High Temperature Glass Seal

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Outline

- Accomplishment of FY07
- Mechanical strength evaluation: plain crofer, aluminized, spinel-coated
- Electrical stability evaluation: aging under DC loading
- Summary
- Future work
FY07 Accomplishment

- Completed seal strength evaluation of high-temperature glass. Evaluated pre-oxidation, aging, coating, and environmental effects on strength.
- Without coating, strength would degrade if a thick Cr$_2$O$_3$ oxide layer present or aged in air. No strength reduction if aged in reducing gas. Cause for strength degradation was SrCrO$_4$ formation.
- Alumina coating is effective in blocking Cr; however, the deposition process needs to be optimized to minimize overdose.
- Spinel coating showed best results with minimum strength reduction even aging in air.
- Tested conventional and high-temperature sealing glasses in SOFC environment and 0.7 V DC loading. Conventional glass showed severe Fe diffusion and rapid increase in conductivity (830°C/∼80hr), while high-temperature glass showed excellent electrical stability over ∼1200hr at 850°C.
High-temperature sealing glass

1. Increase contact bonding strength
2. Increase thermal stability
3. Decrease interfacial reactions
Mechanical strength evaluation

1. Effect of pre-oxidation: Cr$_2$O$_3$ layer thickness
2. Effect of different protective coating: Al$_2$O$_3$, (Mn,Co)$_3$O$_4$
3. Effect of environment: oxidizing, reducing
4. Accelerated condition:
   - 850$^\circ$C/500h in air
   - 850$^\circ$C/250h in 30%H$_2$O, 70%(2.7%H$_2$/Ar)
Interfacial tensile testing

- R. T.
- 0.5 mm/min cross-head speed
- 5-7 samples tested for each condition
- Self-aligned grip fixture
- ½”x½” sample size
Pre-oxidized crofer

To mimic long-term oxidation
1200°C resulted in pores underneath
Outside discrete and non-uniform (Mn,Cr) oxide, inside dense and continuous Cr₂O₃-rich oxide
T<0.5μm (800°C/2h)
Effect of pre-oxidation on tensile strength

crofer/YSO75, pst/crofer, 1/2"x1/2" at RT

average tensile strength, MPa

<table>
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<tr>
<th>Condition</th>
<th>Tensile Strength</th>
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<tr>
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<td>1000C/2h</td>
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<td>1200C/2h</td>
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pre-oxidation conditions

<0.5 μm
~1-2 μm
~6-10 μm
Load-displacement curve showed typical brittle failure

All showed brittle failure: coating, aging, oxide layer thickness, environment
Mixed fracture

As-received

1000°C/2h
Pre-oxidized
Fracture initiated mostly from edge flaws
Effect of aging and environment

Air: 850°C/500h
Wet and reducing: 30%H₂O, 70%(2.7H₂/Ar) 850°C/250h

![Bar graph showing the effect of aging on strength, crofer/YSO75/crofer, 1/2"x1/2"

- no aging
- 850C/500h air aged
- 850C/250h red.aged

average tensile strength, MPa

0 1 2 3 4 5 6 7 8 9 10

effect of aging on strength, crofer/YSO75/crofer, 1/2"x1/2"
Fracture surface of aged sample

Presence of substantial amount of SrCrO$_4$
Aluminized crofer showed no chromate formation.

Plain crofer

Aluminized crofer

SrCrO₄
**Tensile strength of aluminized crofer from pack cementation**

Pack cementation, followed by heat-treatment in air

![Graph showing RT average strength, MPa](image)

- **None**
- **1000°C/2h**
- **1200°C/2h**

**Oxidation conditions**

- **RT average strength, MPa**
- **Average strength, MPa**
- **None**
- **1000°C/2h**
- **1200°C/2h**
Sealing with aluminized crofer from vapor phase deposition

Vapor phase deposition followed by heat-treatment at 1000°C/2h air
As-sealed coupons all fractured through glass.
Glass bonded well to aluminized crofer coupons.
Appreciable amount of Al diffusion
Issue of overdosing Al

Aluminizing by vapor phase deposition followed by heat-treatment at 1000-1100°C/2h air
RT seal strength of spinel-coated crofer/YSO75 glass

$(\text{Mn,Co})_3\text{O}_4$ coated crofer22APU

![RT average tensile strength (spinel coating)](image-url)
Fracture surface of as-sealed Mn$_{1.5}$Co$_{1.5}$O$_4$-coated crofer22APU

Fracture through glass, not at the interface. YSO75 not fully coverage
All 8 samples showed edge flaw
Fracture surface of air aged Mn$_{1.5}$Co$_{1.5}$O$_4$-coated crofer22APU

850°C/500 h air

Suggest 5 μm coating was not enough
Setup for resistivity measurement

Compressive loading

Inconel pressing fixture

Fuel side

Crofer

Glass

Air side

Alumina support pipe

Hybrid mica seal

Power supply

Resistor

Sense

Output

+  

-  

+  

-  

+  

-  

+  

-  

V
Good electrical stability for HT glass on plain crofer22APU

Crofer(as-received)/glass/crofer(as-received) @ 0.7V

YSO75 @ 0.7V & 20% H2O, 2.7% H2/Ar (t<432hrs), 80% H2 (t>432hrs)
power outage @ ~700 h

YSO75 @ 850°C

G18 @ 830°C
EDS showed substantial Fe diffusion

G18 near air side after electrical stability test

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Good electrical stability for HT glass on (Mn,Co)$_3$O$_4$-coated crofer22APU

YSO75 spinel coated 0.7V (30%H2O, 70% (2.7%H2/Ar))

![Graph showing electrical stability over time at 850°C](image)
Materials set evaluation in 2”x2” single cell test @ 800°C

INDEC cell, SS441, spinel coating, LSM contact paste, aluminizing

SS441, YSO77x1, spinel, LSM, H-micax4, 97%H₂ 450 sccm, air 900 sccm

Power density, W/cm²
Mechanical strength tests of M/G/M coupons showed strength degradation for uncoated crofer22APU only if aged in air or started with thick Cr$_2$O$_3$ surface layer.

Aluminizing is effective in blocking Cr; however, overdosing would increase CTE for thin samples and leads to seal failure.

(Mn,Co)$_3$O$_4$-coated crofer showed similar initial seal strength as plain crofer or aluminized ones. Minimal strength degradation when aged in air.

HT glass showed very good electrical stability in SOFC and DC loading at 850°C up to ~1200h.

Successful demonstration of 2”x2” single cell test at 800°C with candidate materials set: HT glass, spinel coating, SS441, and LSM contact paste.
Future work

Materials set validation with single cell (2”x2”) stack testing and standardize the design:

1. Sealing glass: high-temperature, self-healing and composite.
2. Metallic interconnect: SS441 (standard or low Si), crofer22APU
3. Protective coating: (Mn,Co)₃O₄, alumina

- Short-term (200-500h) performance test at 800-850°C
- Short-term thermal cycling test (800°C/24h, cool to RT)x10

- Collaboration with modeling work
- Strengthening of candidate high-temperature glass with reinforcement