Metallic SOFC Interconnect Systems

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ATI Allegheny Ludlum

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Overview

- Surface modification of ferritic (Fe-Cr) stainless steels has shown promise in mitigating the detrimental effects of aluminum and silicon
- Multi-layered interconnect structures have been tested and shown to be effective in eliminating or reducing oxidation on the anode side of the SOFC interconnect

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Overview

- Some of the alloys tested for anode-side layers may possibly reduce hydrogen transport effects
- Other results
  - Alloy development
  - Evaluation of oxidation-resistant, electrically conductive coatings
  - Surface layer adhesion (CMU)
  - Contact layer development (WVU)

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Post-Process Surface Modification

Effect on ASR

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Surface Modifications

- Aluminum and silicon in Fe-Cr alloys generally come from additions made during the steelmaking process
- Both elements have a high affinity for oxygen and form electrically resistive oxides at the scale/alloy interface

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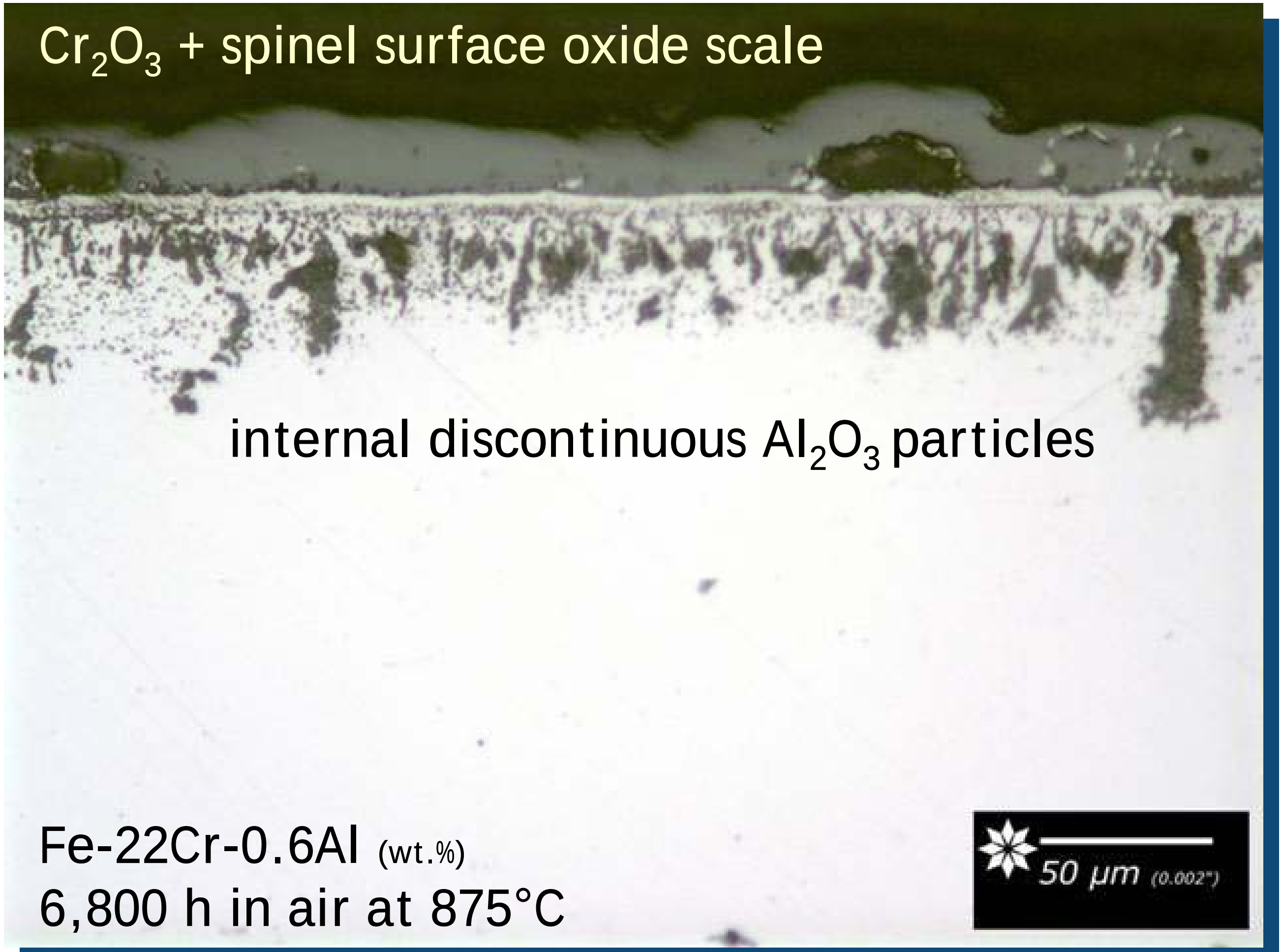
Internal Oxidation of Aluminum



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Surface Modifications

- Surface processing of stainless steel after manufacturing
  - Aluminum sequestration
  - Silicon removal
- Beneficial effect on ASR observed in preliminary evaluation of pre-oxidized specimens

Effect of Aluminum Sequestration

- Aluminum forms internal oxide particles at the scale/alloy interface
  – Increases oxygen uptake (higher weight gains during oxidation testing)
  – Reduces electrically conductive cross-section
- Special processing sequesters aluminum
  – Reduced weight gain (no internal oxidation)
  – Lower ASR
  – Effect reduced at higher temperatures

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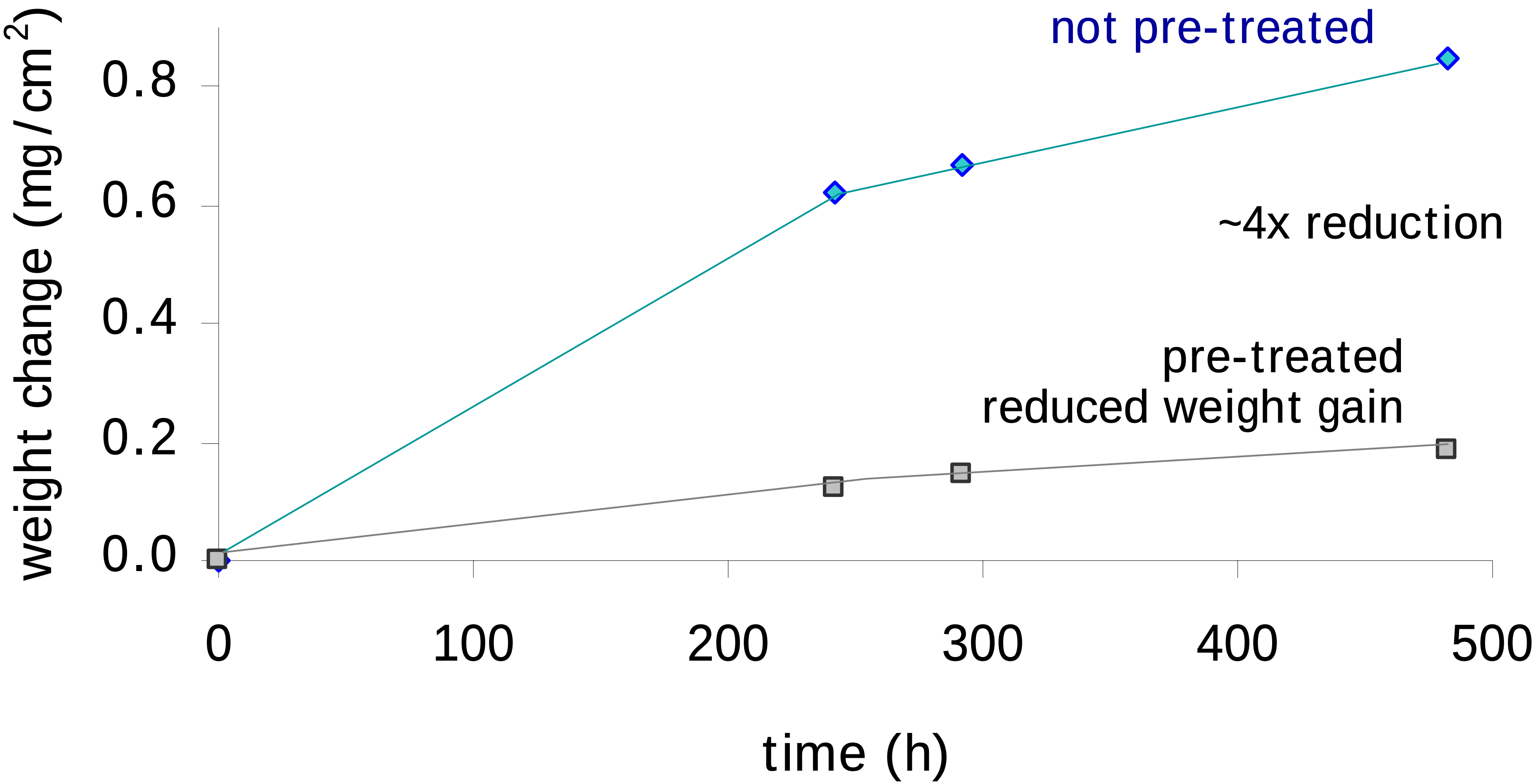
Effect of Aluminum Sequestration on Oxidation Kinetics



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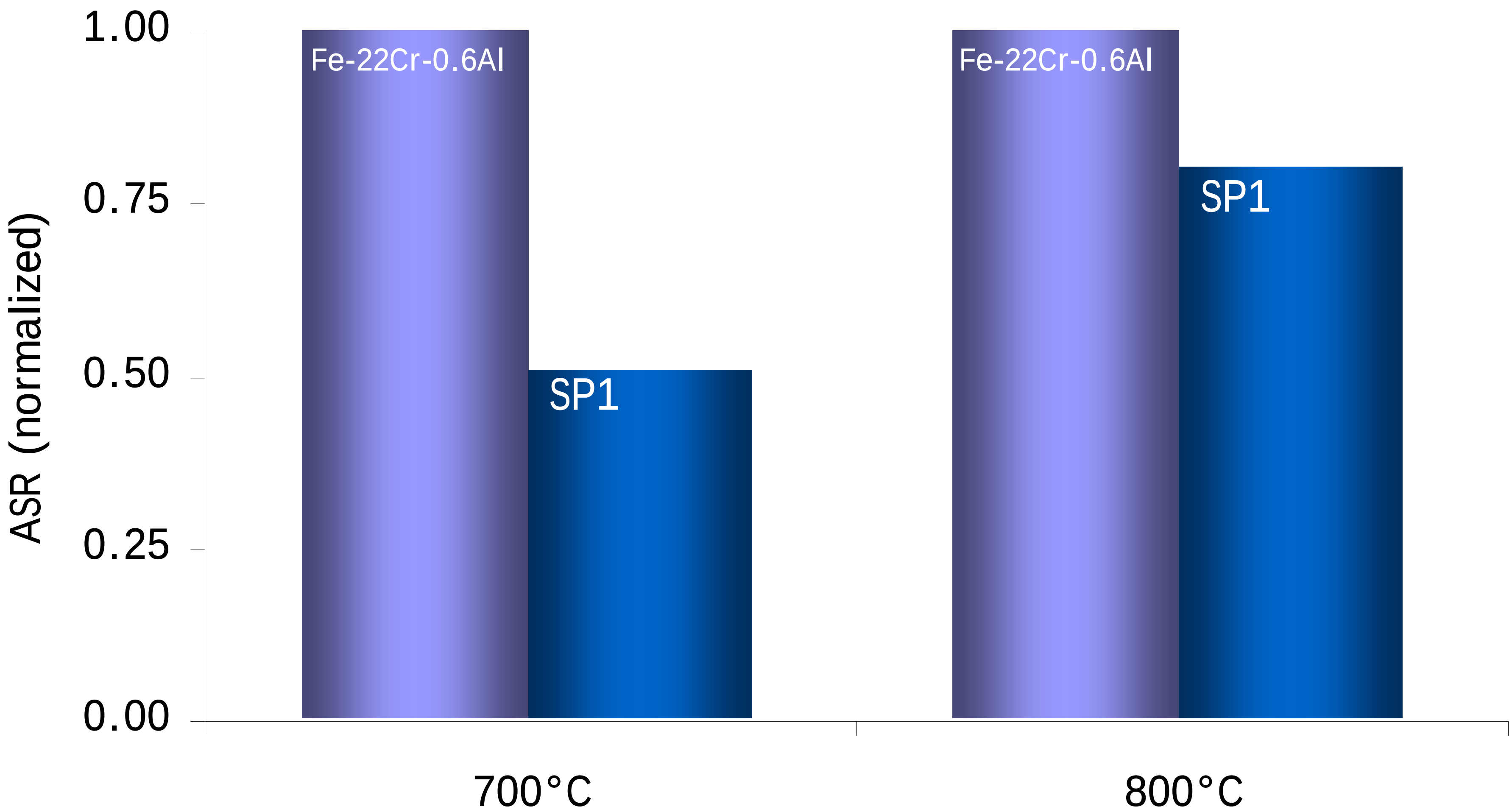
Fe-22Cr-0.6Al alloy
pre-oxidation exposure in air at 800°C

Effect of Aluminum Sequestration



ASR measurement temperature

samples pre-oxidized in air for 500 hours at 800°C

Effect of Silicon Removal

- Silicon forms a very thin layer of electrically resistive silica at the scale/alloy interface
- Special processing removes silicon
  - No effect on oxidation resistance
  - Lower ASR
  - Effect magnified at higher temperatures

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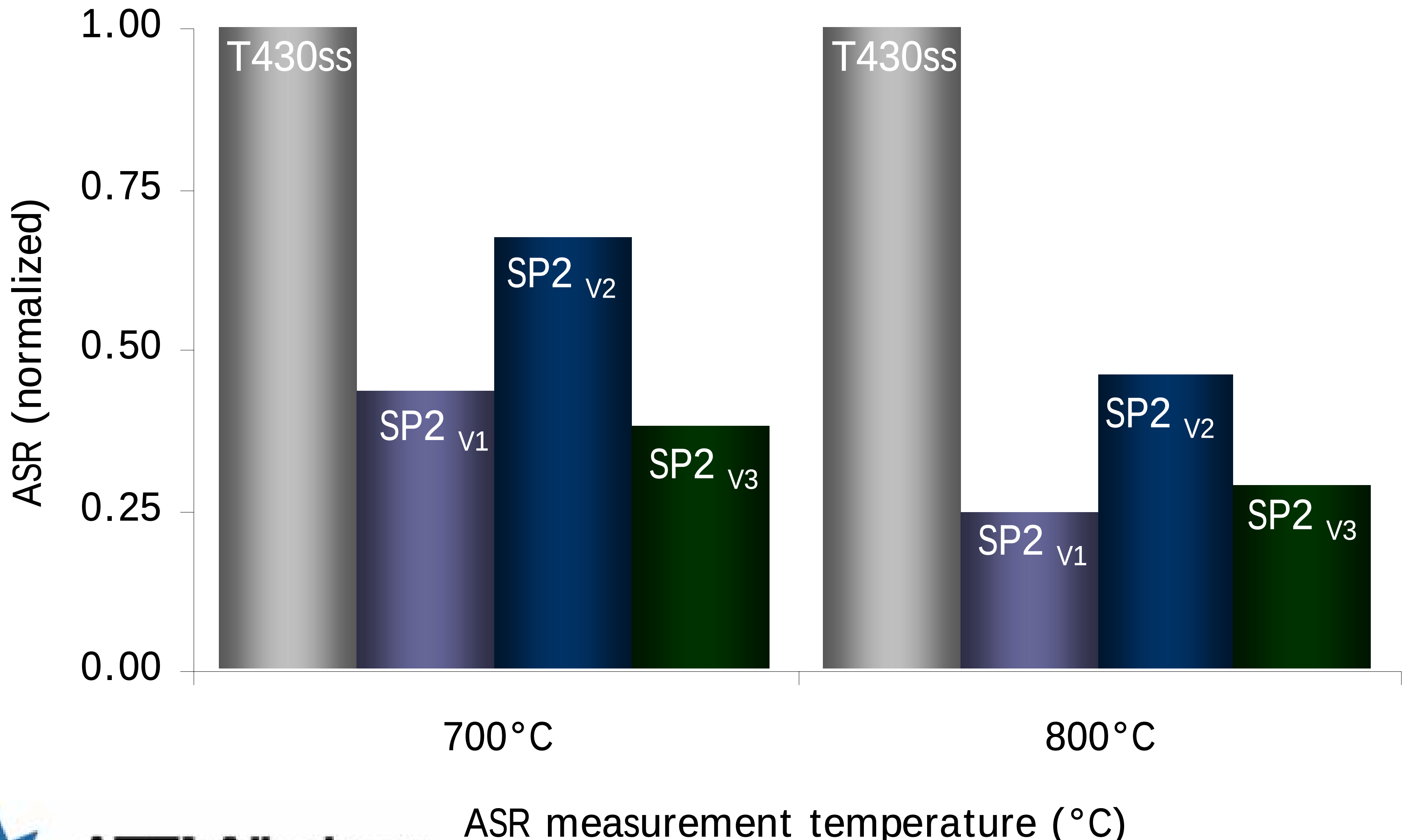
Effect of Silicon Removal



samples pre-oxidized in air for 500 hours at 800°C

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Anode-Side
Surface Modification

Multi-Layered
Metal Interconnects

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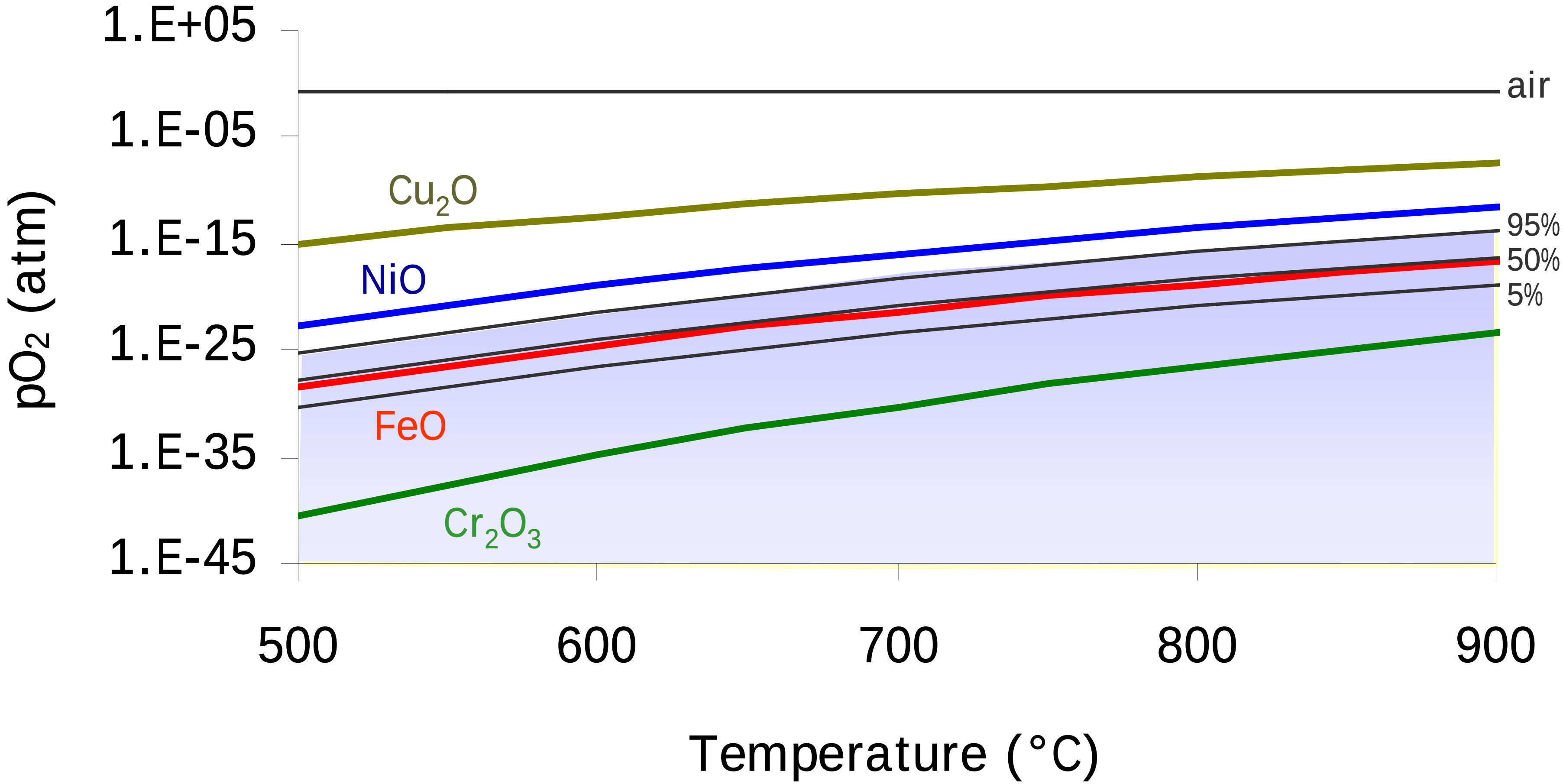
Multi-Layered Metal Interconnects

- SOFC anode gas is a low-oxygen environment
  - Reducing to Cu, Ni
  - Partially reducing to Fe
  - Oxidizing to Cr, Al, Si

Materials Selection



Multi-Layered Metal Interconnects

- SOFC anode gas is a low-oxygen environment
- Most metals/alloys are not generally suitable for monolithic interconnects
  - Excessive oxidation on the cathode side
  - Incompatible physical properties
  - Cost
- Can be used as thin layers on ferritic stainless steel substrates

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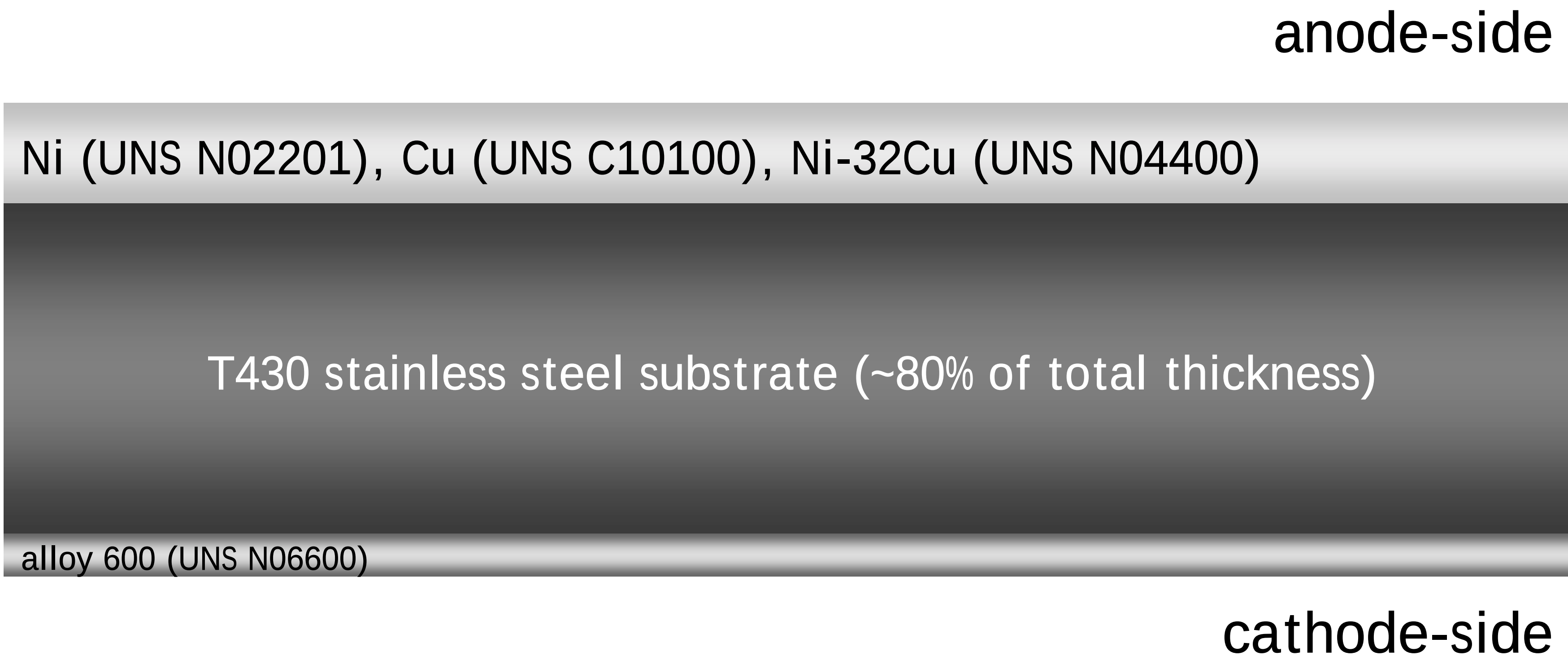
Multi-Layered Metal Interconnects



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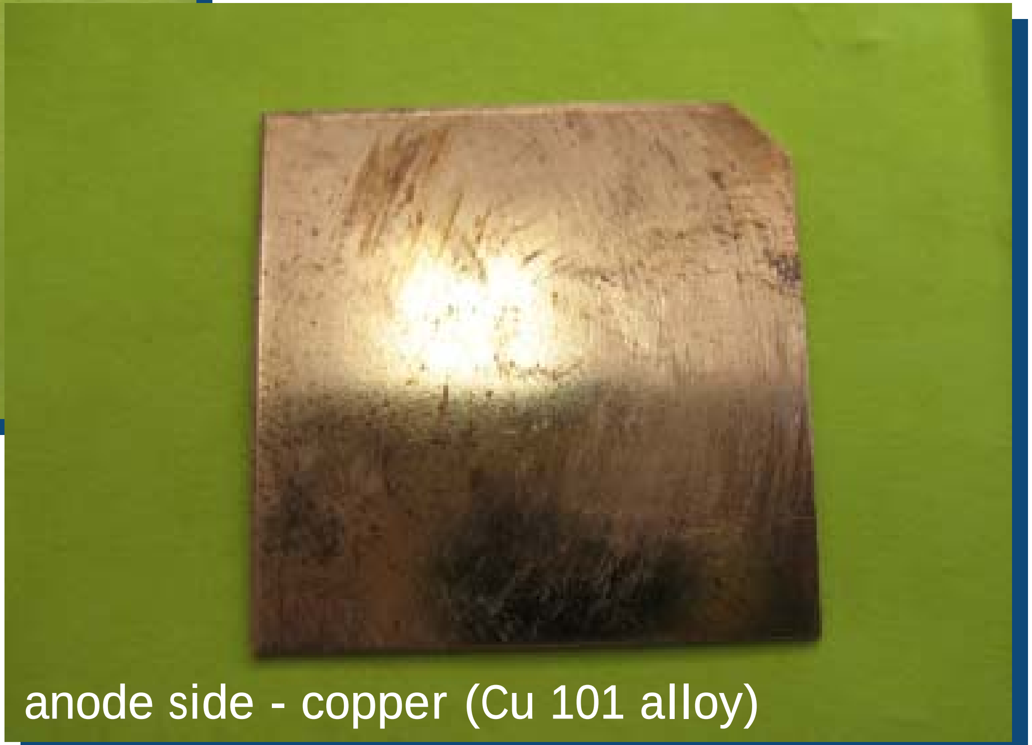
Bi-Layer Interconnect



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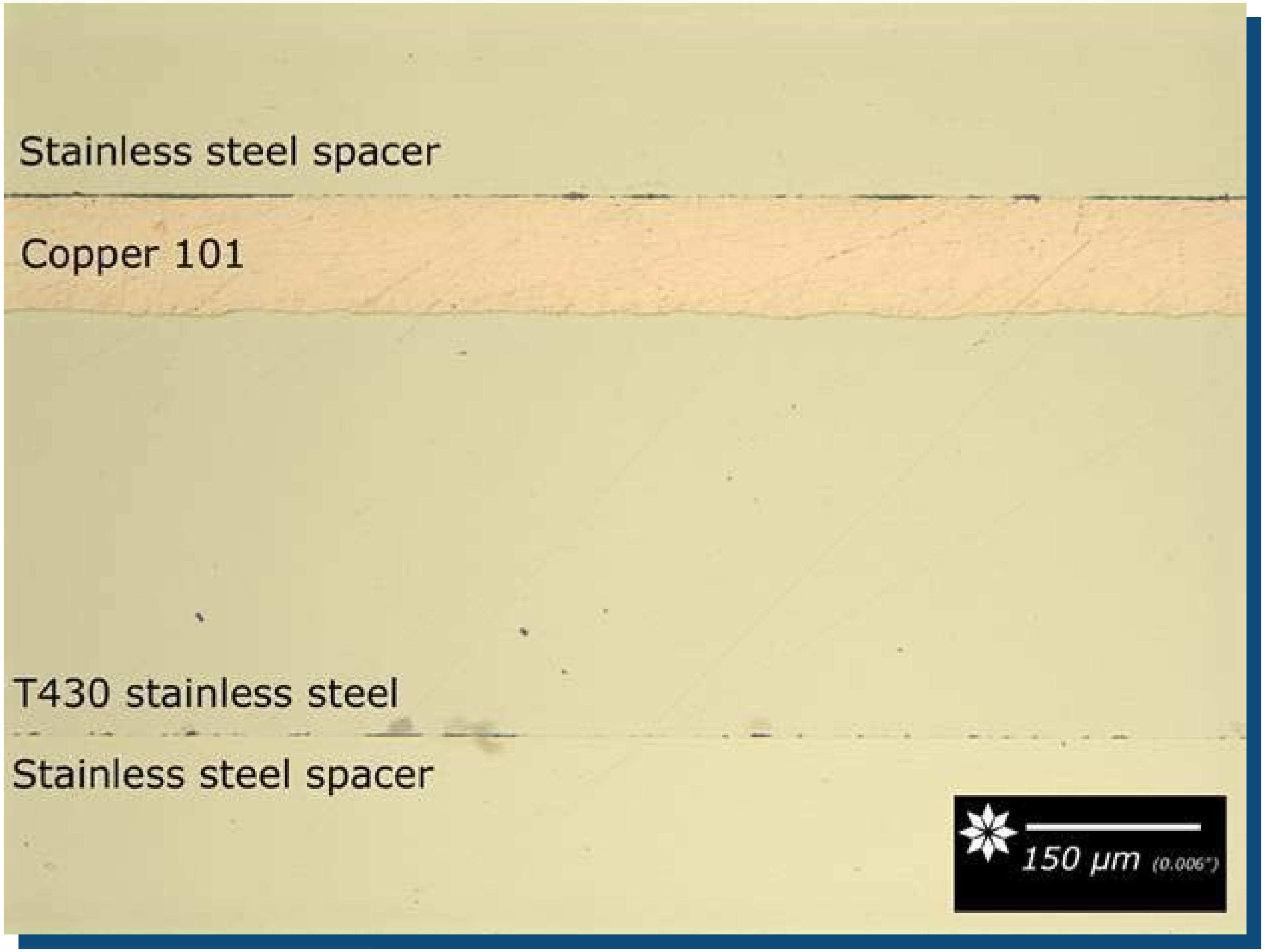
Bi-Layer Interconnect



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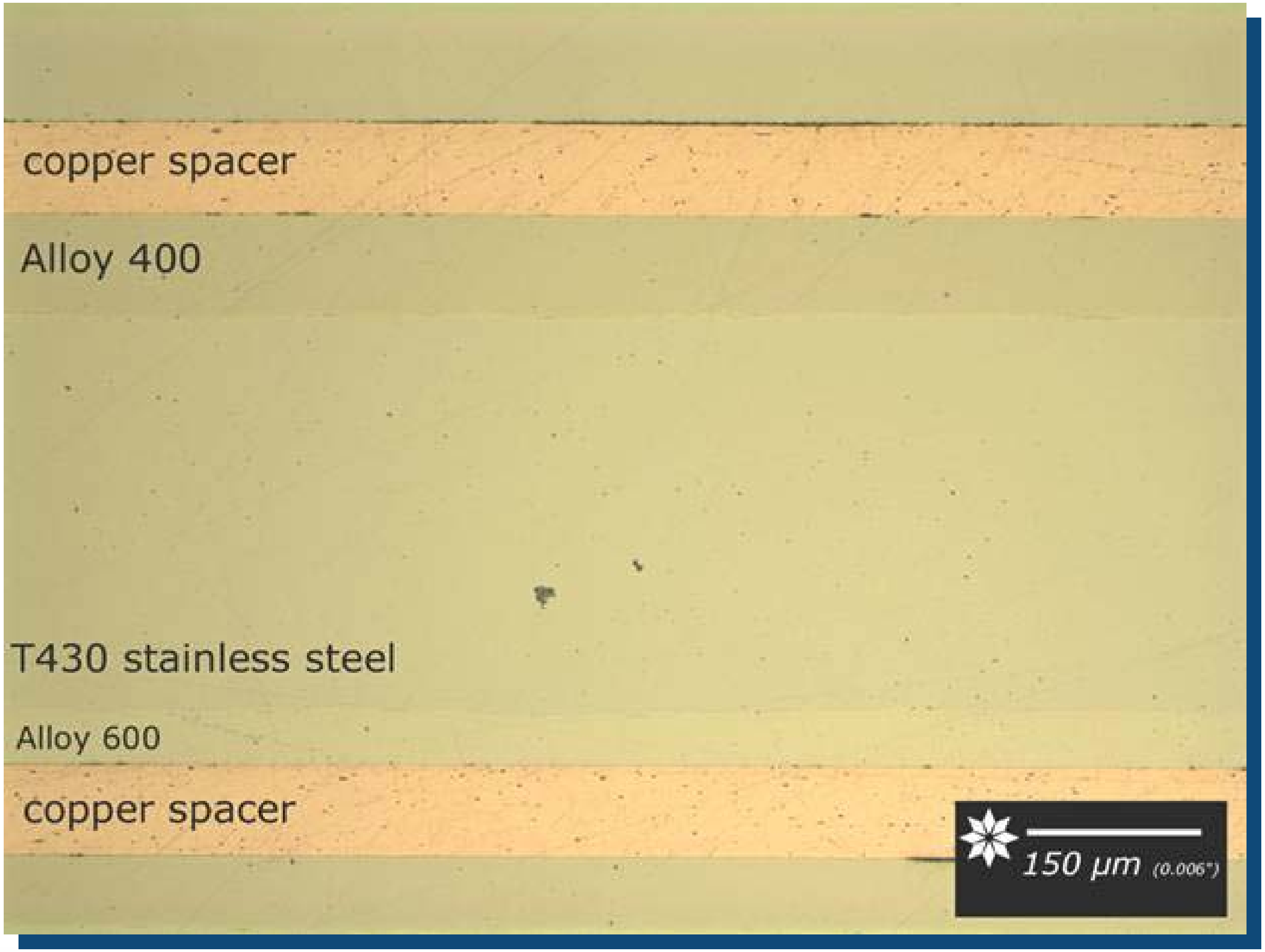
Tri-Layer Interconnect



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Evaluation of Multi-Layered Interconnect Structures

- Physical properties
- Environmental exposures
  - Simulated anode gas (SAG)
    - Ar-4H_2-3%H_2O
    - Ar-4H_2-10%H_2O
    - Ar-4%CH_4-3%H_2O
  - Dual atmosphere
    - Air (cathode side)
    - Ar-4H_2-10%H_2O (anode side)
  - Durability (ΔT)

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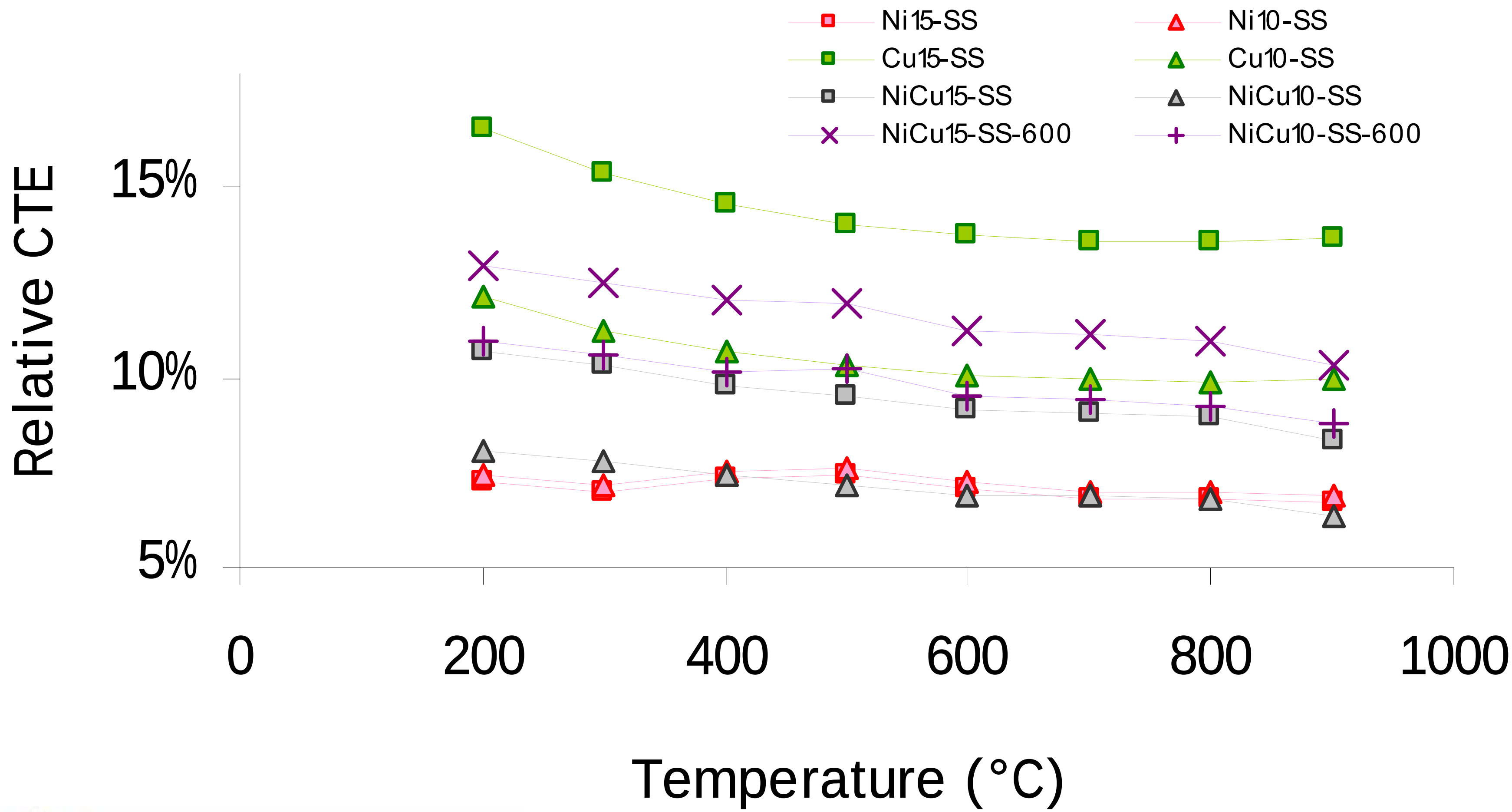
Estimated Linear CTE



expansion with respect to 25°C

CTE relative to Type 430 stainless steel

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Simulated Anode Gas Exposures

- Nickel surface remains bright and free of oxide scale
- Copper surface is mottled dark and metallic, particularly at higher p_{H_2O}
- Manganese oxide film observed to form on the Ni-32Cu alloy
  - MnO is relatively stable
  - Used a commercial alloy with a residual Mn level of approximately 0.4 wt. %

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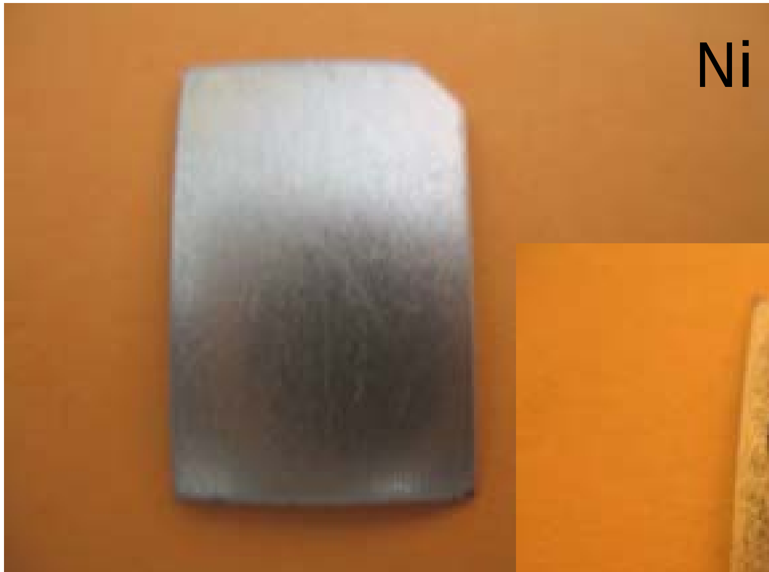
Simulated Anode Gas Exposures

1,372 hours at 800°C

Ar-4%H_2-3%H_2O



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Simulated Anode Gas Exposures

1,221 hours at 800°C

Ar-4%H_2-10%H_2O

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Dual Atmosphere Exposures

- Surface phases on the SAG side consistent with previous exposures
- Anode-side layers appear to provide some resistance to hydrogen migration
  - Fe-rich nodules form on Ni-SS specimens
  - One isolated nodule was found Cu-SS specimens
  - No nodules observed on NiCu-SS specimens

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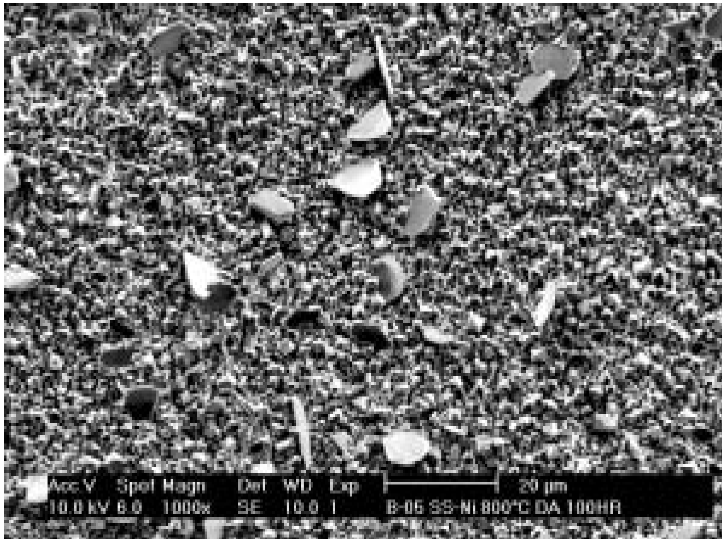
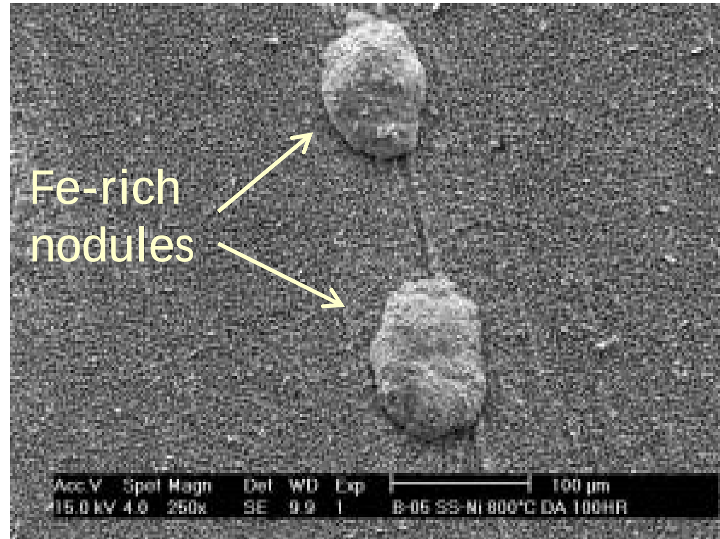
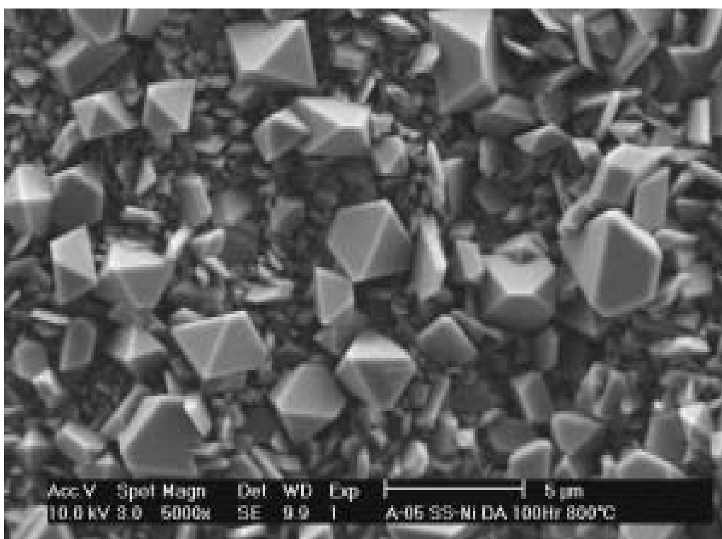
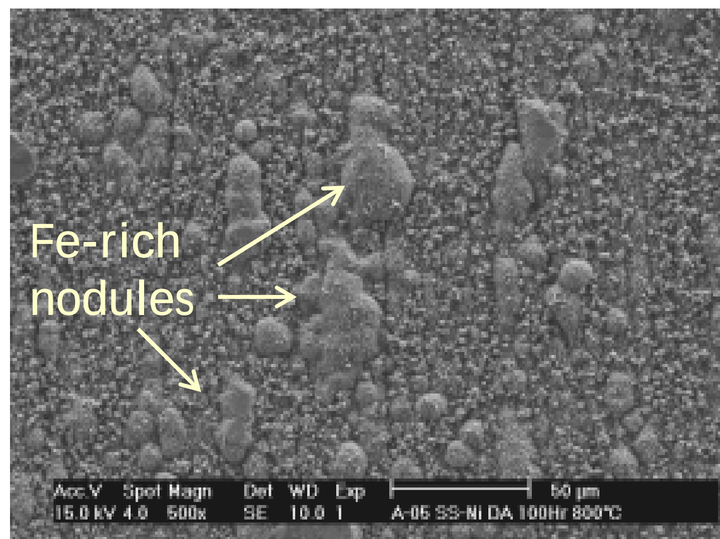
Nickel-Stainless Steel Composite



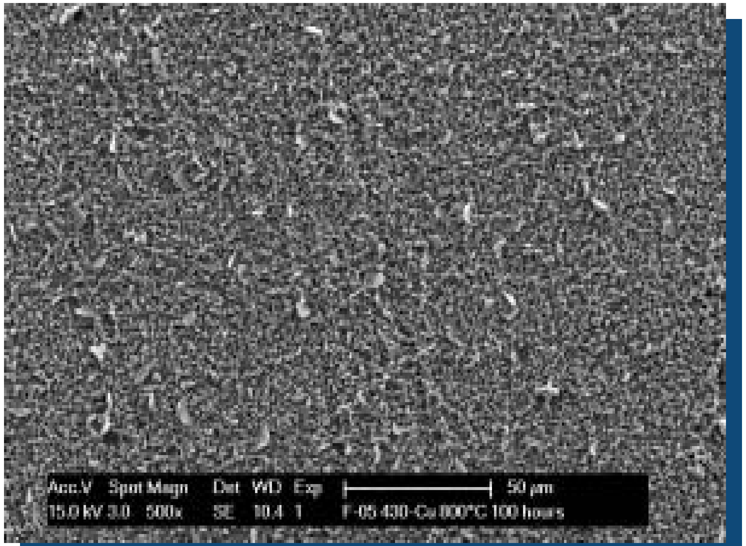


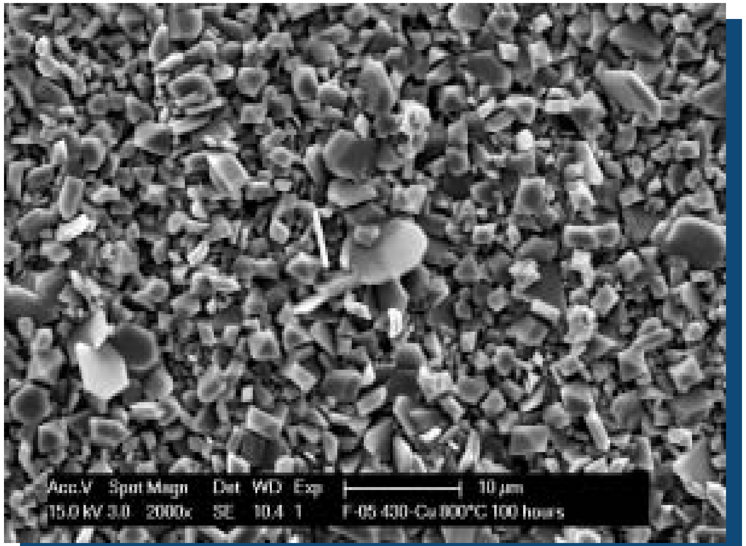


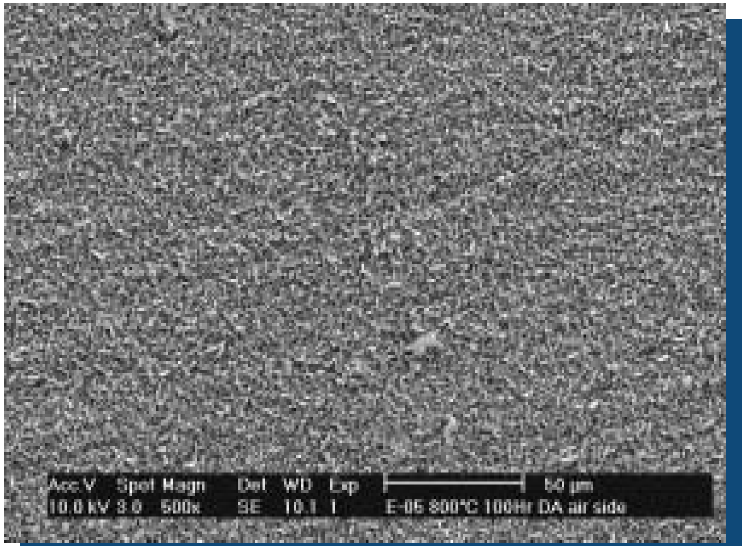


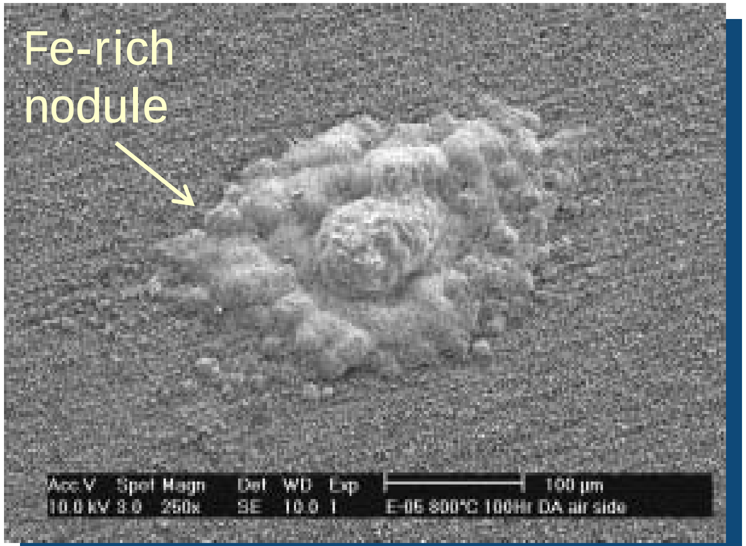
air side

Copper-Stainless Steel Composite



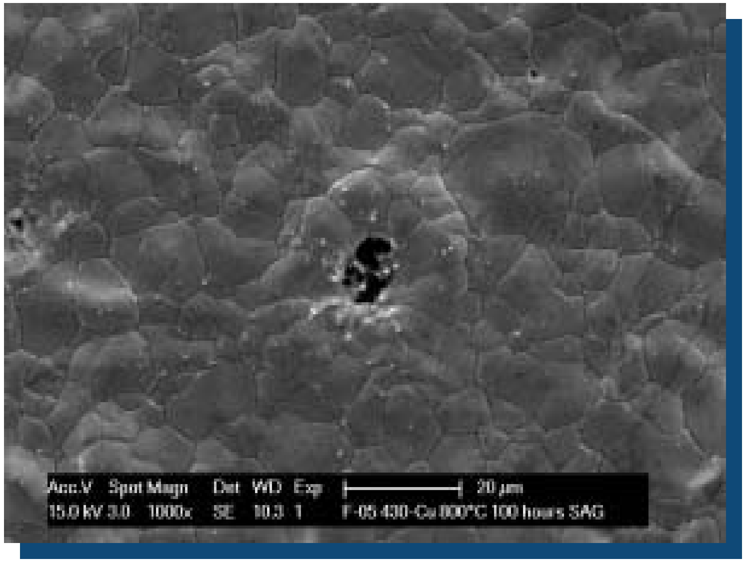




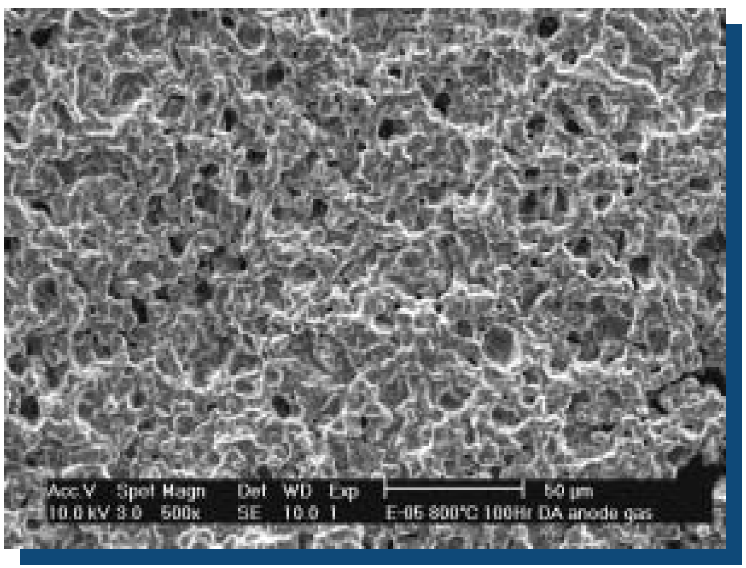


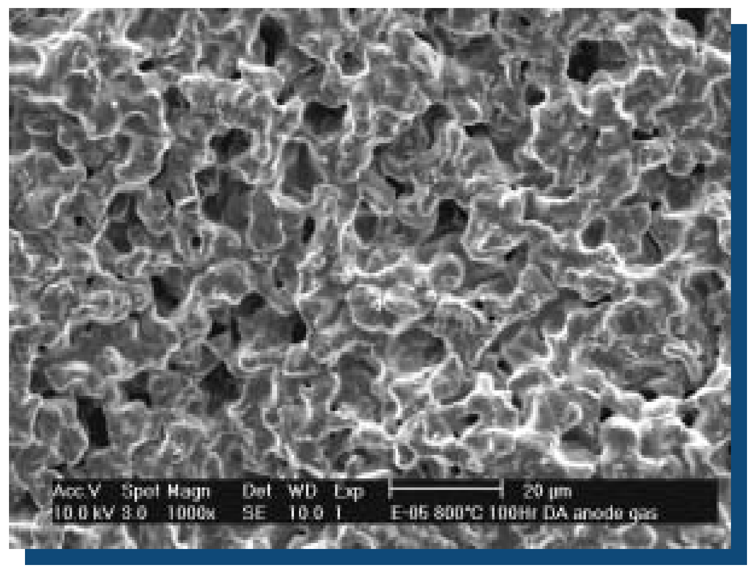
air side

Copper-Stainless Steel Composite



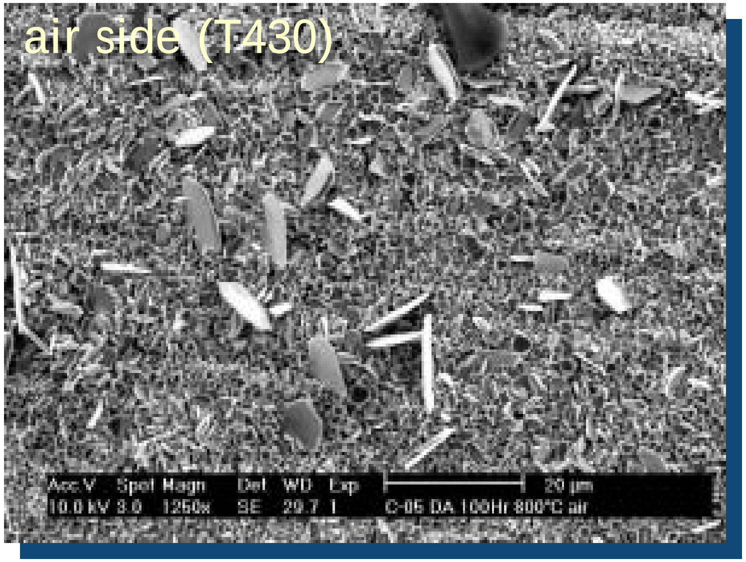
copper layers appear porous after exposure to SAG

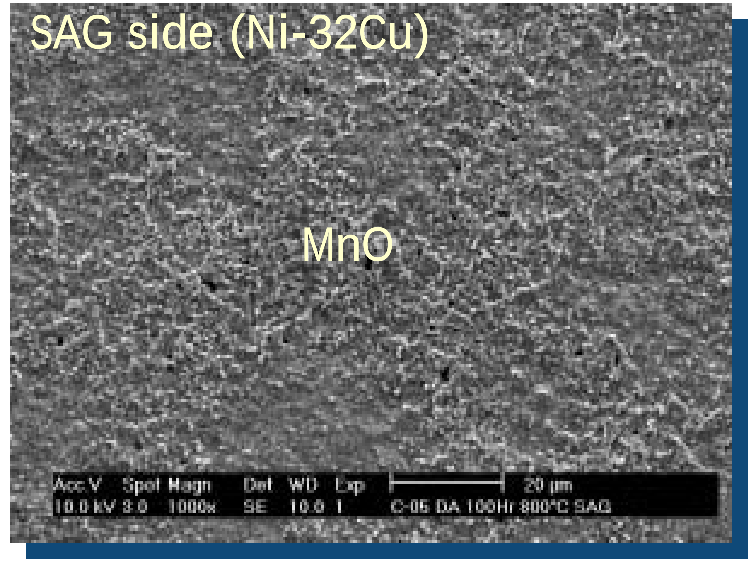




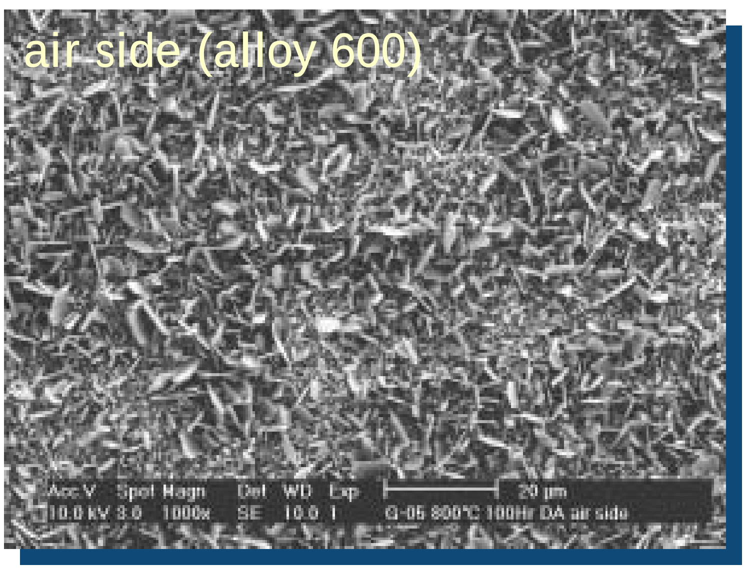
SAG side

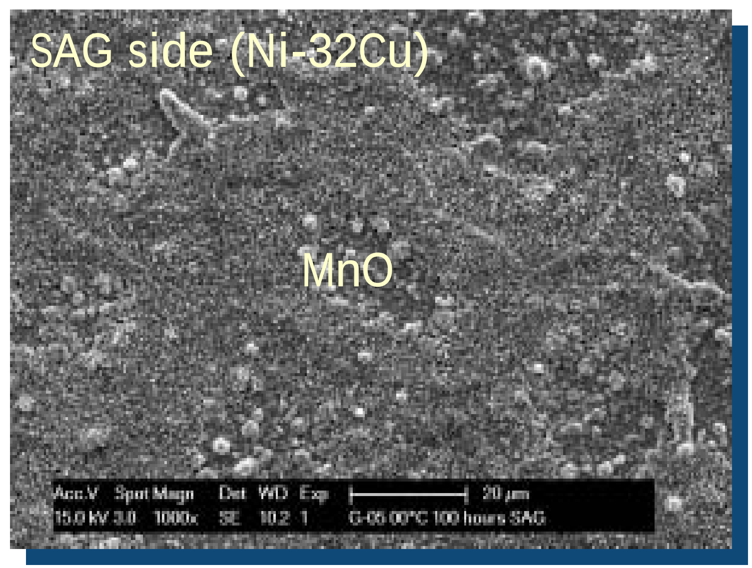
NiCu-Stainless Steel Composite





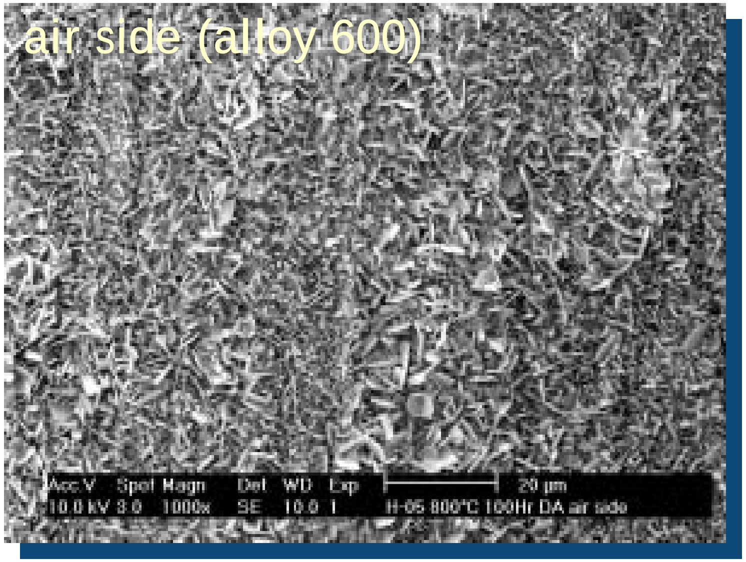
bi-layer

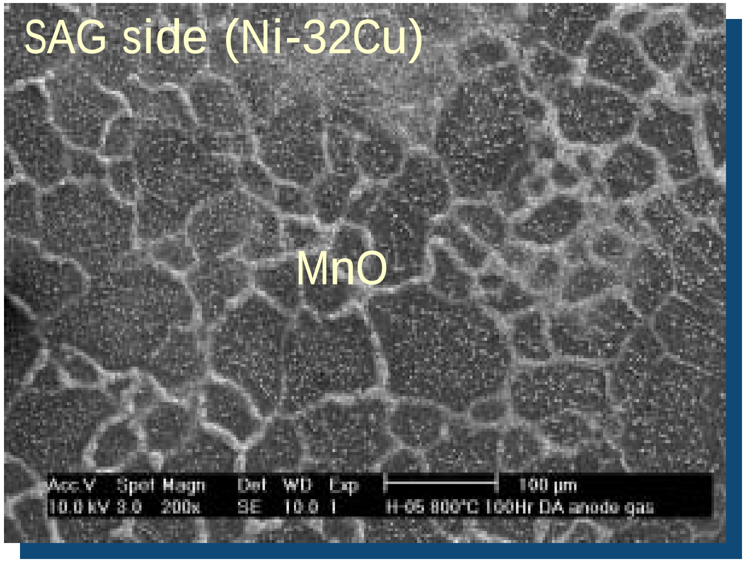




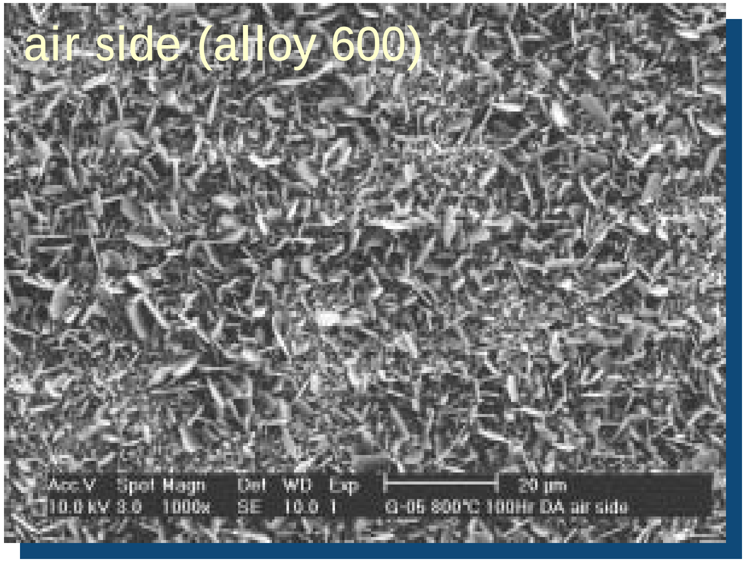
tri-layer

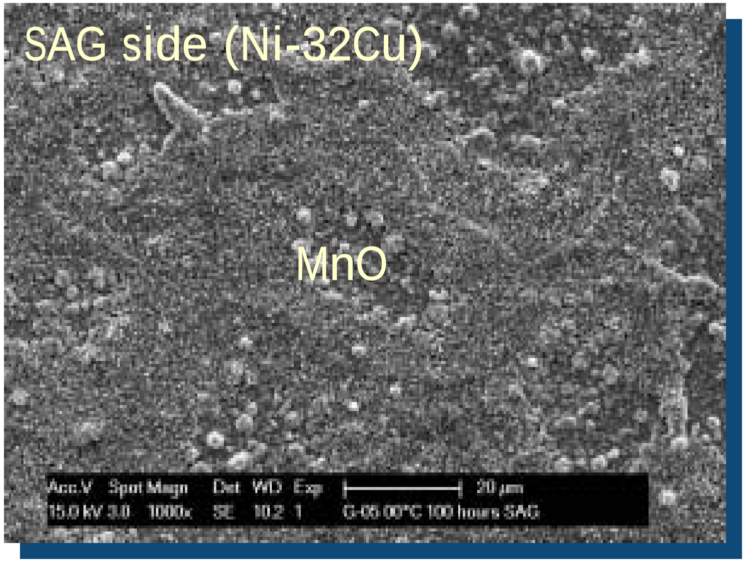
Tri-Layer Composite





NiCu10-SS-600





Summary

- Detrimental effects of aluminum and silicon can be reduced via process modifications
- Multi-layered interconnect structures have been tested and shown to be feasible
  - May reduce or eliminate oxidation on the anode side of the SOFC interconnect
  - Some of the alloys tested for anode-side layers may possibly reduce hydrogen transport (“dual atmosphere”) effects

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Work in Progress

- Optimization and long-term durability testing of post-process treatments for ferritic stainless steel interconnects
- Refinement of alloying concepts for monolithic interconnects
- Further evaluation of oxidation-resistant, electrically conductive coatings for ferritic stainless steel interconnects

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Work in Progress

- Further evaluation of interactions between the SOFC system and interconnect oxidation
- Refinement of techniques for evaluating the adhesion of oxides and coatings on SOFC interconnects (CMU)
- Further evaluation of silver-based cathode contact layers (WVU)

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Acknowledgements

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  - Prabhakar Singh
- Program Subcontractors/Contractors
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  - University of Pittsburgh – Professor Jerry Meier; W. Jackson, S. Laney
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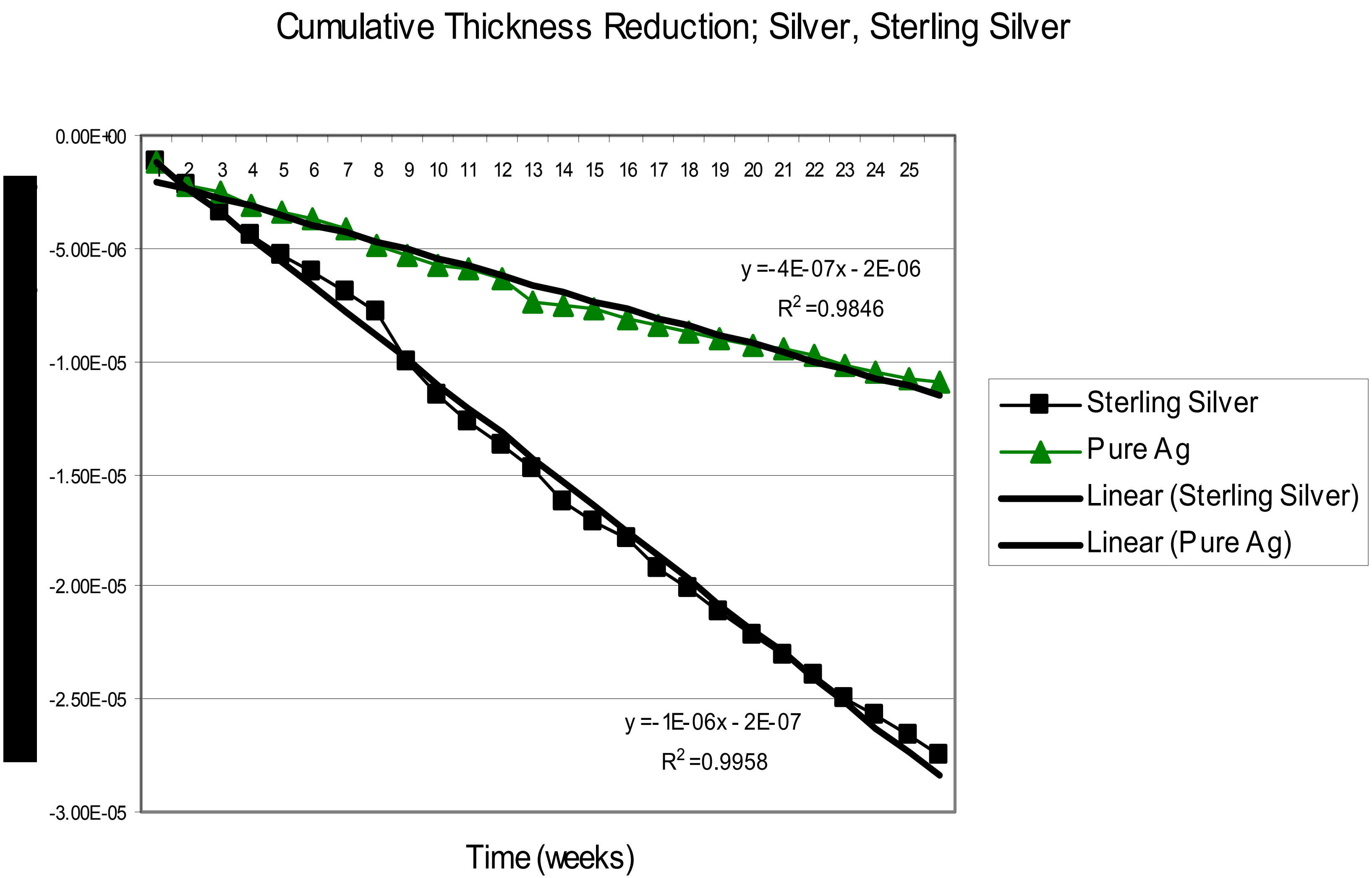
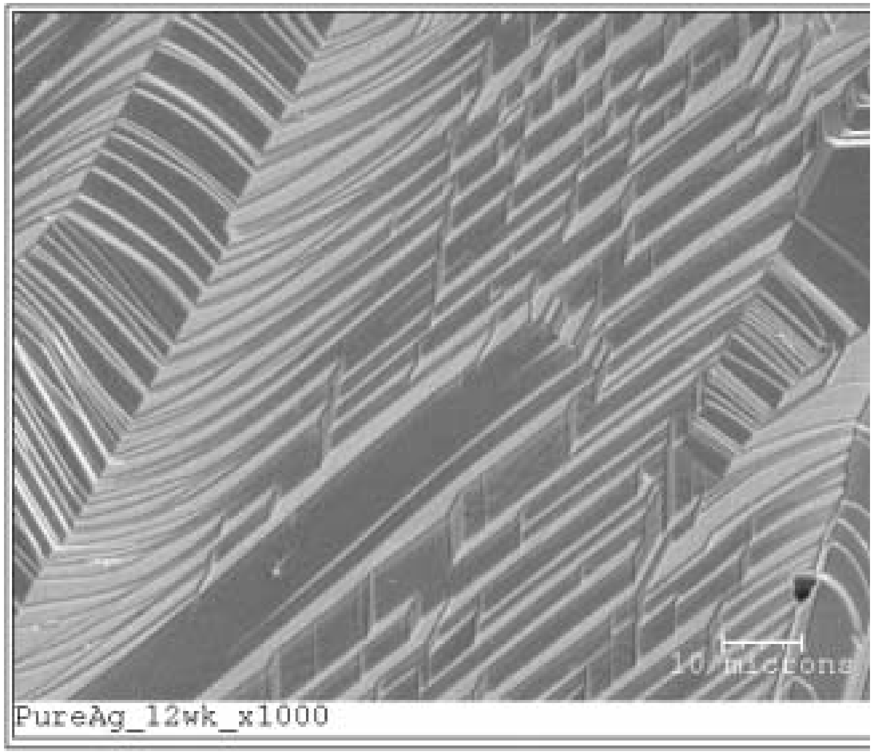
Overview

- Examination of candidate silver cermets for use as contacting material in the cathode chamber of the solid-oxide fuel cell.
- First-year research effort was on sterling silver
  - Thickness reduction data
    - Sterling silver samples vs. Pure silver samples
  - SEM analysis
    - Time series examination of changing sterling silver, pressed Ag/CuO, and pressed Ag/LSM surfaces

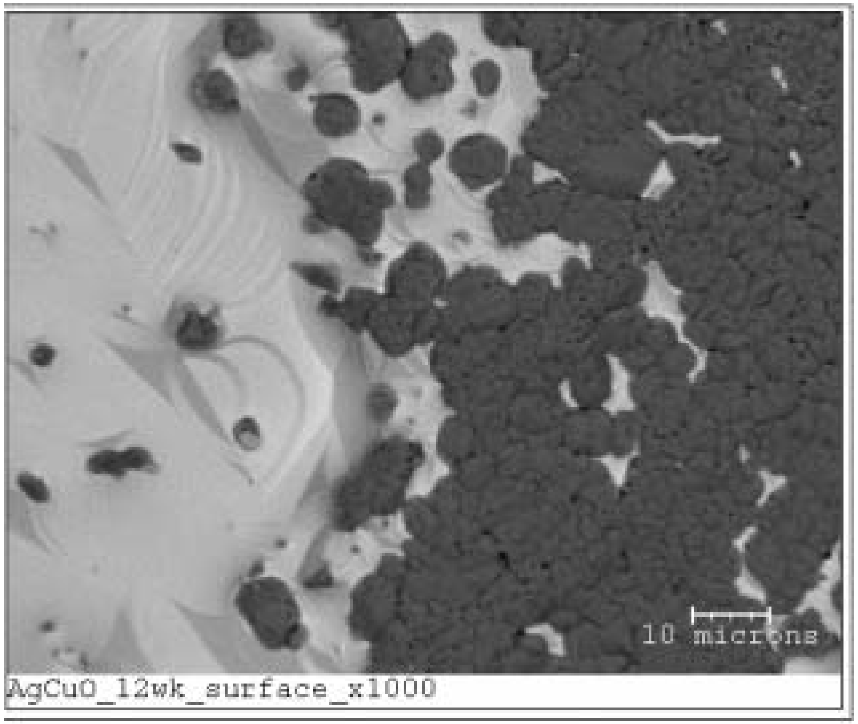

Cumulative Thickness Reduction; Silver, Sterling Silver
[redacted]
0.00E+00
-5.00E-06
-1.00E-05
-1.50E-05
-2.00E-05
-2.50E-05
-3.00E-05
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25
y =-4E-07x - 2E-06
R2 =0.9846
y =-1E-06x - 2E-07
R2 =0.9958
Time (weeks)
Sterling Silver
Pure Ag
Linear (Sterling Silver)
Linear (Pure Ag)

Pure silver exposed surface



- Sample exposed at 800C, 3 l/min air flow for 12-weeks
- Note surface step orientation
- Surface re-orientation to least favorable evaporation state
- SEM micrograph x1000

Silver/Copper-oxide exposed surface



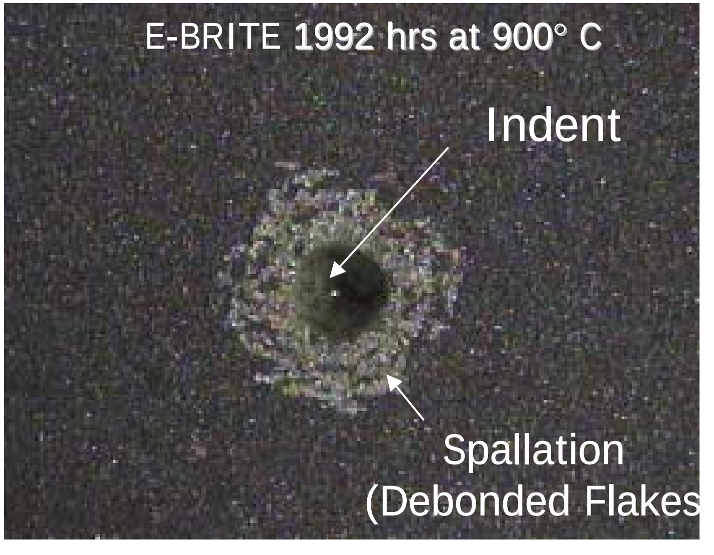
- Sample fabricated by cold-pressing CuO powder (dark areas) into pure silver
- Exposed at 800C, 3 l/min air flow, for 12-weeks
- Silver surface orientation much less pronounced than with pure silver likely not resulting in least favorable evaporation state
- Appears evaporation more pronounced near CuO particles
- Backscatter image x1000

Silver/LSM exposed surface

- Sample fabricated by cold-pressing LSM powder (circled in red) into pure silver
- Exposed at 800C, 3 l/min air flow, for 12-weeks
- Surface orientation similar to that of pure silver

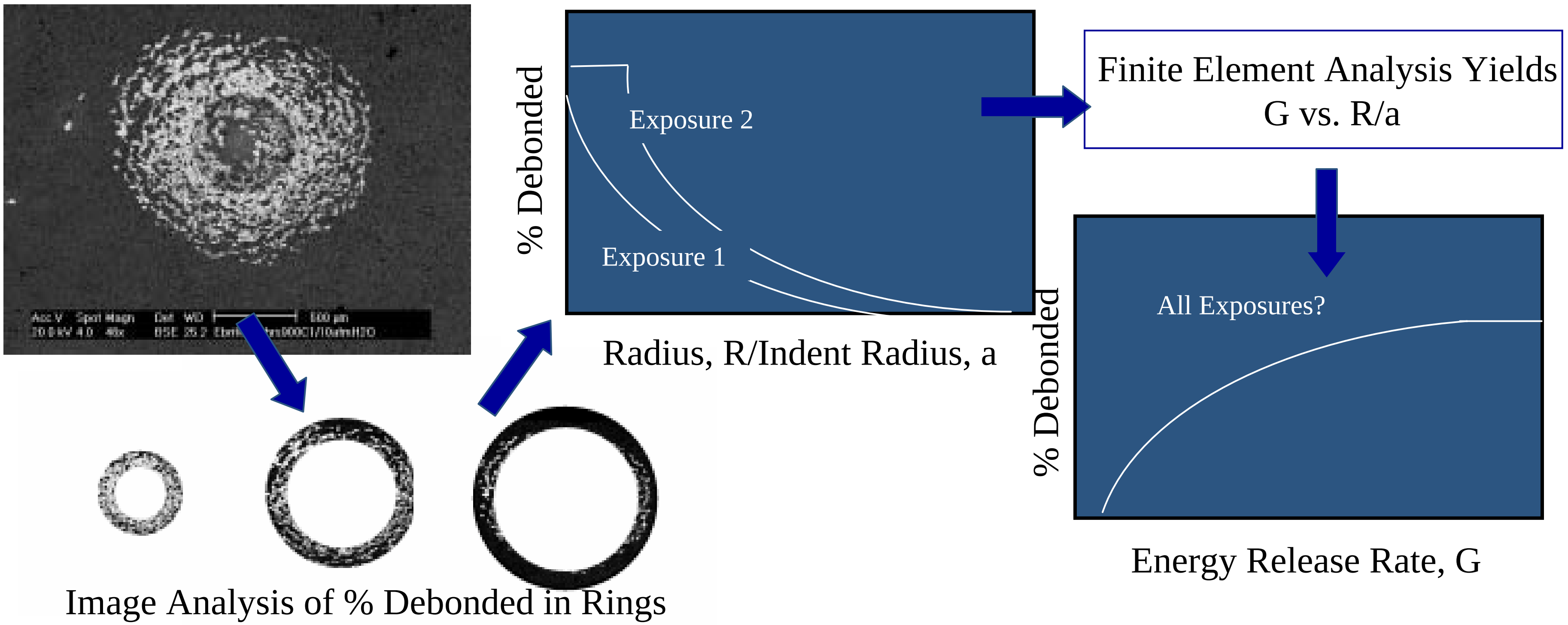
Macro-Scale Indent Tests for Spallation Resistance
J. Beuth, Carnegie Mellon

- *Idea:* Use Indentation to Induce Spalls after Short Exposure Times.
- Use to Rapidly Evaluate Alloy Systems (From ATI) and Coated Alloy Systems (from Arcomac and PNNL)
- Rockwell Hardness Test Performed on Exposed Alloy/Scale Systems or Coated Alloy Systems. *Indent Diameter is just less than 1mm*
- Indented Specimens Show Small Spalls; Density of Spalls Decreases with Radius
- Easy Test to Perform/Easy for SECA Partners to Work into Their Test Programs
- For Alloy Systems: Spallation Changes with Exposure Related to *Scale Thickness*, *Scale Stress* and *Interface Toughness* Changes

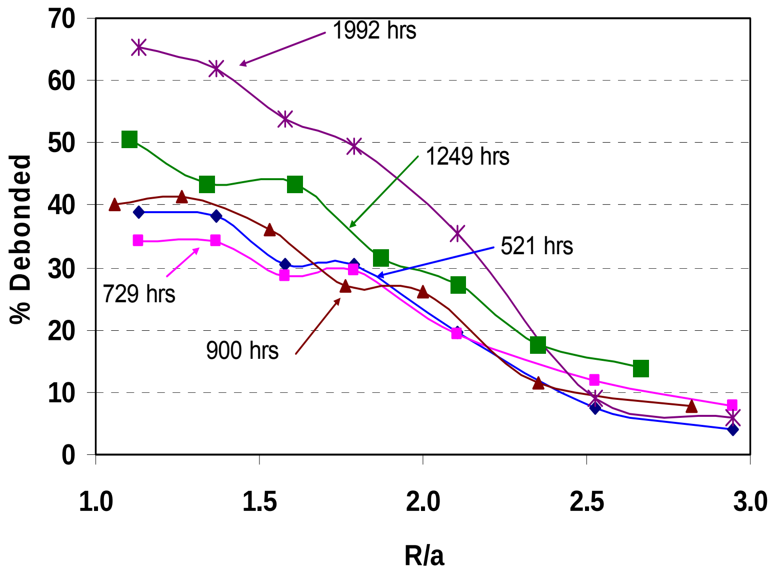


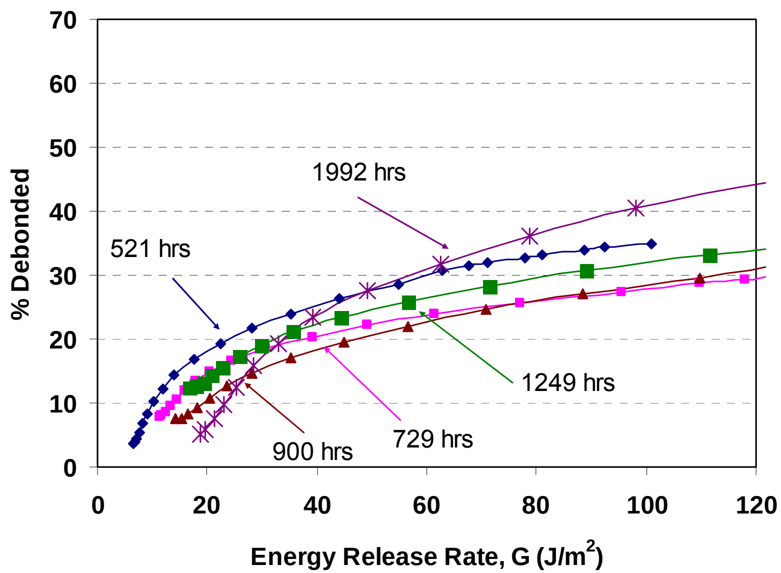
Macro Indent Test Procedures

- *First Plot:* Use Image Analysis to Quantify % of Debonded Scale vs. Radius
- *Second Plot:* Use Energy Release Rate (G) vs. Radius from Fracture Models to Plot % of Debonded Scale vs. G: *G Calculation Includes Measured Oxide Thickness Changes*
- *If a Single Curve Results for all Exposures, then Scale Stress and Interfacial Toughness are not Changing and Scale Thickness Controls Spallation*
- Use this Plot to Predict the % Debonding with Exposure



Macro-Scale Indent Results

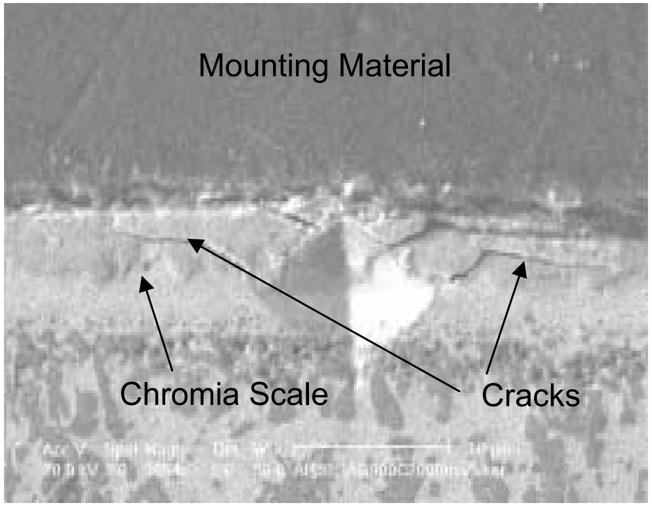




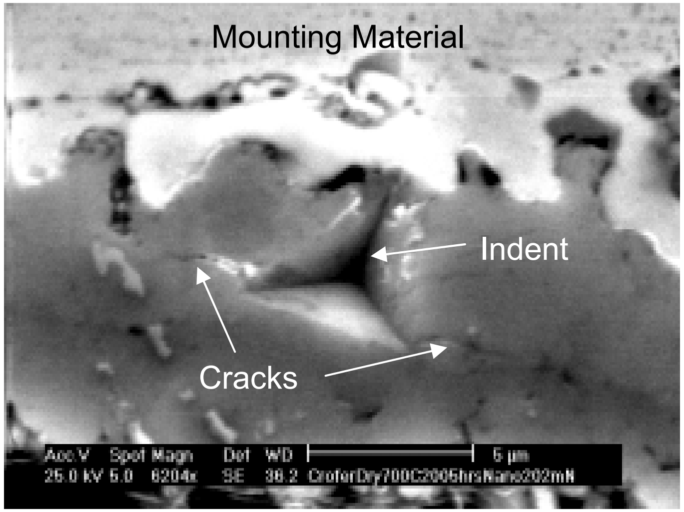
- E-BRITE Exposed at 900° C for up to 1992 hours
- Simulates 800° C Exposures to 25,000 hrs
- *First Plot:* A Fairly Steady Increase in Debonding is seen with Exposure
- *Second Plot:* Fracture Mechanics Analysis of Data Yields a Plot of % Debonding vs. Energy Release Rate
- Second Plot Indicates Stress and Toughness are Not Changing and Scale Thickness is Critical
- Can Relate a % Debonding Limit (an Interconnect Design Criterion on the Y Axis) to a Critical G (on the X Axis)
- Critical G can be Tied to a Critical Scale Thickness and Critical Exposure Time

Micro/Nano-Scale Indent Tests
(Being Developed at Carnegie Mellon)

- An Independent, Direct Means of Determining Whether Scale or Interface Toughness are Changing with Exposure
- Procedure: Micro- or Nano-Indent Mounted Specimens from the Side, Induce Cracking in the Chromia Scale or at the Interface
- Extent of Cracking Tied to Toughness of the Chromia or Interface
- Micro Hardness Test Methods are More Easily Transferred to SECA Partners
- Also a Good Test for Probing Toughnesses of Brittle Layers and Interfaces in Complicated Subcell Structures



Micro (Vickers) Indent



Nano (Berkovich) Indent