Thermochemistry of fuel, fission products and corrosion products in Molten Salt Reactor

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Background and context of research

- The Molten Salt Reactor is among the most promising future nuclear fission reactor technologies as defined by the Generation IV International Forum. It is safe, sustainable, economical and proliferation resistant.
Molten Salt Reactor - components

FUEL

COOLANT

AS CRYSTALLIZED SOLID

$^7\text{LiF} - \text{BeF}_2 - ^{233}\text{UF}_4$

FLUORIDE FUEL FOR A MOLTEN SALT REACTOR
Which are the constrains for a liquid fuel?

NEUTRONIC PROPERTIES
- small capture cross section, moderation capability, low neutronic activation, stable under irradiation

CHEMICAL PROPERTIES
- chemical stability, low corrosion, chemical reactivity, actinide solubility, salt clean-up

THERMAL AND TRANSPORT PROPERTIES
- Low melting point
- Low vapour pressure and high boiling point
- Large heat capacity
- High solubility of actinides

ECONOMIC FEATURES
Molten Salt Reactor – Fuel options

Only a limited number of compounds are suitable from neutronic considerations and fluoride salts are one of the best candidates.

- $^7\text{LiF} - \text{ThF}_4 - \text{UF}_4$
- $^7\text{LiF} - \text{ThF}_4 - \text{PuF}_3 - \text{UF}_4$
- $^7\text{LiF} - \text{BeF}_2 - \text{ThF}_4 - \text{UF}_4$

+ additional components to improve the fuel properties if needed (NaF, KF, CaF$_2$,..)

<table>
<thead>
<tr>
<th>Element</th>
<th>Hastelloy-N (INOR-8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Base</td>
</tr>
<tr>
<td>Cr</td>
<td>7.52</td>
</tr>
<tr>
<td>Mo</td>
<td>16.28</td>
</tr>
<tr>
<td>Ti</td>
<td>0.26</td>
</tr>
<tr>
<td>Fe</td>
<td>3.97</td>
</tr>
<tr>
<td>Mn</td>
<td>0.52</td>
</tr>
<tr>
<td>Nb</td>
<td>–</td>
</tr>
<tr>
<td>Si</td>
<td>0.5</td>
</tr>
<tr>
<td>Al</td>
<td>0.26</td>
</tr>
<tr>
<td>W</td>
<td>0.06</td>
</tr>
<tr>
<td>Cu</td>
<td>0.02</td>
</tr>
<tr>
<td>Co</td>
<td>0.07</td>
</tr>
<tr>
<td>Ce</td>
<td>–</td>
</tr>
<tr>
<td>Zr</td>
<td>–</td>
</tr>
<tr>
<td>B</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>S</td>
<td>0.004</td>
</tr>
<tr>
<td>P</td>
<td>0.007</td>
</tr>
<tr>
<td>C</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Fission products:

- Kr+Xe: 0.606
- Lanthanides + Y: 0.538
- Zr: 0.318
- Sr+Ba: 0.072
- Br+I: 0.015
- Rb+Cs: 0.004
- Mo: 0.201
- Ru: 0.126
- Tc: 0.059
- Nb: 0.014
Thermodynamic modelling

**Development of a thermodynamic database on relevant fluoride salts**

**Fuel composition optimization**

**Addition of fission products and corrosion products to the database**

**Complete understanding of fuel behaviour in operational and accidental conditions**
Database development

EXPERIMENTAL MEASUREMENTS

- Thermodynamic properties of pure compounds (heat capacity, enthalpy of fusion,..)
- Phase determination/stability
- Equilibrium data for phase diagram studies
- Vapor pressure/composition

THERMODYNAMIC MODELING

- Assessment of binary and ternary phase diagrams
- DFT calculations
- Gas phase properties estimates
Thermodynamic model

Binary and ternary system are assessed according to the CALPHAD approach. Three databases were developed:

- **Pure end-members and intermediate compounds**
- **Solid solution**
- **Liquid solution**

**Modified Quasi-chemical Model - Two sublattice Quadruplet approximation**

- Two sublattices: (A,B,...) cations and (X,Y,...) anions
- Variable composition of short range ordering
- Simultaneous treatment of FNN and SNN interactions

\[(A - X - A) + (B - X - B) = 2(A - F - B) \quad \Delta g_{AB/X}\]

**FLUORIDE SYSTEMS (common-anions systems)**
Experimental data

Requirements for fluorides samples:
- Purification step
- Inert atmosphere
- Encapsulation technique

Experimental techniques:
- Differential Scanning Calorimetry
- X-ray Diffraction
- Knudsen Effusion Mass Spectrometry

Differential Scanning Calorimetry
Example of assessed systems

- **Fuel salt with fission products**
  - LiF-ThF$_4$-CsF-CsI system
  
  Fission products with relatively high production yield which deserve strong attention due to their volatility and radiological effects in accidental scenarios.

- **Fuel salt with corrosion products**
  - LiF-NiF$_2$, NaF-NiF$_2$, KF-NiF$_2$ phase diagrams
Fuel salt with fission products

Assessment of the LiF-ThF₄-CsF-CsI system:

- **CsI** is the most stable iodide in the considered mixture
- **CsF** is also formed by the cesium in excess
- Little / negligible presence of I and I₂
- Little / negligible presence of Cs
- Little / negligible presence of IFₓ compounds

![Diagram of the LiF-ThF₄-CsF-CsI system]

- ✓ LiF-ThF₄
- ✓ CsF-ThF₄
- ✓ LiF-CsF
- ✓ CsI-CsF
- ✓ LiF-CsI
- ✓ CsI-ThF₄
Binary phase diagrams – (I)

**LiF-ThF$_4$ system**
- Phase equilibrium points
- Enthalpy of mixing
- LiF and ThF$_4$ activities
- Li$_3$ThF$_7$ enthalpy of fusion

**LiF-CsF system**
- Reviewed properties for CsF
  *(Beneš et al. 2013)*
- Phase equilibrium points
  *(Bukhalova 1965; Thoma et al. 1975)*
- Enthalpy of mixing
  *(Holm and Kleppa 1968)*

**CsF-ThF$_4$ system**
- Phase equilibrium points
- Vapour pressure data
- Activity data for CsF and ThF$_4$ in the liquid solution
- Phase stability
Binary phase diagrams – (II)

CsF-CsI system

- Phase equilibrium points
  (Bukhalova et al. 1973)

LiF-CsI system

\[(A_2X_2)_{quad} + (B_2X_2)_{quad} = 2(ABX_2)_{quad} \quad \Delta g_{AB/X_2}\]

\[(A_2X_2)_{quad} + (A_2Y_2)_{quad} = 2(A_2XY)_{quad} \quad \Delta g_{A_2/XY}\]

\[\frac{1}{2}(ABX_2 + ABY_2 + A_2XY + B_2XY) = 2(ABXY)_{quad} \quad \Delta g_{AB/XY}\]
Binary phase diagrams – LiF-CsI

- Phase equilibrium points from literature (Margheritis, 1973)
- Liquid-liquid immiscibility gap
Binary phase diagrams – LiF-CsI

- Phase equilibrium points from literature (Margheritis, 1973)
- Liquid-liquid immiscibility gap
- New equilibrium point

DSC measurement – Sample LiF-CsI (xCsI = 4 mol%)

[Heat flow graphs for heating and cooling curves showing phase transitions and heat flow over time.]
Ternary systems

- Extrapolation using Kohler or Kohler/Topp interpolation methods.
- Small ternary parameters were introduced.

The developed database is a useful tool to predict the fuel mixture properties during operation.
The LiF-CsF-ThF\(_4\) system

<table>
<thead>
<tr>
<th>Composition</th>
<th>T liquidus /K</th>
<th>P @ 900 K / Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF-ThF(_4) (76.2-23.8)</td>
<td>832 K</td>
<td>2,44 (\cdot) 10(^{-3})</td>
</tr>
<tr>
<td>LiF-ThF(_4)-CsF (75.438-23.562-1.00)</td>
<td>834 K</td>
<td>2,74 (\cdot) 10(^{-3})</td>
</tr>
<tr>
<td>LiF-ThF(_4)-CsF (7.676-23.324-2.00)</td>
<td>837 K</td>
<td>3,06 (\cdot) 10(^{-3})</td>
</tr>
<tr>
<td>LiF-ThF(_4)-CsF (72.39-22.61-5.00)</td>
<td>848 K</td>
<td>4,25 (\cdot) 10(^{-3})</td>
</tr>
<tr>
<td>LiF-ThF(_4)-CsF (68.58-21.42-10.00)</td>
<td>871 K</td>
<td>7,38 (\cdot) 10(^{-3})</td>
</tr>
</tbody>
</table>
Example of assessed systems

- **Fuel salt with fission products**
  - LiF-ThF₄-CsF-CsI system

- **Fuel salt with corrosion products**
  - LiF-NiF₂, NaF-NiF₂, KF-NiF₂ phase diagrams
Corrosion products in MSRs

- **Ni-based alloys** are found to withstand harsh operational conditions in MSRs (high temperatures, contact with corrosive salts).

- **The redox potential** of the salt is a key parameter for corrosion issues and it is controlled by the $\text{UF}_4/\text{UF}_3$ ratio.

- However during **irradiation**, this ratio increases and corrosion products can be dissolved in the mixture:
  
  \[
  \text{Cr (alloy) + 2UF}_4(\text{salt}) \rightarrow \text{CrF}_2(\text{salt}) + 2\text{UF}_3(\text{salt})
  \]
  
  \[
  \text{Ni (alloy) + 2UF}_4(\text{salt}) \rightarrow \text{NiF}_2(\text{salt}) + 2\text{UF}_3(\text{salt})
  \]

**Study of the phase equilibria of fuel salt with corrosion products as a function of temperature and salt composition**
The LiF-NiF$_2$ system

Pure NiF$_2$ synthesis
\[ T_{\text{fus}} = (1628 \pm 5) \text{ K} \]

\[ \text{L} \]
\[ \text{L} + \text{NiF}_2 \]
\[ \text{Li}_2\text{NiF}_4 + \text{NiF}_2 \]
\[ \text{Li}_2\text{NiF}_4 + \alpha \]

Solid solution $\alpha = (\text{Li}_{1-2x}\text{Ni}_x\text{F})$

Petrov et al., 1961.
The NaF-NiF₂ and KF-NiF₂ systems

This work


Petrov et al, 1952.

Thoma et al., reproduced from Mamantov and Smith, 1975.

This work


Wagner and Balz, 1952.
Conclusion

➢ The generation of a reliable and consistent thermodynamic model is very important for multi-components system, such as the molten salt fuel mixture.

➢ A database containing the most relevant fluoride salts, including fission products and corrosion products is being developed in collaboration between the Joint Research Centre - Karlsruhe and Delft University of Technology.

➢ It is a powerful tool which allows the optimization of the fuel composition for MSR fuels and the prediction of their thermodynamic properties and behaviour during irradiation.
Thank you