Sealing Materials for Solid Oxide Fuel Cells

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Outline

Goal: Develop stable, resilient sealing materials for SOFCs
• Reviewing the problem; initial glass development research
• Progress over the past six months
  - Glasses with greater CTE’s
  - Developing composite materials
• Summarizing our program
The sealing problem is a challenge

1. **Challenging compositional design problem**
   - Uncommon combination of properties
   - Investigate uncommon families of glasses

2. **Glass-ceramics are a likely option**
   - Crystallization studies - seal processing and long-term material stability

3. **Interfacial chemistry**
   - Glass-metal reactions
   - Material stability/volatility
     - Thermochemical stability
Sealing glass properties depend on composition

Glass forming system under study:
- Alkaline earth/zinc pyrosilicates
  - 35-50 SiO$_2$
  - 30-50 RO (R=Mg, Ca, Sr, Zn; no Ba)
  - 0-10 B$_2$O$_3$, Al$_2$O$_3$, TiO$_2$, etc.

Design targets include:
- 10<CTE<13 ppm/°C
- 800°C<T$_{seal}$< 900°C
- Thermochemical and thermomechanical stability

"As made glasses"

ZnO/(SrO+CaO)=0.00
ZnO/(SrO+CaO)=0.35
ZnO/(SrO+CaO)=1.00

G36
CTE$_{RT-600}$=11.4x10$^{-6}$/°C

G27

LG38
CTE$_{RT-600}$=8.4x10$^{-6}$/°C
Sealing glass properties depend on composition

Glass forming system under study:
- Alkaline earth/zinc pyrosilicates
  - 35-50 SiO₂
  - 30-50 RO (R=Mg, Ca, Sr, Zn; no Ba)
  - 0-10 B₂O₃, Al₂O₃, TiO₂, etc.

Design targets include:
- 10<CTE<13 ppm/°C
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"As sealed glasses"

ZnO/(SrO+CaO)=0.00
ZnO/(SrO+CaO)=0.35
ZnO/(SrO+CaO)=1.00

CTE₉₀₀ = 12.4x10⁻⁶/°C
CTE₉₀₀ = 10.0x10⁻⁶/°C
CTE₉₀₀ = 5.5x10⁻⁶/°C
Thermal properties of sealing glasses are controlled by the ZnO/RO ratio.

- ZnO/(SrO+CaO)=0.00
  - CTE=12.4 ppm/°C
- ZnO/(SrO+CaO)=0.35
  - CTE=10.0 ppm/°C
- ZnO/(SrO+CaO)=1.00
  - CTE=5.5 ppm/°C

As-sealed G27

(1) - Ca₂ZnSi₂O₇
(2) - CaSrAl₂Si₂O₇

As-sealed G36, 750°C for 10 days

As-sealed LG38

2θ (degree)
Representative crystalline phases in the UMR glass-ceramics

- **Pyrosilicates**
  - CaSrAl$_2$SiO$_7$, Ca$_2$ZnSi$_2$O$_7$
- **Orthosilicates**
  - Sr$_2$SiO$_4$, Zn$_2$SiO$_4$
- Composition is most important parameter for final phase distribution.

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**Graphs**

**As-sealed (850°C/4 hrs)**

- CaSrAl$_2$SiO$_7$
- Ca$_2$ZnSi$_2$O$_7$

**28 days/750°C**

- Crofer APU22/G#27
  - 750°C/100 hrs
Glass#27 possesses a good CTE-match with YSZ

- As sealed
- 3 days/750°C
- 7 days/750°C
- 14 days/750°C
- 28 days/750°C

Expansion of residual glass

CTE match below 650°C

Glass #27

Temperature(°C)

ΔCTE(glass-YSZ)
Greater CTE's are needed for some SOFC designs

- Compositional modifications include
  - Replacing ZnO with CaO and SrO
  - Reducing Al$_2$O$_3$ content
  - Modifying relative SiO$_2$ and B$_2$O$_3$ contents
- About fifteen new compositions prepared this past reporting period
Glass #36 may be more appropriate for some SOFC designs.

\[ \alpha_{\text{RT-800}} = 119 \times 10^7 / \text{°C} \]

\[ \alpha_{\text{RT-800}} = 100 \times 10^7 / \text{°C} \]
Crystallization Kinetics of Glass#36/DTA Analyses

Held at 750ºC/air
Held at 800ºC/air
The CTE of glass#36 changes at 800°C

CTE (10^-6 / °C)

Temperature (°C)

'as sealed' - 890°C/2hrs
12.3 ppm/°C
11.4 ppm/°C

After one week at 800°C

Long term (1000 hrs) are underway
Ca-silicate phases form on crystallization

'as sealed', 890°C

(1) CaSiO$_3$
(2) CaSrSiO$_4$
Initial Hermeticity Tests - Mixed Results

Crofer-Glass (UMR-36) seal
Annealed at 800°C, tested at RT
Raj Singh - U. Cincinnati

Leaker/500 hrs

As Made
After annealing 50 hours
After annealing 100 hours
We use DTA to characterize processing effects on properties.

Finer particles crystallize more readily.
We use DTA to characterize processing effects on properties.

Kissinger analysis: DTA heating rates

Fine Particles, 355 kJ/mole

Coarse Particles, 346 kJ/mole
Glass#51 has promising dilatometric characteristics

Graph showing temperature (C) vs % Linear Change with different sample conditions:
- 'as sealed', 10.3 ppm/C
- 2 weeks at 750C, 11.1 ppm/C
- 4 weeks at 750C, 11.5 ppm/C
Sr-silicate phases form on crystallization

As sealed G#51
(1) - Sr$_2$Al$_2$SiO$_7$
(2) - SrSiO$_3$

Two weeks at 750°C
(1) - Sr$_2$Al$_2$SiO$_7$
(2) - SrSiO$_3$
Glass stability in wet forming gas (800°C)

ΔWeight at 800°C (g/cm²)

More stable materials have
• Less residual glass
• Lower B₂O₃-contents

- G#27
- G#36
- G#51
- G#52

Days

University of Missouri-Rolla
Glass-metal adhesion strength measured by pin-pull test

Romulus adhesion testing machine- Quad Group Inc.

~300μm glass coatings on interconnect substrates; ‘as sealed’ and after heat treatments

<table>
<thead>
<tr>
<th>Coating</th>
<th>Condition</th>
<th>Adhesion Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G51/430SS</td>
<td>‘as sealed’</td>
<td>20.9±6.9 MPa</td>
</tr>
<tr>
<td>G51/430SS</td>
<td>750ºC/700hrs</td>
<td>20.7±10.2 MPa</td>
</tr>
<tr>
<td>G52/430SS</td>
<td>‘as sealed’</td>
<td>19.8±3.8 MPa</td>
</tr>
<tr>
<td>G52/430SS</td>
<td>750ºC/700hrs</td>
<td>18.9±2.6 MPa</td>
</tr>
</tbody>
</table>
Sealing materials can be modified by adding fillers

- Tailor CTE
- Control crystallization
- Affect interfacial reactions
- Relieve thermal stresses
  - Controlled cracking in glass matrix; healing by viscous flow of residual glass
  - Design CTE and elastic mismatches
## Composite Overview

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE (ppm/°C)</th>
<th>Elastic Modulus (GPa)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>G36</td>
<td>12.1</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>13.3</td>
<td>207</td>
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<tr>
<td>Mo</td>
<td>5.1</td>
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<tr>
<td>316SS</td>
<td>17</td>
<td>193</td>
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<tr>
<td>Ti-Ni</td>
<td>34-83</td>
<td></td>
<td>Phase transition</td>
</tr>
<tr>
<td>WC</td>
<td>5.2</td>
<td>669</td>
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<tr>
<td>SiC</td>
<td>4.3</td>
<td>483</td>
<td></td>
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<tr>
<td>Quartz</td>
<td>7.0→13.3</td>
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<td>Phase transition</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>7.0→10.5</td>
<td>138-210</td>
<td>Phase transition</td>
</tr>
</tbody>
</table>
Dilatometric characteristics depend on filler.
Composite crystallization behavior will be characterized by DTA.
Experiments Underway

- Composite processing
  - Dense seals using tape-casting techniques

- Composite properties
  - Tailoring CTE
  - Induced cracking?

- Composite reactivity
  - Filler/matrix compatibility'
  - SOFC interfaces
SOFC Seal Summary

- SOFC seals offer an interesting materials challenge
- RO-polysilicate compositions have promising combinations of properties
  - Polysilicate glass-ceramics can be designed with thermal and chemical properties desired for some SOFC seal designs.
  - Thermo-chemical and thermo-mechanical stabilities are critical for long-term applications.
- Composite seals based on RO-polysilicate glasses
  - Reduce stresses due to thermal cycling?

Thank you for your attention!