RECENT PROGRESS IN THE DEVELOPMENT OF ELECTRICALLY INSULATING COATINGS FOR A LIQUID LITHIUM BLANKET

B. A. Pint, P. F. Tortorelli, A. Jankowski, J. Hayes, T. Muroga, A. Suzuki, O.I. Yelisseyeva and V.M. Chernov

Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6156, USA
Chemistry and Materials Science, Lawrence Livermore National Laboratory P.O. Box 808, L-352, Livermore, CA 94551, USA
Fusion Engineering Research Center, National Institute for Fusion Science, 322-6 Oroshi, Toki, Gifu, 509-5292, Japan
G. V. Karpenko Physico-Mechanical Institute NASU, L’viv, 79601, Ukraine
SSC-RF A. A. Bochvar Institute of Inorganic Materials, 123060, P.O. Box 369, Moscow, Russia
The magneto hydrodynamic problem
For self-cooled liquid metal blanket and magnetic field

MHD force causes:
- a load to the pumping system
- additional stress on structures

A solution is required for this concept to be viable
MHD coatings

High resistivity material insulates the system

Critical for vanadium alloy concept:
- good compatibility of vanadium with Li
- O/H embrittlement problem with He coolant

Critical for most liquid metal blanket concepts:
- very attractive from system design standpoint

MHD coating material requirements:
High resistivity ($\geq 10^5 \ \Omega \cdot \text{cm}$)
Thin (avoid heat transfer problem) (10µm)
Resistant to radiation
Adherent to channel wall
Compatible with Li (the most difficult to meet?)

System requirements: 25,000h, 400°-700°C(?)
Change in emphasis

Recent reviews focused on CaO and AlN as the best candidates

However, Li compatibility results showed problems:

CaO dissolved: polycrystalline CaO and single crystals

AlN dissolved: when tested with V alloy capsule (not with Mo capsule)

issue of N gettering
CaO: Coatings showed similar problem
Results from Park et al., Argonne National Laboratory

Longer term testing showed similar results as bulk CaO specimens
≈50% coating loss by 1000h
Total lifetime estimated as <3,000h
Effect of substrate O content not significant

600°C, 700h test in Li-2.8at.%Ca
Vapor-deposited CaO O-loaded vanadium alloy substrate
Why the disconnect?
Between screening/theoretical studies and experimental observations of Li compatibility

Predictions of compatibility relied on:

\[ \text{CaO + 2Li} \leftrightarrow \text{Ca + Li}_2\text{O} \]

and assumed Li saturated with O

Poor assumption:
O solubility changes greatly with temperature

In a temperature gradient, saturation problem:
  - If Li saturated at high T, Li$_2$O precipitates at low T
  - If Li$_2$O precipitates, Li will no longer be saturated

Without saturation, a different criteria is needed
A saturation criteria for dissolution

The more relevant reaction is:

\[
\text{CaO} \leftrightarrow \text{Ca(Li)} + \text{O(Li)}
\]

CaO problem: both Ca and O very soluble in Li

Similarly for AlN:

\[
\text{AlN} \leftrightarrow \text{Al(Li)} + \text{N(Li)}
\]

For V capsule: N gettered by capsule
dissolution not inhibited

For Mo capsule: no gettering, N saturates

Other issues: AlN reaction with O or Ti in V-Cr-Ti
Coating fabrication with low O
Sawada et al. 3-10 at.% O in coating
What is left?
Few materials are compatible with Li Screening of bulk ceramics in Li at 800°C

<table>
<thead>
<tr>
<th>Materials</th>
<th>ΔG_f° (kJ/mol O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>-1025</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-1045</td>
</tr>
<tr>
<td>Li₂O</td>
<td>-1122</td>
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<tr>
<td>Er₂O₃</td>
<td>-1206</td>
</tr>
<tr>
<td>CaO</td>
<td>-1207</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>-1211</td>
</tr>
<tr>
<td>Sc₂O₃</td>
<td>-1213</td>
</tr>
</tbody>
</table>

Several show promise at 800°C in static Li testing Er₂O₃ and (Y,Sc)O₃ mass gains due to specimen porosity Suzuki: adding Zr and Sc to CaO reduced mass losses

Y₂O₃ showed most promise and pursued first by U.S.
**Y$_2$O$_3$ coatings by EB-PVD**

10 made at LLNL (by electron beam - physical vapor deposition) deposited on polished V-4Cr-4Ti 13mm disk measured thickness of 12.5µm (laser profilometry) fine grain size (0.5µm):

8 Li capsule tests at 700°-800°C, 100-2,000h results varied from no loss to major spallation

X-ray diffraction: Y$_2$O$_3$ before, some LiYO$_2$ after

Surface morphology change, Ti-rich oxides by Auger
**Y$_2$O$_3$ coatings: resistivity results before and after Li exposures**

![Graph showing resistivity results vs. temperature for Y$_2$O$_3$ coatings.](image)

- **As-received coating** showed lower resistivity than **literature values** and much lower than measurement on sintered bulk Y$_2$O$_3$ possibly due to Au in cracks/pores (2 other specimens shorted)

- **1000h/800°C** lower resistance: likely degradation by YLiO$_2$

- **Cycled specimen (800°C/3x100h):** showed no degradation

- **First attempt at Y$_2$O$_3$** showed problems but some promise

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**Testing to 800°C**
- Initially limited to 500°-600°C upgraded specimen heater
- **Au electrode + guard**
- 5.1mm diameter guard ring to limit leakage
- **Constant voltage:** 1-5V
- **Current:** measure to $<10^{-12}$A

**Vacuum:** $10^{-6}$Torr or less limit V-4Cr-4Ti oxidation
New coatings: Fabrication & Testing

- Japan: RF sputtering of AlN, Er₂O₃ and Y₂O₃ also using vacuum arc process
  Issues: thickness, adhesion, crystallinity

- Properties:
  Resistivity (figure of merit for coatings)
  most start out very high
  Radiation induced conductivity (Tanaka et al.)
  found expected, acceptable effect
  Li compatibility
  mostly disappointing results

High quality coatings are needed to assess Li compatibility to avoid issues related to processing
Interest remains for in-situ coatings as an attractive method for covering complex parts.

Ukraine/Russia - fundamental evaluation of mechanisms at long time, problems with V in CaO and Li & Ca in V alloy.

Japan - using ANL process for CaO to make Er$_2$O$_3$. Charge V-4Cr-4Ti with O, anneal, 300h/600°C Li-0.006%Er.
Candidate materials

CaO - dropped from consideration on the U.S. MHD coating development program because of dissolution problems observed for both bulk specimens (at ORNL) and coatings (at ANL).

$Y_2O_3$ - completed Li capsule testing of PVD $Y_2O_3$ coatings on V-4Cr-4Ti substrates; problem with $YLiO_2$ formation

AlN - excellent bulk testing results in Mo; potential compatibility problem with V-4Cr-4Ti

$Er_2O_3$ - promising bulk testing results; awaiting coating development

$(Y,Sc)O_3$ - promising bulk testing results; recently showed adequate $\rho$; awaiting coating development

Change in emphasis reflected in ICFRM-11 posters
MHD coating metrics

Proposed by ORNL and adopted by U.S. in 2002:
Isothermal Li exposure:
  coating: 5-15μm thick
  duration: ≥1000h
  temperature: 700°C or 50°C above max. T
  less than 10% solute additions to Li

Post exposure performance:
  less than 10% dissolution/reaction
  maintain electrical resistivity (≥10^5 Ω-cm)

Cyclic Li exposure
  heat to temperature, 10-100h hold, cool
  after 3 cycles, coating should show no spall
  and meet isothermal performance

One or more coatings must meet metrics prior to
U.S. beginning Li loop construction/testing
Defects in coatings

U.S.-Japan committee led by Dai Kai Sze
Good interaction from design side
Previous literature on MHD coating defects

Theoretical calculations indicate very few defects can be tolerated ($10^{-7}$ fraction)
- concern about through thickness cracks
- assuming Li wets (fills) cracks causing short

Real coating likely has $10^{-2}$-$10^{-4}$ defects
review of ceramics literature not promising

Allowable crack fraction may be altered by design

Conclusion: major problem is likely
Review of crack literature led to one more issue...
Cracking due to tensile stresses

Maximum crack spacing $\lambda_{\text{max}}$ normal to a load $\sigma_m$

$$\lambda_{\text{max}} = \pi \ d \ \sigma_m / \tau_m$$

d = film thickness, $\tau_m$ = ultimate shear stress
and $\sigma_m = E \cdot \varepsilon_f$

$E$ = coating modulus, $\varepsilon_f$ = coating fracture strain

Values of $\tau_m$ are not readily available (determine by $\lambda_m$)
Variety of assumptions for oxide coatings based on:
- hardness
- low fracture strain of oxides
- interface energy

Resulting estimate: $\lambda_{\text{max}} = 10-100 \cdot d \approx 1\text{mm}$

Unless the V alloy is unstressed, there will be cracks
A new paradigm (but not a new idea)

There will be defects in the ceramic coatings Either as-deposited or due to tensile cracking

Reasonable assumption that Li will wet cracks (Once Li in cracks how could they heal?)

Therefore, a metallic overlayer is needed to prevent Li from wetting the cracks in the coating

Vanadium is the logical choice for the overlayer

Flowing Li

Vanadium overlayer

Ceramic insulating coating

Vanadium alloy substrate
Metallic outer layer

Need to reconsider the entire system
- Insulating ceramic no longer in contact with Li
  However, some reasonable compatibility needed
- Compatibility issue now switches to vanadium layer
  Maximum 100µm thickness (D.-K. Sze input)
  Tortorelli-Sze literature review leaves questions
  several papers show no problem
  several paper show a big problem
  only loop experiments will provide answer
- How to coat a refractory metal layer?
- At 100µm, maybe a free-standing sleeve (?)
  pressurized 600°C heat exchangers made from 75µm SS
Summary

Change in emphasis
CaO has been dropped by the US program
AlN has significant technical problems
Looking for elements with low solubility in Li
Y$_2$O$_3$ and Er$_2$O$_3$ are being investigated

Change in strategy
defect assessment led to system change
outer layer needed to prevent Li crack wetting

Change in the critical issue
single layer - Li compatibility
MeO$_x$ <-> Me(Li) + O(Li) may have no solution
double layer - processing issues increase
fabrication method? quality?
Lithium Capsule Testing at ORNL

CaO, Y_2O_3 -> V-Cr-Ti inner capsule

AlN -> requires Mo inner capsule to avoid N gettering from Li

Type 316 capsule protects the V or Mo capsule from oxidation

Inverting the capsule allows the lithium to drain from specimen