Sealing/Joining Technology for Gas Separation Membranes and SOFCs

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Materials Joining: An Enabling Technology

- **Project Objectives: To develop joining/sealing technology that enables gas separation processes and high-temperature power generation**
- **Project Accomplishments:**
  - New low-cost process for ceramic joining: air brazing
  - Several new families of air braze filler metals
  - Patent issuing on joining Al_2O_3 using Al-based conversion technique
  - Successful joining of porous H_2 separation support tubes
  - Demonstration of the viability of ceramic membrane joining for SOFCs and H_2 and O_2 separation membranes
- **Present Focus:**
  - Develop joining materials/practices that meet current DOE-FE needs on electrochemical devices
    - Process optimization
    - Performance feedback from prototypic devices/equipment fabrication and operation
  - Understand structure-bonding/property relationships in joining systems under development
    - Alloying effects
    - Environmental exposure testing

Develop coal as a potential source of clean hydrogen fuel for use in fuel cells, turbines and various process applications

- **Hydrogen separation membranes – to remove H_2 from the coal gas stream and enable higher product yield due via the water-gas-shift reaction**
- **Oxygen separation membranes – to enhance H_2 production and coal gasification/combustion efficiencies by eliminating dilution effects of N_2 in air and simultaneously mitigate NO_x formation**
- **Solid oxide fuel cells – to augment power generation efficiency via electrochemical conversion**

Application Projects

Knowledge Transfer

- Fabrication of an Oxygen Concentrator
- Hermetic Joining of Electrochemical Sensors
- Joining of Microchannel Recuperators for CHP
- pSOFC Sealing

FE-ARM Project

- Materials Joining

Leveraged Collaborations

- Washington State University, Argonne National Laboratory, and Marshall Space Flight Center: structural and property analysis of molten Ag-CuO
- Alfred University and Aachen University: employing the new brazing technique in joining large tubular oxygen separation membranes to metallic gas manifolds
- Delphi Corporation: demonstrating the use of a new binary braze filler metal in joining solid oxide fuel cell components
- Battelle Memorial Institute: demonstrating the use of air brazing metal in fabricating high-temperature microchannel devices
- Bechtel Bettis Inc.: developing a new braze filler metal alloy for use in YSZ electrochemical probes to be employed in pressurized water reactor applications
- Aegis, Inc. and Williams Advanced Materials: demonstrating methods of manufacturing air braze filler metals for various energy applications
- Corning Inc.: demonstrating the use of a new ternary braze filler metal in joining solid oxide fuel cell components
- Ceramic Tubular Products: developing ceramic joining approaches for nuclear energy applications

Fundamental Studies

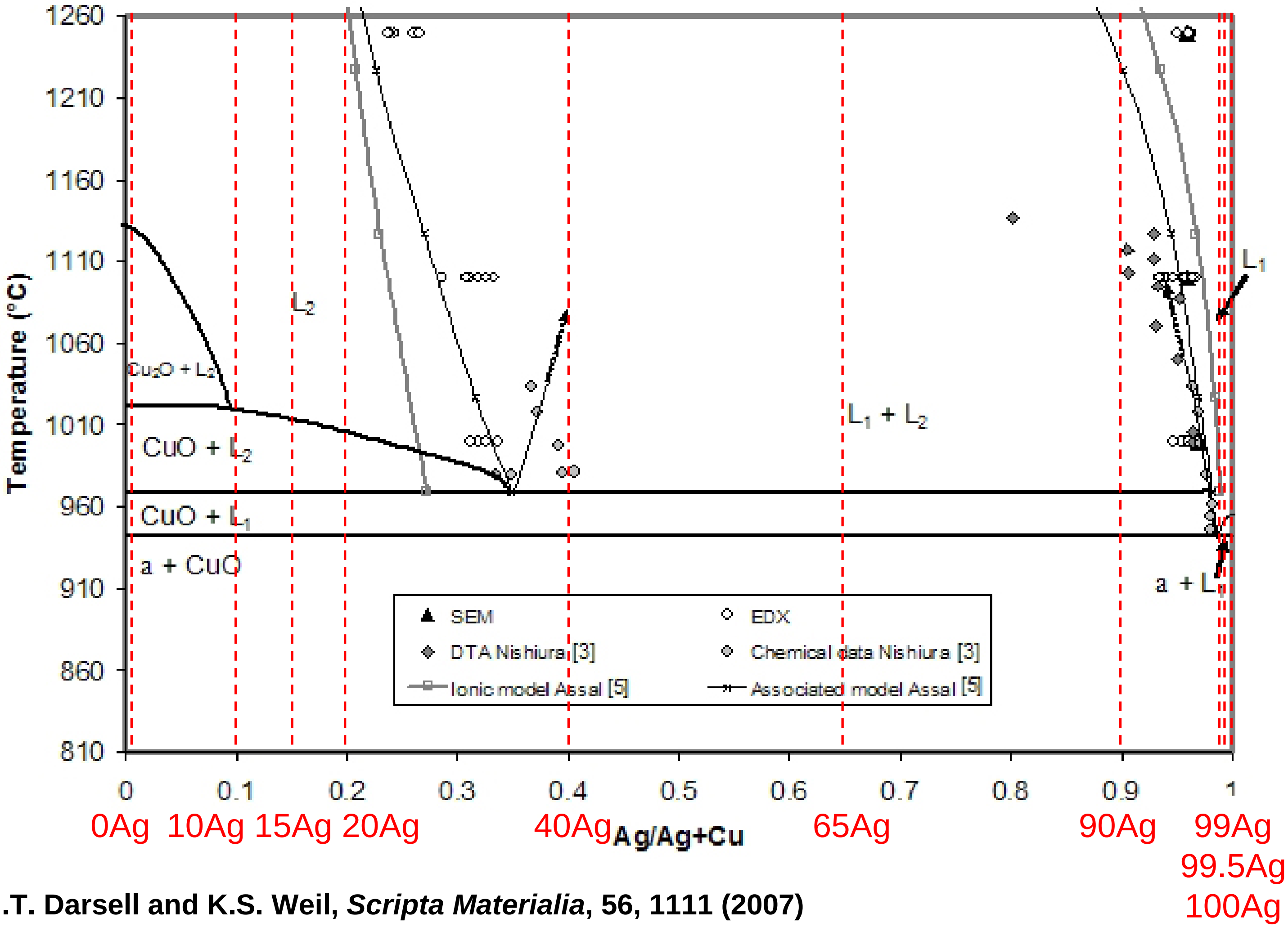
- Structure-bonding/property relationships
- Alloying effects: Pd, Al, TiO_2
- Two-phase wetting phenomena
- Effect of particle additions

Applied Studies

- Braze process optimization
- Demonstration in prototypic devices/equipment
- Low-cost fabrication techniques
- Environmental exposure testing

Fundamental Studies

Understanding Mutual Solubility in Ag-CuO

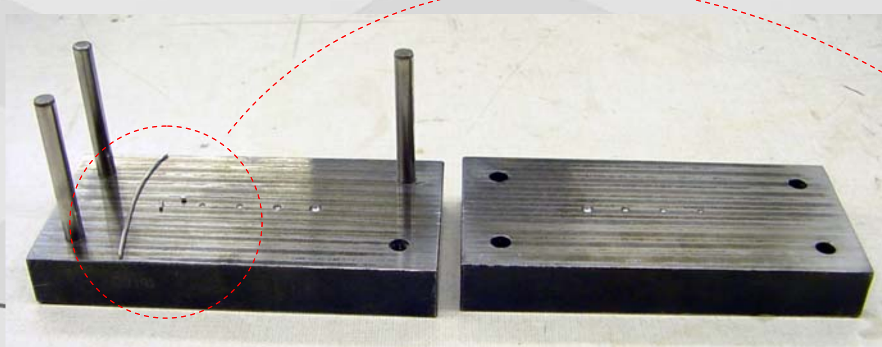


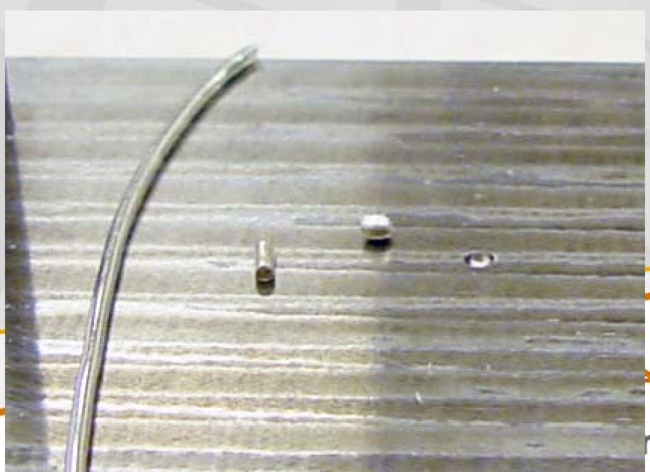
J.T. Darsell and K.S. Weil, *Scripta Materialia*, 56, 1111 (2007)

Study Objectives and Approach

- **Objective: to gain an understanding of the physicochemical properties of metal-metal oxide solutions via the characterization of molten Ag-CuO alloys as a function of composition and temperature**
- **Approach:**
  - **Atomistic structure:**
    - **Aerodynamic levitation – containerless study avoids contamination due to dissolution of substrate material into the high temperature melt**
    - **Laser heating**
    - **High energy x-ray scattering – the Advanced Photon Source (APS) synchrotron at ANL provides x-rays with sufficient energy for full penetration of levitated samples**
  - **Density, surface tension, and viscosity:**
    - **Electrostatic levitation at Marshall Space Flight Center (MSFC) – containerless, to avoid contamination**
    - **Laser heating**
    - **Digital processing of images from a high-speed video**
    - **Induced surface oscillations – natural frequency (surface tension) and rate of decay (viscosity)**
  - **Correlation of structure and properties**

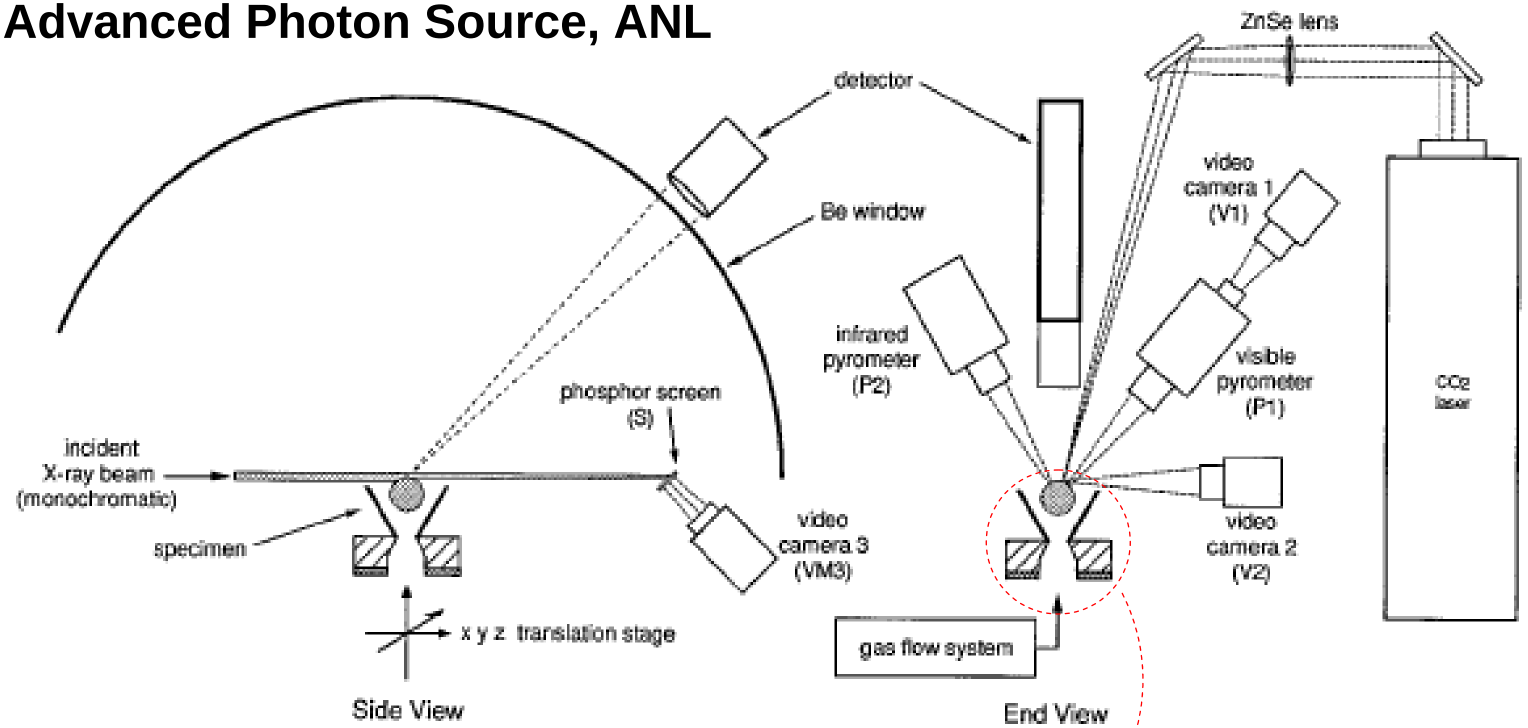
- High (99.999%) purity Ag-Cu alloy wires were fabricated at Williams Advanced Materials:
  - 99.999mol% Ag (100Ag); 99.46mol% Ag (99.5Ag); 98.87mol% Ag (99Ag)
  - 90.43mol% Ag (90Ag); 65.38mol% Ag (65Ag); 40.39mol% Ag (40Ag)
  - 19.99mol% Ag (20Ag); 15.08mol% Ag (15Ag); 10.08mol% Ag (10Ag)
  - 99.999 mol% Cu (0Ag)
- Segments of wire were pressed in a pair of hemispherical dies to form 2 - 3 mm spheres
- 65Ag – 99.5Ag: pre-oxidized at 600 - 650ºC for 1 – 2.5 hours to darken the surface for better absorption of laser energy
- Other compositions: oxidized in-situ during heating and melting





Experimental Apparatus: Aerodynamic Levitation

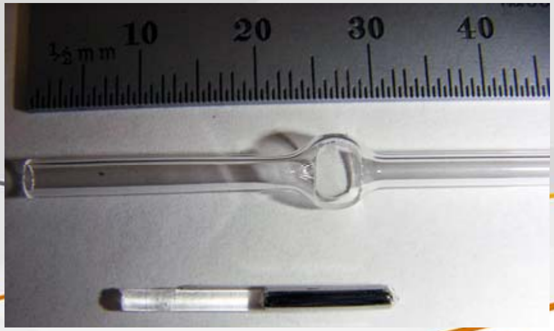
Advanced Photon Source, ANL

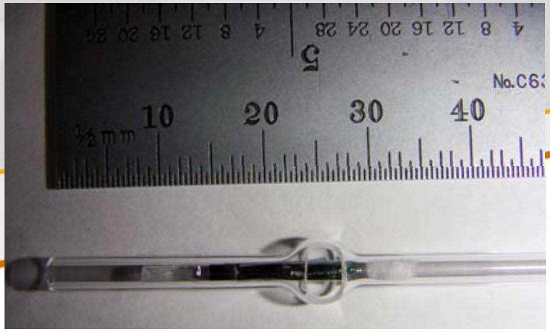


S. Krishnan, et al., *Rev. Sci. Instrum.*, **68**[9] 3513-8 (1997)

Status: Aerodynamic Levitation

- **0Ag – 65Ag**
  - Obtained X-ray scattering patterns of the liquid alloys at various temperatures
  - Data reduction is currently in progress
- **90Ag – 100Ag**
  - Too reflective to couple with the laser well enough to melt
- **The high purity wires of 90Ag – 100Ag alloys were cut into 1 – 2 cm long segments**
- **The wire segments were placed in a 1.5 mm dia thin-walled carbon-coated fused quartz capillary tube**
  - These measurements were not containerless, therefore:
    - X-ray scattering measurements were performed on the empty capillary tube
    - The signal from the empty capillary tube will be subtracted from the measurement run when it contained a sample





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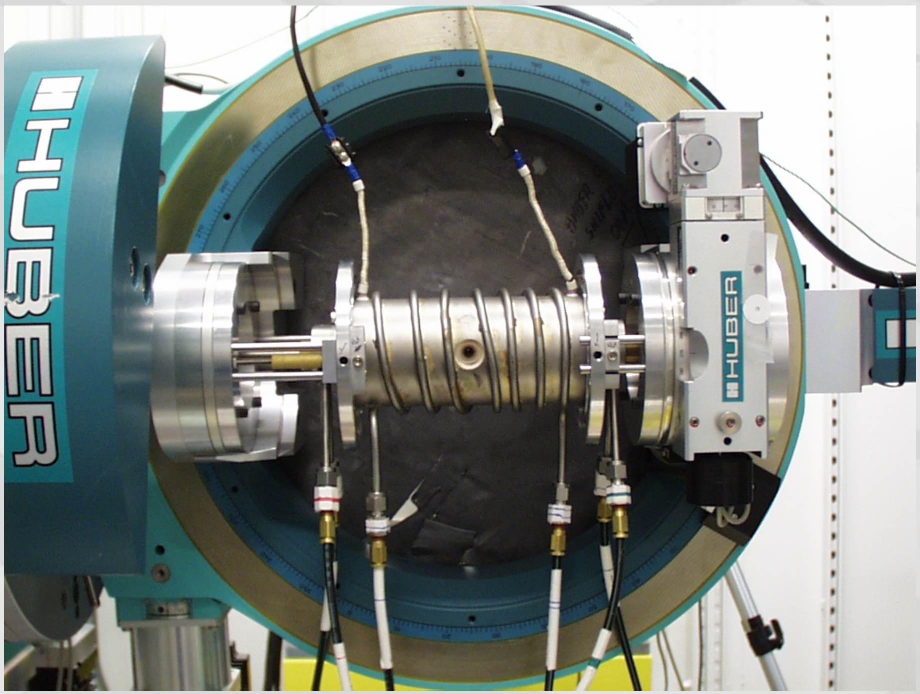
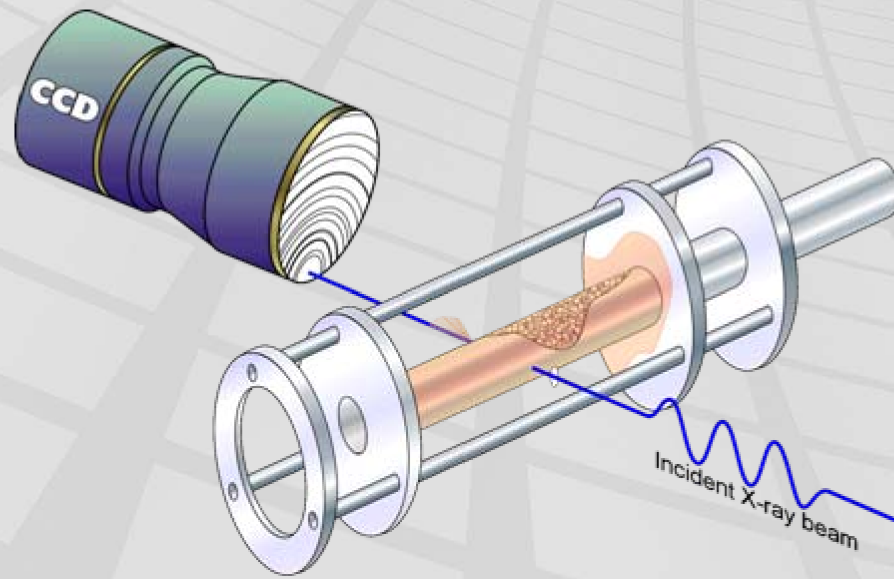
Capillary Tube X-ray Scattering Measurements

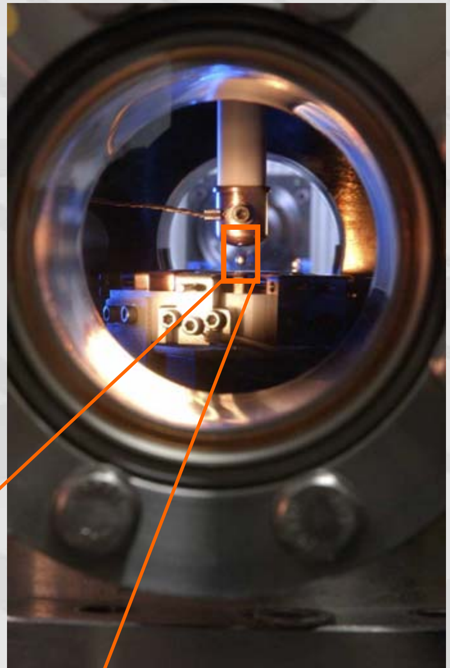
- **X-ray scattering patterns have been obtained for the liquid 65Ag – 100Ag alloys at various temperatures**
- **Data reduction is currently in progress**



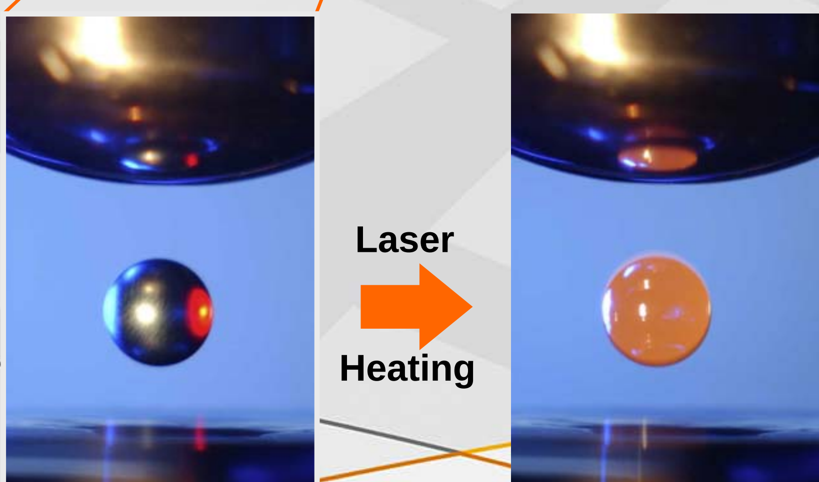


Status: Electrostatic Levitation

Electrostatic Levitator at Marshall Space Flight Center



- Preliminary work at MSFC to determine levitation and heating parameters for Ag-CuO alloys has shown that it is difficult to maintain levitation during heating
- Method works with end-point compositions, but not with the alloys thus far
- Currently attempting electrostatic levitation of samples that were previously melted on the aerodynamic levitator at ANL



Surface tension: Rayleigh's formula

$$f_l = \sqrt{\frac{l\,(l-1)\,(l+2)\,\gamma}{3\pi m}}$$

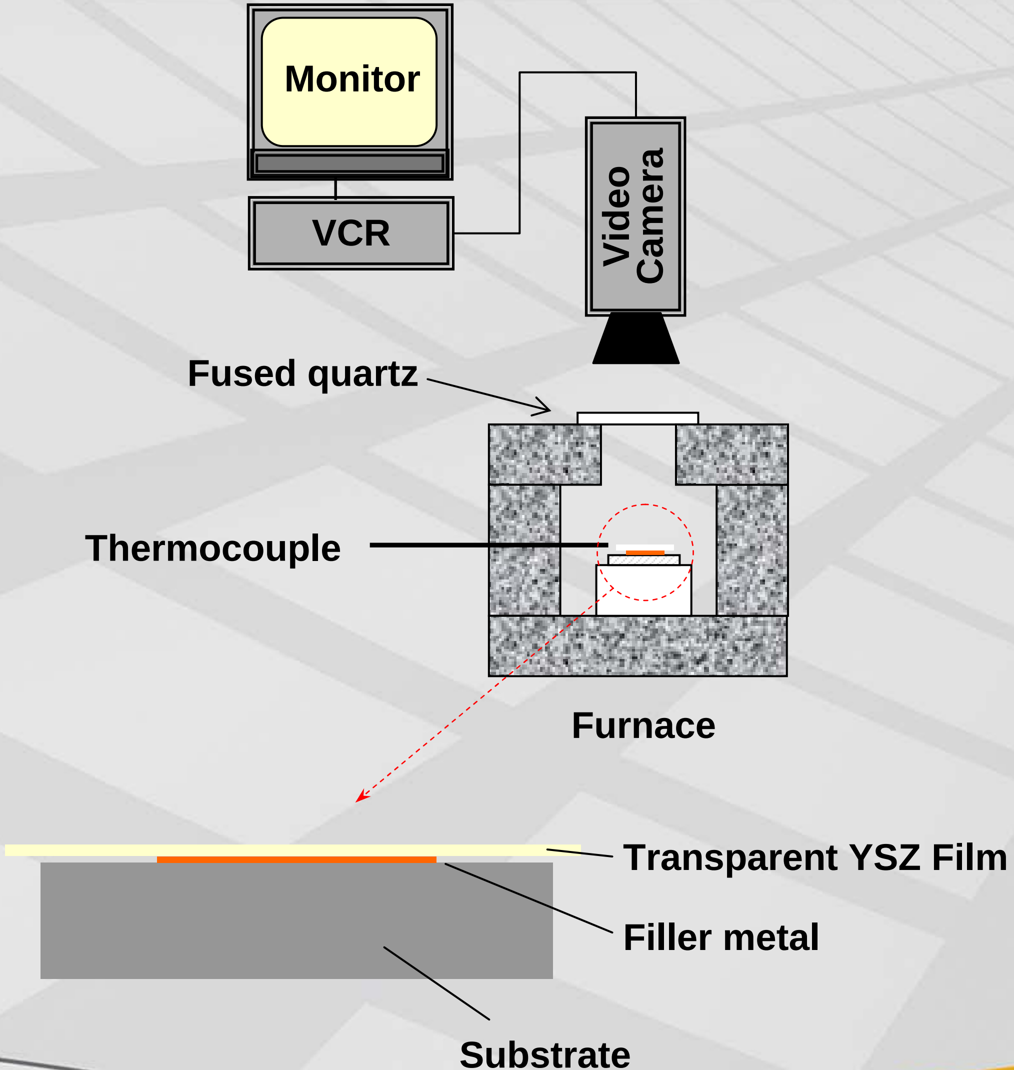
f = *natural frequency*
l = *oscillation mode*
γ = *surface tension*
m = *mass*

Viscosity: Lamb's formula

$$\tau_l = \frac{\rho R_o^2}{(l-1)\,(2l+1)\,\mu}$$

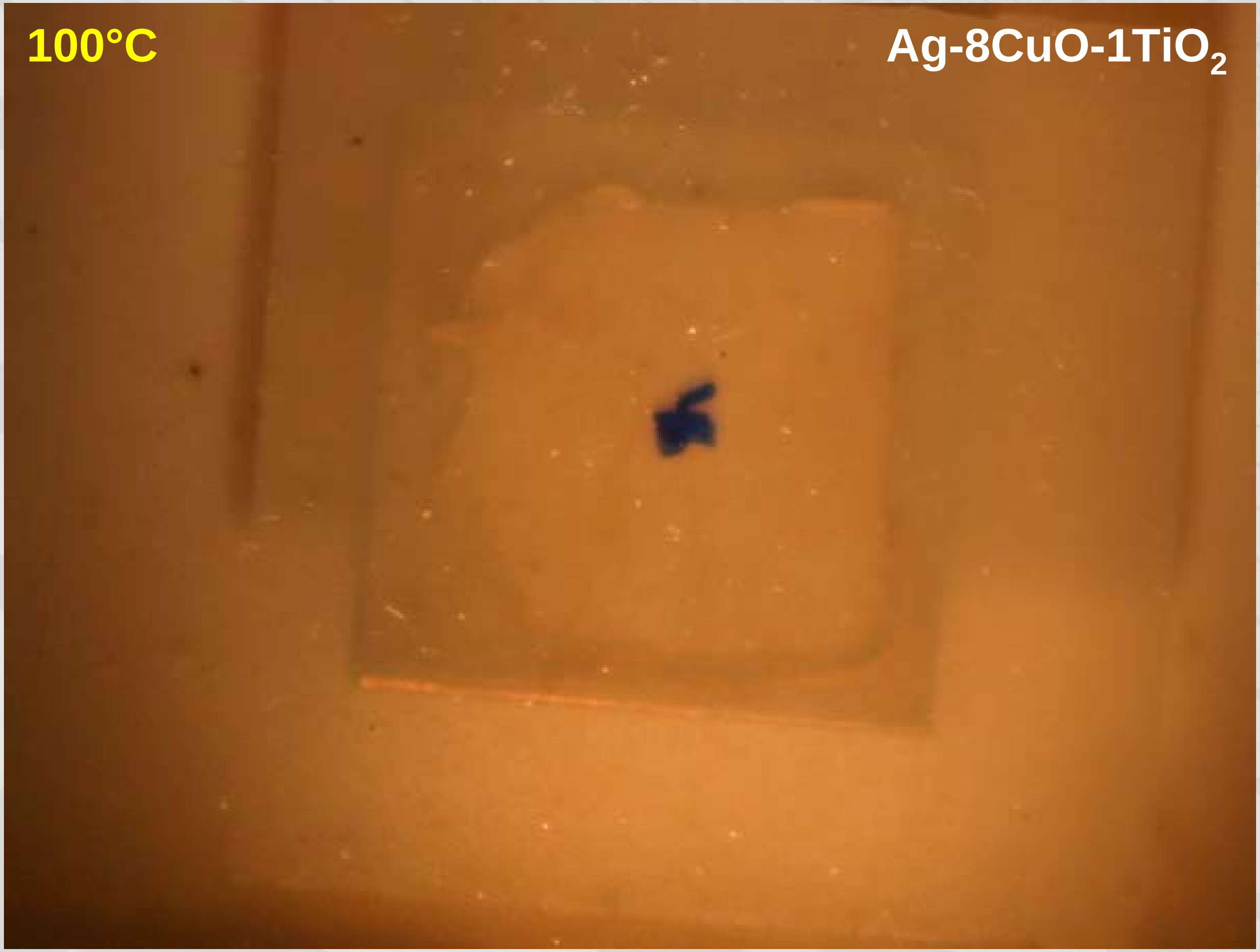
τ= exponential time constant
l = oscillation mode
ρ= density
R_o = undeformed spherical radius
μ = viscosity

In-Situ Wetting Transition Studies



Heat at 5°C/min from RT to 1000°C

In-situ Images of the Brazing Process



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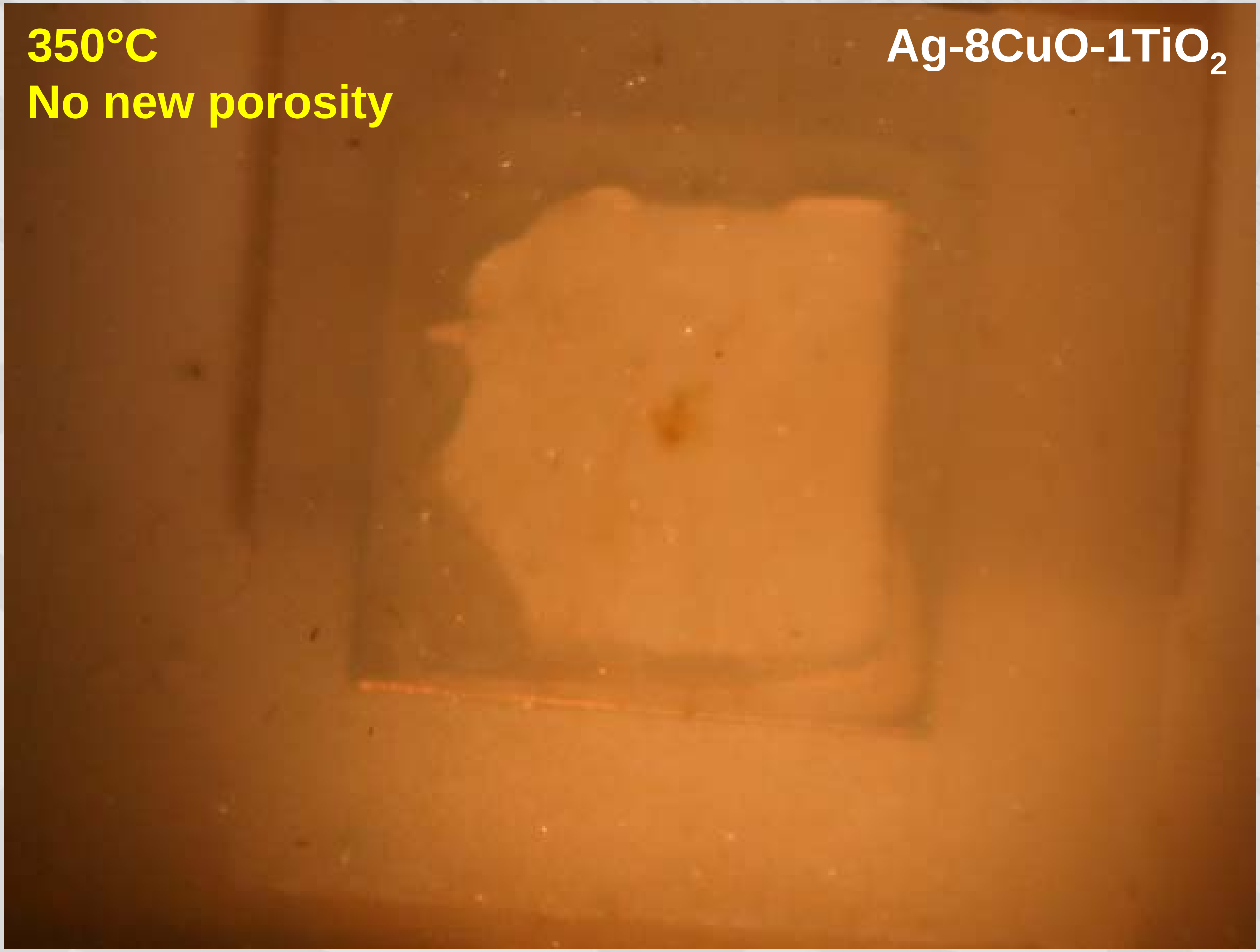

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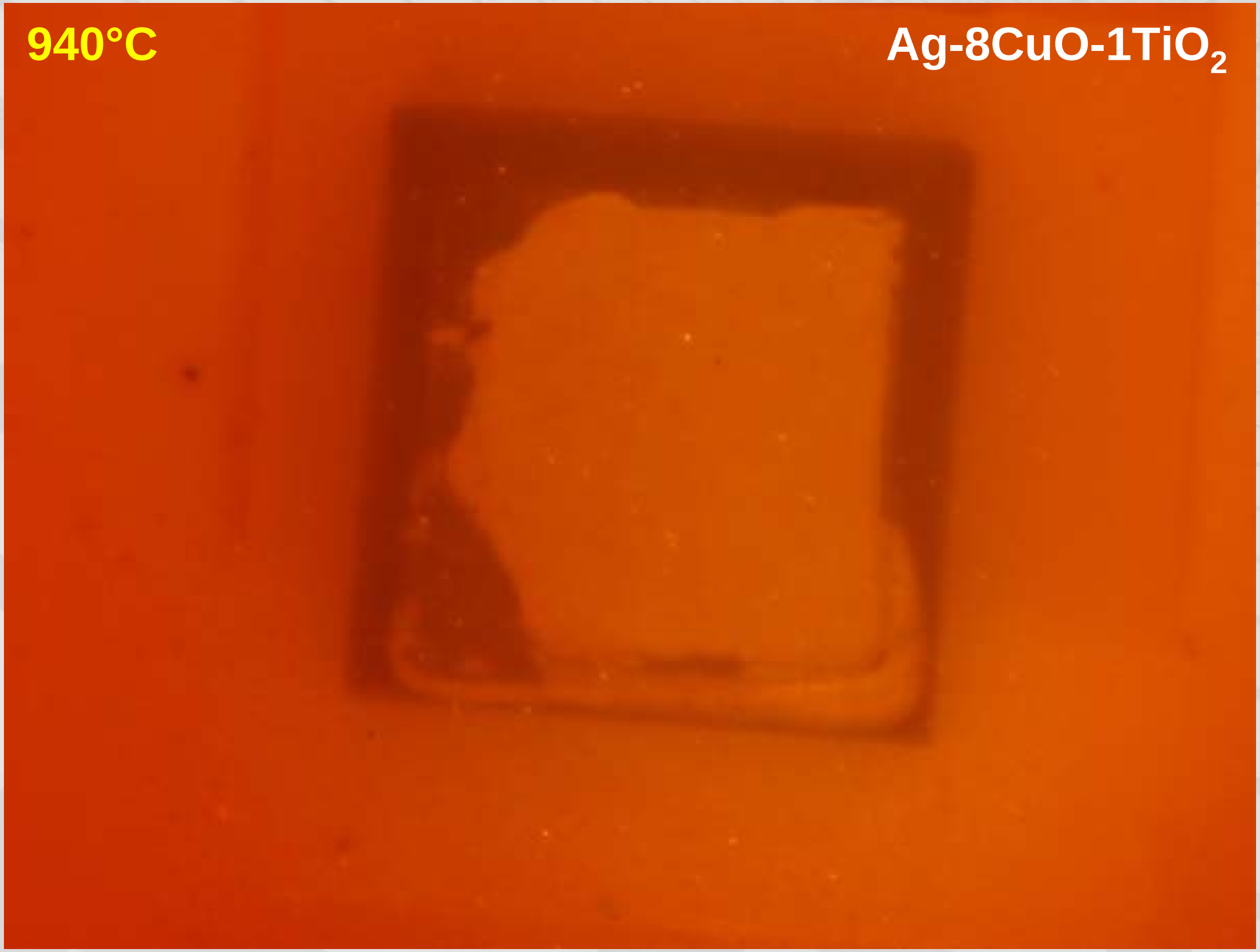

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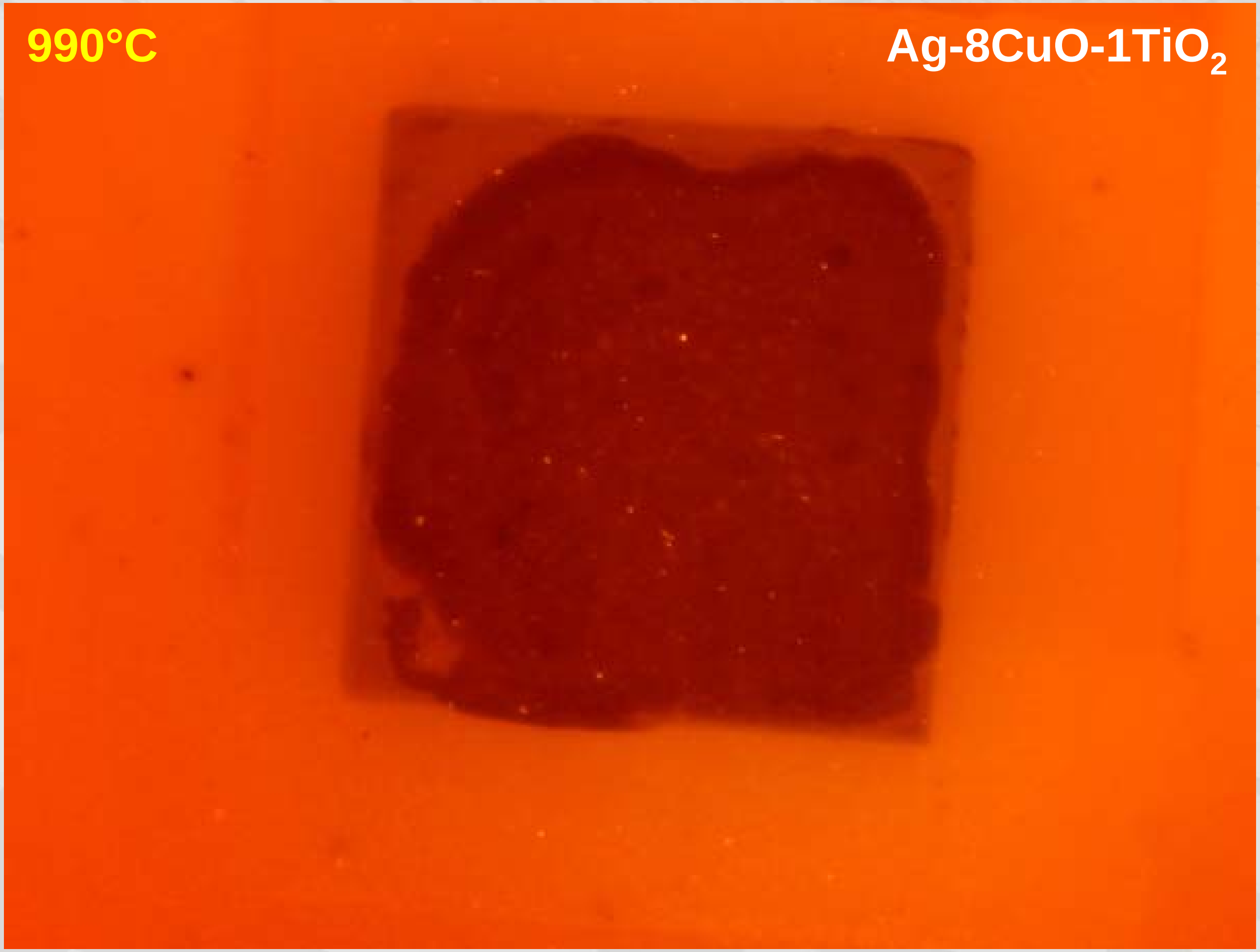

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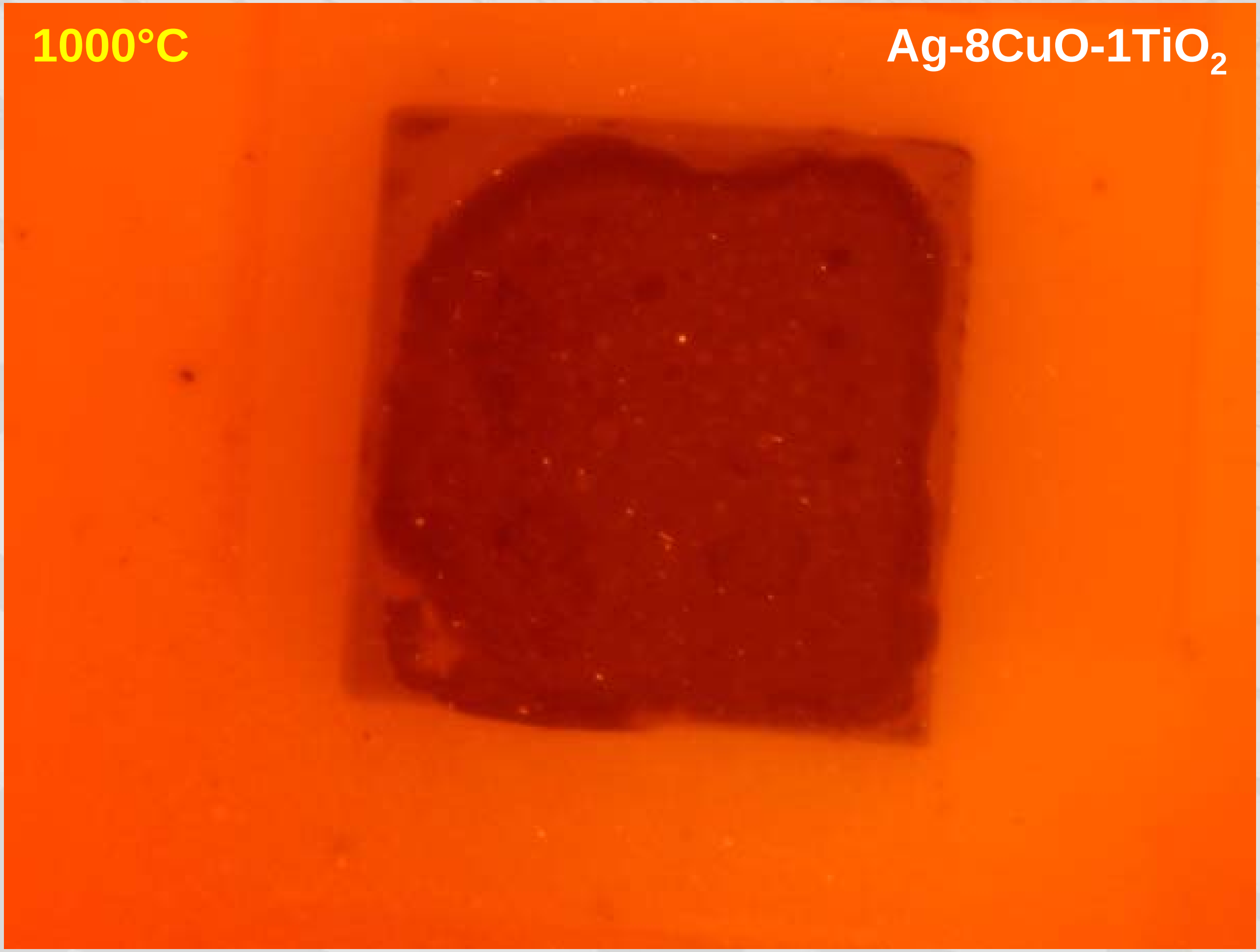

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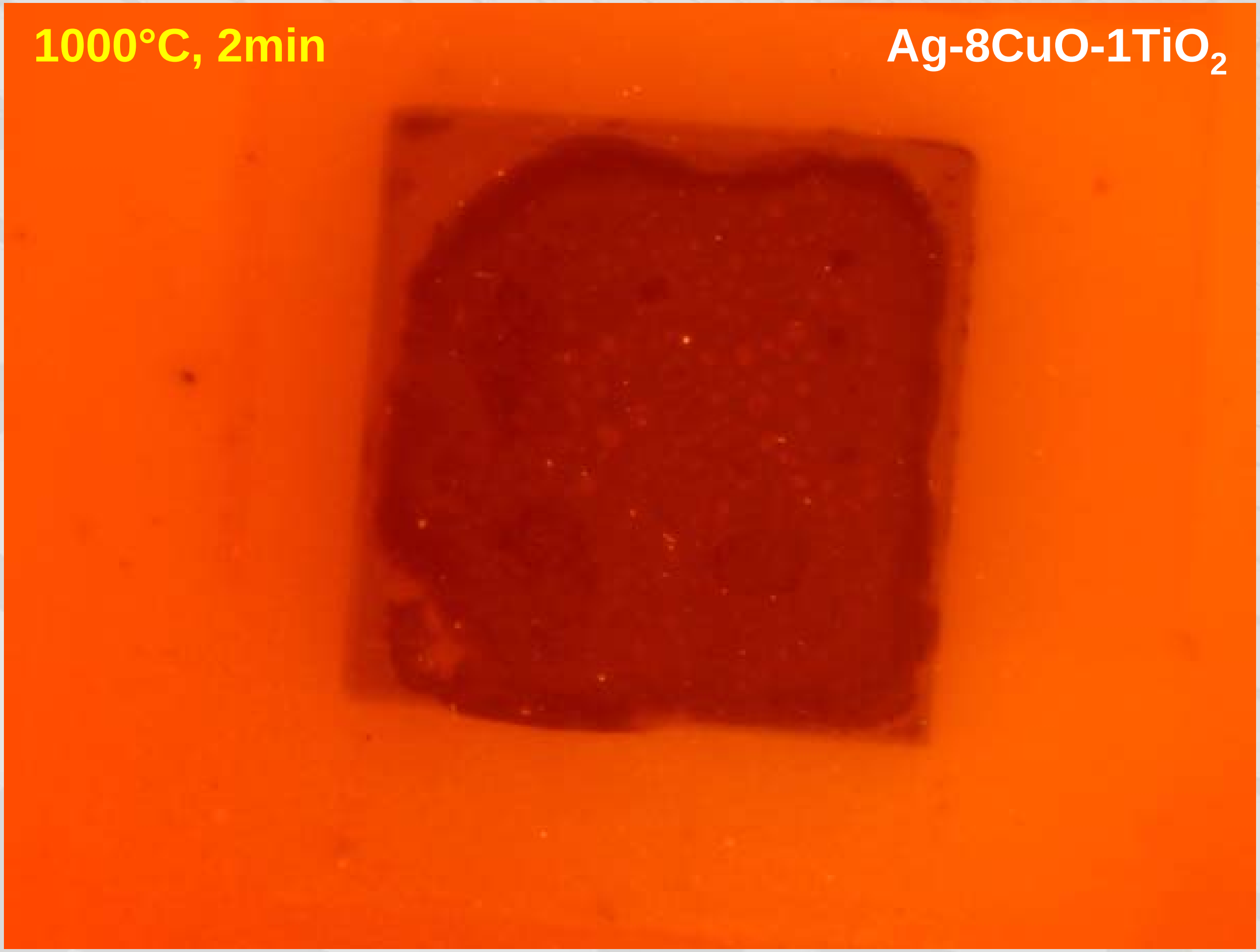

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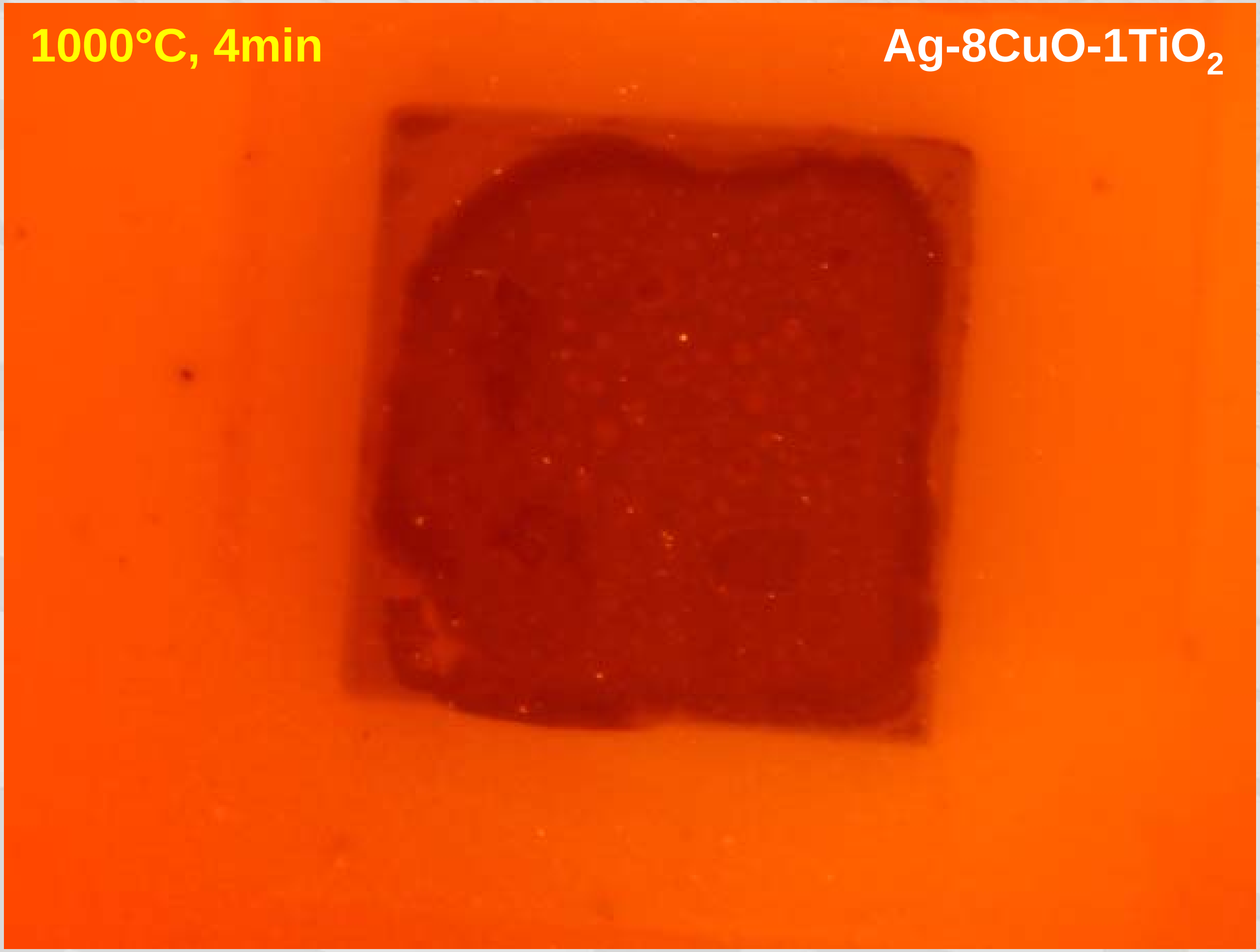

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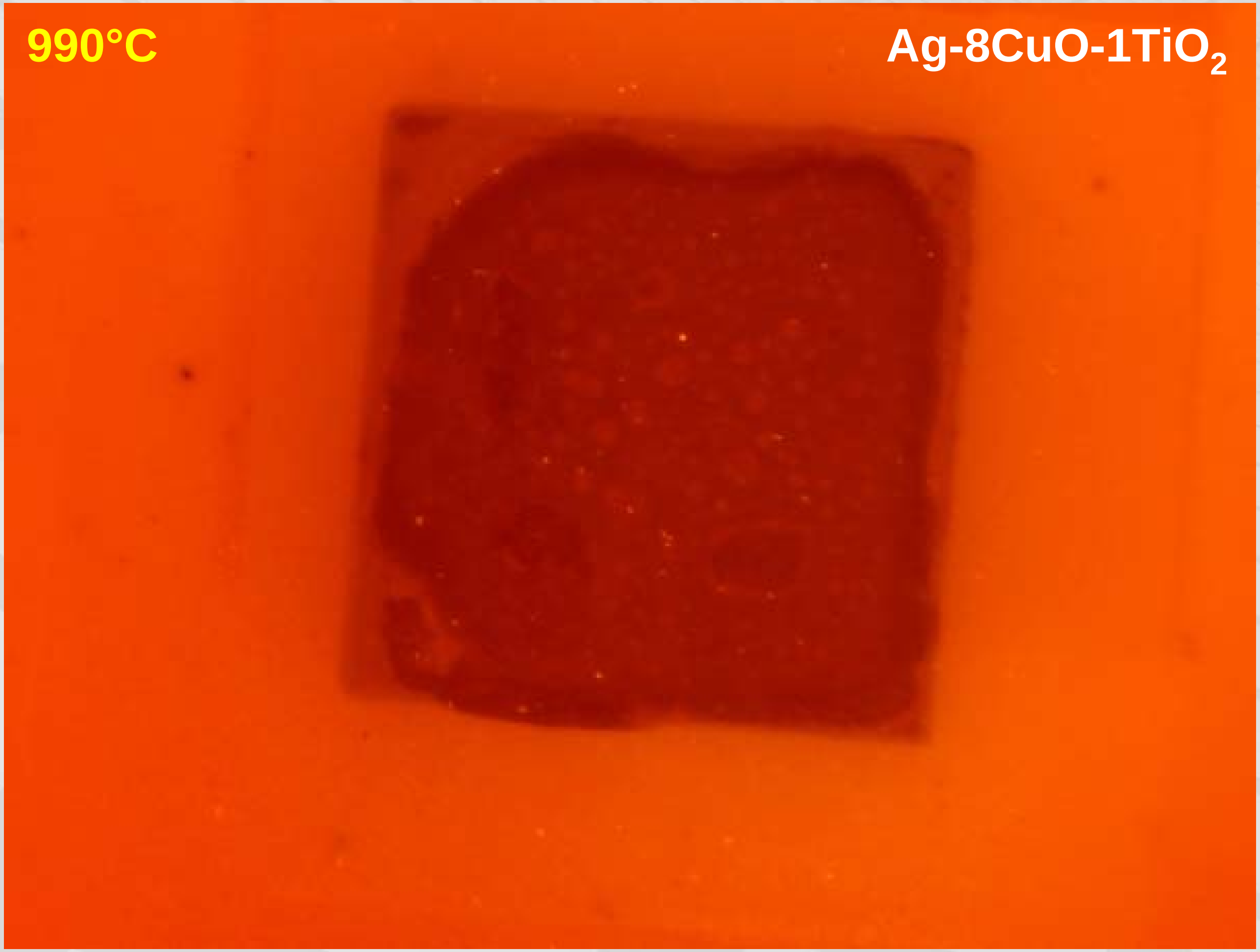

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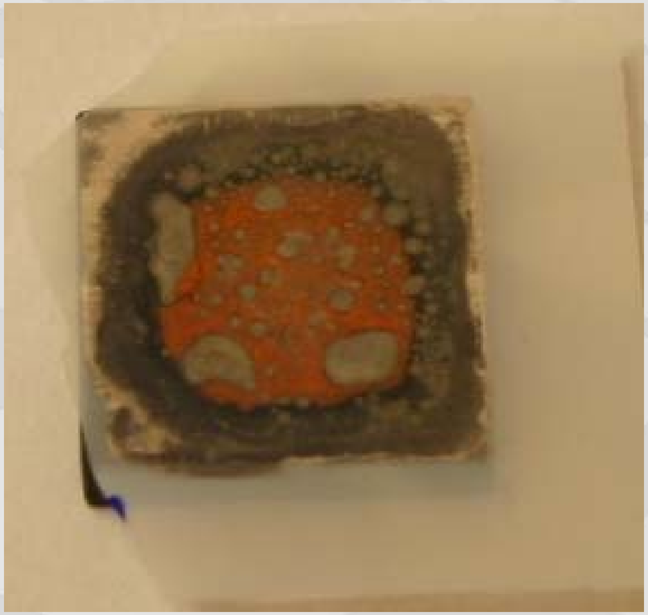

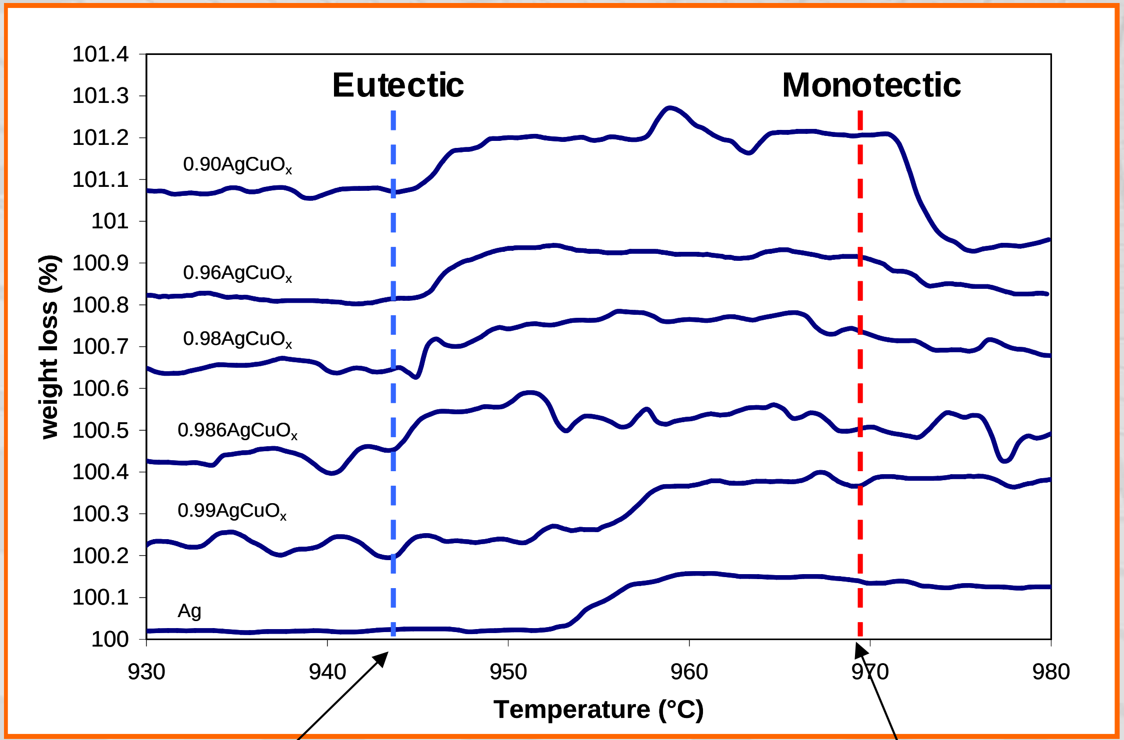

O uptake in liquid

CuO to Cu_2O

Applied Studies

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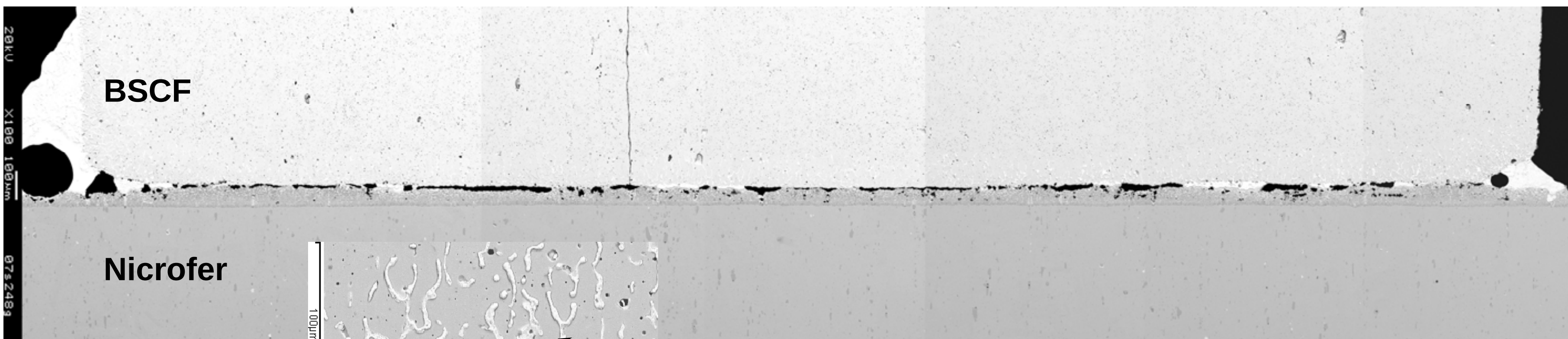
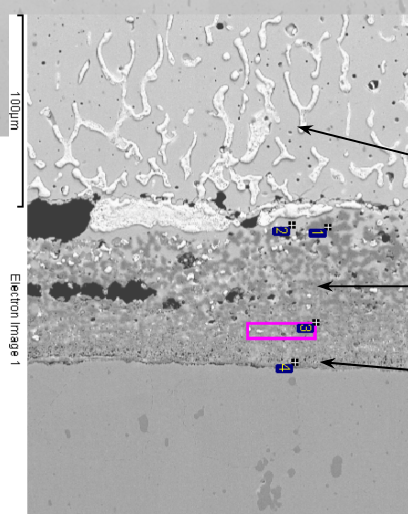
Brazing of Oxygen Separation Tubes

- **Objective: optimize the air brazing process to hermetically seal BSCF to Nicrofer 6025**
  - **BSCF: $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (CTE = 18.5 x 10^{-6} K^{-1})**
  - **Nicrofer 6025: 0.2 C, 2Al, 11 Fe, 25 Cr, bal. Ni (CTE = 17.0 x 10^{-6} K^{-1})**
- **Test Variables**
  - **Filler metal composition**
  - **Intermediate and soak temperature(s)**
  - **Intermediate and soak time(s)**
  - **Heating/cooling rates**
- **Experimental methodology**
  - **Determine the initial filler metal composition based on prior wetting/reactivity data**
  - **1st series of brazing trials: employ the standard heat treatment schedule and examine effects (interfacial analysis)**
  - **2nd series of brazing trials: incorporate compositional/heat treatment schedule modifications and examine “robustness” of the changes using the Box approach**
  - **Fine tuning brazing trials: joint analysis and hermeticity testing**

Trial 1 Joining Conditions:

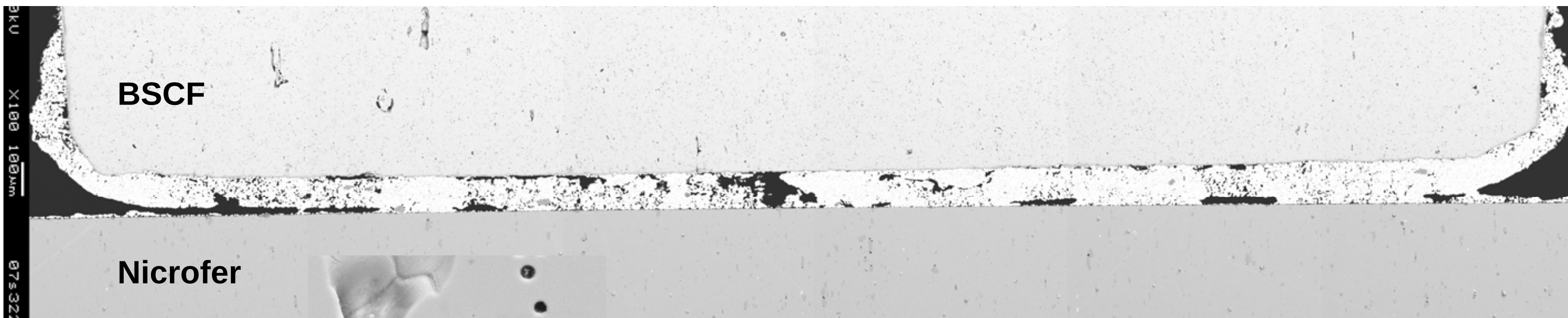
- Filler metal: 8mol% CuO in Ag
- Applied as a 70% solids paste mixture via stencil printing - 125μm (5mil) thick layer
- Heat treated in air at 3°C/min to 980°C and held for 10min

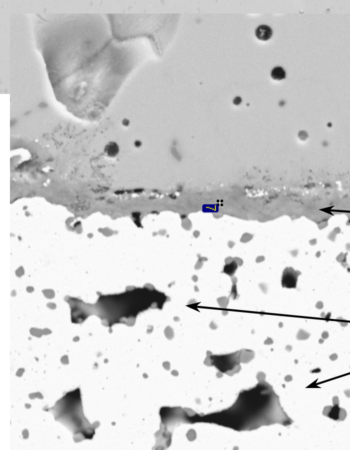




Trial 4 Joining Conditions:

- Filler metal: 8mol% CuO in Ag
- Applied as a 70% solids paste mixture via stencil printing - 125μm (5mil) thick layer
- Heat treated in air at 10°C/min to 970°C and held for 0min, cooled at 10°C/min





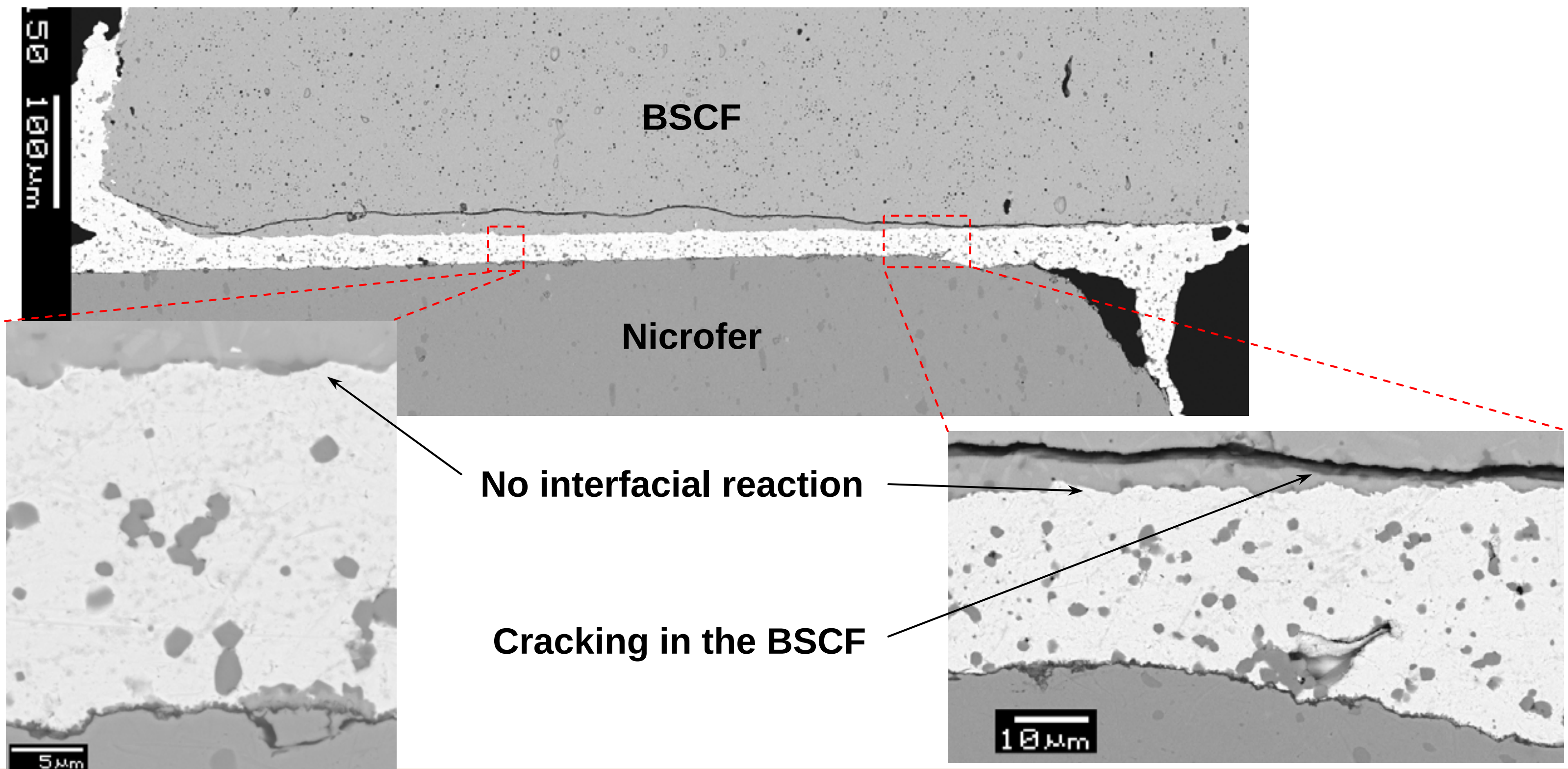
Dissolution confined to a 1mm thick layer between the ceramic and filler metal

Some porosity in the filler –potential concern that it did not fully melt

Higher Soak Temp, Rapid Cooling

Trial 6 Joining Conditions:

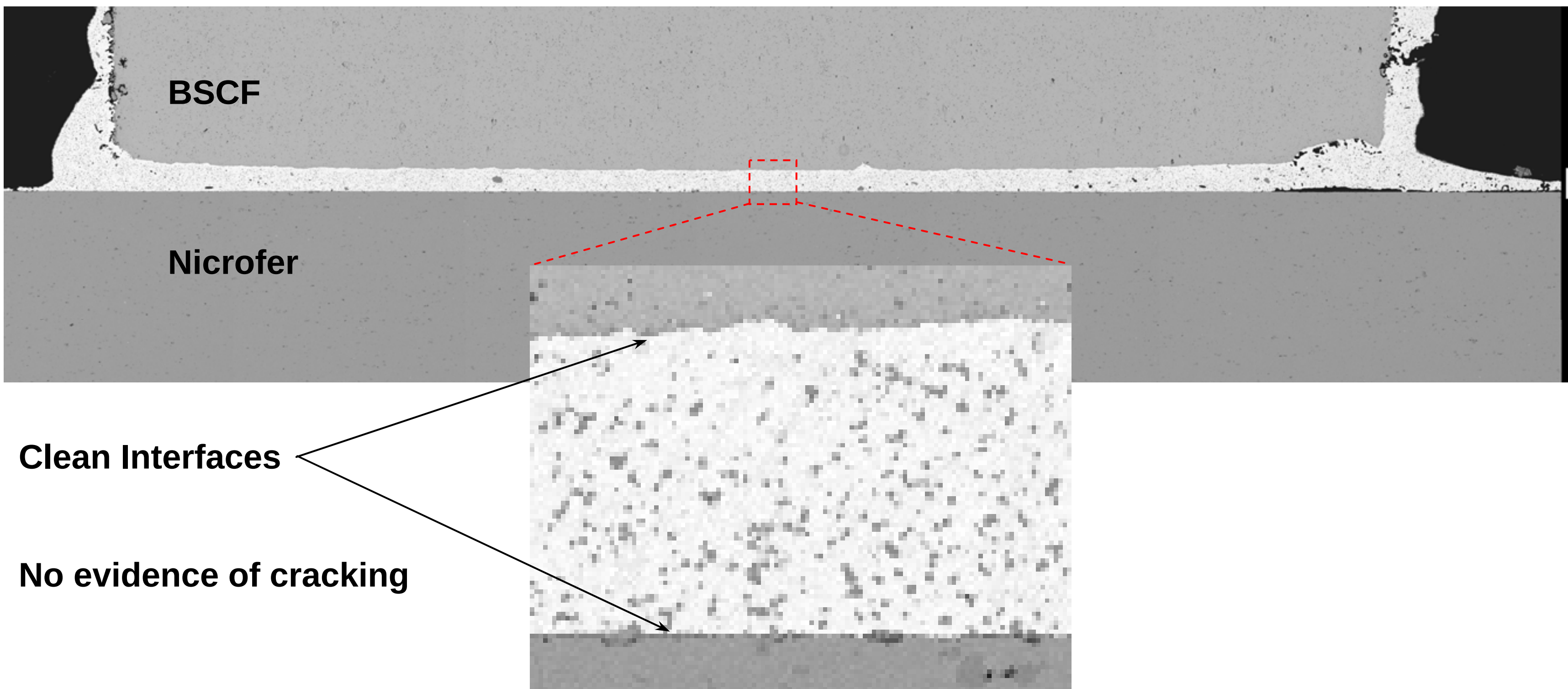
- **Filler metal: 8mol% CuO in Ag**
- **Applied as a 70% solids paste mixture via stencil printing - 125μm (5mil) thick layer**
- **Heat treated in air at 10°C/min to 990°C and held for 0min, cooled at 100°C/min to 900°C and at 10°C/min to 300°C**



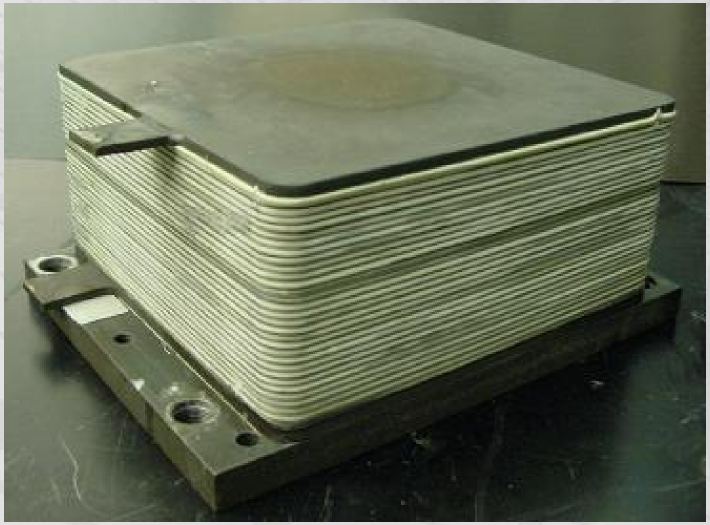
Rapid Cooling to 930°C

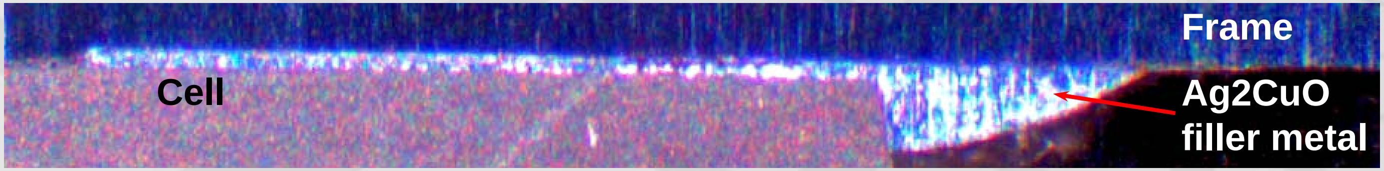
Trial 7 Joining Conditions:

- **Filler metal: 8mol% CuO in Ag**
- **Applied as a 70% solids paste mixture via stencil printing - 125μm (5mil) thick layer**
- **Heat treated in air at 10°C/min to 990°C and held for 0min, cooled at 100°C/min to 930°C and at 10°C/min to 300°C**



SOFC/Reformed Natural Gas Studies

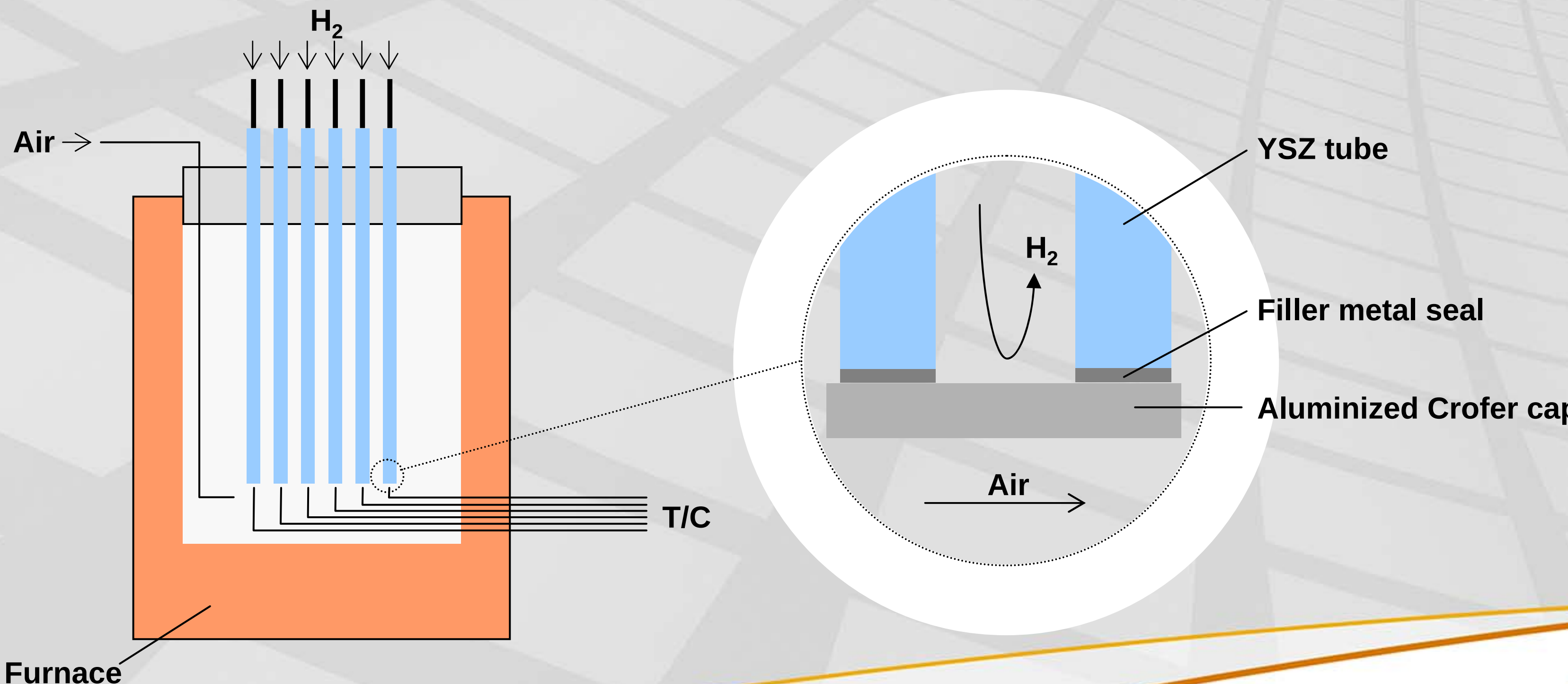




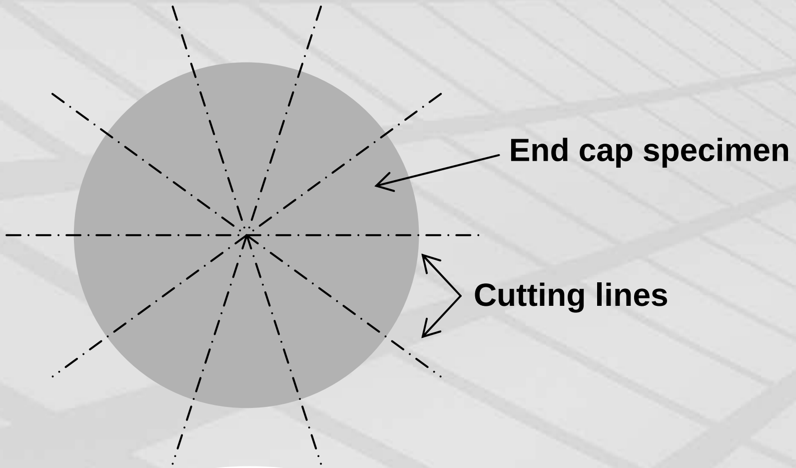
- **In short-to-mid-term (0 – 2000h) testing, Ag-CuO braze seals work well (reformed natural gas fuel, 750°C, slow load/thermal cycling)**
- **Some problems with excessive filler metal flow**
- **After ~2000h, begin to see signs of dual atmosphere degradation**

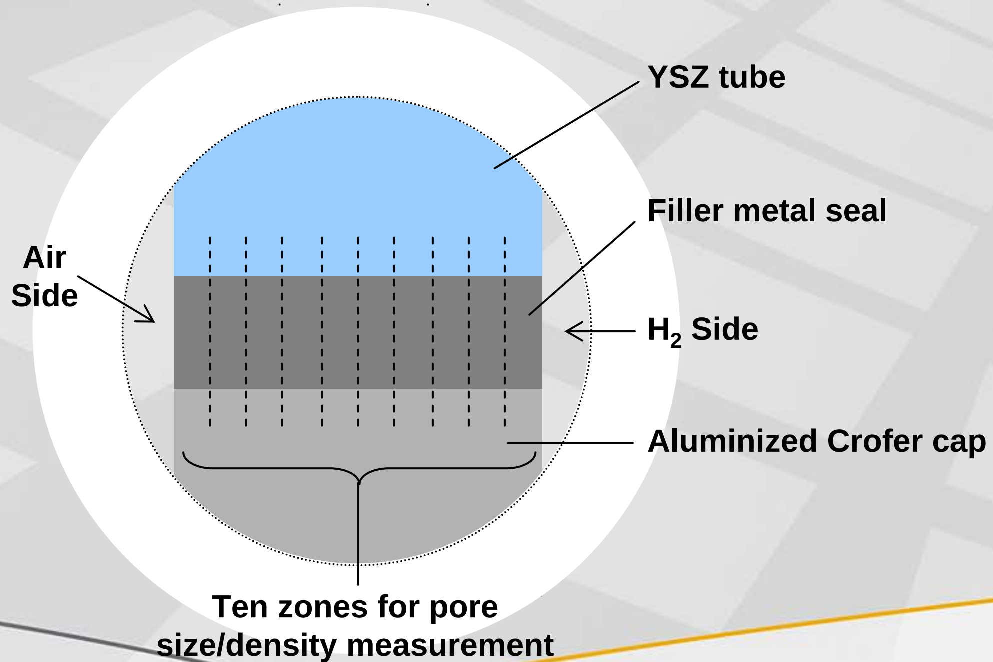
Tracking Dual Atmosphere Effects

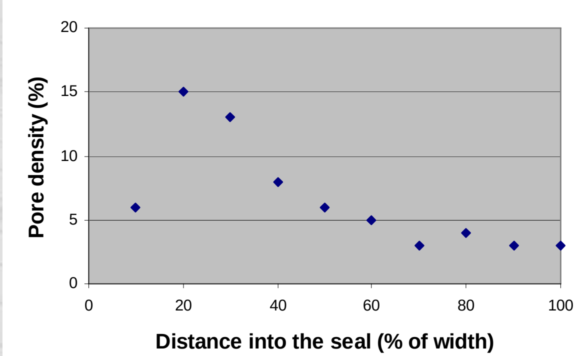
- Statistical test methodology
- Two test temperatures: 750 and 850°C
- Exposure times: 500, 1000, 2000, 3000, 4000, and 5000 hrs
- YSZ sensor will track seal integrity

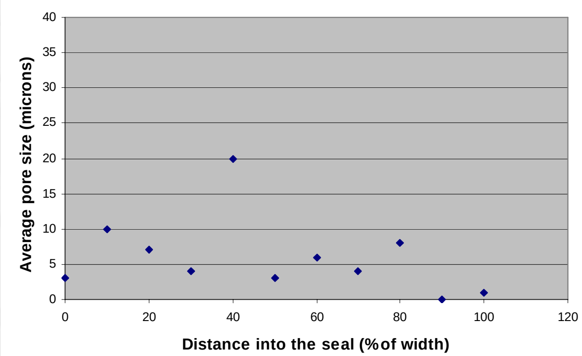


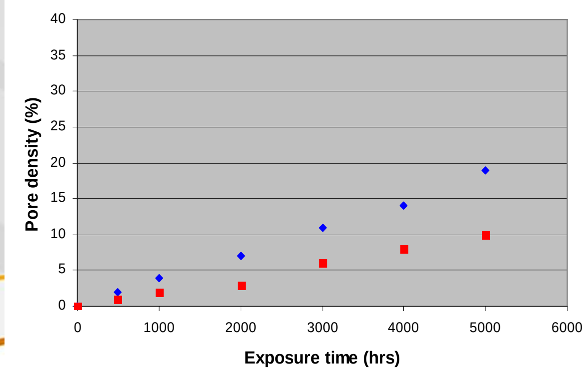
Tracking Dual Atmosphere Effects



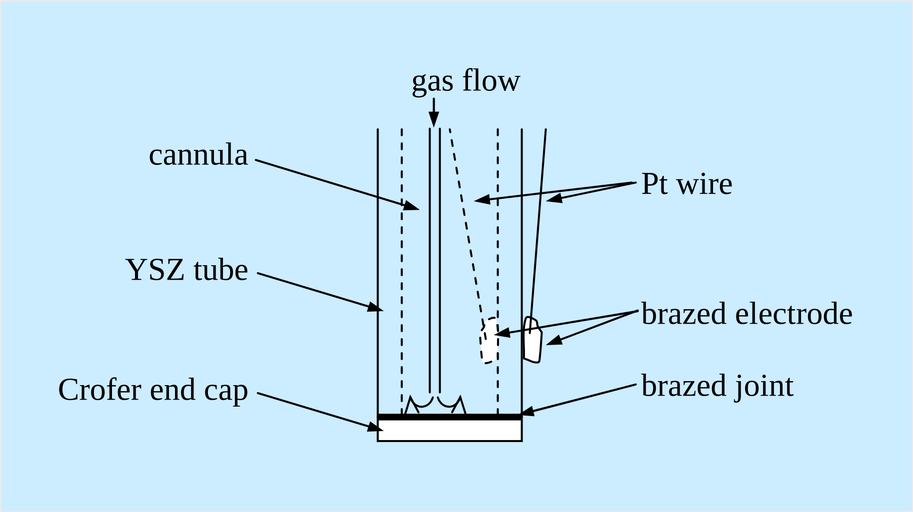


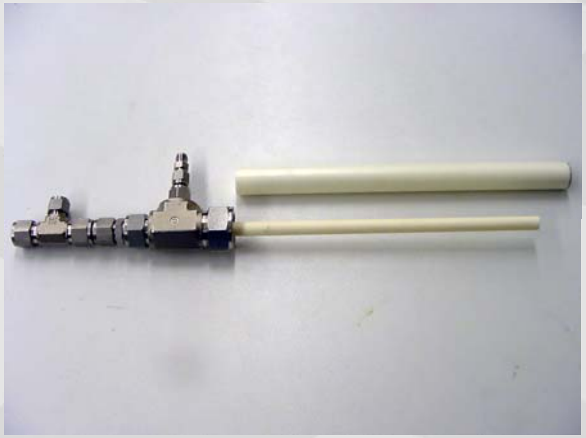


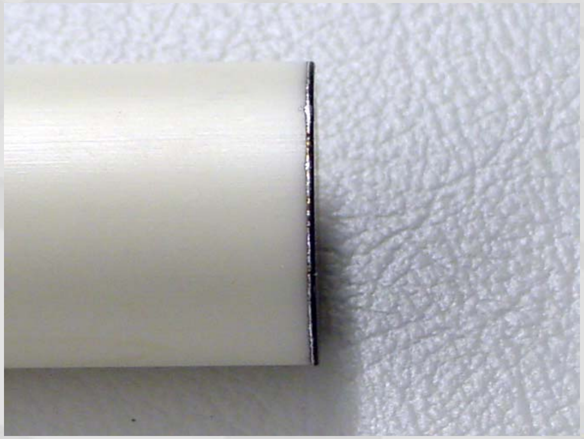




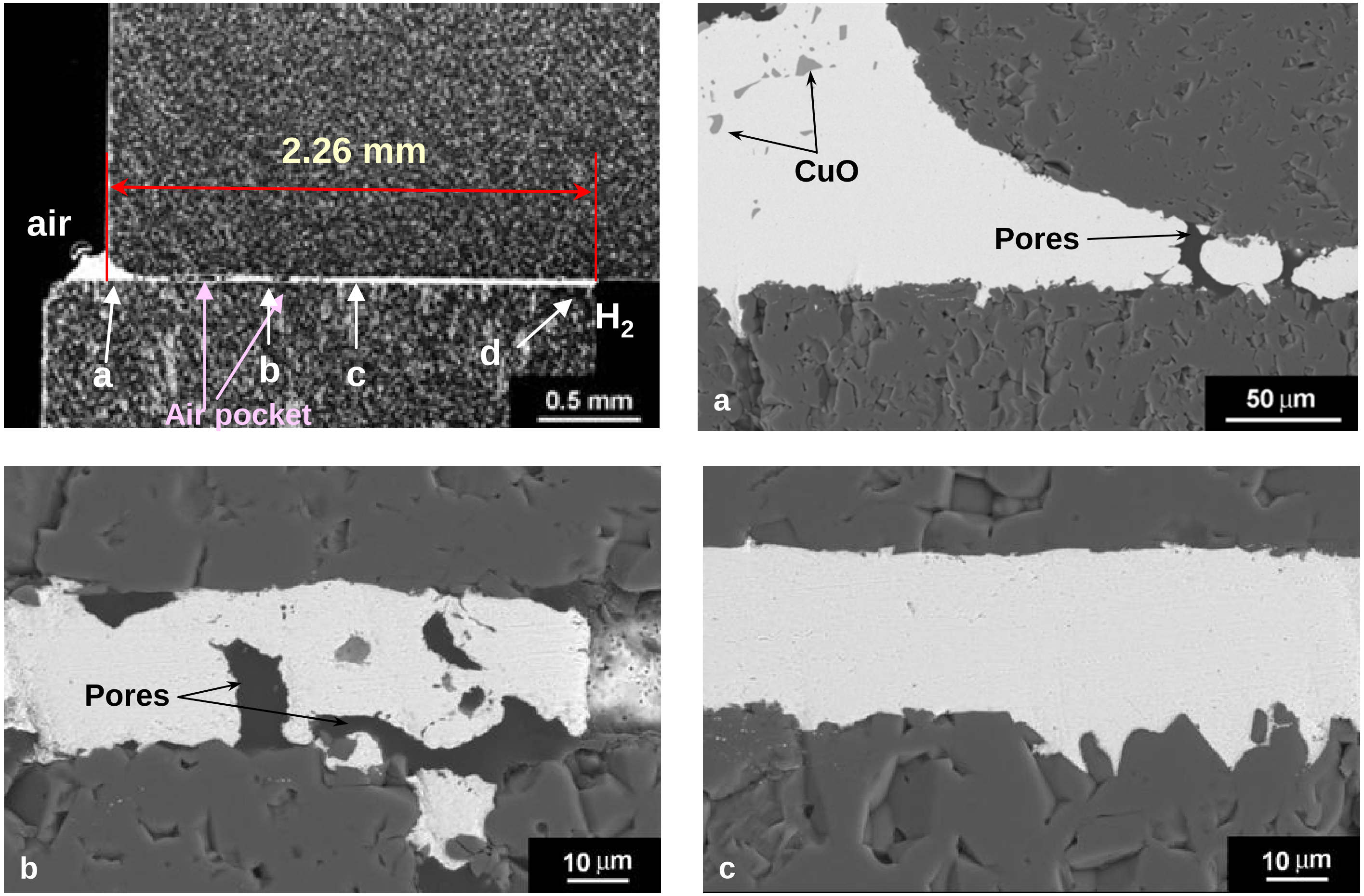
Testing Underway







Ag2CuO brazed at 980°C; dual atm exposure at 850°C for 500hrs



Conclusions

- **Materials joining – processes that enable a wide variety of technologies important to efficient fossil fuel utilization:**
  - **Gas separation (H_2/O_2)**
  - **SOFC fabrication**
  - **Electrochemical sensors**
- **Fundamental studies – focused on obtaining information that enables the design of joining processes that meet DOE-FE needs:**
  - **Structure-bonding/property relationships**
  - **Alloying effects: Pd, Al, TiO_2, CoO**
  - **Two-phase wetting phenomena**
  - **Effect of particle additions**
- **Applied studies – focused on solving near-term DOE-FE joining issues:**
  - **Braze process optimization**
  - **Demonstration in prototypic devices/equipment**
  - **Low-cost fabrication techniques**
  - **Environmental exposure testing**

Future Work

- Complete our physicochemical studies on Ag-CuO
- Examine dual atmosphere effects in air brazed joints
- Explore non-silver based air braze systems
- Investigate transient liquid phase concepts → development of air braze filler metals with higher re-melt temperatures
- Develop and evaluate joining processes for:
  - Various high temperature materials
    - Refractory metal alloys
    - Metal matrix composites
    - Coated alloys
    - ODS alloys
    - SiC and SiC_f/SiC composites
  - Low-cost, high-temperature recuperator for CHP applications
  - High-temperature, ceramic-based microchannel devices

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Collaborators

- Argonne National Laboratory
  - Chris Benmore
- Materials Development , Inc.
  - Rick Weber
- Battelle Memorial Institute
  - Paul George
- Aachen University
  - Sabine Dabbarh
- Aegis Technology, Inc.
  - Tim Lin
  - Chuck Tan
- Corning, Inc.
  - Dillip Chatterjee
- Alfred University
  - Alan Meier
  - Jared Friant
- Bechtel Bettis Laboratory
  - Jim Hardy
- Marshall Space Flight Center
  - Jan Rogers
  - Trudy Allen
- Delphi Corporation
  - Karl Haltiner
  - Shubhashish Mukerjee

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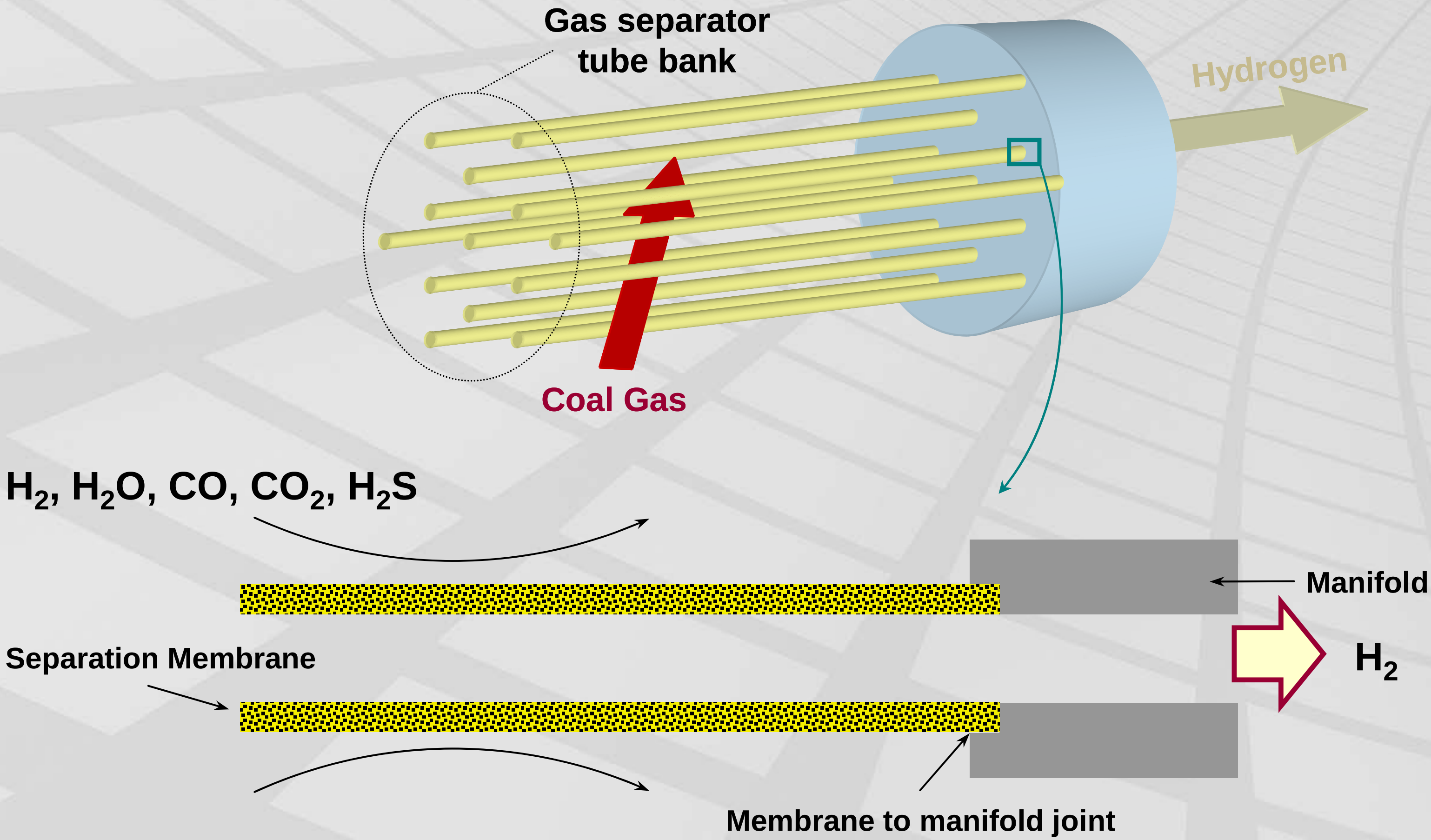
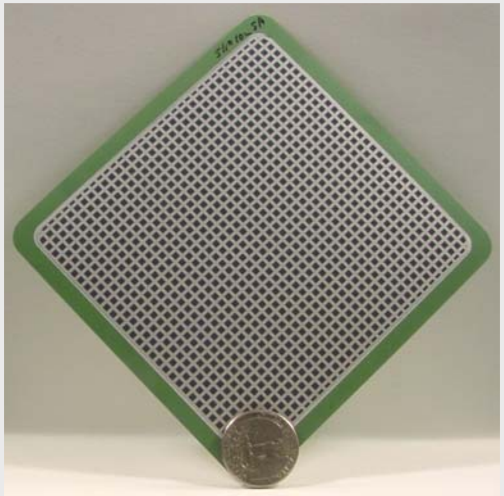
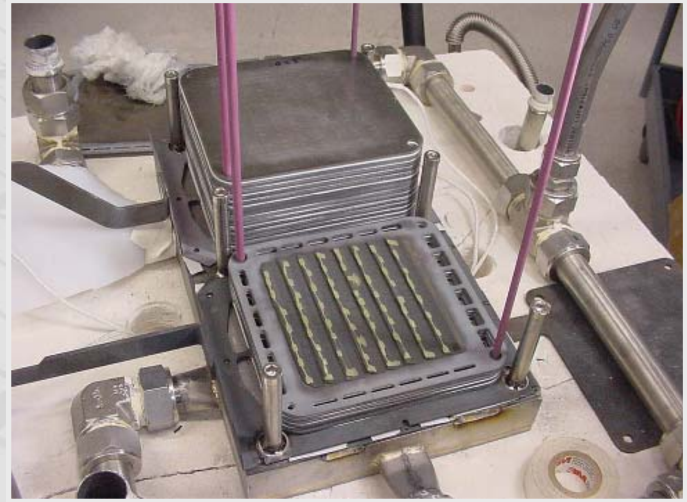
Applications: H_2 & O_2 Separations



Applications: Solid Oxide Fuel Cells & Sensors

SOFC





Water Quality Probe