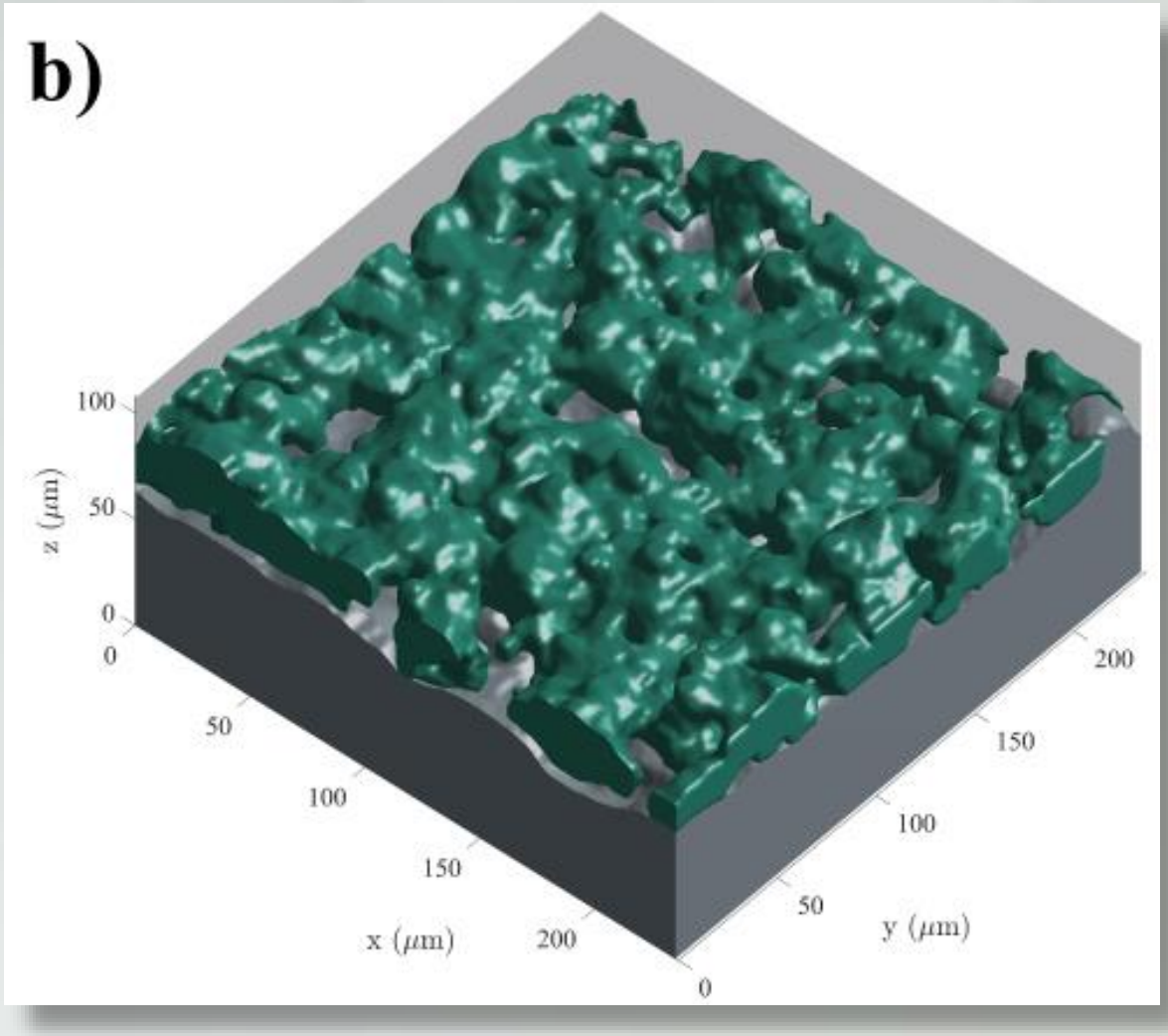
Porous Nickel Layers Can Be Used Instead of Reactive-Air Brazes to Bond Metals to Ceramics





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

Porous Nickel Layers Can Also Be Used For Ceramic-Ceramic Bonding

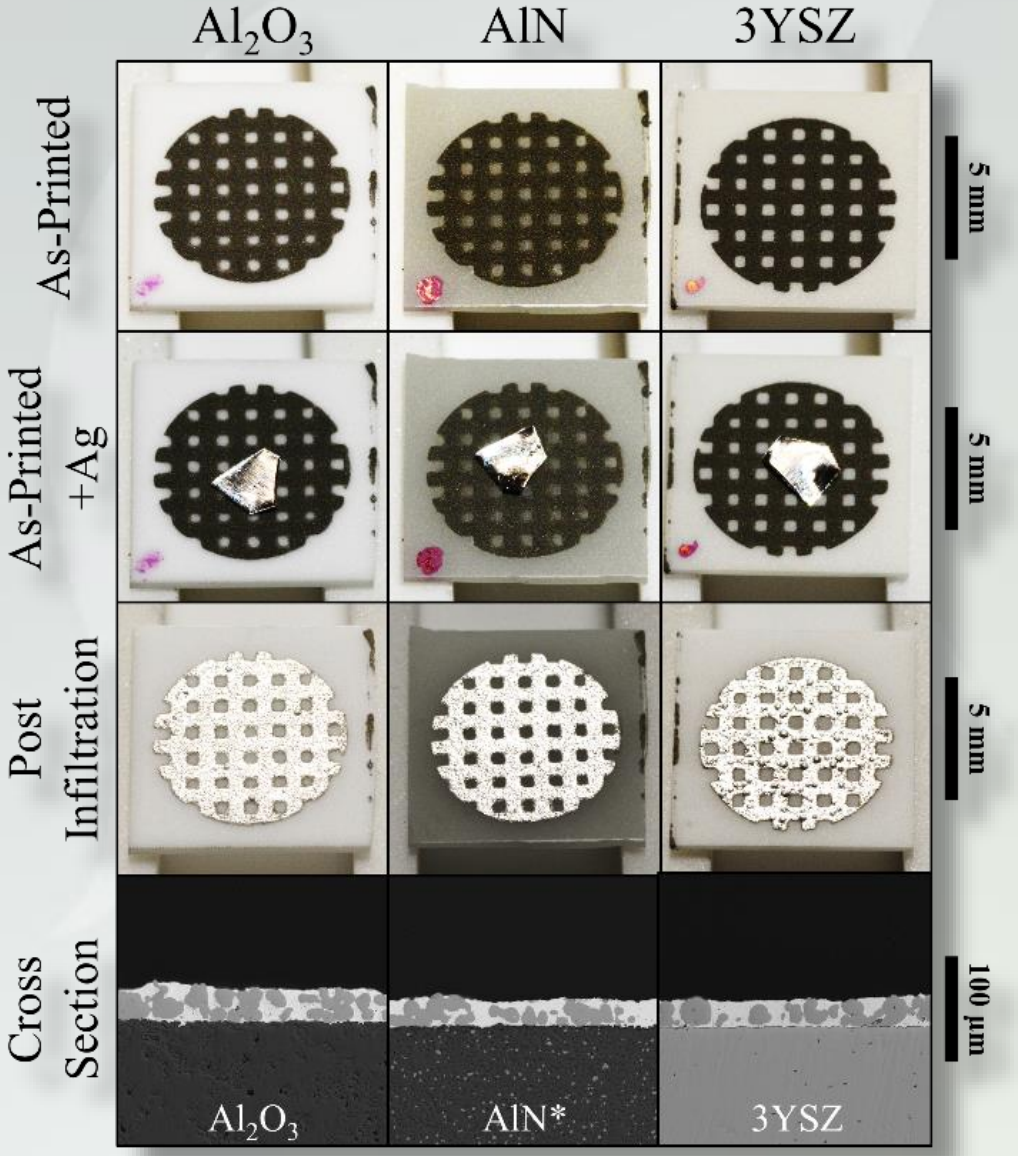


Ni is Green, Pores are Black, Sapphire is Gray, and Silver is Transparent

This 3D X-Ray Tomographic Reconstruction was Obtained at Argonne National Laboratory

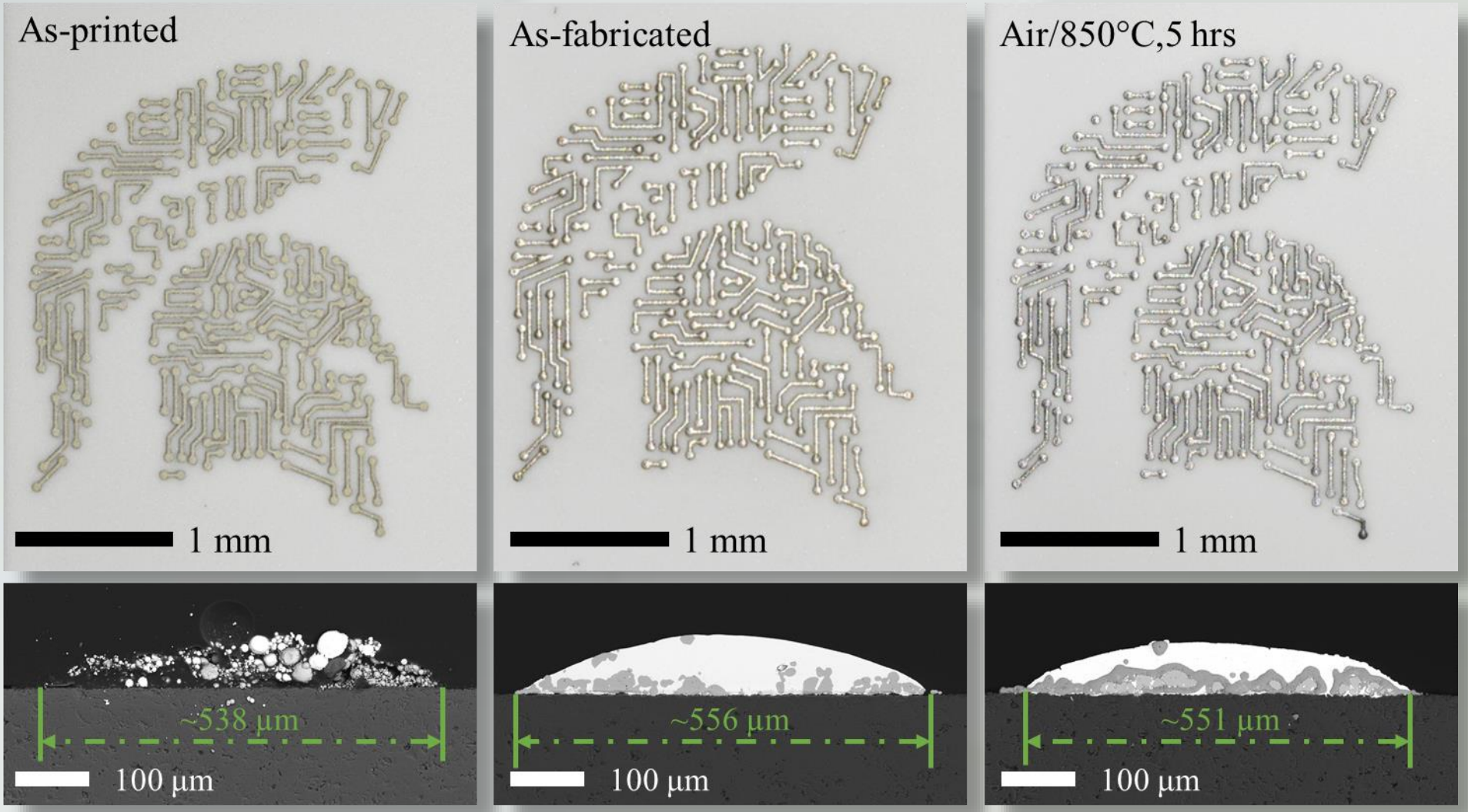
Hu *et al.*, *Scripta Materialia.*, v196 p113767 (2021).

Patterned Silver Circuits Can Also Be Made by Infiltrating Molten Silver Into a Pre-Patterned Nickel Network



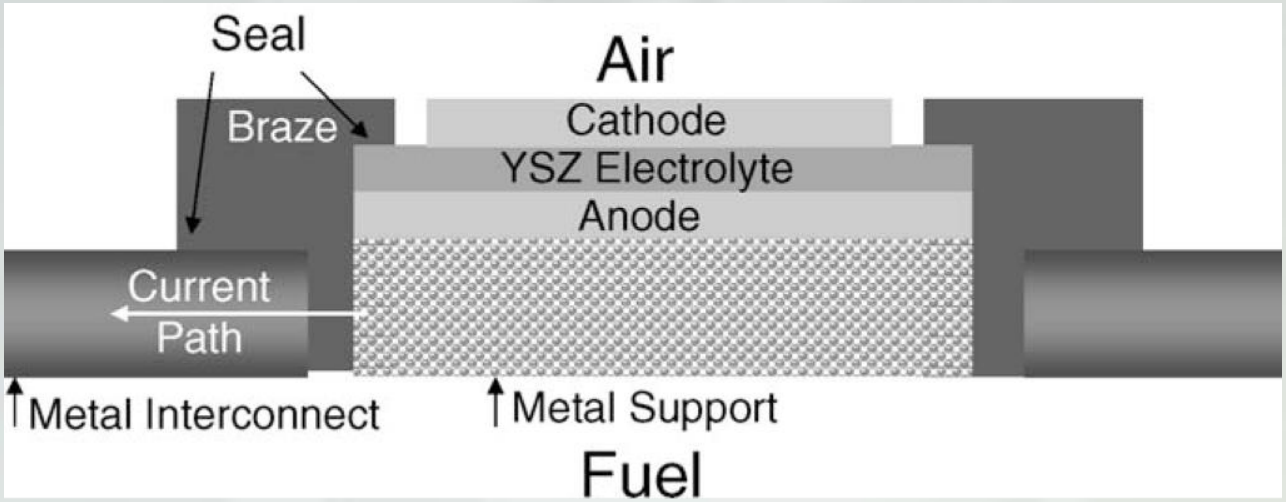
Hu *et al.*, *Scripta Materialia.*, v196 p113767 (2021).

Patterned Silver Circuits Can be Made by Applying Silver Ink Over Nickel Ink and Firing Together

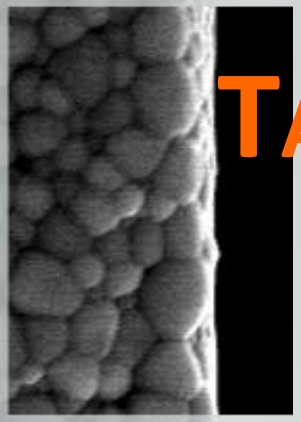


Hu *et al.*, *Scripta Materialia.*, v196 p113767 (2021).

Low Resistance Electrical Contacts Between Stainless Steel Are Needed for Metal-Supported Solid Oxide Cells

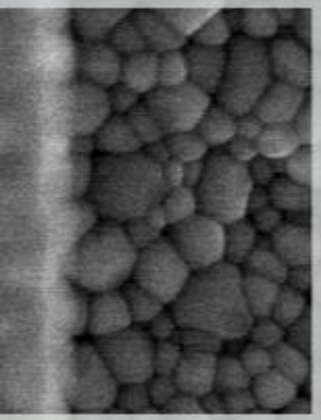


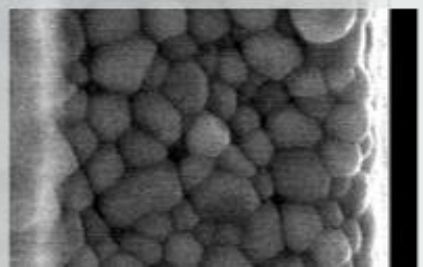
Tucker *et al.*, *J. Power Sources.*, v160 p1049 (2006).



Talk Outline

1. Motivation
2. **Porous Interlayers that Both:**
   1. **Promote Ag Wetting**
   2. **Inhibit Stainless Steel Surface Oxide Formation**
3. Conclusions

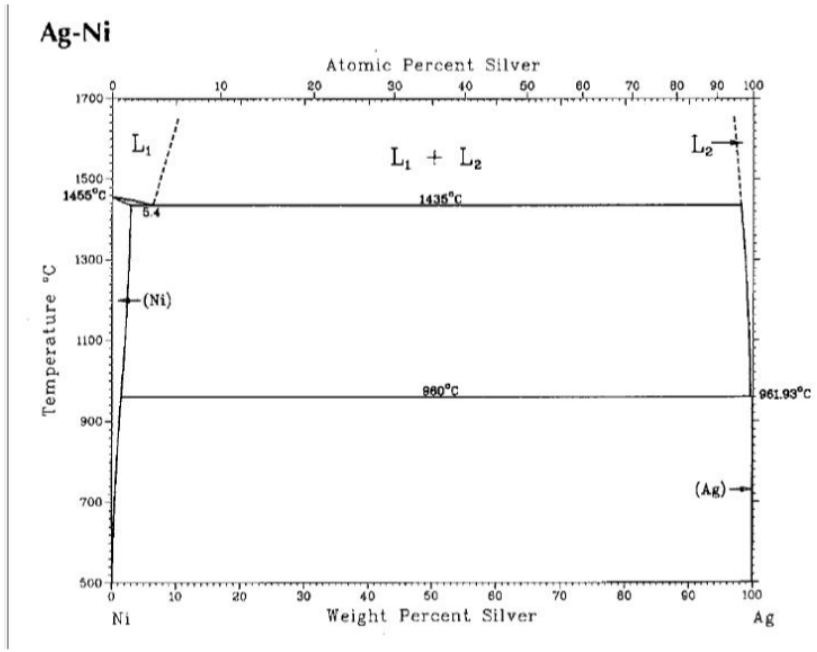




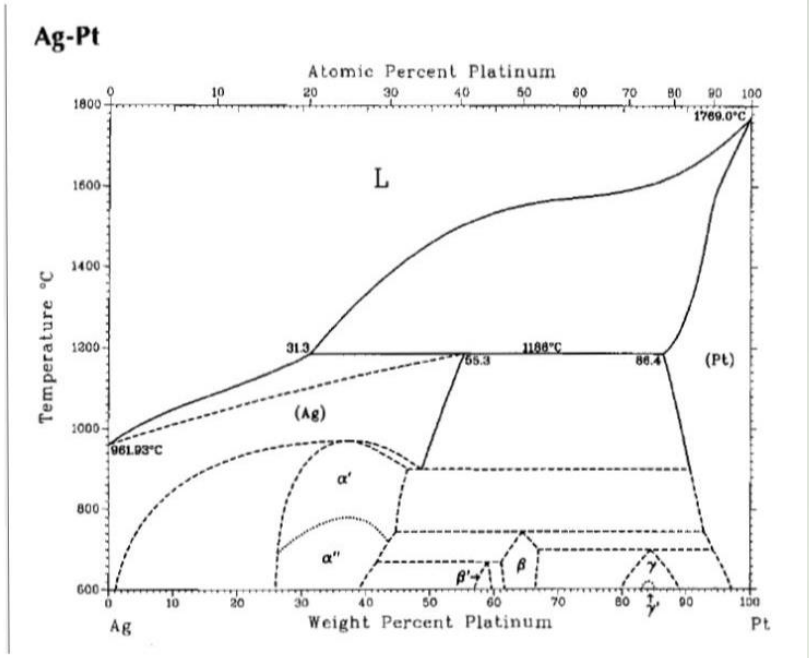
Wetting Promoting Interlayer Phase Diagram Characteristics

- The Interlayer Must Remain Solid Well Above the Ag Melting Temperature of 962°C
- To Promote Ag Wetting, There Must Be Some Ag Solubility in the Interlayer Material
- To Ensure the Interlayer Doesn't Disappear Before Joint Manufacture is Complete, The Interlayer Should NOT have Complete Solid Solution with Ag

Binary alloy phase diagrams Ag-Ni



Binary alloy phase diagrams Ag-Pt

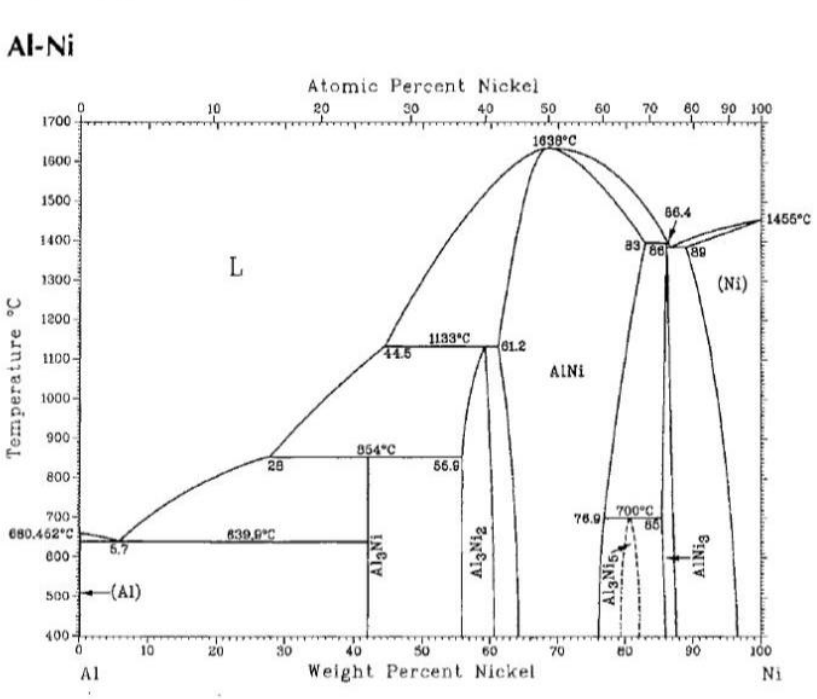


Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

Chemical Gettering Interlayer Phase Diagram Characteristics

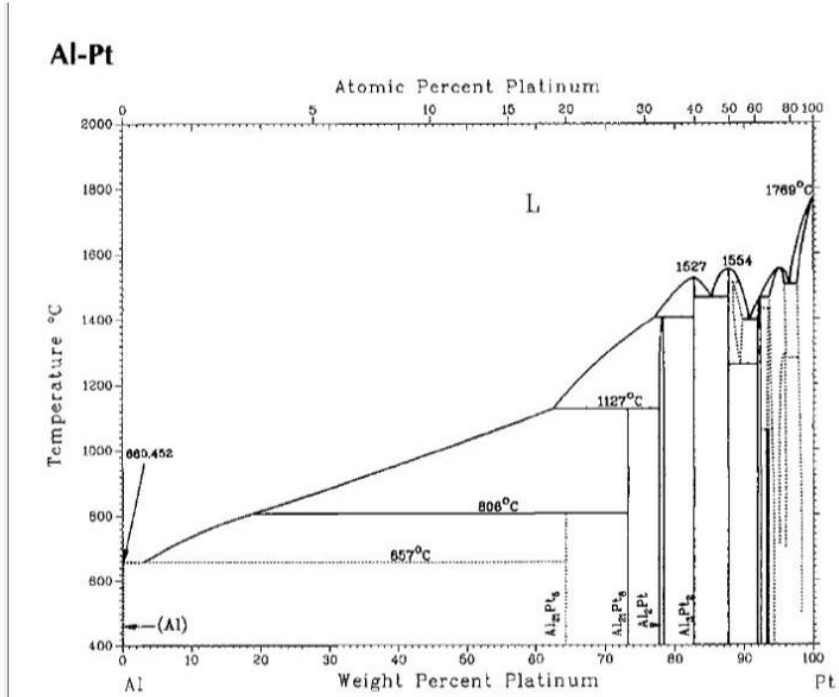
- To Have a Chance of Serving as an Effective Surface Oxide Getter, the Interlayer Material Should Form Intermetallics with Stainless Steel Oxide Scale Cations (Al, Cr, etc).

Binary alloy phase diagrams AI-Ni



ASM Handbook, Volume 03 - Alloy Phase Diagrams
Copyright © 1992 ASM International

Binary alloy phase diagrams AI-Pt



ASM Handbook, Volume 03 - Alloy Phase Diagrams
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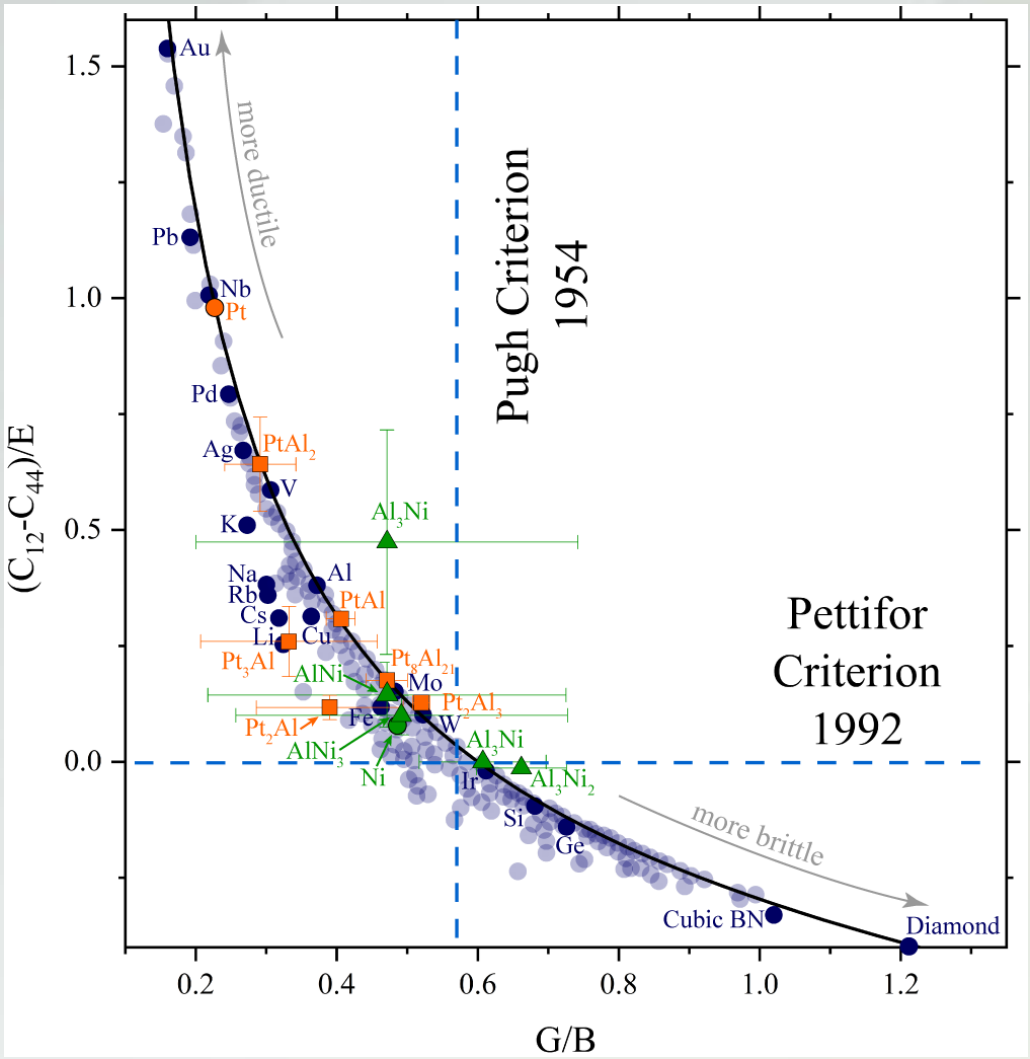
Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

Interlayer Mechanical Property Considerations

- Interlayer Reaction Products Must Have Similar or Greater Ductility than Ni



Elastic Constant Data was Obtained from Materials Project

Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

Ni and Pt Are Likely Good Interlayer Materials, Others May Also Be Possible

Gaseous at room and elevated temperature

No aluminide phases

Unwettable by Ag

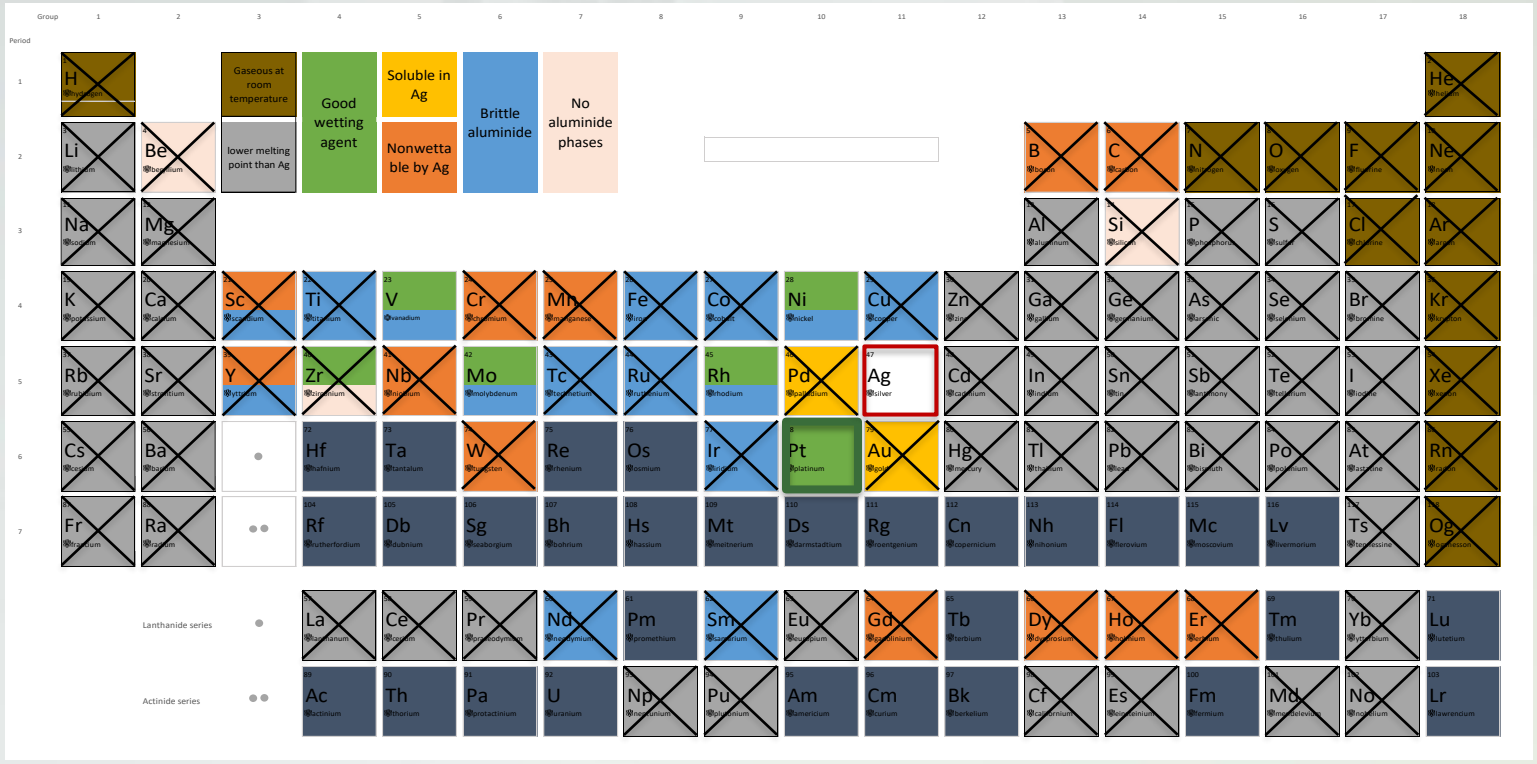
Insufficient Data

Lower melting point than Ag

Potentially brittle aluminide phases

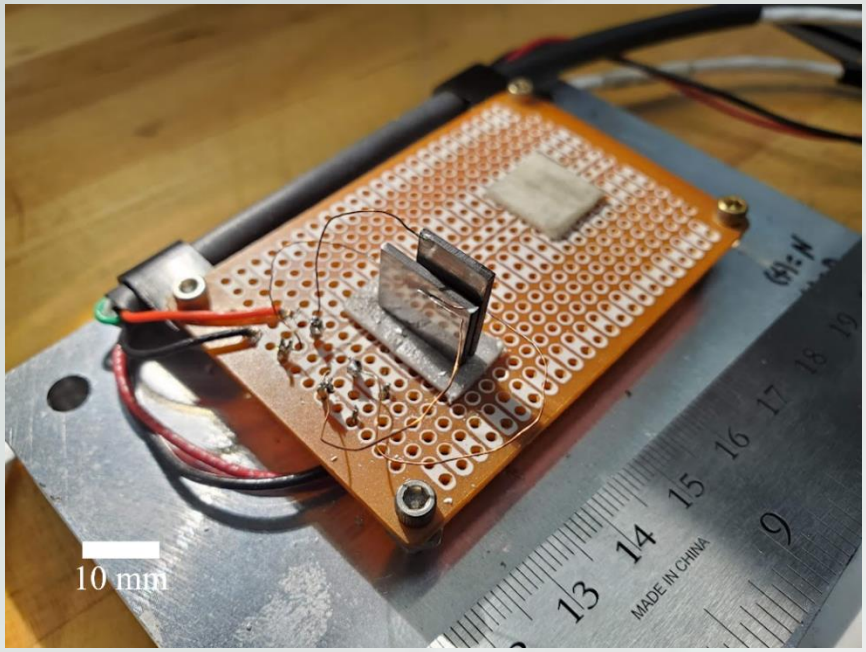
Extremely, soluble in Ag, as implied by the phase diagram

Potentially wettable by Ag, as implied by the phase diagram

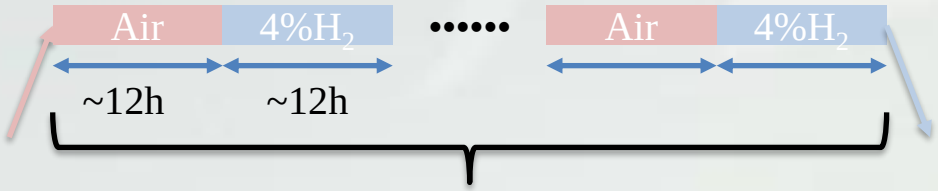


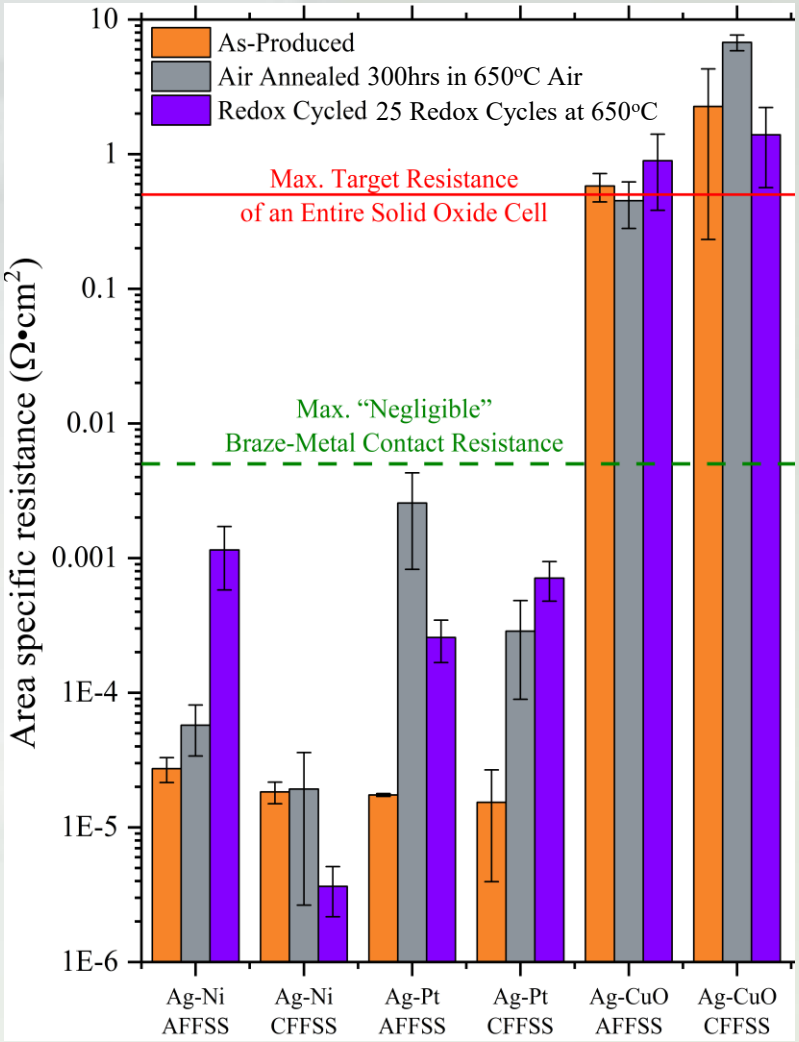
Hu *et al.*, *J. Electrochem. Soc.*, *Submitted.* (2025).

Ag-Ni and Ag-Pt Electrical Contacts Perform Significantly Better Than Conventional Ag-CuO RAB Joints



Measurements assume contact resistance is the dominant source of resistance.

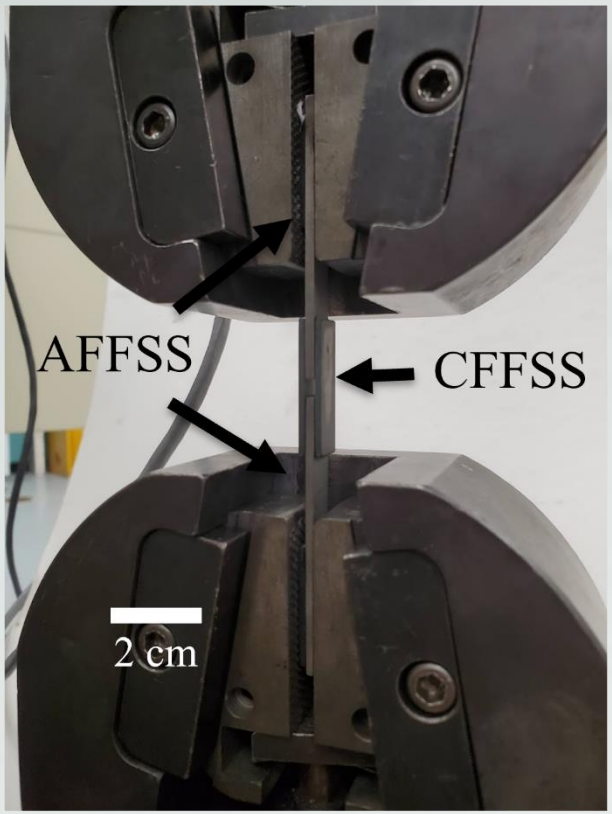


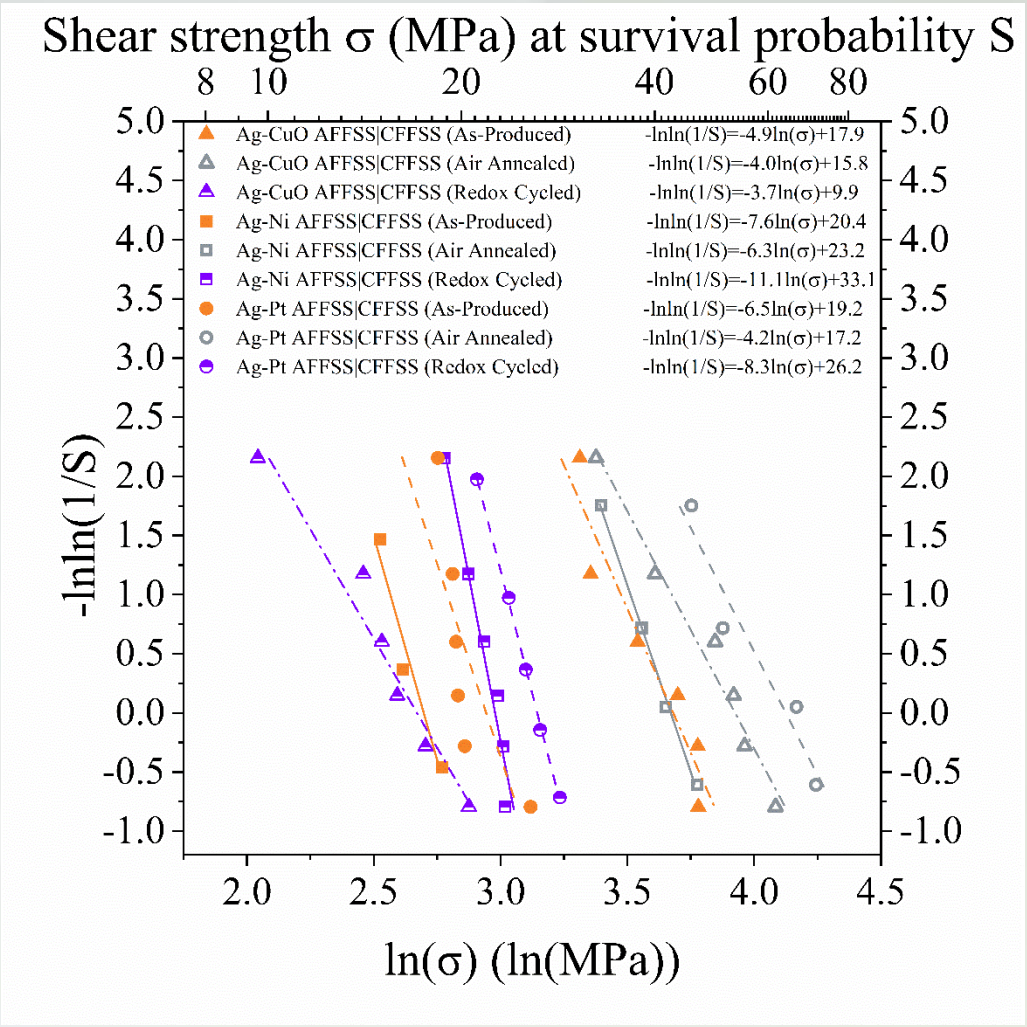


AFFSS = Alumina-Forming Stainless Steel, CFFSS = Chromia-Forming Stainless Steel

Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

Ag-Ni and Ag-Pt Stainless Steel Joints Have Strengths Similar, Or Greater, Than Those Made With Ag-CuO

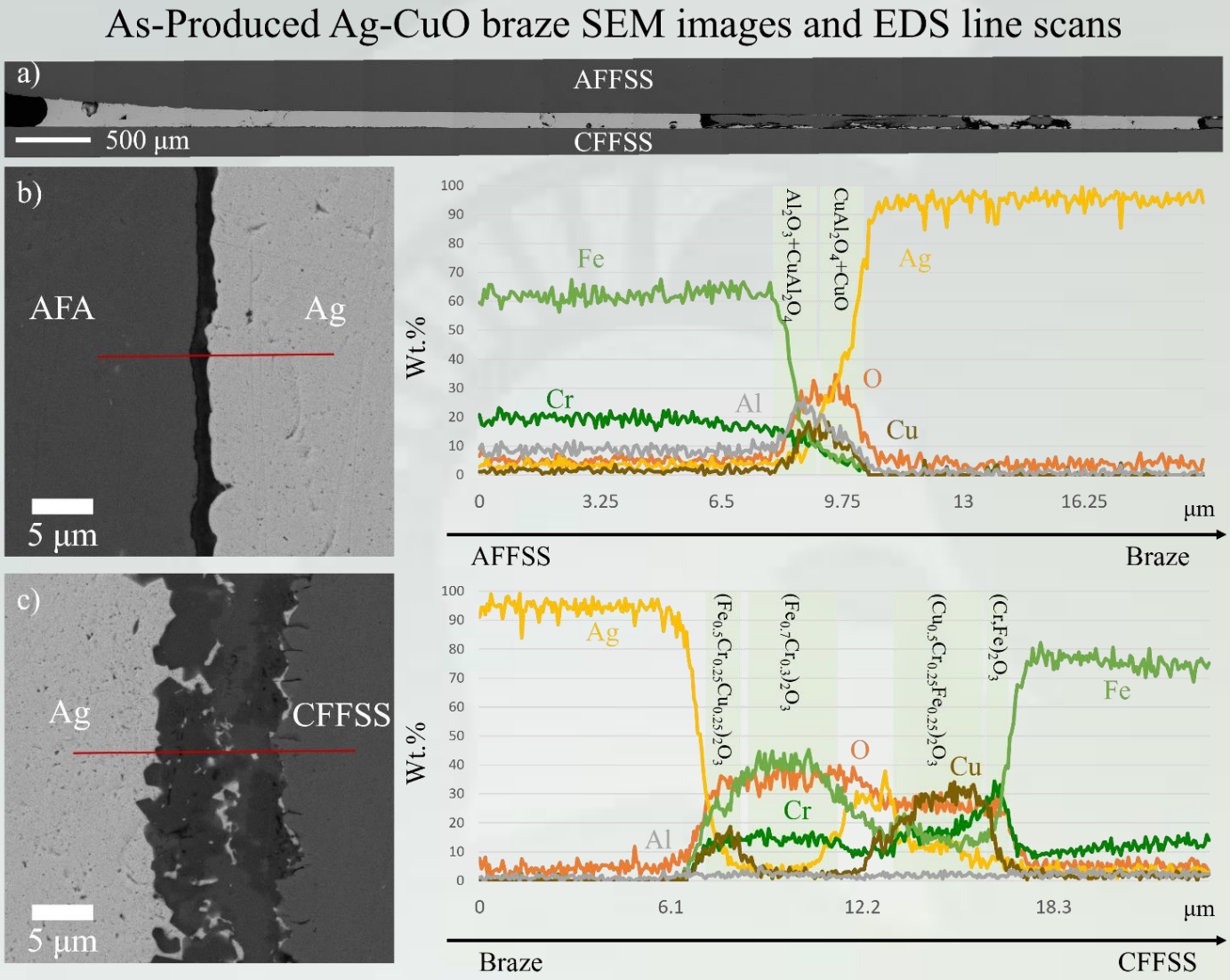




AFFSS = Alumina-Forming Stainless Steel, CFFSS = Chromia-Forming Stainless Steel

Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

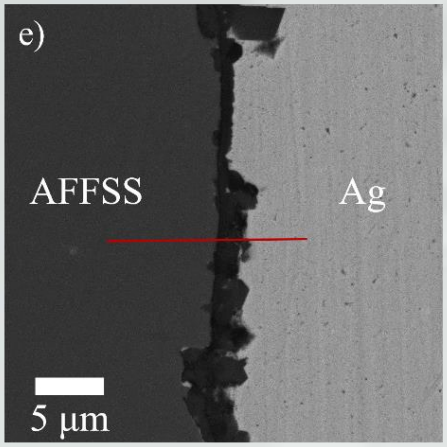
Ag-CuO Produces Defective Joints with Thick $CuAl_2O_4$ Layers

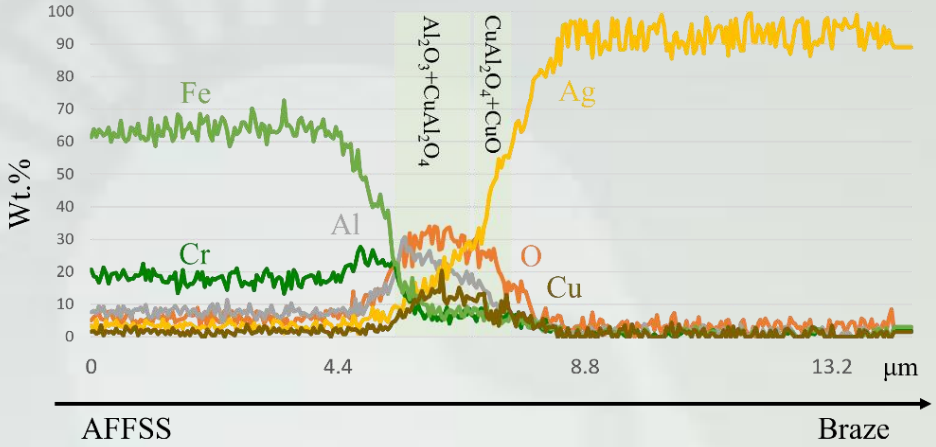


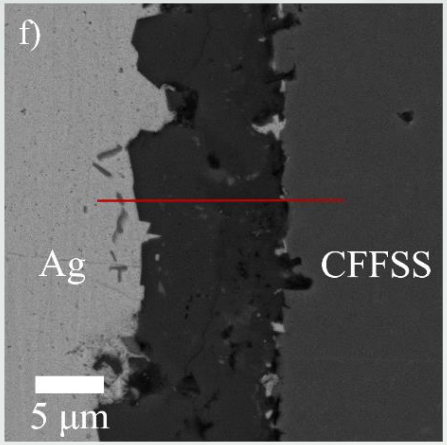
Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

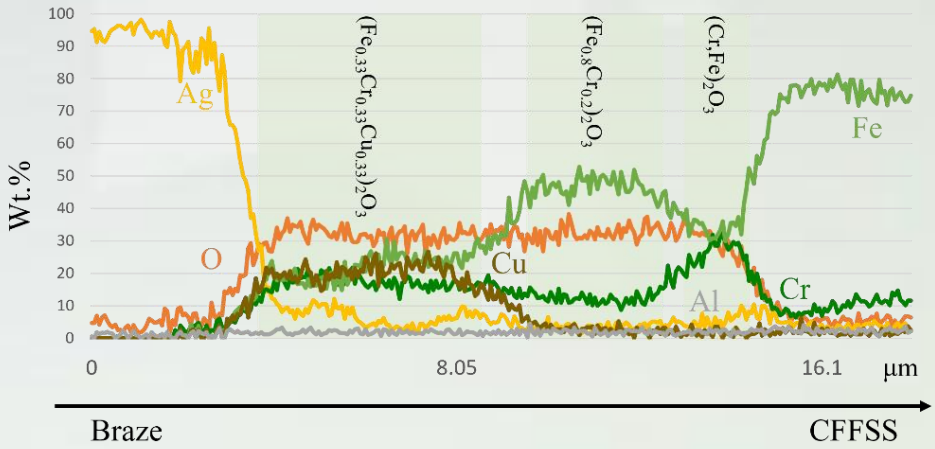
Since It Was Made In Air, the Ag-CuO Microstructure Doesn't Change Much With 300hrs in 650°C Air

Air-Annealed Ag-CuO braze SEM images and EDS line scans



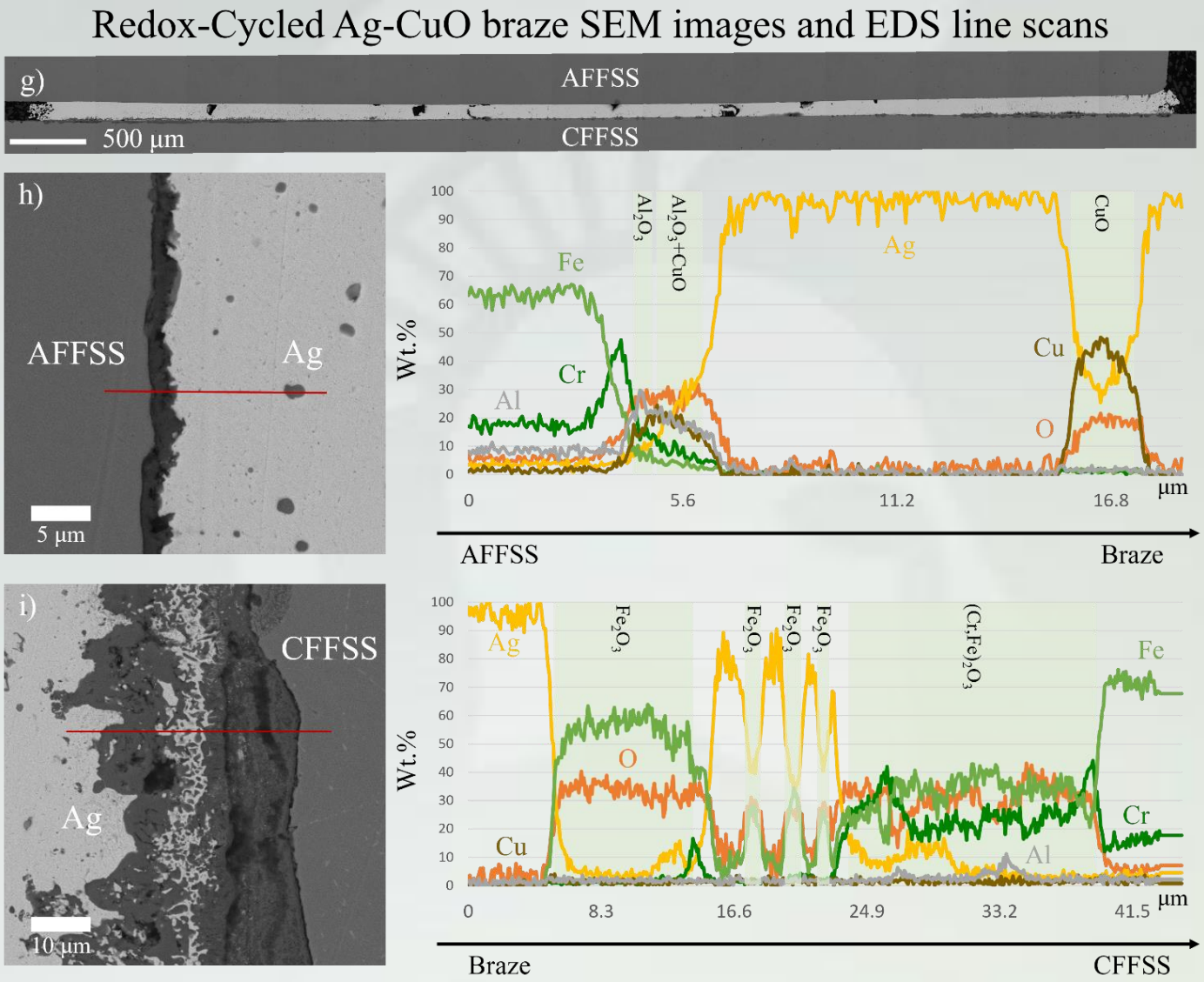






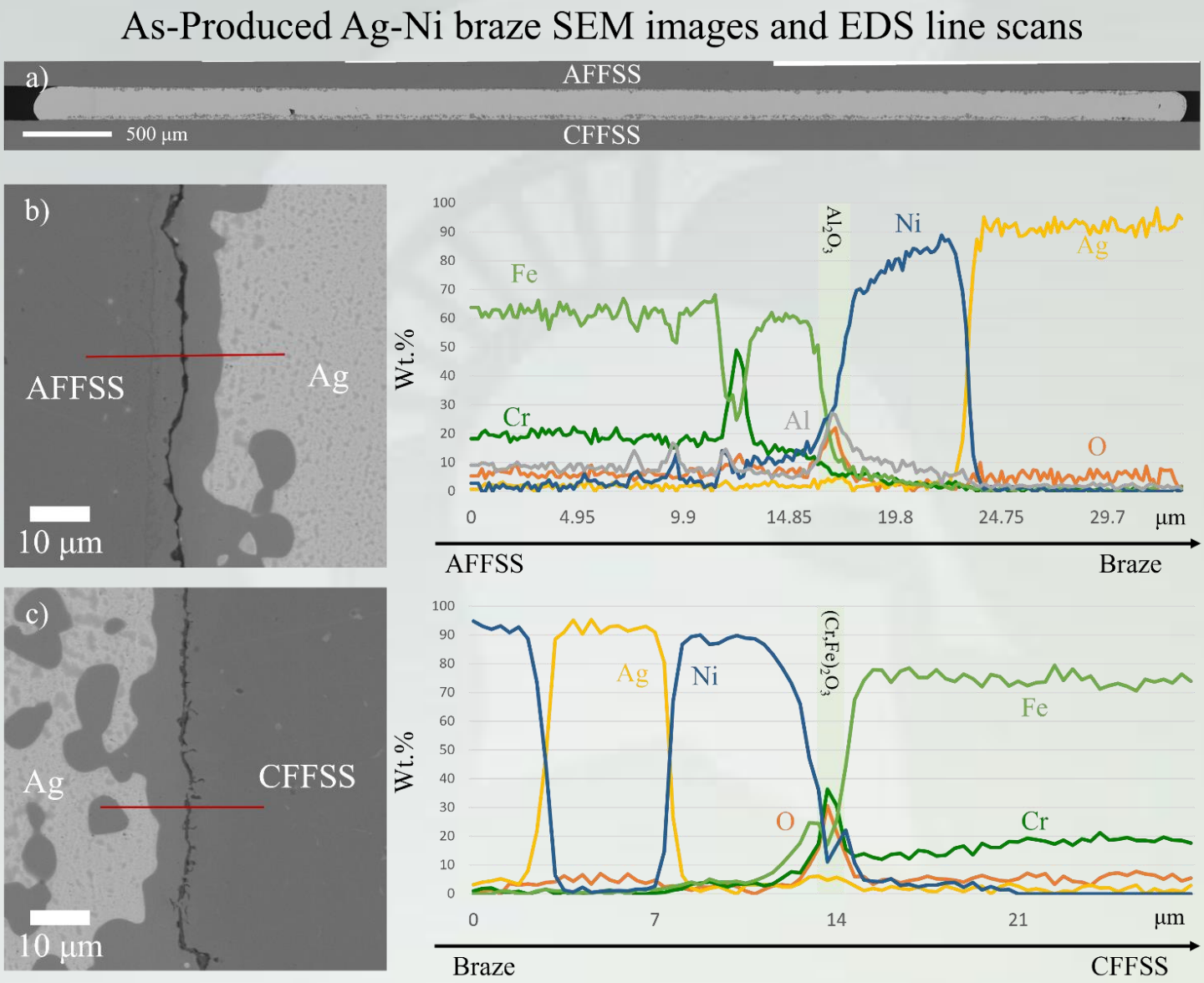
Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

The $CuAl_2O_4$ Spinel in Oxidized or As-Produced Ag-CuO Joints Breaks Down with Redox Cycling



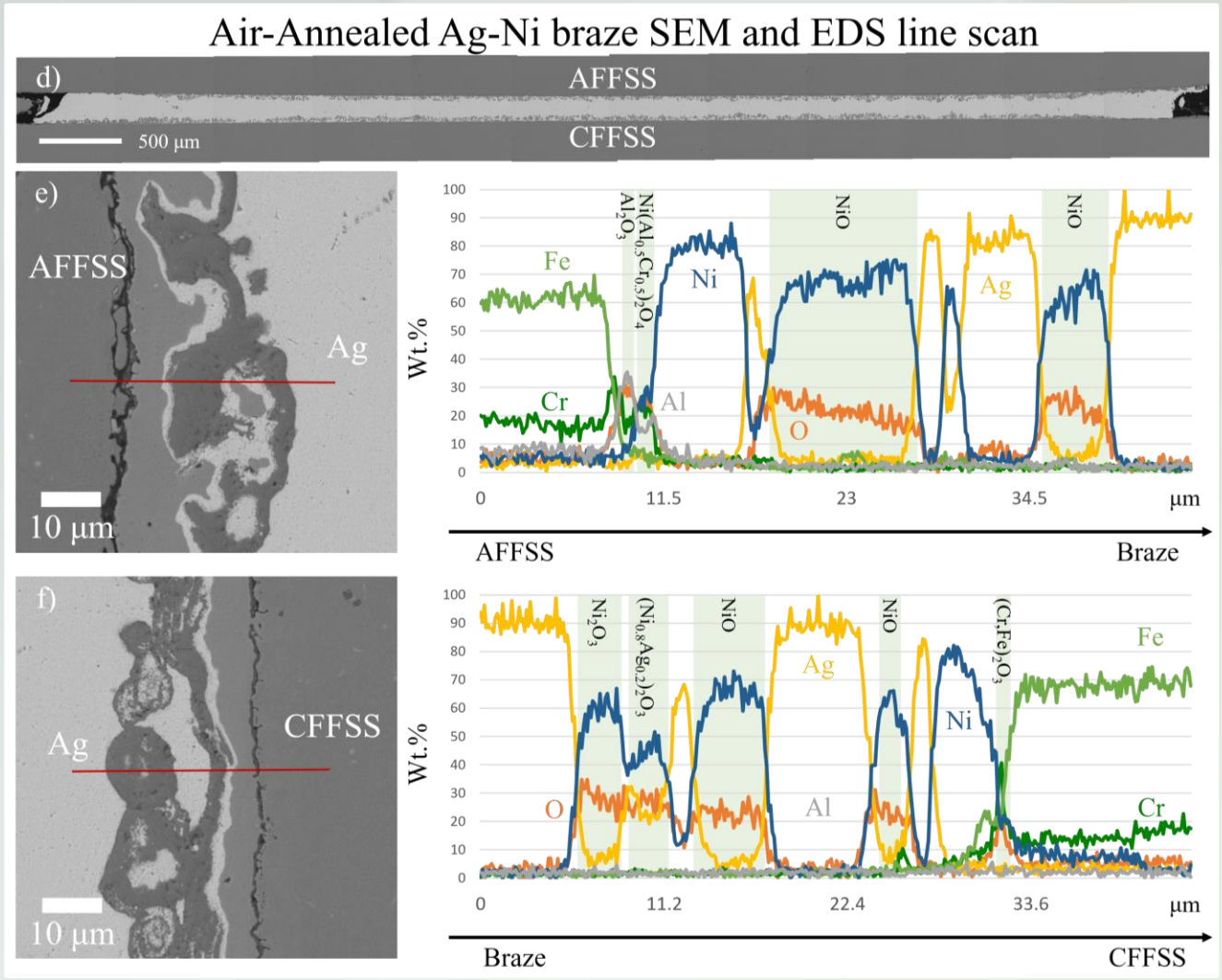
Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

Ag-Ni Produces Dense AFFSS to CFFSS Electrical Contacts



Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

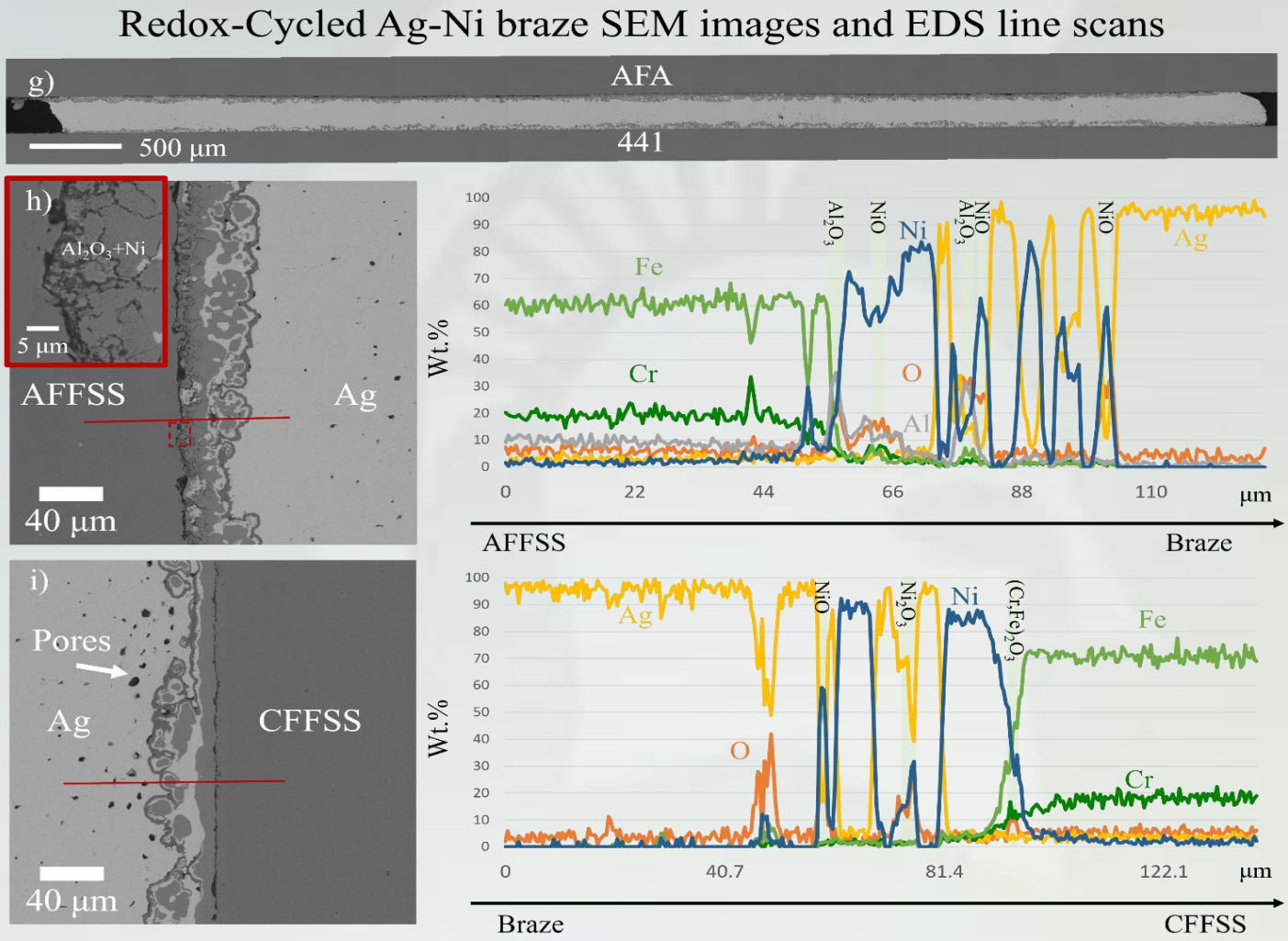
Ni Getters Al During 300 hrs of 650°C Sir, Reducing the Thickness of the Alumina Scale



AFFSS = Alumina-Forming Stainless Steel, CFFSS = Chromia-Forming Stainless Steel

Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

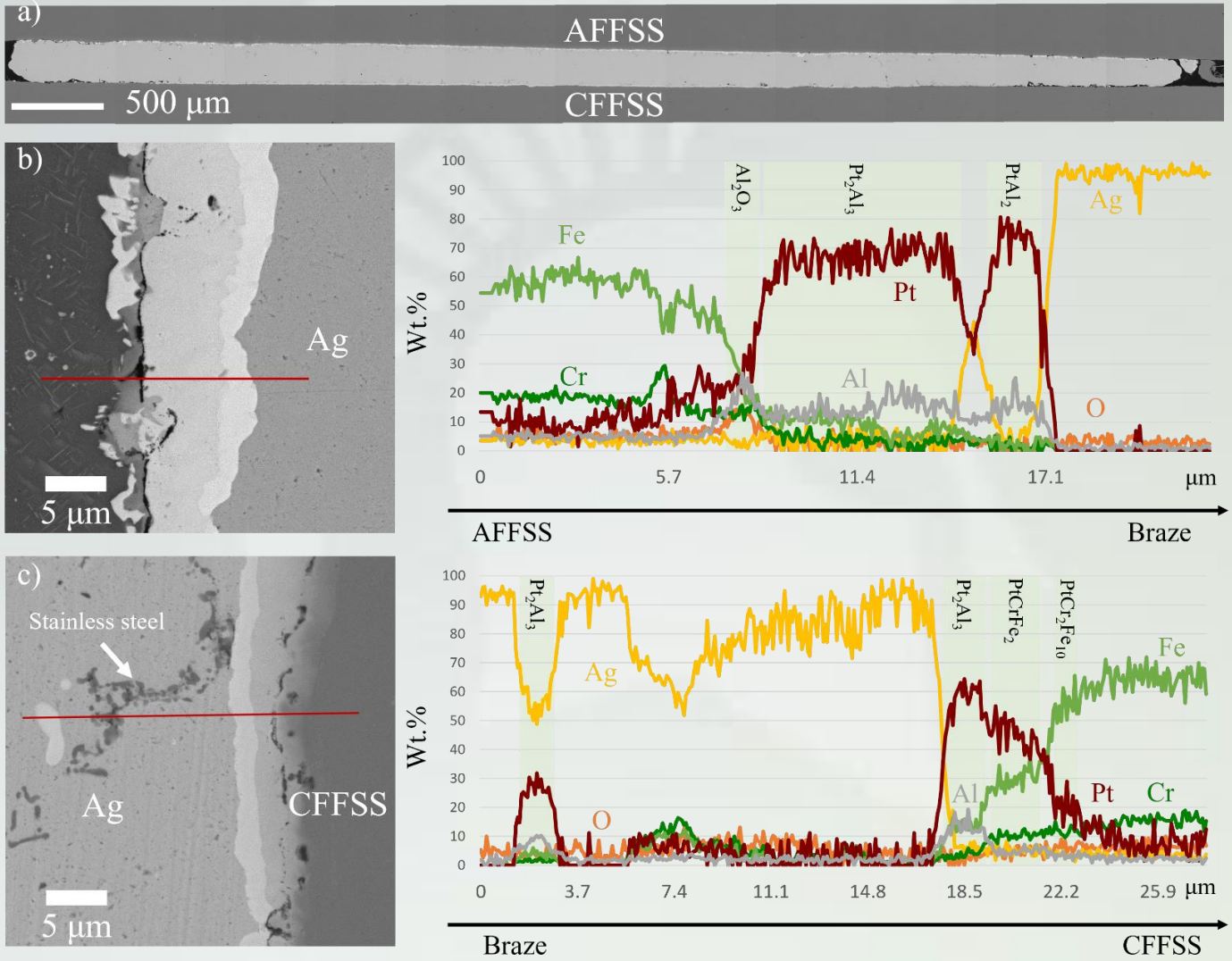
The $Ni(Al,Cr)_2O_4$ Spinel in Oxidized Ag-Ni Joints Breaks Down with Redox Cycling



Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

Ag-Pt Produces Dense AFFSS to CFFSS Electrical Contacts, Pt Getters Al During Manufacturing

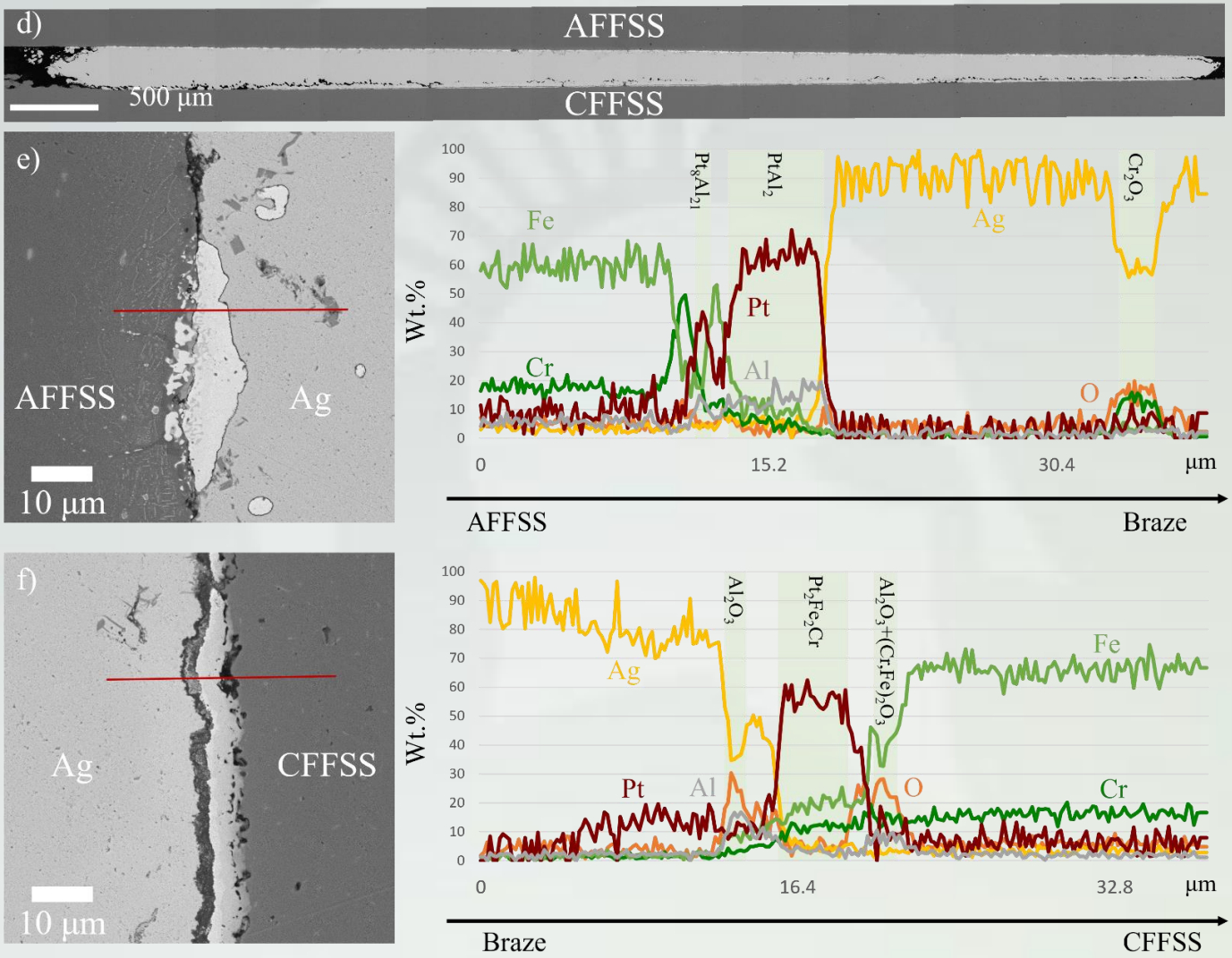
As-Produced Ag25Pt braze SEM images and EDS line scans



Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

Ag-Pt Contacts Have Regions That Are Al_2O_3-Free After 300 hrs in 650°C Air, Most of Pt Dissolves into the Ag

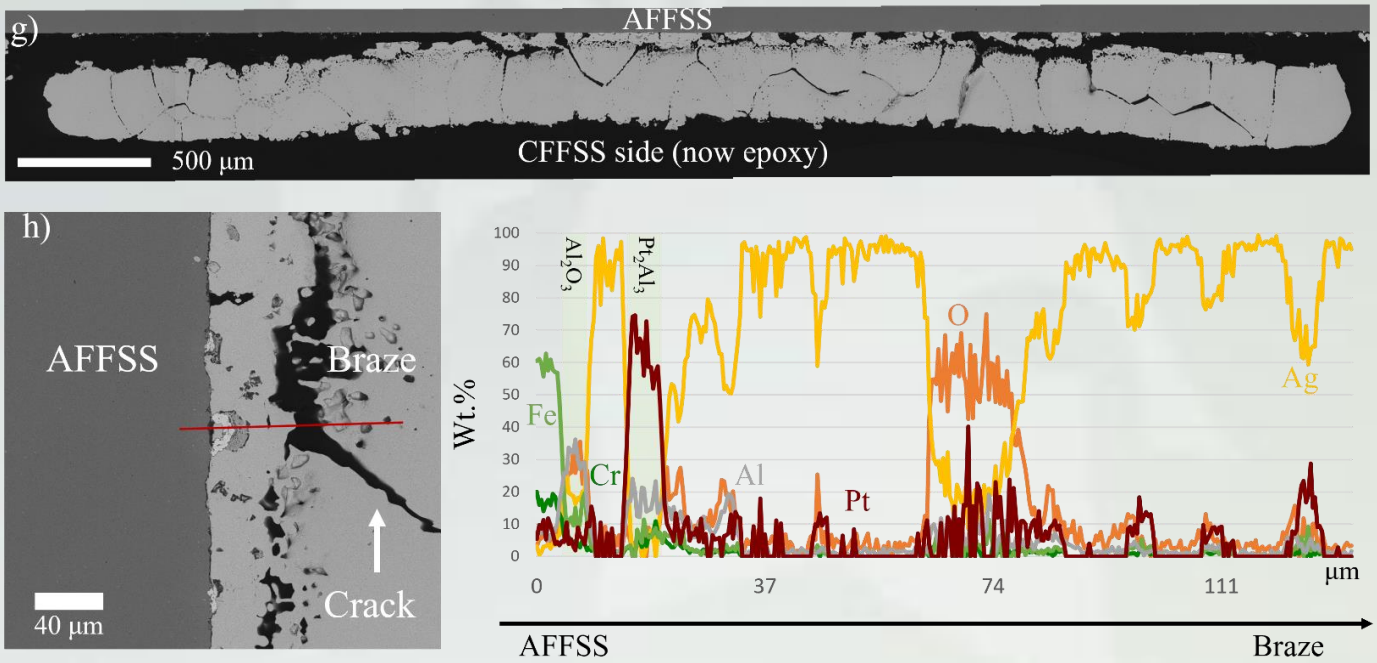
Air-Annealed Ag25Pt braze SEM images and EDS line scans



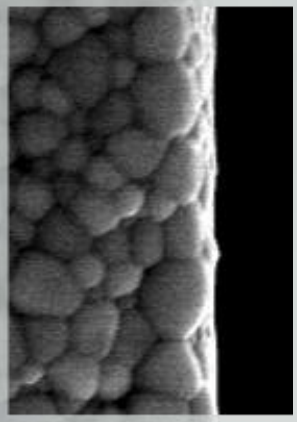
Hu *et al., J. Electrochem. Soc., Submitted.* (2025).

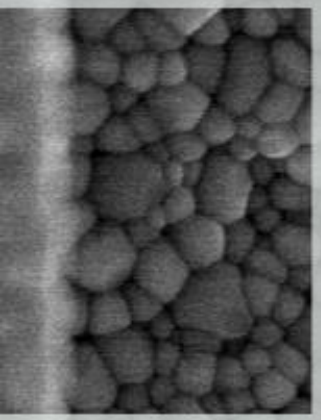
Due to Solid Solution Embrittlement Caused by Pt Dissolving into the Ag, Ag-Pt Braze Joints Do Not Survive Redox Cycling. Pt Likely Also Catalyzes Water Pocket Formation at the Grain Boundaries

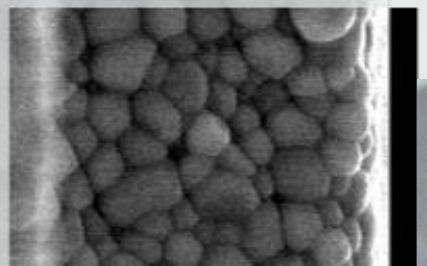
Redox-Cycled Ag25Pt braze SEM images and EDS line scans



Hu *et al., J. Electrochem. Soc., Submitted.* (2025).







Conclusions

- Porous Ni or Porous Ni interlayers promote the wetting, spreading and adhesion of silver on alumina-forming ferritic stainless steel (AFFSS) and chromia-forming ferritic stainless steel (CFFSS).
- Porous Ni or Porous Pt interlayers can also chemically getter surface-segregating steel constituents (particularly Al from the AFFSS), **dramatically reducing the electrical contact resistance by several orders of magnitude**.
- Ag-Pt joints become brittle and porous after redox cycling
- After redox-cycling or 650°C isothermal aging in air, Ag-Ni braze joints displayed shear strengths that were larger than, or similar to, those of Ag-CuO braze joints.
- The Ag-Ni contacts were made here by firing screen printed Ni and Ag inks at 1025°C in Carbon- and NiO-buffered Argon.
- Flux-free, torch-made Ag-Ni electrical contacts to stainless steel (for SOC tabs etc.) should also be possible