Glass Seal Development for Tubular Cells in High Temperature Electrolysis Application

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Introduction:
PNNL is working with an industrial partner to develop glass sealants for tubular cells for high temperature electrolysis under the Department of Energy’s Technology Commercialization Fund (TCF) Program. The objective is to develop suitable glass sealants based on PNNL’s SOFC glass seal (Ba-Ca-Al-B-Si) and alumina coating technologies to advance the partner’s SOEC technology to commercialization.

Q1: Glass formulation and thermal property characterization
Q2: Ageing effect on thermal properties and wetting study
Q3: Bonding strength and interfacial reaction study
Q4: Validation test with mini-tube reactor design in dual environment and post-mortem analysis in progress

1. Plain glass formulation and thermal properties

<table>
<thead>
<tr>
<th>Glass</th>
<th>αT (1000°C-50°C)</th>
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<th>αT (1000°C-50°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G18</td>
<td>4.88 x 10^-6</td>
<td>4.88 x 10^-6</td>
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<tr>
<td>G04</td>
<td>4.25 x 10^-6</td>
<td>4.25 x 10^-6</td>
<td>4.25 x 10^-6</td>
<td>4.25 x 10^-6</td>
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<tr>
<td>G03</td>
<td>4.50 x 10^-6</td>
<td>4.50 x 10^-6</td>
<td>4.50 x 10^-6</td>
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2. Thermal expansion behavior of crystalized plain glass

Typical appearance of as-made plain glass that was melted in a Pt crucible at 1800°C Ba-Al-Si and cooled. Note that glasses G03 to G04 were transparent as shown above, while G03 were opaque indicating colorless crystallization. Glass G03 was also transparent (not shown here). The observed transparency and absence of surface crystallization suggests good homogeneous glass formulations.

3. Composite glass approach with high CTE phases and fibers

<table>
<thead>
<tr>
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<th>αT (1000°C-50°C)</th>
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<tbody>
<tr>
<td>G18/LSCF</td>
<td>4.88 x 10^-6</td>
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<td>4.88 x 10^-6</td>
<td>4.88 x 10^-6</td>
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<tr>
<td>G18/YSZ</td>
<td>4.88 x 10^-6</td>
<td>4.88 x 10^-6</td>
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4. Thermal properties of composite glass

Linear thermal expansion of the composite glass phase as a function of ceramic phase concentration. CTE values differ greatly from model predictions. The cause was attributed to reaction between ceramics and the parent glass. Only BaCrO4 showed minute reaction with the G18 glass matrix; however, thermodynamic calculations predict gas evolution when exposed to reducing environments. XRD, 10G/YSZ and G18/YSZ(20/282) were further pursued.

5. Good wetting behavior over a wide temperature range

6. Glass bonding strength with YSZ layer

7. Leak testing of cup seals with iso-propanol

8. Interfacial EDS analysis of composite glass G18/LSCF2828 with YSZ layer

9. Validation of composite glass in dual environment

Summary and Conclusions:
- Formulated 6 glasses: 5 showed good glass behavior, one crystallized upon casting.
- CTE of as-made plain glasses were lower than targeted values – crystallized glass G04 had the closest match; however, sealing behavior was undesirable due to rapid crystallization.
- 3 high CTE ceramic phases were identified as candidates for composite glass sealants using G18 glass as the matrix material.
- Chemical compatibility was studied for the high CTE ceramic = G18 composite. BaCrO4 was the least reactive, while Inoculite and LSCF reacted most with G18 glass melt.
- Composite G18/BaCrO3/LSCF2828 and G18/4%YSZ(20/282) were selected for further study. Both showed good wetting on YSZ over a wide temperature range for sealing.
- Interfacial EDS analysis of G18/LSCF on YSZ showed BaCrO3 formation which grows over time at 900°C to form a dense and continuous layer. No distinct microstructural difference was observed after aging in air or reducing/humid environment.
- Fatigue testing showed strong bonding of candidate composite glasses with YSZ while glass with YSZ fiber showed slightly higher strength, likely due to strong fiber reinforcement.
- Small reduction in bond strength after aging is likely attributed to crystallized microstructure.

Acknowledgment:
This work was funded by the U.S. Department of Energy’s Technology Commercialization Fund. Thanks to Evelyn Lopez, Rin Burke, Shaillesh Vora, and Jai-Woh Kim for their helpful support and guidance.

Presented at the 23rd Solid Oxide Fuel Cell Project Review Meeting, October 2022, Pittsburgh, PA