COOLANT STRUCTURAL MATERIALS

COMPATIBILITY

APEX Task III.6a

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KEY ISSUES FOR LIQUID METAL/STRUCTURE COMPATIBLITY

EFFECTS

1. Corrosion/Mass Transfer
   - Uniform or selective dissolution
   - Inter-granular penetration
   - Interstitial-element transfer

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- Wall Thinning
- Degradation of Strength

2. Deposition of Corrosion Products

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- Pumping Power
- Efficiency
- Safety

(1) CORROSION/MASS TRANSFER

- **Variables:**
  - Liquid metal and type of impurities (N, O, C, etc.)
  - Composition and microstructure of wall
  - Temperature
  - Exposure time
  - System parameters :
    - flow velocity, MHD, delta-T, surface area, bi-metallic or mono-metallic loop, system temperature profile.

- **Effects on Property Deterioration:**
  - Liquid metal embrittlement (LME)
  - Oxidation, nitridation, carburization-decarburization
  - Fatigue crack propagation
  - Creep ductility loss

Task-III.6a APPROACH

- **Investigation Approach:**
  - Empirical Literature Data Extrapolation
  - Thermodynamics of main compounds, for example:
    - Li-Fe, Li-V, Li-W, Li-SiC
    - Sn-V, Sn-Fe, Sn-W, Sn-SiC
    - Flibe-Fe, Flibe-V, Flibe-W, Flibe-SiC

- **GOAL of Investigation:**
  Identify Temperature and Impurity Limits:

Data-Base Matrix

	Available Data	Lacking Data
Liquid Metal	Li, Li17-Pb83, FliBe, Sn	
Structural Materials (Experimental)	Li & LiPb : V-Ti-Cr V-Cr-Ti-Zr Fe-C-Cr-Ni-Mo, HT9	Li & LiPb : W, W-Re, ODS-W, SiC Flibe,Sn-V,Fe,W, SiC
Insulating Ceramics (Mostly thermodynamic analysis, some experimental)	Li-Oxides: Y_2O_3, CaO, Al_2O_3, MgO, SiO_2, Cr_2O_3 Li-Carbides: β-SiC, TiC, ZrC, TaC Li-Nitrides: BN, AlN, TiN, ZrN, VN, CrN	No info on SiC and FliBe or SiC and Sn-Li; SiC unstable in Li, but stable in Li-Pb[1] Flibe, Sn & all
Impurities (effects on compatibility)	Li containing O, N, C, H	Sn-Li, Flibe

[1] Hubberstey, 1997

AVAILABLE DATA BASES

- Simple Phase Diagrams are available for:
  - Lithium-Vanadium (Li-V):
  - Li-Fe (compounds are thermodynamically unlikely to form: Positive enthalpy of formation)
  - Tin-Vanadium (Sn-V)
  - Tin-Iron (Sn-Fe)
  - Thermo-physical data for Li and Sn are available

- FliBe (LiF-BeF_2):
  - Detailed phase diagram is available
  - Thermo-physical data are available for:
    - density, expansivity, viscosity, electro-conductivity, specific conductance, specific heat, enthalpy, entropy, free energy, heat of mixing, thermal conductivity, thermal diffusivity, Prandtl number, vapor pressure, compressibility, sound speed, kinematic viscosity, surface tension, some interfacial surface tension, solubility values (gases, Ni, Fe, Al), optical properties, self-diffusion coefficients.

Thermodynamic Modeling for Chemical Stability of Coatings in Lithium

- As a function of (1) non-metal solute concentration (x_x), and (2) Temperature (T)
- Free energy changes of reactions ($\Delta_r G$):

$$M_x O_y(c) \xrightarrow{\text{liquid Li}} yO(Li) + xM(c)$$

$$\Delta_r G = (1/x)\left[y\overline{G}_o(Li) - \Delta_f G^o(M_x O_y) \right]$$

$\Delta_f G^o$ Standard free energy of formation data (need data for Sn to evaluate Sn-Li systems)

$\overline{G}_o(Li)$ Solute free energy is given by:

$$\begin{aligned} \overline{G}_o(Li) &= RT\ln a_o \\ &= RT\ln a_o^* + RT\ln x_o / x_o^* \\ &= \Delta_f G^o(Li_2O) - 2\overline{G}_{Li}(Li) + RT\ln x_o / x_o^* \end{aligned}$$

a_o^* : oxygen activity at saturation
x_o : oxygen concentration
x_o^* : oxygen conct. at saturation

Thermodynamic Modeling for Chemical Stability of Coatings in Lithium

- Principal non-metal solutes in liquid lithium are: Li_2O, Li_3N, Li_2C_2, and LiH
- Solve for free energy change of reaction ($\Delta_r G$) (similar for N and C):

$$\Delta_r G = (1/x)\left[y\left\{ \Delta_f G^o(Li_2O) - 2\overline{G}_{Li}(Li) + RT\ln x_o / x_o^* \right\} - \Delta_f G^o(M_xO_y) \right]$$

- Use established solubility expressions for oxygen, nitrogen, and carbon in Li:

$$\ln x_O = 1.428 - 6659\ (T/K)^{-1}, \quad 530 < T/K < 715$$
$$\ln x_N = 2.976 - 4832\ (T/K)^{-1}, \quad 468 < T/K < 723$$
$$\ln x_C = 1.100 - 5750\ (T/K)^{-1}, \quad 477 < T/K < 908$$

Thermodynamic Modeling for Chemical Stability of Coatings in Lithium

- Based on the above model the chemical stability of coatings can be determined:

Coating	$\Delta_f G^o_{O,N,C}$ (kJ/mol)	$\Delta_r G$ (kJ/mol-metal)	Stability
Oxides:			
Sc_2O_3,	-1679	93.5	Stable
Y_2O_3,	-1678	93.4	Stable
CaO	-554	56.8	Stable
La_2O_3	-1570	39.2	Stable
Nitrides			
ZrN,	-291	210	Stable
TiN,	-263	182	Stable
AlN,	-219	137	Stable
BN,	-206	124	Stable
TaN	-187	106	Stable
Carbides:			
ZrC	-189	115	Stable
TiC	-175	101	Stable
TaC,	-141	67	Stable
NbC	-134	60	Stable

Thermodynamic Modeling for Relative Stability of Coatings in Lithium

- The stability of coatings is critical for minimizing MHD pressure drop effects.
- Oxides, Nitrides, and some Carbides have been investigated as potential coating candidates for vanadium alloys.
- Most stable ceramic coatings (in order of stability):
  - Oxides:
    - Sc_2O_3, Y_2O_3, and CaO
  - Nitrides:
    - ZrN, TiN, AlN, BN, TaN
  - Carbides:
    - ZrC, TiC, TaC, NbC

Conclusions

- The most stable coatings for a Lithium are:
  - Oxides: Y_2O_3, Sc_2O_3
  - Nitrides: ZrN
  - Carbides: ZrC

- Plan to apply thermodynamic model to determine the stability of coatings in a Sn-Li and in Flibe.