Sandia National Laboratories

# Engineered Glass Composites for Sealing Solid Oxide Fuel Cells

Ronald Loehman, Mathieu Brochu, Bryan Gauntt, Raja Shah, Dale Zschiesche and Hans-Peter Dumm

Sandia National Laboratories
Albuquerque, NM USA

Richard Brow
University of Missouri-Rolla
Rolla, MO

SECA Core Technology Program Review , May 11 – May 13, 2004 Boston, USA

Supported by the U.S. Dept. of Energy under Contract DE-AC04-94AL85000

# Outline

- Composite approach to SOFC sealing
- Glass and composite properties
- Composites applied to different seal designs
- Demonstration of different seal properties
- Summary and conclusions

# Composite seals can be engineered to provide a wide range of chemical and mechanical properties

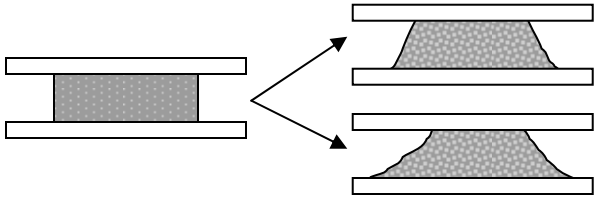
- Composite approach allows glass and filler to be optimized independently
- Glass phase is above its Tg at SOFC operating temperature to reduce thermal and mechanical strains
- Control viscosity, CTE, etc. by adding unreactive powder
- Volume fraction of glass phase can be reduced to minimum for seal

$$\alpha = \frac{\alpha_1 K_1 V_1 + \alpha_2 K_2 V_2}{K_1 V_1 + K_2 V_2}$$

$$\eta = \left( 1 + \frac{\kappa\phi}{1 - \left( \phi / \phi_{\max} \right)} \right)^2$$

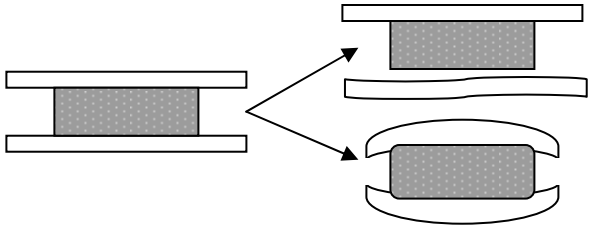
# Glass composites allow us to design for specific seal properties

## Viscosity

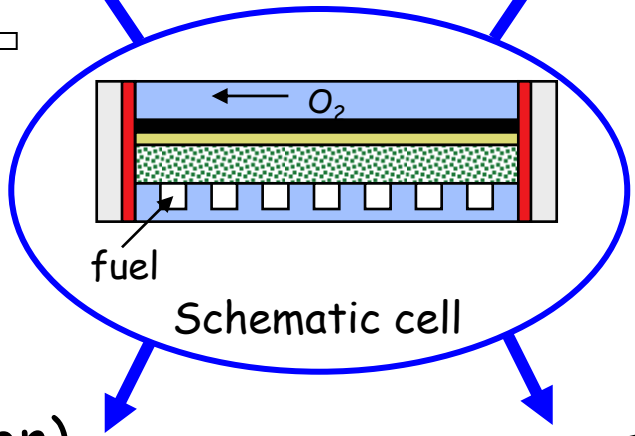


- Flow of glass composite
- Creep of seal

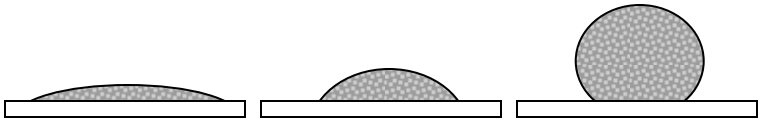
## Coefficient of thermal expansion



- Residual stresses
- Interfacial decohesion




## Wettability (adhesion)



- Contact angle
- Interfacial strength

anode
electrolyte
cathode
interconnect
manifold
sealant

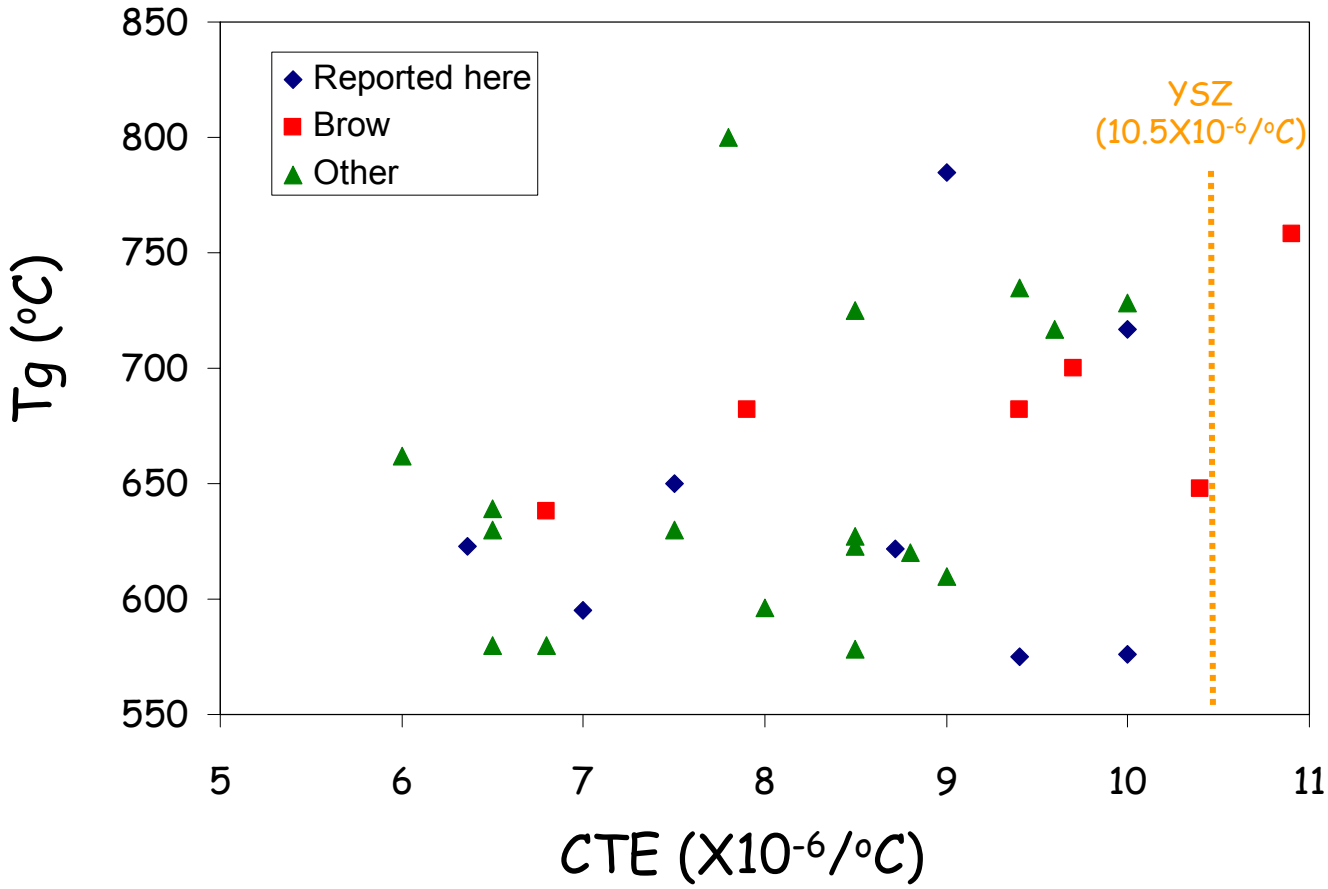
## Interfacial reaction


Sealing and high temp processes:
- Growth of interfacial rx layer
- Potential dissolution of additive
- Crystallization of glassy phase

# We are studying a wide variety of glass/powder additive composites

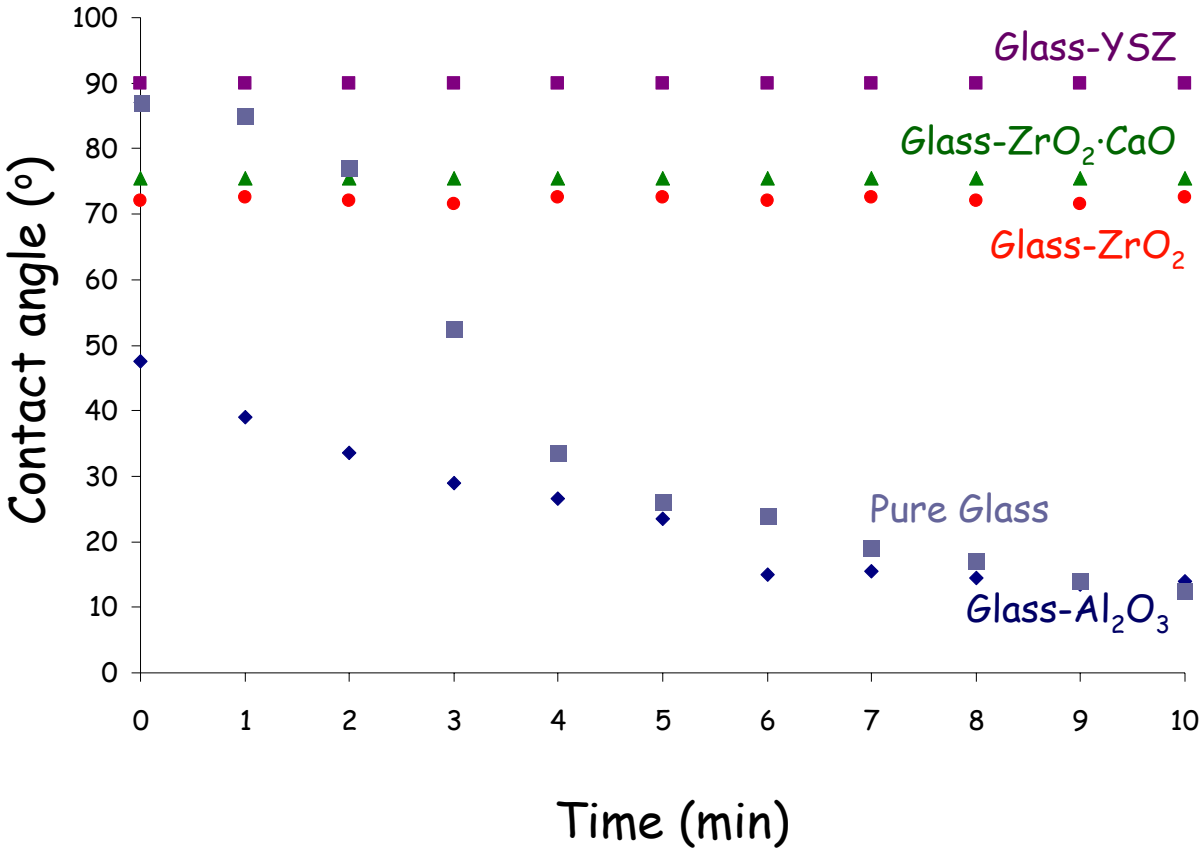
15 Glass compositions
5 Ceramic powders
3 Metallic powders
5 Particle sizes
2 Particle aspect ratios
7 Volume fractions of additive
6 Sealing temperatures

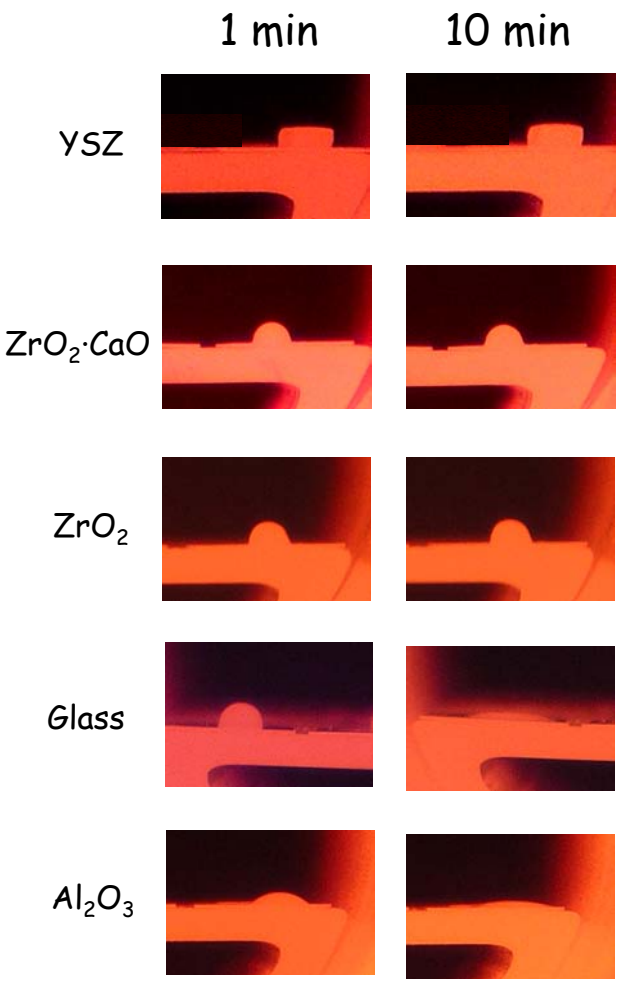
# We are considering glasses with a wide range of properties



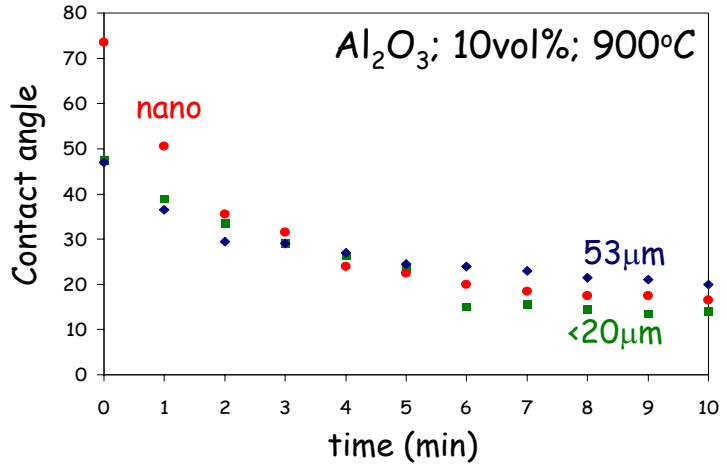
# Wetting and flow can be controlled by varying the ceramic powder additive

(Glass 14a; 900°C; 10vol%; powder<20μm)



# Glass composite viscosity varies with amount and size of filler particles



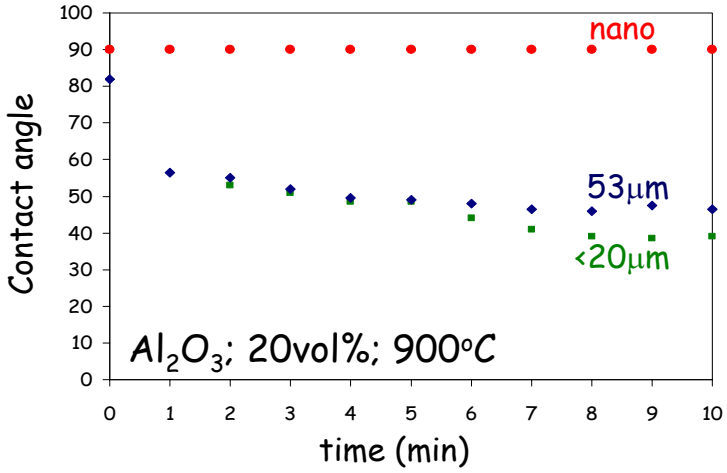

Viscosity increases with decreasing filler particle size and with increasing filler concentration

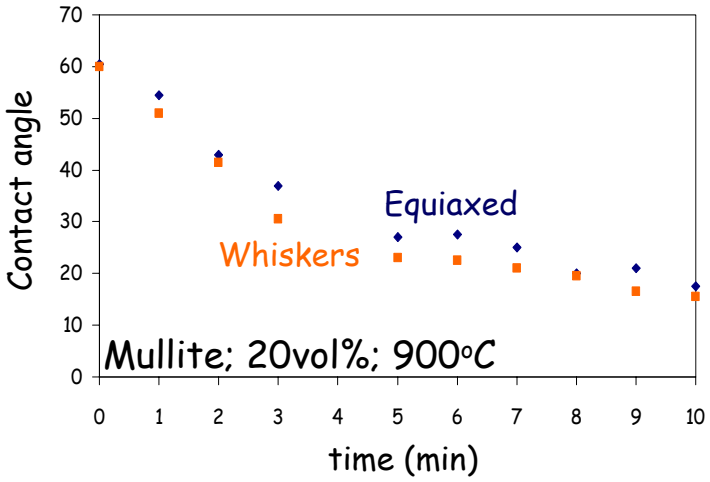
$$\eta = \left(1 + \frac{\kappa\phi}{1 - \left(\phi / \phi_{max}\right)}\right)^2$$

$K \alpha$ 1/particle size

$\phi\Phi$ = particle packing density

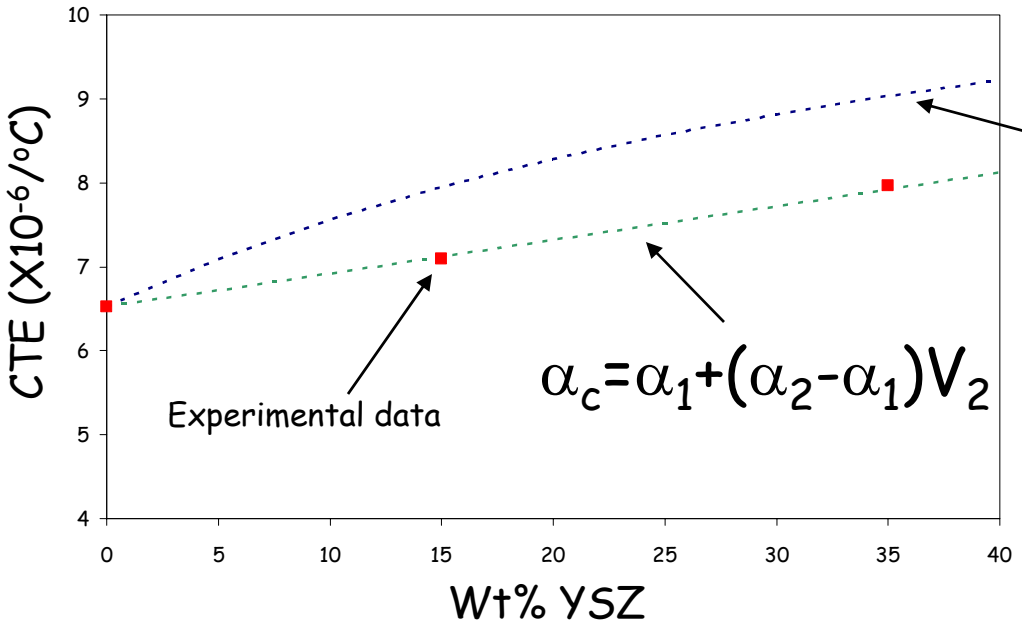
$\phi_{max}$ (volume fraction)



# Composite coefficient of thermal expansion varies with ceramic addition

## Composite CTE depends on individual CTE and modulus values



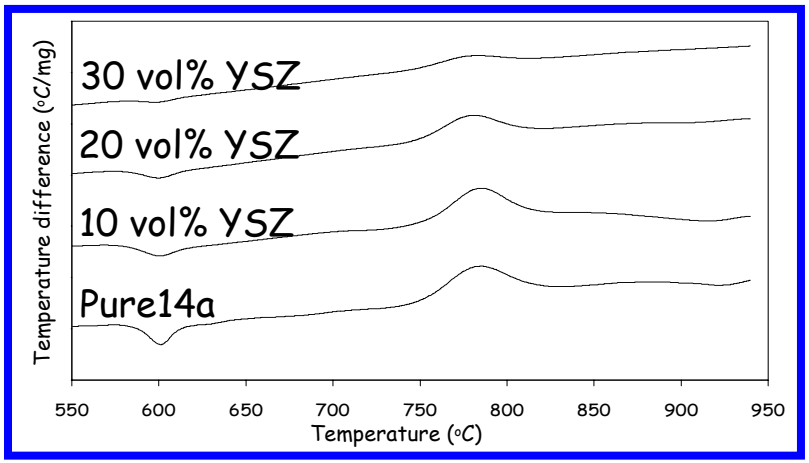

$$\alpha = \frac{\alpha_1 K_1 V_1 + \alpha_2 K_2 V_2}{K_1 V_1 + K_2 V_2}$$

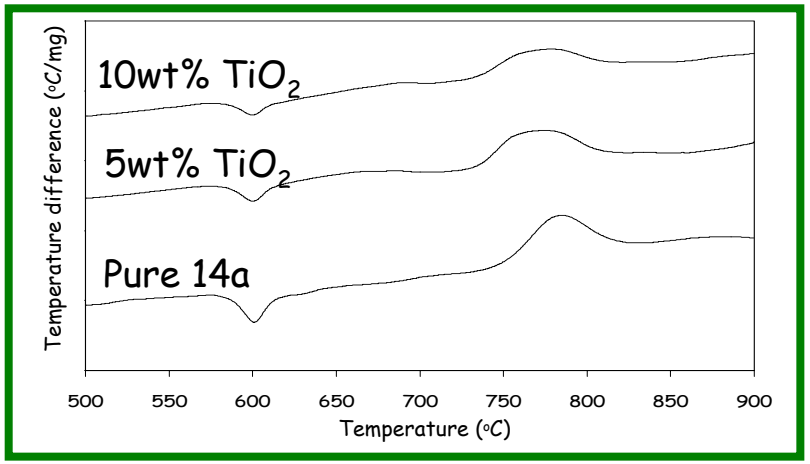
$K_i$ = Young modulus

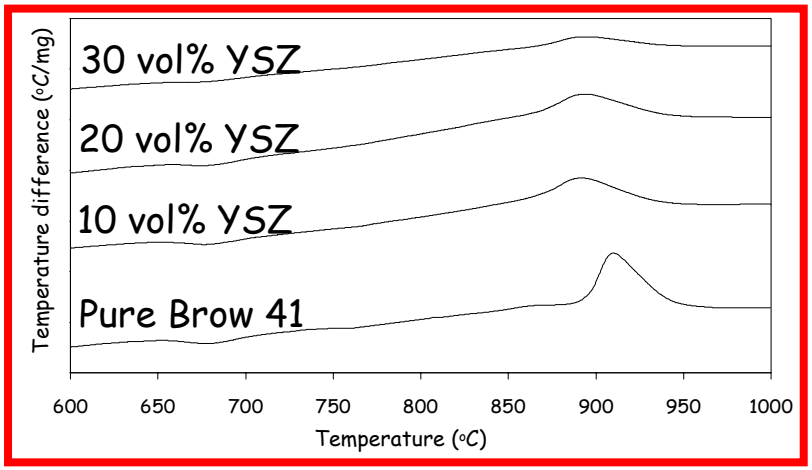
$V_i$ = volume fraction

In this case, a simple rule-of-mixture is a better fit

# Glass crystallization can be controlled by varying the glass and ceramic powder compositions



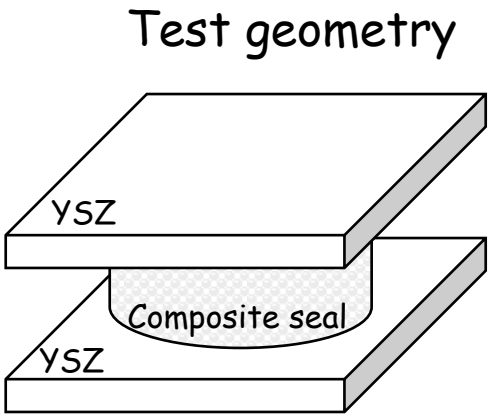

Glass systems:

· Crystallization is independent of reinforcement (glass 14a)

· Crystallization is dependant on reinforcement (glass Brow 41)

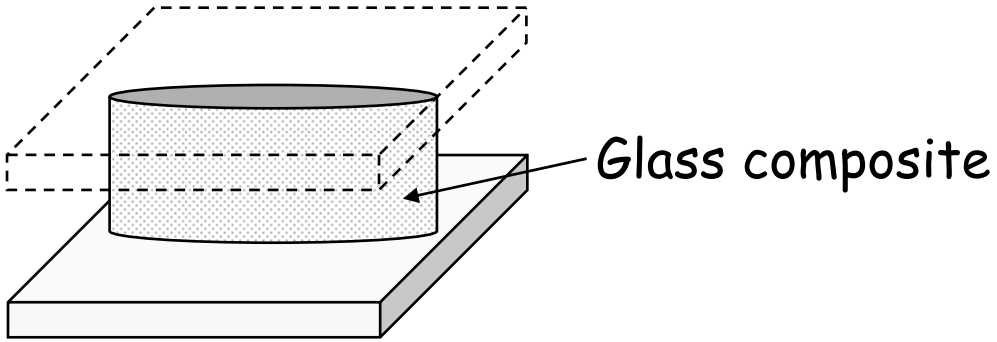
· Controlled crystallization of independent system (glass 14a + $TiO_2$)

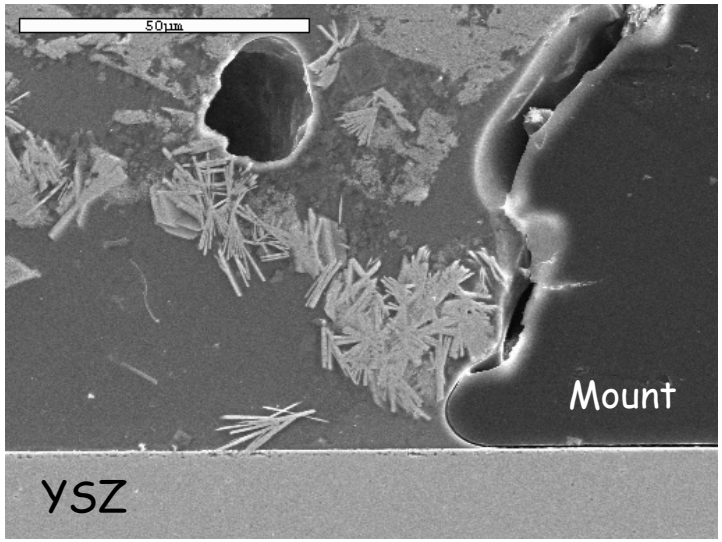
# Glass composites can be used to make a wide variety of different seal designs




- Basic glass composite seals
- Multi-layer seals
- Thermal shock resistant seals
- Glass/Metal Composite Seals
- Electrically conductive seals
- Thermal shock resistant and electrically conductive seals

# Example of basic glass composite seal with glass crystallization




Seal Characteristics

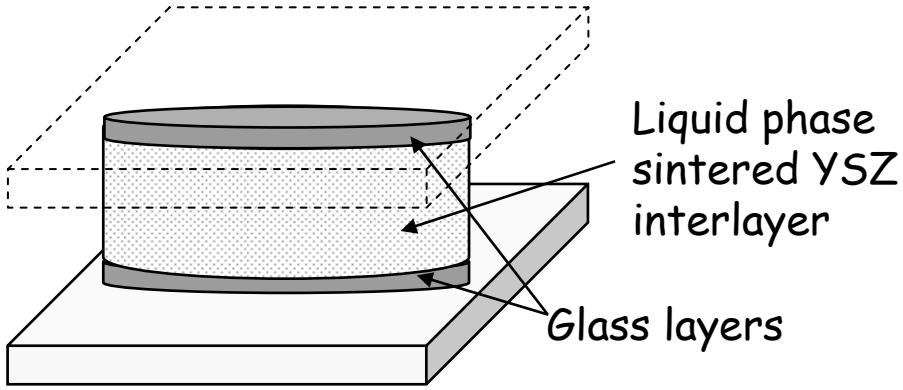
| | |
|---|---|
| $T_g$ | 575°C |
| Onset Cryst | 750°C |
| Max Cryst T | 810°C |
| Powder/ Vol% | YSZ / 30 |
| $CTE_{(200\text{-}550°C)}$ | $8.9 \times 10^{-6}/°C$ |

Sealing parameters

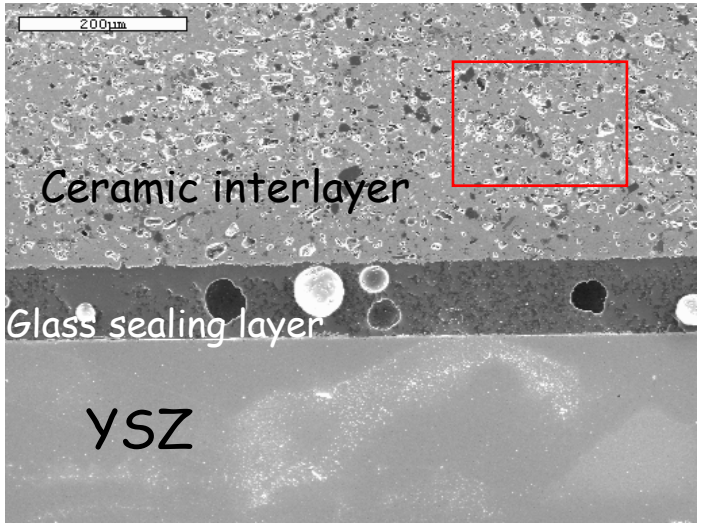
| | |
|---|---|
| Temp | 900°C |
| time | 10 min |

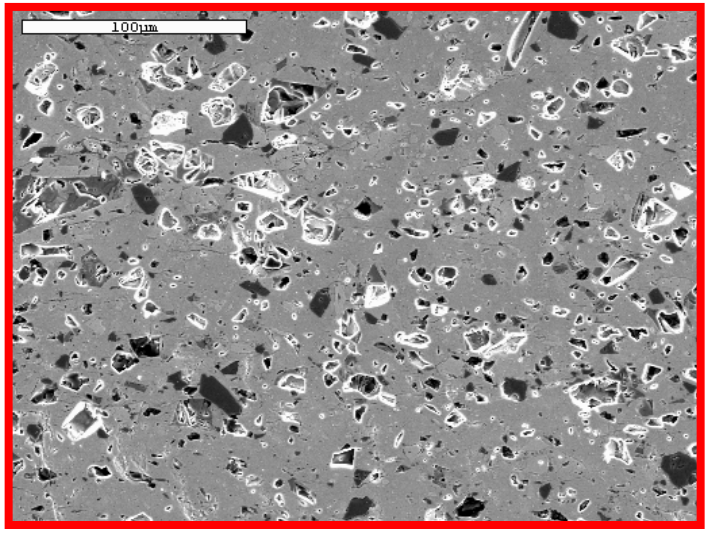
# Glass composites can be used to make multi layer seals

Concept: reduce sealing glass to thin interfacial layer



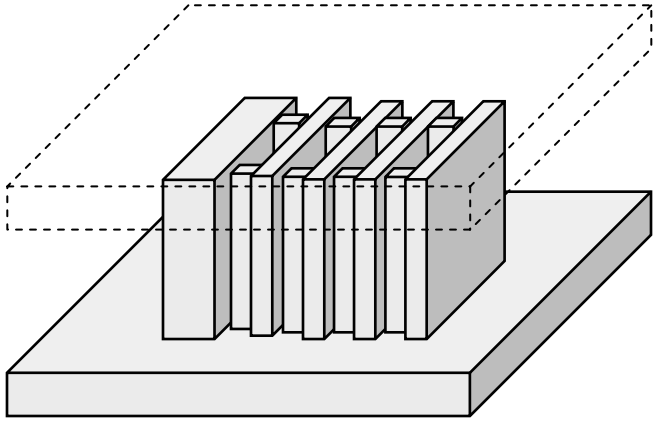

- Ceramic: 70 vol% YSZ
- Glass: Tg=703°C , CTE = 9.7x10$^{-6}$/°C
- Composite CTE = 10.2x10$^{-6}$/°C (200-700°C)

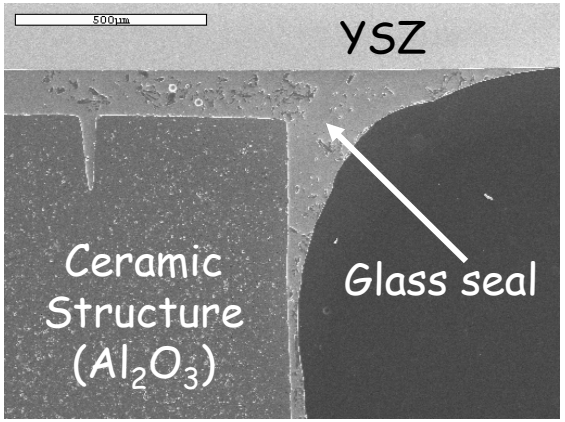


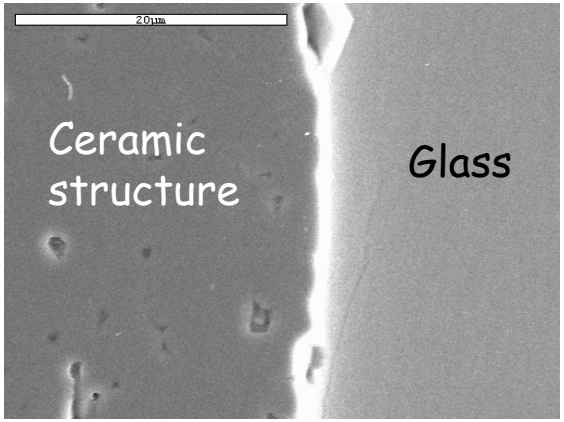



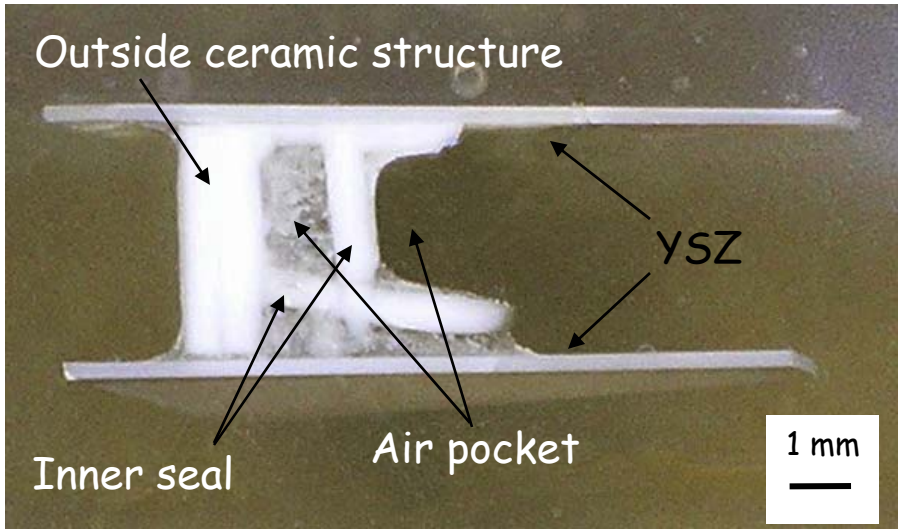

Ceramic interlayer:
70vol% YSZ – 30vol% Glass
Note: no pressure applied

# Robocast cellular structure proposed to make thermal shock resistant seals



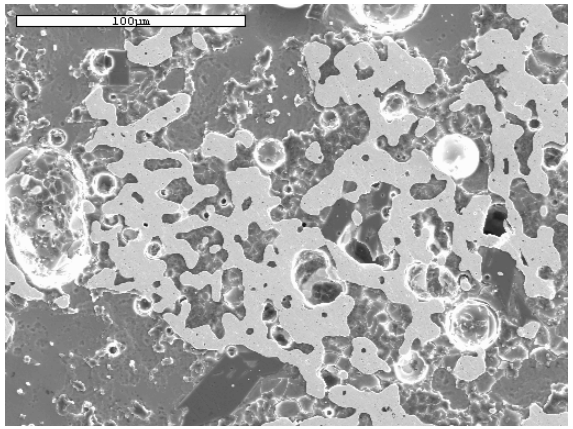


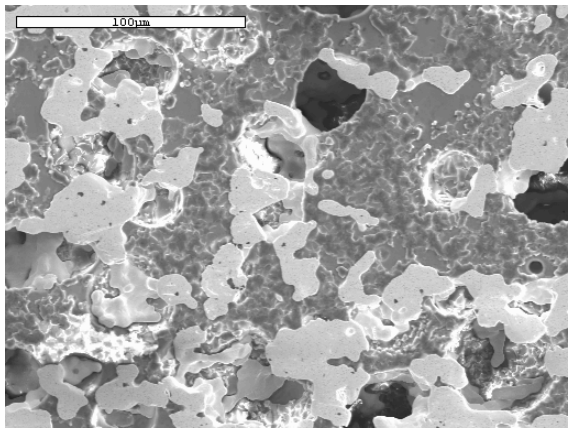




- Cellular ceramic structure provides strength and some compliance
- Compatible glass coating provides seal

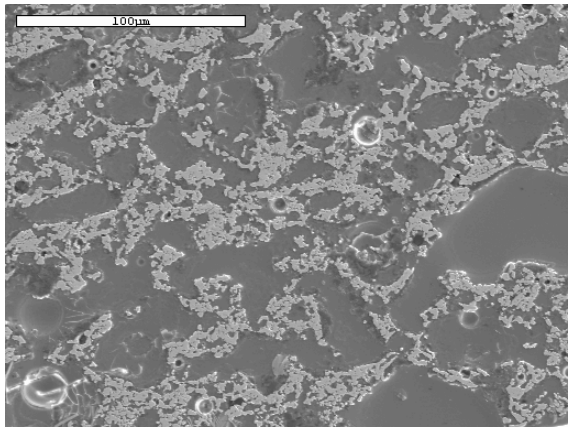
# Glass-metal composite seals can provide electrical connectivity




14a-20vol% Ag
0.5-1.0 µm



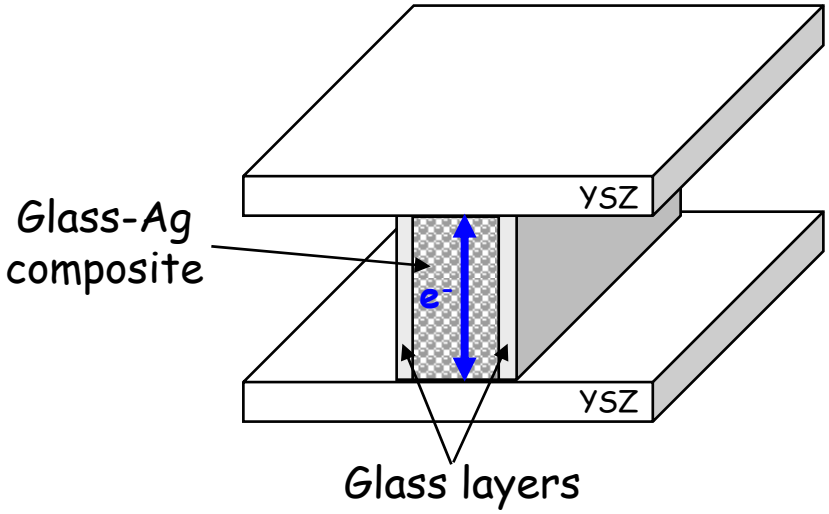

14a-20vol% Au
5.5-9.0 µm




14a-20vol% Pd
0.5-1.7 µm

- Percolating network obtained for all metallic additives
- Some dissolution of Ag in glass matrix (EDS analysis)
- No dissolution of Au or Pd in glass matrix (EDS analysis)

# Glass-Ag composites make electrically conductive seals

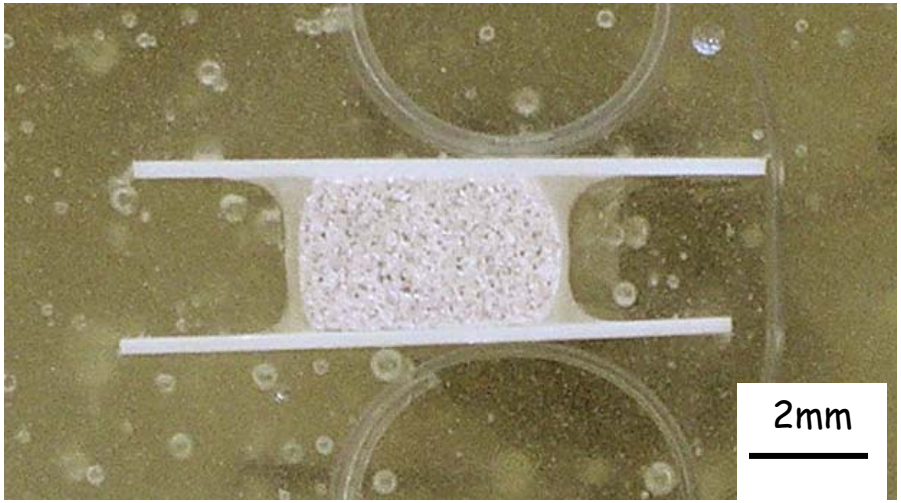


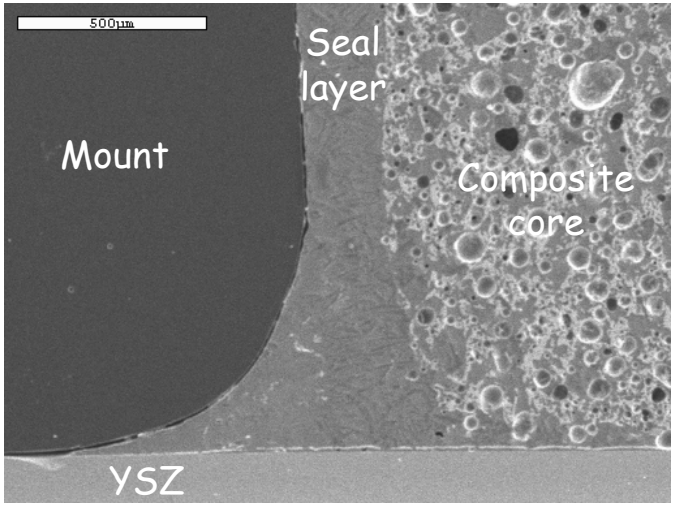

Electrical resistance measurement



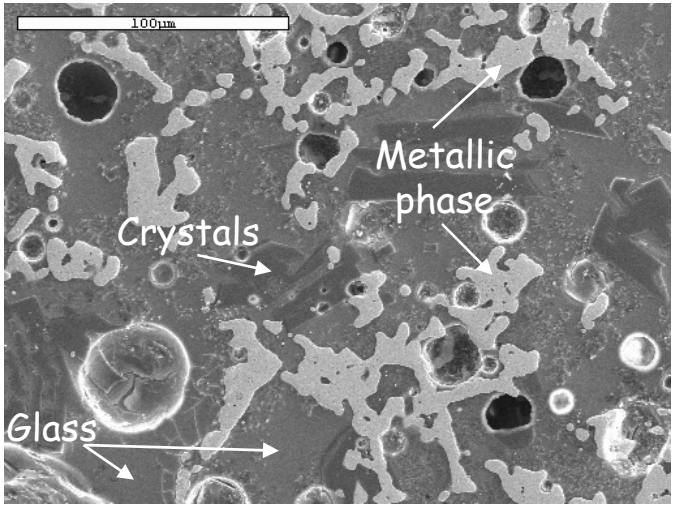
- Vol fraction of metallic phase slightly above the percolation limit
- Glass wets and coats metal to make composite and to provide seal
- Metal encapsulated by glass on exterior

# Micrograph shows electrically conductive seal with glass 14a-Ag composite

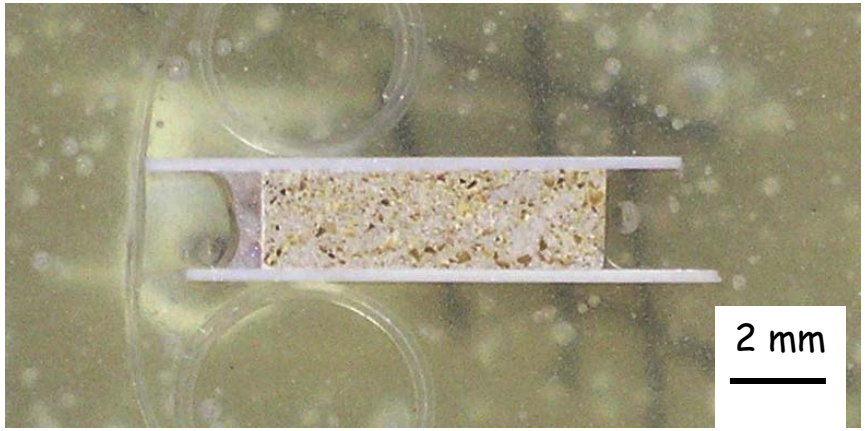


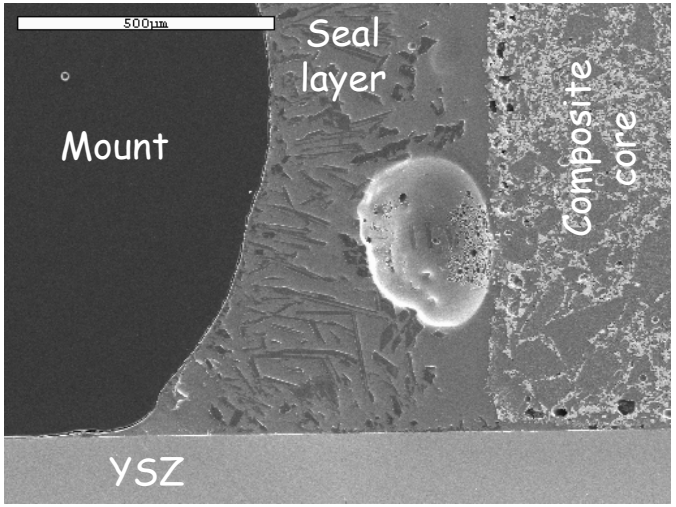



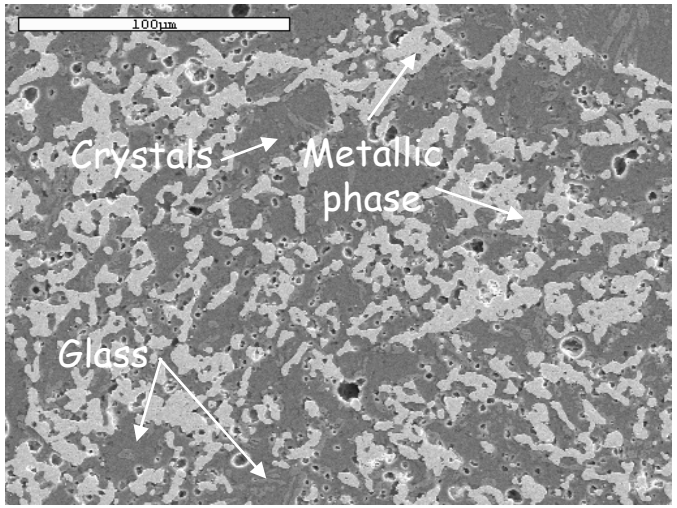

- Glass: Tg=575°C , CTE=9.4X10$^{-6}$/°C
- Filler metal: 20 vol% Ag
- Composite: Tg=566°C, CTE=10.5X10$^{-6}$/°C
- Resistance: <0.1 ohm



# Micrograph shows electrically conductive seal with Brow 37 glass-Ag composite

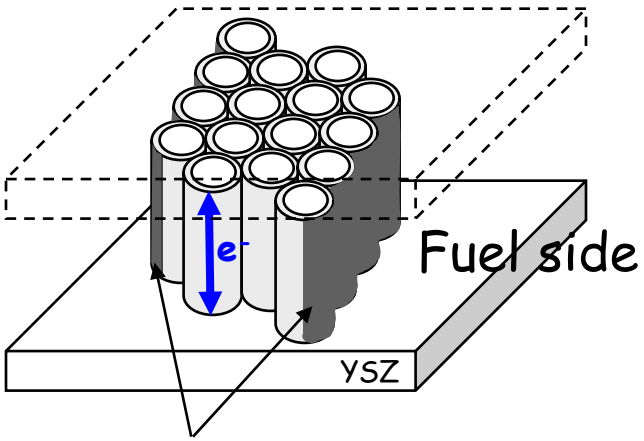


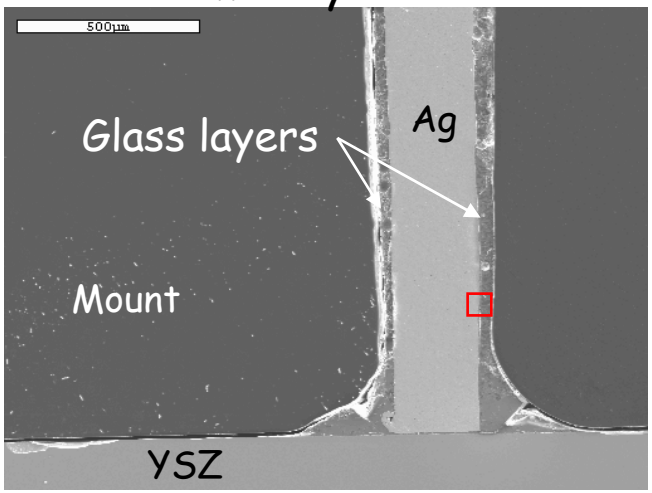

- Glass: Tg=620°C , CTE=6.8x10$^{-6}$/°C
- Filler metal: 20 vol% Ag
- Composite: Tg=582°C, CTE=9.1x10$^{-6}$/°C
- Resistance: <0.1ohm

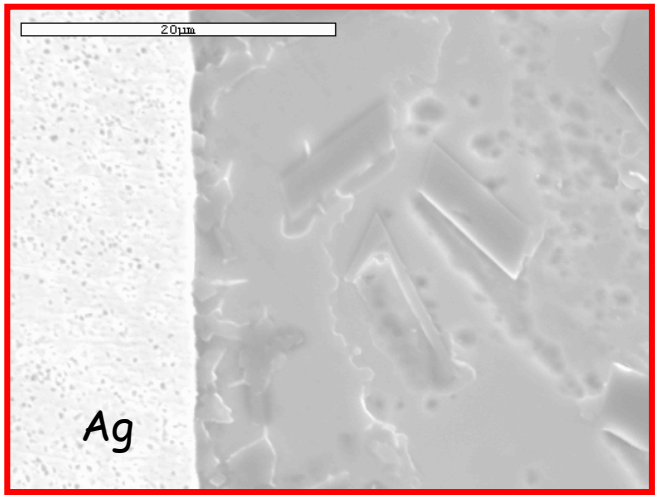
# Electrical Conductive Seal with high thermal shock resistance




Glass seal layers

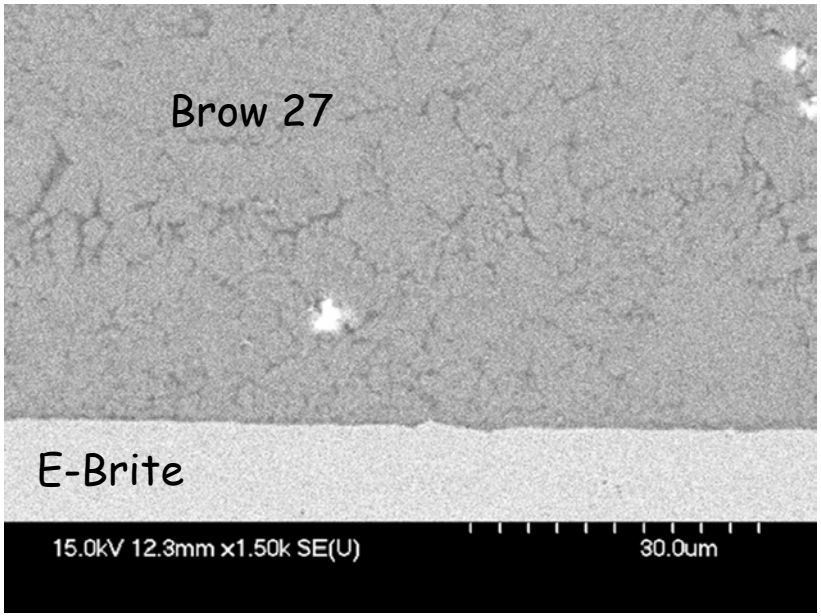
Preliminary results




Tubular metallic structure provides electrical conductivity and may provide some compliance that will increase thermal shock resistance

# Work by R. Brow shows his glass 27 is compatible with E-brite alloy




Exposure for 96 hours at 750°C

# Work in Progress

- Analyzing interfacial reactions
- Thermal cycling and long time exposure at service temperature (environmental exposure)
- Mechanical testing of composite seal materials
- Mechanical testing of seal adhesion on YSZ substrates
- Development of seals on alloys such as E-brite

# Conclusions

- Glass and crystalline compositions can be optimized independently
- Glass composites allow a wide range of properties and seal designs
- Composite approach seems very promising for sealing SOFCs
- We are ready to try to adapt this approach to specific vertical team needs

# Your research team