FLiBe Electrochemistry and Materials Corrosion Research at UW-Madison

Thomas Chrobak, Karl Britsch, Dr. Guoping Cao, Dr. Kumar Sridharan, Dr. Mark Anderson
Tritium Workshop, Salt Lake City, UT
10/27/2015
Outline

• Introduction to LiF-BeF$_2$ (FLiBe)
  – Fluoride Salt Chemistry
  – Molten Salt Corrosion

• Electrochemistry Studies on Fluoride Salts
  – FLiBe Redox Measurements

• Static Corrosion Test
  – Experimental design and materials

• FLiBe Natural Circulation Flow Loop
  – Flow-assisted corrosion testing in FLiBe convection loop
Research Questions to be answered

- Will a 0.3V difference in the redox potential of FLiBe salt cause a significant increase in corrosion behavior?
  - (-1.71V) As-purified vs. (-1.41V) Be-reduced

- Does the presence of graphite in the salt facilitate corrosion?
  - Liner vs. without liner

- What is the effect of flow on corrosion?

- Is there a significant difference in corrosion behavior of samples in the cold or hot leg of a natural circulation flow loop?

- What is the compatibility of new selected materials?
More Research Questions for Consideration

• What is the optimum amount of Be that should be added to FLiBe?
  – Balance between over and under-reduction → smallest quantity possible sequentially added

<table>
<thead>
<tr>
<th>Stoichiometric</th>
<th>vs.</th>
<th>Excess</th>
<th>?</th>
</tr>
</thead>
</table>

• Does the over-abundance of Be metal in the salt cause enhanced corrosion to carbon-containing parts?
  – Possible formation of a BeC passivation layer that can keep salt redox low while protecting C from further corrosion?
  – Increased wetting of glassy carbon crucible following Be reduction
    • Convex surface before reduction vs. concave surface after reduction.
Why Use FLiBe as Liquid Salt Coolant?

- Higher outlet temperatures lead to:
  - More valuable process heat applications
  - Greater cycle efficiencies → \( \eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H} \)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>300</td>
<td>15</td>
<td>0.55</td>
<td>3970</td>
<td>8.8×10⁻⁵</td>
</tr>
<tr>
<td>Helium</td>
<td>850</td>
<td>7.5</td>
<td>0.29</td>
<td>20.9</td>
<td>4.2×10⁻⁵</td>
</tr>
<tr>
<td>Sodium</td>
<td>550</td>
<td>Atmospheric</td>
<td>62</td>
<td>1008</td>
<td>2.3×10⁻⁴</td>
</tr>
<tr>
<td>Lead</td>
<td>550</td>
<td>Atmospheric</td>
<td>18.25</td>
<td>1499</td>
<td>1.67×10⁻³</td>
</tr>
<tr>
<td>FLiBe</td>
<td>650</td>
<td>Atmospheric</td>
<td>1.0</td>
<td>4683</td>
<td>5.6×10⁻³</td>
</tr>
</tbody>
</table>

- No ideal heat transfer fluid exists
- Molten fluoride salts offers a good compromise of properties
Properties of FLiBe meet most requirements for FHR Salt

- Molten Salt Primary Coolant Requirements
  - ✓ Exhibit chemical stability at T > 800 °C
  - ✓ Stable in an intense radiation field
  - ✓ Consist of low thermal cross section elements
  - ✓ Melt at useful temperature (<500 °C) without being volatile
  - ? Compatible with high-temperature alloys and graphite

- LiF-BeF₂ – FLiBe as primary coolant
  - + Atmospheric pressure operation
  - + Good heat transfer properties
  - + Neutron transparent
  - + Wealth of MSRE experience
  - – Tritium production from $^6$Li
  - – Beryllium toxicity
  - – Corrosive without chemistry control or proper materials

<table>
<thead>
<tr>
<th>Isotope</th>
<th>F</th>
<th>Be</th>
<th>Li-7</th>
<th>B-11</th>
<th>Zr</th>
<th>Rb</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Cross Section</td>
<td>0.009</td>
<td>0.010</td>
<td>0.033</td>
<td>0.05</td>
<td>0.18</td>
<td>0.37</td>
<td>0.53</td>
</tr>
</tbody>
</table>

MSRE Salt. Blue tint from dissolved UF₄
Overall Corrosion Process

- Impurity-driven corrosion dominates initial phase
- Thermodynamically-driven leads to continuous corrosion

Possible Corrosion Solutions

- Minimize thermal gradients?
- Use high Ni, low Cr Alloys?
  - Implement chemistry control of salt with redox potential measurement to maintain high salt quality
Thermodynamically Driven Corrosion

- Non-favorable reactions slowly occurring
- Assisted by a temperature gradient and mass flow

\[ \text{BeF}_2 + \text{Cr} \leftrightarrow \text{Be} + \text{CrF}_2 \]

\[ Keq = \frac{[\text{Be}][\text{CrF}_2]}{[\text{BeF}_2][\text{Cr}]} \]

\[ Keq = 8.66 \times 10^{-13} \quad \text{at 700 °C} \]

\[ Keq = 2.76 \times 10^{-14} \quad \text{at 600 °C} \]
Impurity Driven Corrosion

- Thermodynamically favorable reactions due to unstable impurities
- Occurs quickly in initial corrosion stages

Metal Fluoride Impurity Reactions

\[ M_{\text{alloy}}(s) + M_{\text{imp}}F_x(d) \rightarrow M_{\text{alloy}}F_y(d) + M_{\text{imp}}(s) \]

Moisture Impurity Reactions

\[ \frac{x}{2}H_2O + M_{\text{salt}}F_x \rightarrow M_{\text{salt}}O_{\frac{x}{2}} + xHF \]
\[ xH_2O + M_{\text{salt}}F_x \rightarrow M_{\text{salt}}(OH)_x + xHF \]
\[ M_{\text{alloy}}(s) + xHF \rightarrow M_{\text{alloy}}F_x(d) + H_2 \]
Fluoride Salt Corrosion Mechanisms

- Salt constituents are more stable than metal fluorides
- Almost no corrosion expected from pure FLiBe
- How can we ensure purity of FLiBe? → Redox potential

**Free Energies of Salt Fluorides and Corrosion Products**

- 0.17 MoF6
- 0.5 NiF2
- 0.5 FeF2
- 0.5 CrF6
- 0.5 BeF2
- LiF

**Corrosion Products** (less stable)

**Salt Constituents** (more stable)
Experimental facilities for electrochemical testing of FLiBe

- HP 3616A Power Supply
- Ar glovebox. O₂ and Moisture <1 ppm
- Radiant heater, PID used to maintain 500±0.5°C
Dynamic reference probe design for compact redox potential testing of FLiBe

- O-Ring
- BN Spacer
- Glassy Carbon Anode
- Mo Cathode
- Mo Indicator
- Mo TC well
- K-Type TC
Dynamic Reference Electrode Measurements

- Combination of Dynamic and Static Techniques

First Phase
- Beryllium is plated from the salt onto an electrode (1)

Second Phase
- Voltage is cut, beryllium allowed to redissolve back into the salt
- Be|BeF$_2$ reference voltage is formed from dissolution reaction (2)
- As plated products deplete, voltage relaxes back to zero (3)

(Afonichkin, 2009)
Redox Probe Measurement Process

Phase I: Plating

Phase II: Voltage Measurement
Plateau voltage of Be dissolution indicates redox potential of FLiBe

Procedure:
• Start after plating time + 1 second
• (current point – moving average) < $V_c$?
  • If true, move on to next point, update average
• Points collected and averaged until end point exceeds a set cutoff voltage, $V_c$.

Blue: Original data
Red: Plateau data points
Green: Average of red points
-Used as Redox Voltage
Redox potential testing of purified, unreduced UW-made FLiBe

- 24 Measurements total, average of -1.708V with standard deviation of 6.2 mV
- Average standard deviation within each batch of 3.11 mV
- All batches will be mixed together prior to crucible loading
Production, purification and reduction of UW-made FLiBe

As-received BeF₂ As-received LiF

HF/H₂ → H₂ → Filtration 600 – 630°C

UW FLiBe

Beryllium and Filtration 650°C

Beryllium Reduced
Video of FLiBe being poured from vessel into tray in glovebox
Glovebox inventory of FLiBe for all future experiments

Total of 2.2 kg of UW-made FLiBe currently stored in glass jars in Ar glovebox.

Four nickel crucibles are fully filled and stored in jars.

Approximately 250 g of granulated salt was separated for one crucible in corrosion test.
Next static corrosion experiment will test multiple variables

- Metrics to test against corrosion:
  - Redox potential effect
    - HF/H₂ Purified salt (redox potential = -1.71V)
    - Beryllium Reduced salt (redox potential = -1.41V)
  - Effect of carbon from IG-110 graphite crucible
    - Corrosion test with or without liner for 316 SS
  - New materials testing in FLiBe
    - GA SiC-SiC
    - Mo-Hf-C alloy
    - Zr/C-W Cermet
# Experimental Design of Static Corrosion Experiment in FLiBe

<table>
<thead>
<tr>
<th>Crucible 1: -1.7V UW FLiBe</th>
<th>Crucible 2: -1.4V UW FLiBe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hole 1:</strong> SiC ➔ 3x SiC-SiC samples, 1x bulk SiC sample</td>
<td></td>
</tr>
<tr>
<td><strong>Hole 2:</strong> Nuclear Graphite ➔ 3x matrix graphite samples, 1x IG-110 sample</td>
<td></td>
</tr>
<tr>
<td><strong>Hole 3:</strong> No liner. Mo-Hf-C ➔ 3x Mo-Hf-C alloy samples with Mo wire suspension*</td>
<td></td>
</tr>
<tr>
<td><strong>Hole 4:</strong> No liner. W-Zr-C ➔ 3x W-Zr-C Cermet samples with W wire suspension*</td>
<td></td>
</tr>
<tr>
<td><strong>Hole 5:</strong> No liner. 316 SS ➔ 3x 316 samples with SS wire suspension*</td>
<td></td>
</tr>
<tr>
<td><strong>Hole 6:</strong> With 316 SS liner. 316 SS ➔ 3x 316 samples with SS wire suspension*</td>
<td></td>
</tr>
</tbody>
</table>

*Avoid dissimilar materials in contact in FLiBe wherever possible*
Immediate Future Work

- Flow-assisted corrosion in natural circulation FLiBe loop
  - Corrosion samples in hot and cold legs of loop
  - Thermo-physical properties of FLiBe can be measured
  - Surge tank on top of loop for in-situ salt measurements and chemical control
FLiBe Natural Convection Loop 1/2

- FLiBe natural convection loop to be built
  - Incorporate Be-addition, redox measurement, and corrosion tests.
  - Use ports in surge tank for:
    1. Sacrificial Be rod with bellow
    2. 3-electrode redox probe
    3. Port-hole
    4. Anything else?
• 1” OD Stainless Steel tubing
  – Composition matching important
• Two double ball valves to support in-loop corrosion tests.
Thank you for your attention!

Questions?