Brazed Seals

Alternative Sealing Technology for Solid Oxide Fuel Cells

U.S. Department of Energy, Office of Fossil Energy,
SECA Program

7th Annual SECA Workshop
September 12 – 14, 2006

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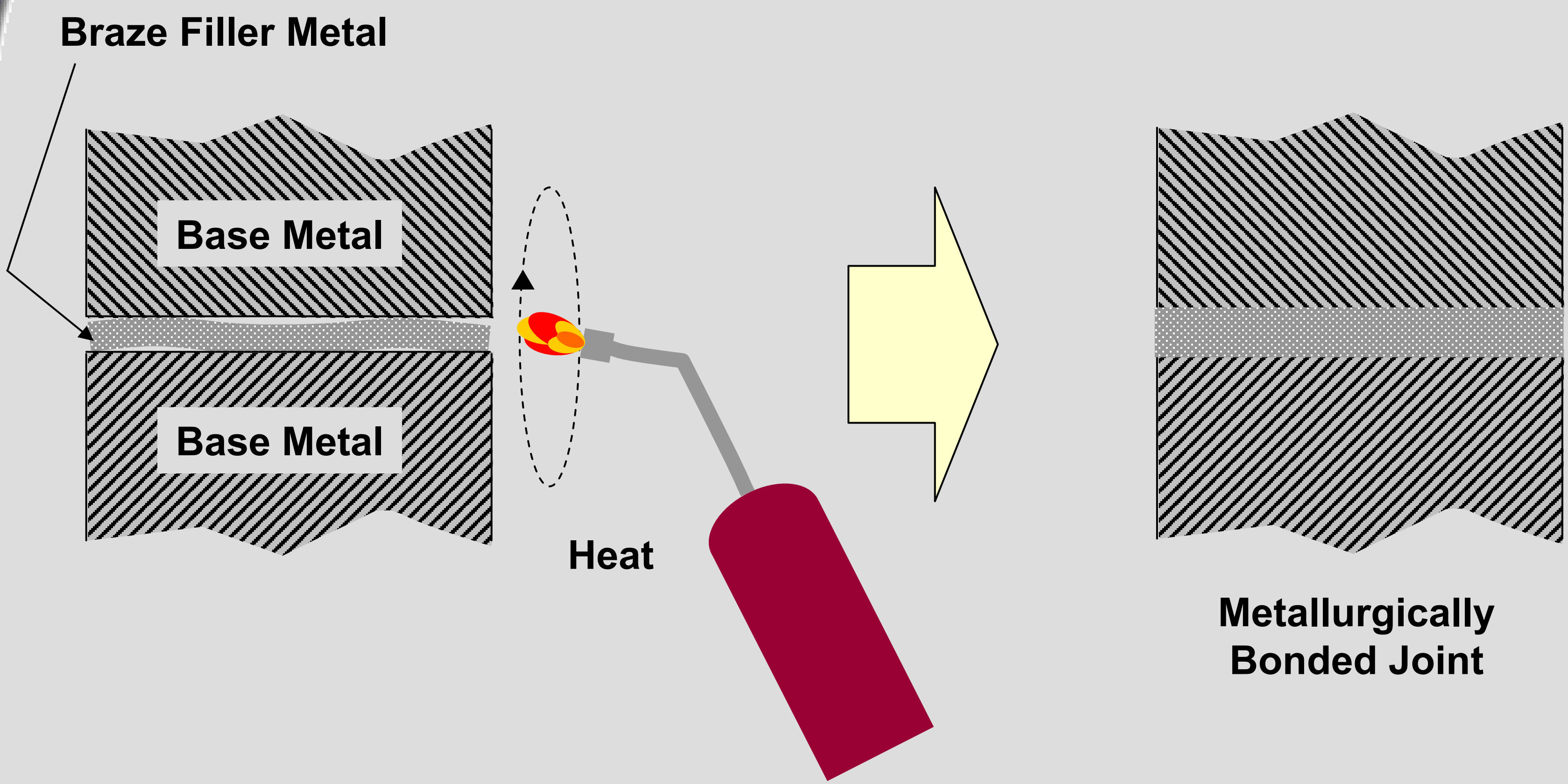
What is Brazing?

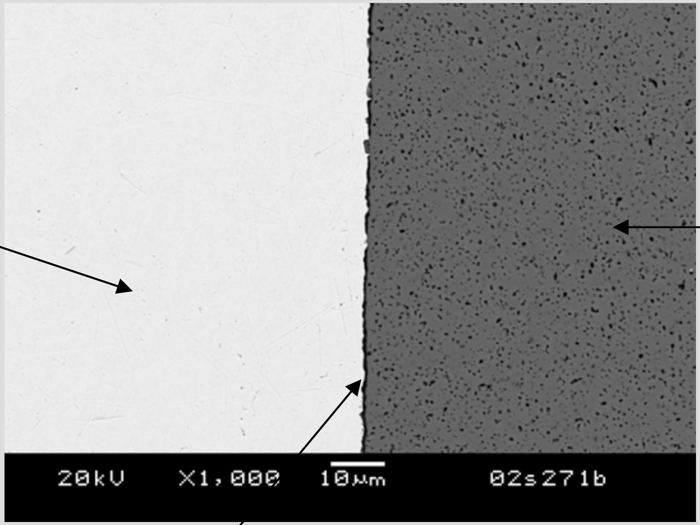
Definition: A filler metal is heated to melting and under capillary action fills the gap between the sealing surfaces. When cooled, a solid joint forms.



Active Metal Brazing: A specialized technique that employs a reactive element such as titanium to facilitate wetting between the filler metal and a ceramic substrate

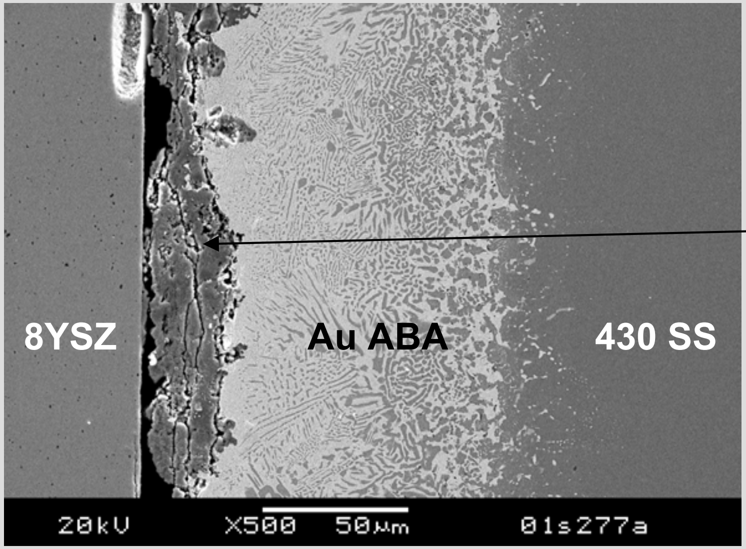
Typical Filler Metals: Au-Ni-Ti, Au-Ni-V-Mo, Ag-Cu-Ti, Pd-Ni-V

Process Conditions: Vacuum or inert gas environment
850ºC or higher



Issues with Active Metal Brazing

Joint Oxidation



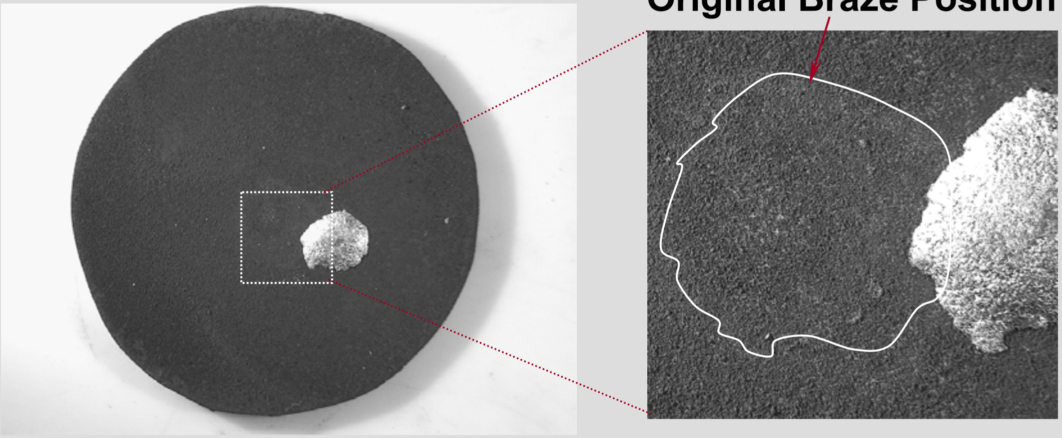
KS Weil and JP Rice, *Scr. Mater.*, 52 (2005) 1081

$(Cr,Fe)_2O_3$ scale formation after 200hrs air exposure at 700°C

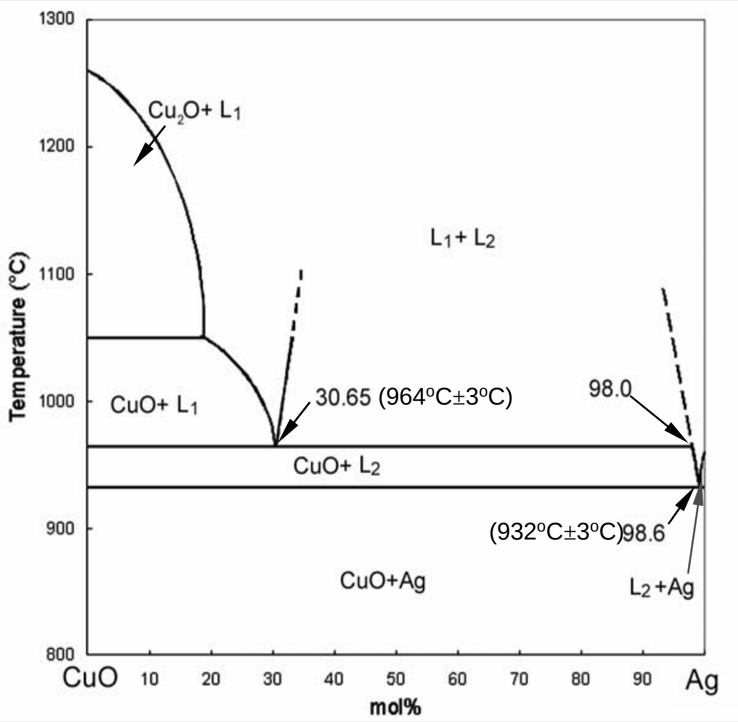
Cathode Decomposition

Under vacuum at T > 700ºC:

$$LaFeO_3 \rightarrow \tfrac{1}{2} La_2O_3 + \tfrac{1}{2} Fe_2O_3$$

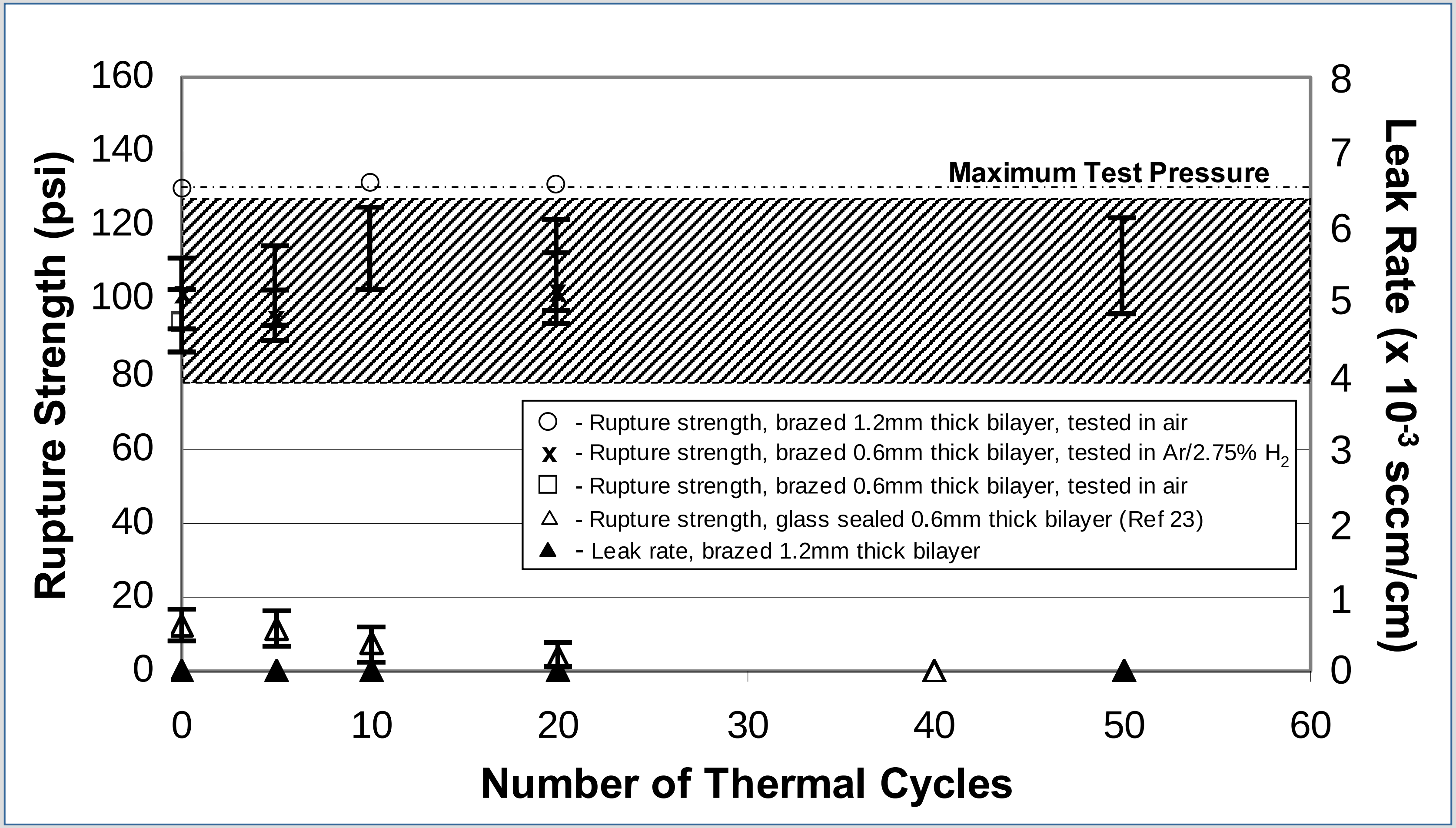


- A new method of ceramic-to-ceramic and ceramic-to-metal joining
- Uses a unique filler metal system: a soluble metal oxide dissolved in a noble metal – e.g. CuO in Ag
  - Is conducted in open air (i.e. in a simple muffle or continuous belt furnace)
  - Does not require fluxing or the use of inert cover gas
  - Confers oxidation resistance and ductility to the joint



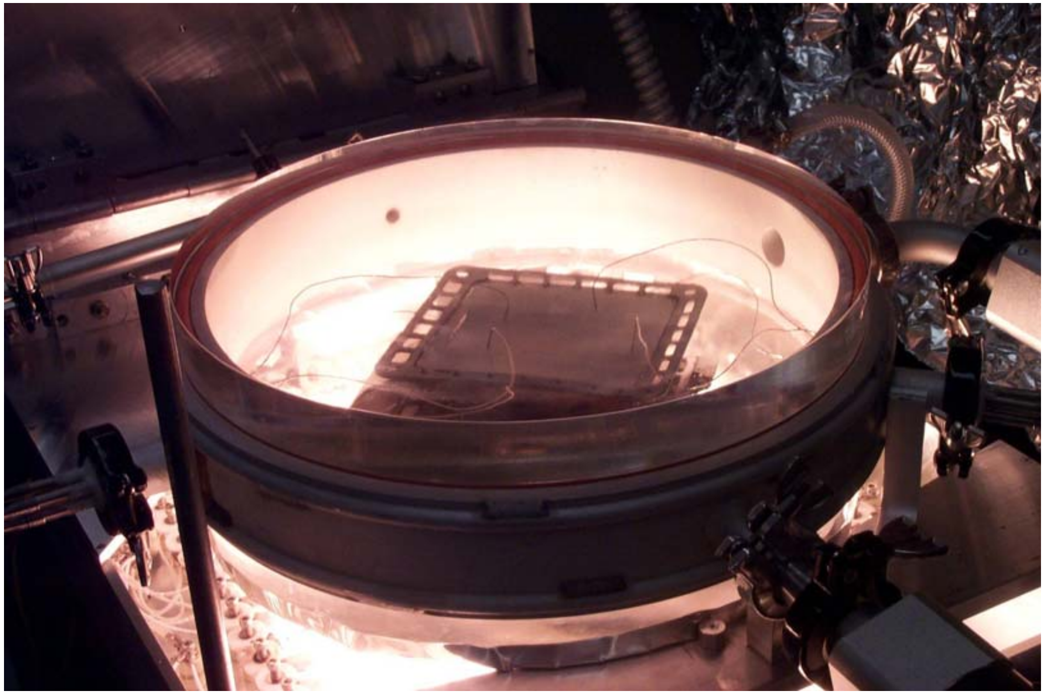
Shao et al, *J. Am. Ceram. Soc*. [1993] 2663

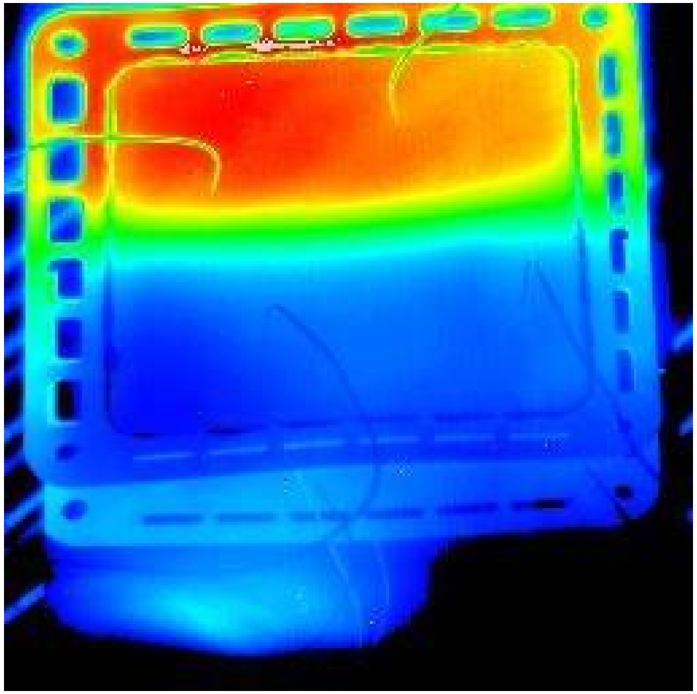
Thermal Cycling (75ºC/min, RT → 750ºC):



KS Weil, CA Coyle, JT Darsell, GG Xia, and JS Hardy, *J. Power Sources*, 152 (2005) 97

Preliminary testing with full-scale components is very encouraging:



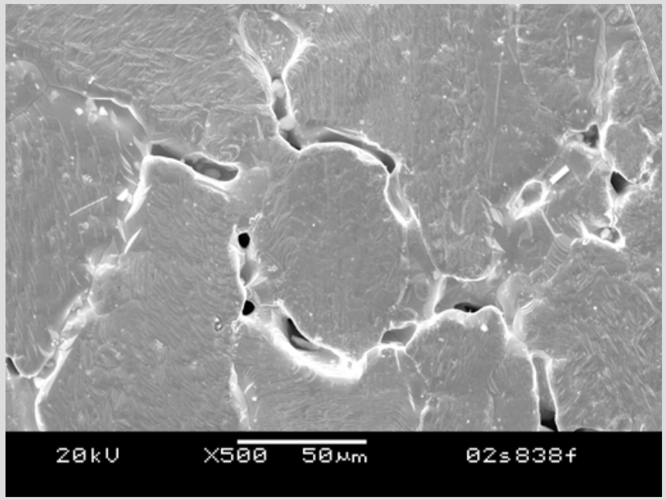


Seal remains hermetic after testing through five thermal cycles

Potential Concerns

- **High-temperature degradation in a dual atmosphere environment**

Pure Silver



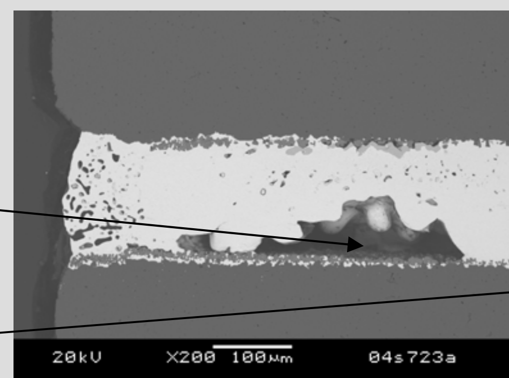
Singh et al., *J. Mater. Eng. Perform.*, 13 (2004) 287

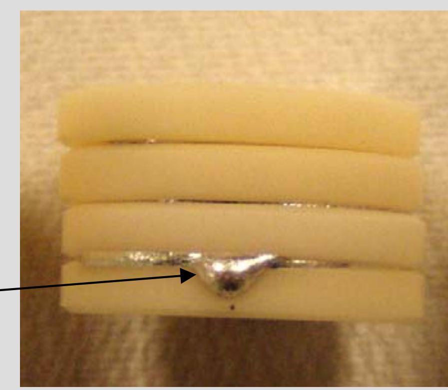
- **Process consistency**

Pore formation due to poor wetting and/or cooling upon shrinkage

and

“Squeeze-out”





Summary of Findings to Date

- **Dual atmosphere degradation**
  - **Observed three different types of pore defects – all of which we suspect can be mitigated**
  - **Phenomenon is not significant with respect to short-term use (up to 2000hrs) – no loss in hermeticity, but a measurable loss of strength**
  - **Could potentially be problematic over longer periods of operation**

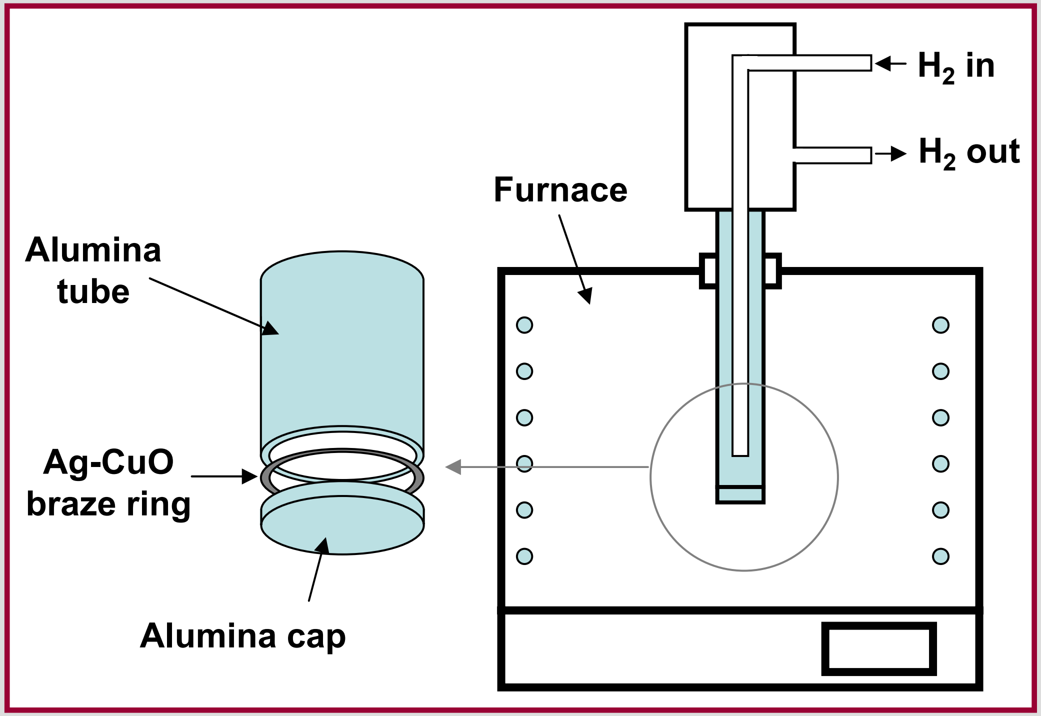
- **Al-Ag-CuO air braze filler metals are being investigated to eliminate long-term dual atmosphere degradation**
  - **Initial alloy compositions have been successfully synthesized, but require further optimization with respect to joint strength**
  - **Observe improved joint strength upon H_2 exposure**
  - **Dual atmosphere testing currently in progress**

- **New composite filler metal composition (containing Al_2O_3 particulate) looks very promising**
  - **Joint strength equal to that of the base material (Al_2O_3)**
  - **Can combine with the Al-alloyed material to develop a very durable air braze filler metal**

Dual Atmosphere Degradation: Experiments

- **Tube testing – 200 - 2000hr aging tests conducted at 800ºC with flowing H_2 inside and flowing air outside**
- **Examined the following variables: exposure time (200, 1000, and 2000hrs), filler metal composition (Ag2CuO and Ag8CuO), and braze temperature (980ºC and 1100ºC)**

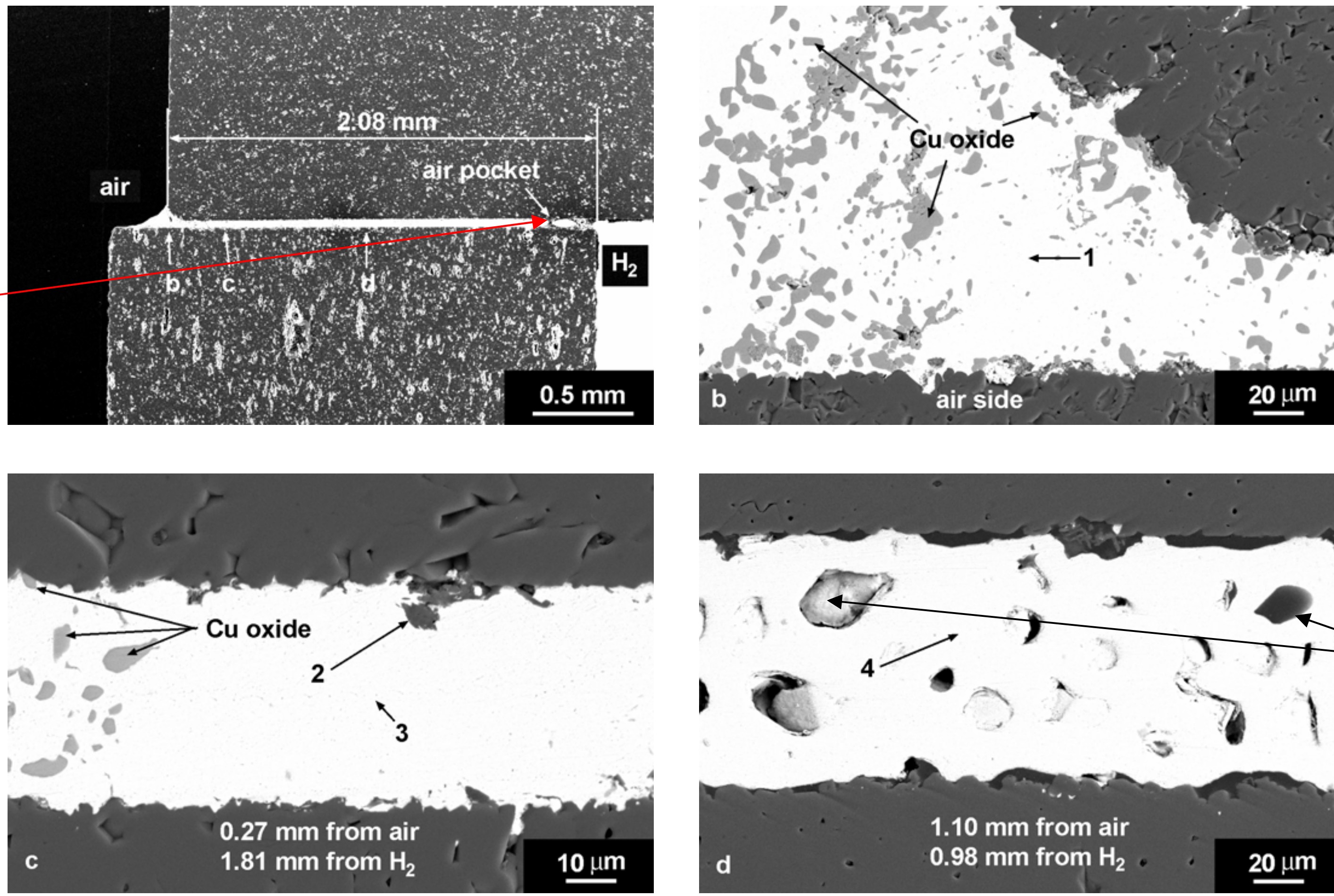
Sealed Tube Exposure Test



- **Three types of pores were found:**
  - **Air pockets formed during processing (Type 1) - large (mm in size) and often found near the center of the joint**
  - **Pores (Type 2) formed within 5hrs of exposure due to CuO reduction : $CuO + 2H_{diss}\,Ag \rightarrow Cu_{diss}\,Ag + H_2O\uparrow$ - >5μm in size, found first along the boundary exposed to H_2**
  - **Pores (Type 3) formed around ~2000hrs due to $H_{diss} + O_{diss} \rightarrow H_2O\uparrow$ - sub-micron to micron in size and only found after "extensive" dual atmosphere exposure (within the center of the joint)**
- **In all cases, the porosity remains isolated (not interconnected)**
- **In all cases, the tubes are hermetic at the end of testing**
- **Progression of Type 2 pore front appears to scale with √t fit, which suggests a means of estimating the lifetime of an Ag-CuO seal based on dual atmosphere degradation**

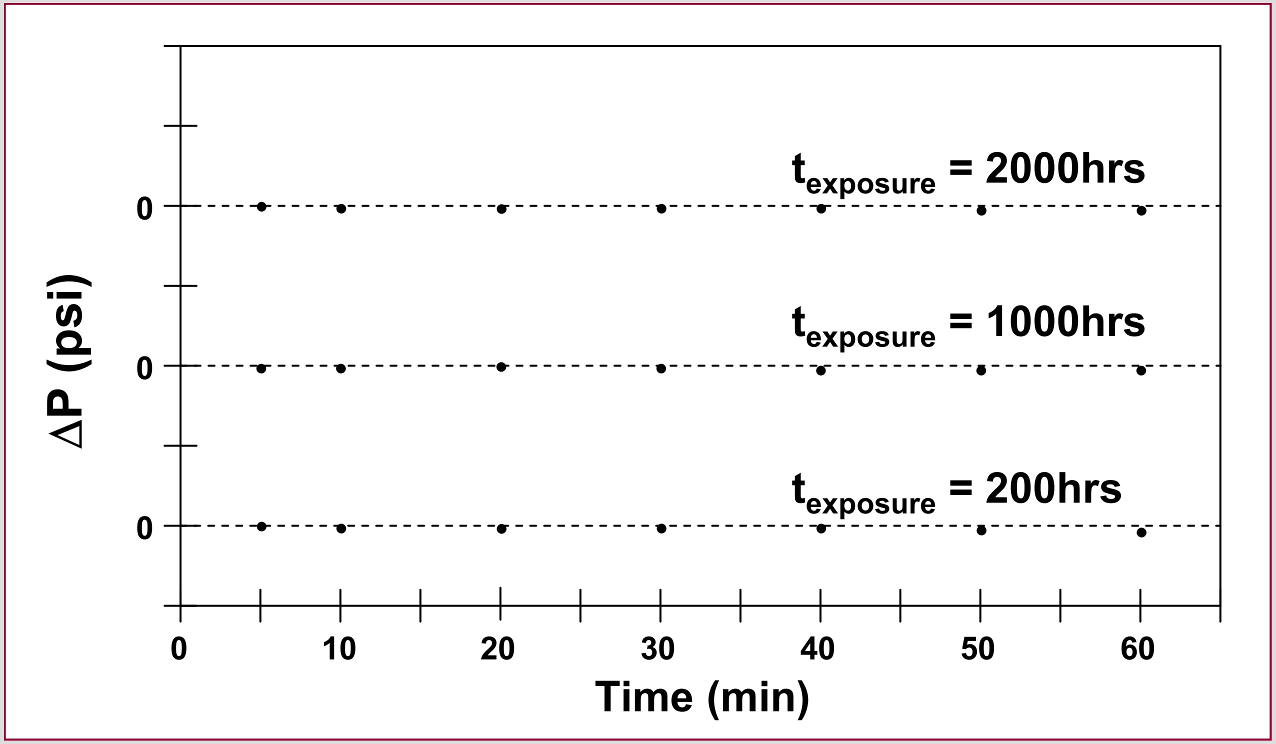
Ag8CuO brazed at 980°C; dual atm exposure at 800°C for 1000hrs

Type 1 Pore



Type 2 Pores

Seal hermeticity:



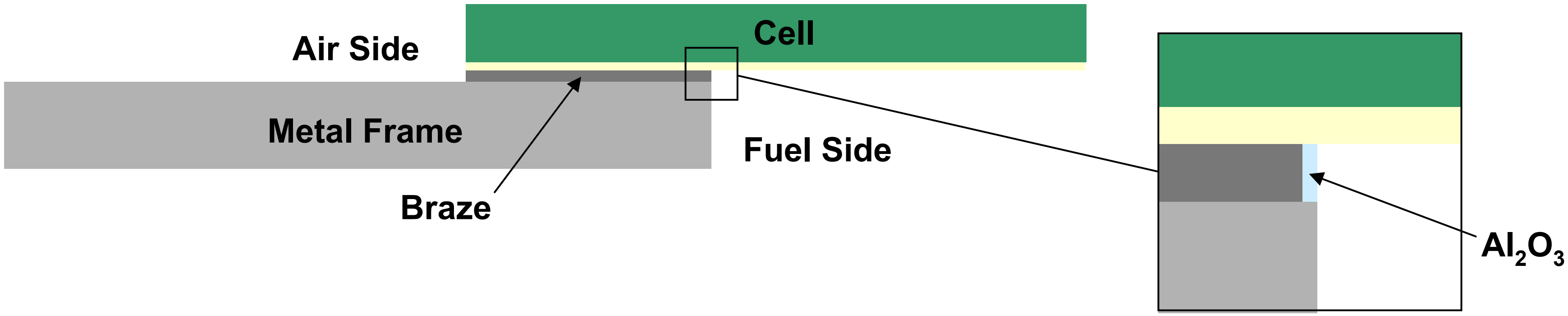
Progression of the Type 2 pore front appears to scale with $\sqrt{t}$.

Based on this, we can roughly extrapolate the lifetime of the seal:

$t_{95\%\ Degradation}$ **~ 5,200hrs at 800ºC and ~ 12,600hrs at 750ºC**

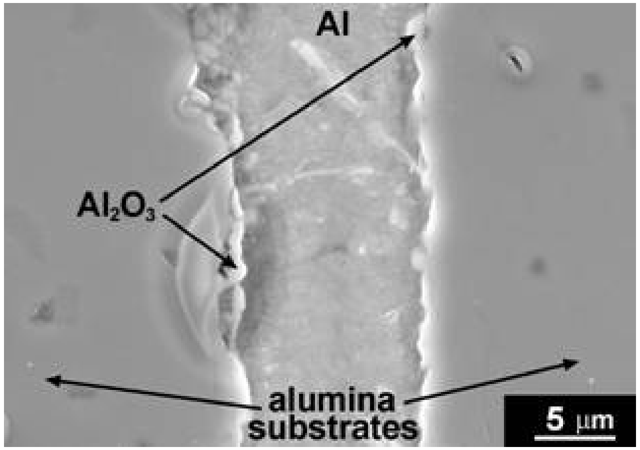
∴ standard filler metal needs to be modified for longer-term use

Concept: develop a passivation layer that inhibits H and O diffusion and eliminates pore Types 2 & 3



Prior work on $Al_2O_3/Al/Al_2O_3$ joining:

1000ºC, 10hr, Air:

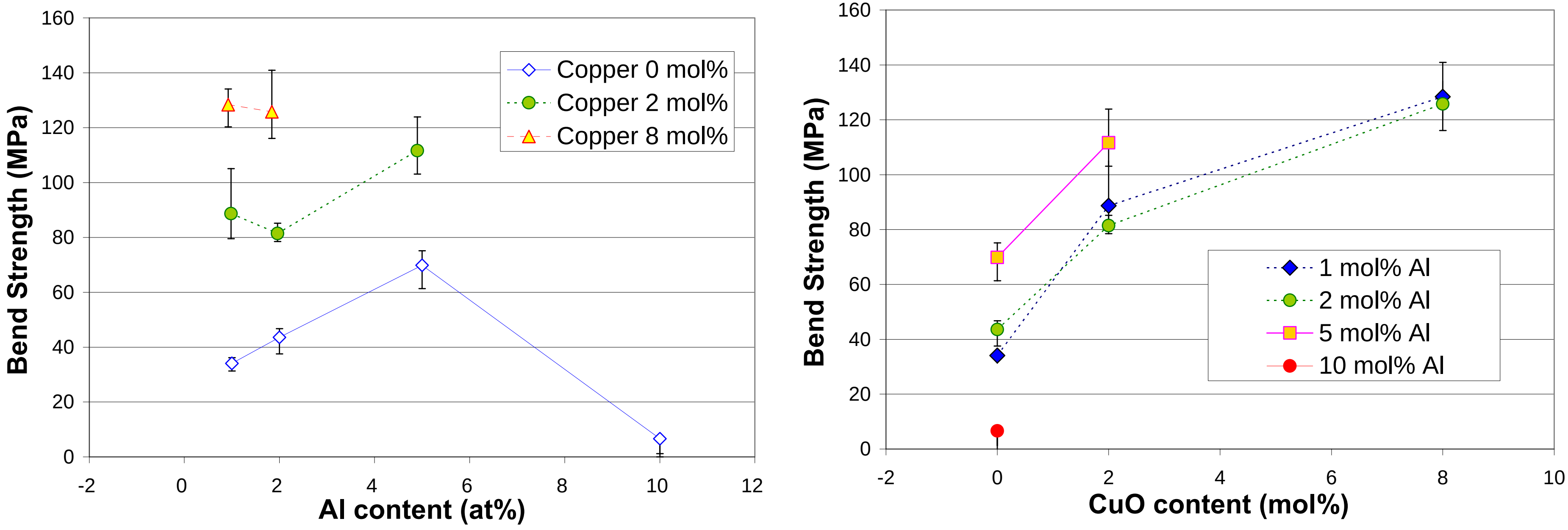


Forms an adherent Al_2O_3 scale that protects the underlying metal

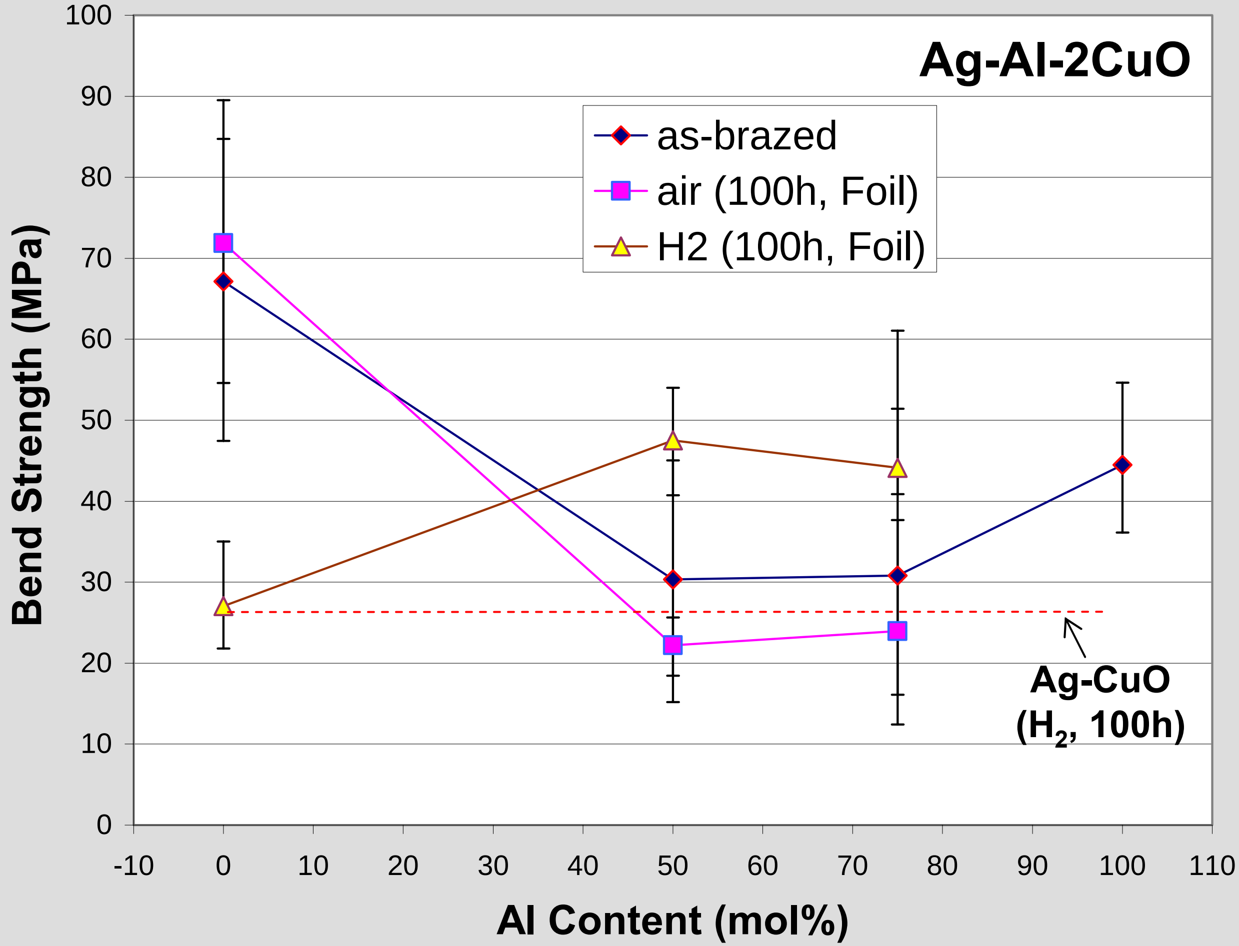
JY Kim, JS Hardy, and KS Weil, *J. Mater. Res.*, 19 (2004) 1717

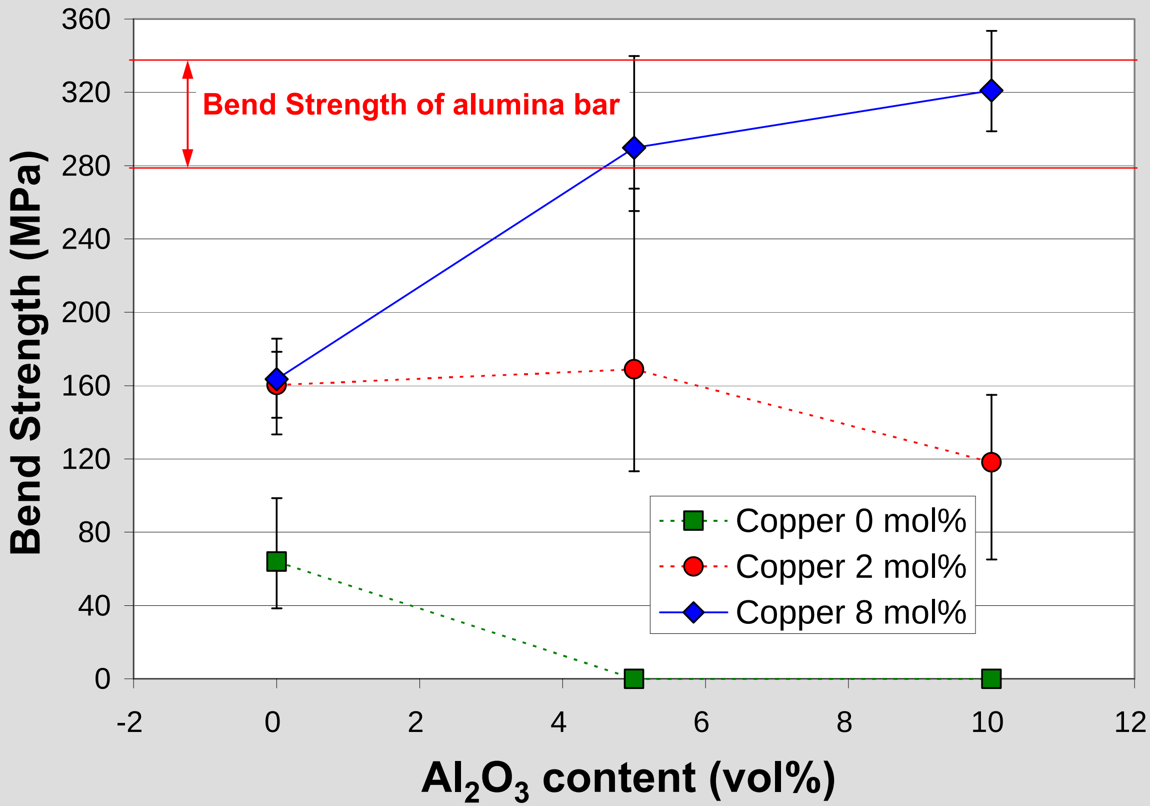
Ag-Al-(CuO) Filler Metal Alloys

- Started by fabricating Ag-Al binary compositions
- Observed adequate joining, but found poor joint strength
- Turned to the Ag-Al-CuO system



Observe improved strength after H_2 exposure

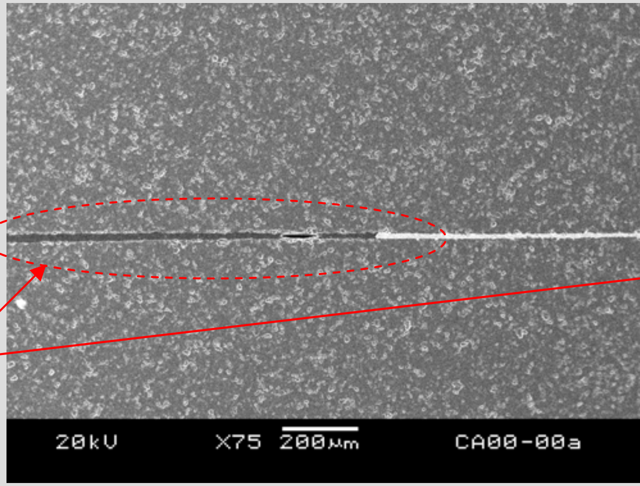




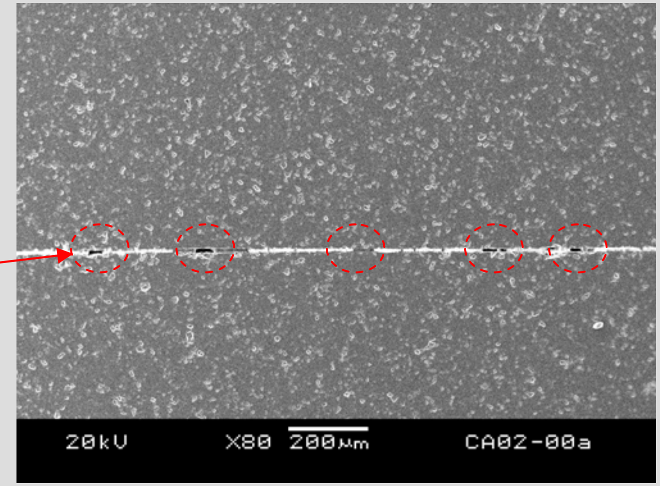
- **Alumina addition to high CuO content filler metals leads to a dramatic increase in bend strength.** ***The joints are as strong as the ceramic substrate!***
- **For no or low CuO, the alumina addition did not improve bend strength**

Al_2O_3-modified Ag-CuO Filler Metal

Ag-2CuO

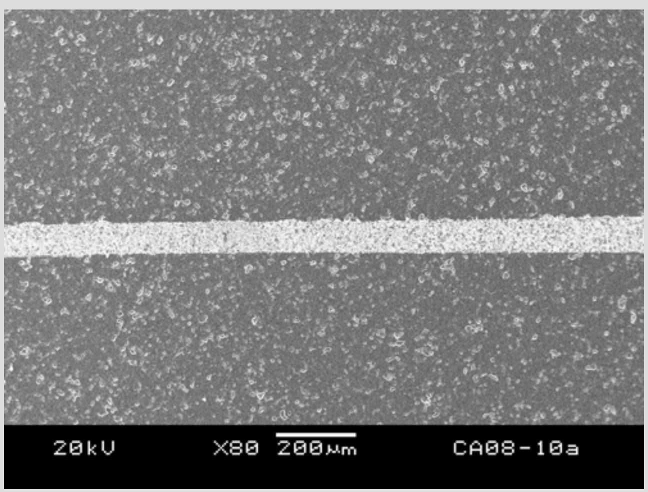


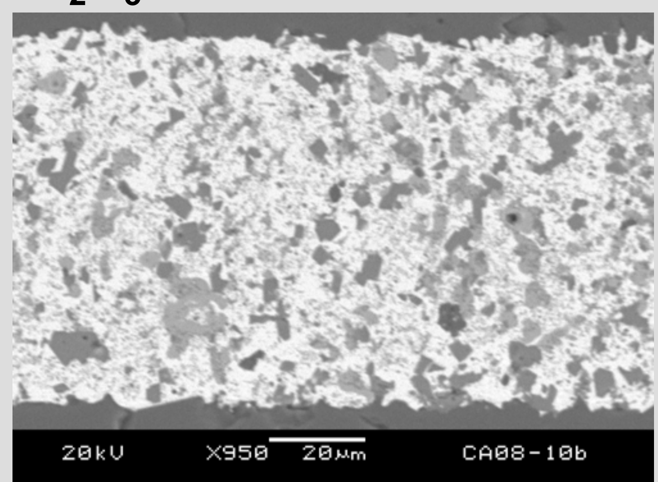
Ag-4CuO



Type 1 Pores

Ag-8CuO-10Al_2O_3





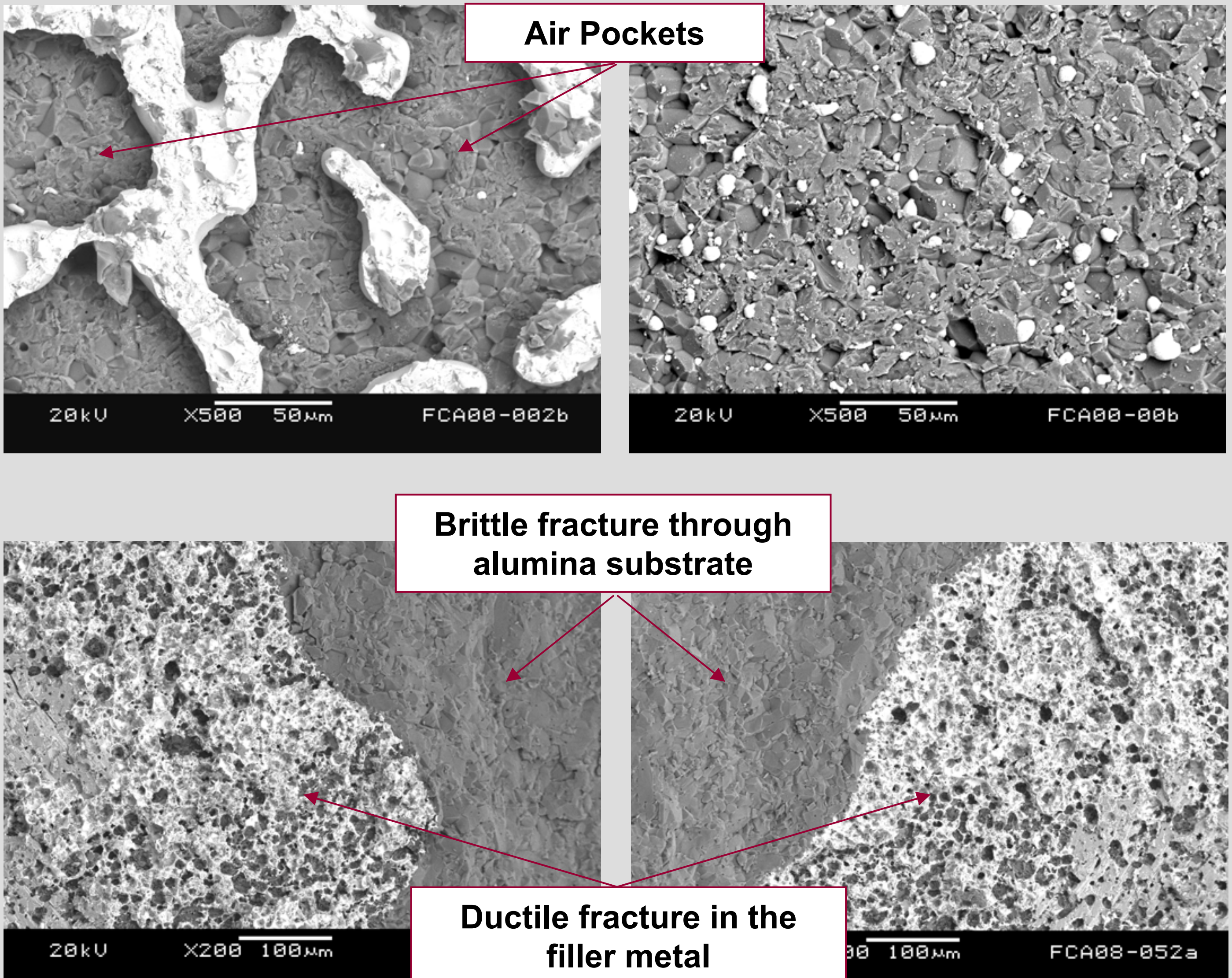
No squeeze out or porosity observed in the Al_2O_3-modified filler metals

Al_2O_3-modified Ag-CuO Filler Metal

Ag8CuO

0 vol% Al_2O_3

5 vol% Al_2O_3



- Have identified three types of pores that can form in Ag-CuO air brazed joints exposed to a high-temperature, dual atmosphere environment
  - Type 1 – air pockets formed during joining
  - Type 2 – micron-sized pores formed due to reduction of CuO ppts
  - Type 3 – pores formed along the matrix grain boundaries due to reaction between dissolved H and O (observed at ~2000hrs of exposure)
- The pores do not appear to be problematic in short-term testing (2000hrs or less)
- Can eliminate Type 1 pores using filler metals containing Al_2O_3 particulate and a high CuO content
- Preliminary testing indicates that Type 2 and possibly Type 3 pores can be eliminated by adding Al as an alloying agent

Next Steps

- Investigate the use of Al_2O_3 in combination with high CuO-containing Ag-Al-CuO filler metals as a means of achieving high strengths and mitigating dual atmosphere degradation
- Examine the mechanical properties of Ag-Al-CuO-Al_2O_3 brazed joints after single atmosphere exposure for $t_{exposure}$ < 1000hrs and compare with prior results obtained on bend specimens joined using the Ag-CuO, Ag-Al, and Ag-Al-CuO filler metals
- Conduct 1000+hr dual atmosphere exposure testing on tube specimens sealed using the Ag-Al-CuO-Al_2O_3 filler metals
- Conduct post-exposure hermeticity testing and metallographic analysis
- Carry out preliminary joining studies using prototypic SOFC materials

Acknowledgements

- John Hardy, Joe Rice, Jim Coleman, Nat Saenz, and Shelly Carlson

- Support: U. S. DOE, Office of Fossil Energy, SECA program

The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. DOE under Contract DE-AC06-76RLO 1830