High-Temperature Viscous Sealing Glasses for Solid Oxide Fuel Cells

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Sealing Glasses: SOFCs, Aerospace

Specialty Glasses for New Applications

RadSpheres  Commercial Blood-Typing Cards  DermaFuse
Why consider a viscous glass seal for an SOFC?

- Potential for *lower thermal stresses* through viscous relaxation at operational temperatures
  - Less critical that seal has CTE match to dissimilar materials

- Potential for ‘re-sealing’ at operational temperatures through viscous flow
Objectives

➢ Develop glass compositions that exhibit stable thermomechanical/thermochemical properties, including viscosity, for use as seals for SOFCs

  Requisite Thermal and Physical Properties
  a) Long-term stability in viscosity (650-850°C)
  b) $T_g$: < 650°C: thermal stress will be relieved
  b) $T_{soft}$: < 650°C: requisite flow for re-sealing behavior
  c) $T_{Liq}$: < 800°C (as low as possible): stable, a small volume fraction of crystals
  d) $CTE(RT-subT_g)$: 10-12.5 x 10^{-6}/°C (YSZ- SS441)

➢ Conduct hermetic sealing tests

  SOFC Materials
  a) Aluminized SS441
  b) NiO-YSZ supported YSZ electrolyte bilayers
  Supplied by PNNL

➢ Characterize thermochemical reactions

  a) Volatilization of glass components
  b) Interfacial reactions with SOFC components
Promising compositions were identified

➢ To date, prepared a total of >90 compositions (including Phase I) and measured properties ($T_g$, $T_s$, $T_{Liq}$, and CTE) of all of the compositions

➢ Preferred Compositions Exhibit Promising Sealing Behavior

<table>
<thead>
<tr>
<th></th>
<th>Glass 2</th>
<th>Glass 4</th>
<th>Glass 28</th>
<th>Glass 73</th>
<th>Glass 75</th>
<th>Glass 77</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass system</td>
<td>BaO-B$_2$O$_3$-SiO$_2$</td>
<td>BaO-RO-Al$_2$O$_3$-B$_2$O$_3$</td>
<td>BaO-RO-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_g$ (°C) measured from CTE curve</td>
<td>619</td>
<td>599</td>
<td>581</td>
<td>624</td>
<td>623</td>
<td>625</td>
</tr>
<tr>
<td>Dilatometric $T_s$ (°C)</td>
<td>650</td>
<td>632</td>
<td>615</td>
<td>640</td>
<td>650</td>
<td>656</td>
</tr>
<tr>
<td>CTE 40-500°C (/°C)</td>
<td>8.19x10^{-6}</td>
<td>7.32x10^{-6}</td>
<td>7.48x10^{-6}</td>
<td>8.48x10^{-6}</td>
<td>8.17x10^{-6}</td>
<td>9.25x10^{-6}</td>
</tr>
<tr>
<td>Liquidus T (°C)</td>
<td>805</td>
<td>790</td>
<td>795</td>
<td>800</td>
<td>810</td>
<td>810</td>
</tr>
</tbody>
</table>
DSC Analysis

- Differential Scanning Calorimetry (DSC) Reveals That The Candidate Sealing Glasses Do Not Readily Crystallize
  - No Crystallization Peaks Up to 1000°C
  - Similar results were found for other candidate compositions
Liquidus Temperature

- Liquidus Temperature (ASTM C829-81), 72 hours in a gradient furnace

- Glass 73: Clear Glass
  - Liquidus Temperature: 800±10°C

- Slightly Cloudy Glass

- Glass 75: 810±10°C

- Glass 77: Liquidus Temperature as low as possible
  - Liquidus Temperature: 810±10°C

Liquidus Temperature as low as possible
Stable Viscosity

Viscosity measurements provide valuable performance information

- High temperature measurements (1-10⁴ Pa-s) by the rotating spindle technique
- Low temperature measurements (10⁵-10¹¹ Pa-s) by the parallel plate technique
- Viscosity-temperature curves fit using the Corning viscosity model (JC Mauro, PNAS, 2009)

Long-term viscosity measurements in progress

<table>
<thead>
<tr>
<th>Glass</th>
<th>Fitting Parameters</th>
<th>(T_g) (°C)</th>
<th>Isokom (T(°C), \log(\eta)) (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m)</td>
<td>(T_g) (°C)</td>
<td>Dilatometric</td>
</tr>
<tr>
<td>Glass 73 as-cast</td>
<td>48.46</td>
<td>610</td>
<td>624</td>
</tr>
<tr>
<td>Glass 73 500hr at 800°C in air</td>
<td>39.54</td>
<td>598</td>
<td>Not Measured</td>
</tr>
</tbody>
</table>
Flowing Wet Forming Gas (5%H₂ 95%N₂)

Glass 73 Weight Loss at 750°C in Flowing Wet Forming Gas

Stagnant Dry Air

Glass 73 Weight Loss at 750°C in Stagnant Dry Air

**Weight Loss estimated for 40,000 hrs**

<table>
<thead>
<tr>
<th>Test Condition at 750°C</th>
<th>Volatility Rate (g/mm²/hr)</th>
<th>Total Weight Loss (%) at 40,000 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowing wet forming gas</td>
<td>2.0×10⁻⁸</td>
<td>4.5</td>
</tr>
<tr>
<td>Stagnant dry air</td>
<td>1.7×10⁻⁸</td>
<td>1.9</td>
</tr>
</tbody>
</table>
Hermetic Sealing Tests

Schematic seal performance test system

Sandwich sample:

- Glass pastes were made from powders (-45 µm) mixed with a solution of PVB binder and acetone, and used to bond NiO/YSZ bi-layer to aluminized steel (SS441) substrate (materials from PNNL)

- Sandwich seals fired in air at 850°C for 8 hours
Glass 73 seal has survived 100 thermal cycles (750°C to RT) in dry air at a differential pressure of 0.5 psi (26 torr) over the course of > 3,300 hours without failure and the test was deliberately terminated for analysis.
To date, Glass 73 seal has survived **81 thermal cycles (750°C to RT)** under **wet forming gas** at a differential pressure of 0.5 psi (26 torr) over the course of **> 2,800 hours** without failure and the test continues.
Re-Sealing Tests

- Tried to break a seal by fast cooling as possible in the furnace, but no seal failure
- Glass 73-Coupon A: No seal failure up to 15 psi, 850°C

![Graph showing temperature and ΔP increments for Glass #73 Coupon A]

- ΔP increased in 0.5 PSI increments until 12.5 PSI held for 0.5 hours. No seal failure.
- ΔP increased in 0.5 PSI increments until 7 PSI held for 0.5 hours. No seal failure.
- ΔP increased in 0.5 PSI increments until 6 PSI held for 2.5 hours. No seal failure.
- ΔP increased in 0.5 PSI increments until 6 PSI held for 3 hours. No seal failure.
- Cycling from 800°C to RT
- Constant T of 800°C
- Constant T of 850°C
- Constant ΔP of 0.5 PSI while cycling from 800°C to RT
Glass 73-Coupon B: No seal failure up to 15 psi, 850°C

- ΔP increased in 0.5 PSI increments from 3.5 PSI to 7.5 PSI. No seal failure.
- ΔP increased in 0.5 PSI increments from 8.0 PSI to 13.5 PSI. No seal failure.
- ΔP increased in 0.5 PSI increments from 13.5 PSI to 14.5 PSI. No seal failure.
- ΔP increased in 0.5 PSI increments from 14.5 PSI to 15.0 PSI. No seal failure.
- ΔP of 15 PSI held for 5.5 hours. No seal failure. Test terminated.

Cycling from 800°C to RT

Constant T of 850°C
Glass 73-Coupon C: Thermally cracked and healed

- Seal originally found to be hermetic
- Glass seal deliberately cracked by high cooling rate quench (> 25°C/s)
- Crack healed after re-heating to 725°C for 2 hrs

Foaming in soapy water
No foaming in soapy water
## Re-Sealing Tests-cont. (ex-situ)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
<th>Observation</th>
<th>Viscosity log(η) (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>2</td>
<td>Healed</td>
<td>3.4</td>
</tr>
<tr>
<td>750</td>
<td>2</td>
<td>Healed</td>
<td>5</td>
</tr>
<tr>
<td>725</td>
<td>2</td>
<td>Healed</td>
<td>5.7</td>
</tr>
<tr>
<td>700</td>
<td>2</td>
<td>Healed once, but not healed second time; more tests in progress at 700°C or below</td>
<td>6.4</td>
</tr>
</tbody>
</table>

### Glass Fitting Parameters

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<td>11 9 6.6 4 2</td>
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<td>623 655 705 785 886</td>
</tr>
</tbody>
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Possible Healing as low as 700-725°C
Reactivity Characterization
Glass 73

800°C for 168 hours in air

- Excellent wetting and bonding to both aluminized metal and YSZ
- Some interfacial reactions between glass and metal, long-term characterization will be required
- No major interfacial reactions between glass and ceramic substrate
- No major Cr or Fe migration to glass seal
- Some Al migration to the interface of glass seal
- No elemental migration to glass seal or to ceramic substrate
Long-Term Reactivity Characterization

- Glass 73 reaction couple: 100 Thermal cycles (750°C to RT) > 3,300 hours, dry air
- More analysis in progress

Bubble: a few large bubbles
Crack
Al- or Si-rich phase(s)
On-going & Planned Work

- Refine and optimize glass compositions
- Study long-term viscous behavior
- Characterize long-term thermochemical reactions
- Hermeticity and ‘re-sealing’ behavior
- Characterize porosity
- Stack tests (PNNL)
Acknowledgements

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