MHD Coating: Understanding and Status

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Introduction

Need durable insulating coating compatible with lithium for vanadium structural system to be viable.

System requirements: 25,000h, 400°-700°C ?

Objective

To assess the long-term, high temperature (500°-800°C) compatibility of high electric resistance coatings with lithium.

Task I: Screening tests on bulk ceramics

- confirm thermodynamic calculations, define T_{max}
- avoid coating parameters as variables
- eliminate candidates -> focus coating development

Task II: Static lithium tests on ceramic coatings

Task III: Dynamic (loop) testing of coatings

MHD Coating Metrics

Proposed by U.S. and adopted this year:

- Isothermal Li exposure:
  - coating: 5-15μm thick
  - duration: ≥1000h
  - temperature: 700°C or 50°C above use T
  - less than 10% additions to Li
- Post exposure performance:
  - less than 10% dissolution/reaction
  - maintain sufficient resistance
- 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 beginning Li loop testing

Lithium Doping

Rather than compare the reaction energy:

$$CaO + 2Li \leftrightarrow Ca + Li_2O$$

The reaction of the ceramic with lithium occurs until equilibrium is achieved in solution:

$$CaO = (\underline{Ca})Li + (\underline{O})Li \qquad \text{or}$$
$$AlN = (\underline{Al})Li + (\underline{N})Li$$

thus, $k_r = a_{Ca} \cdot a_O \qquad \Delta G = R \cdot T \cdot \ln k_r$

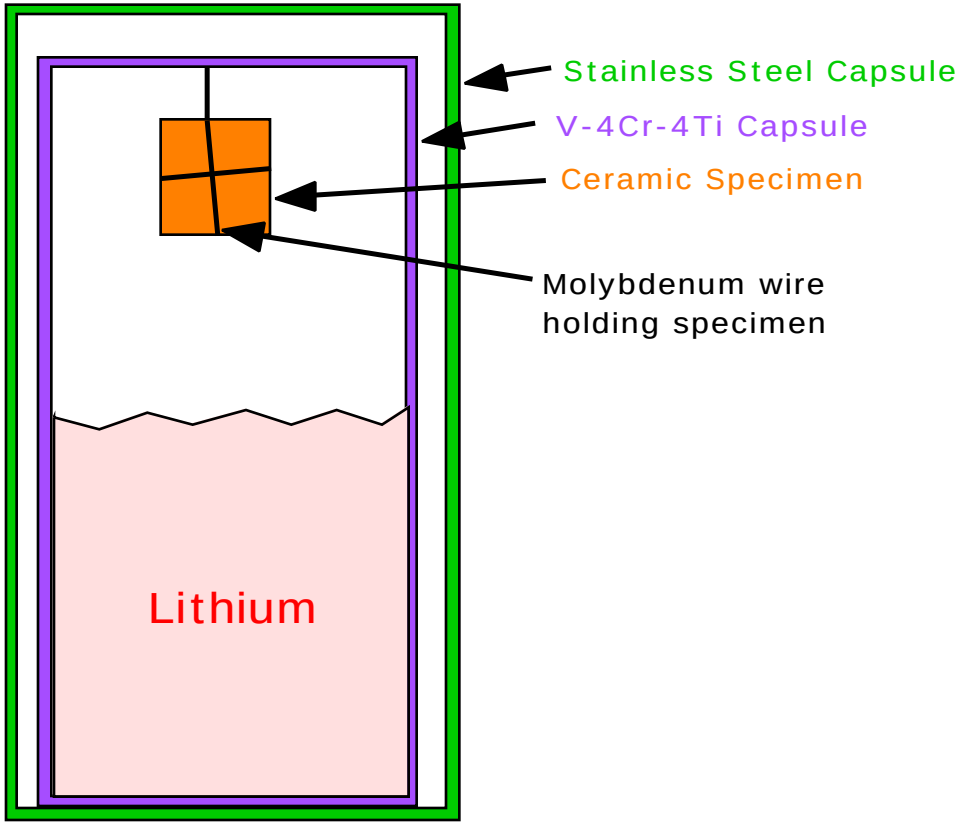
Corrosion control likely will depend upon maintaining the proper levels of corrosion product in the lithium

Rather than purifying the Li, expect to get less corrosion of ceramics by doping the lithium

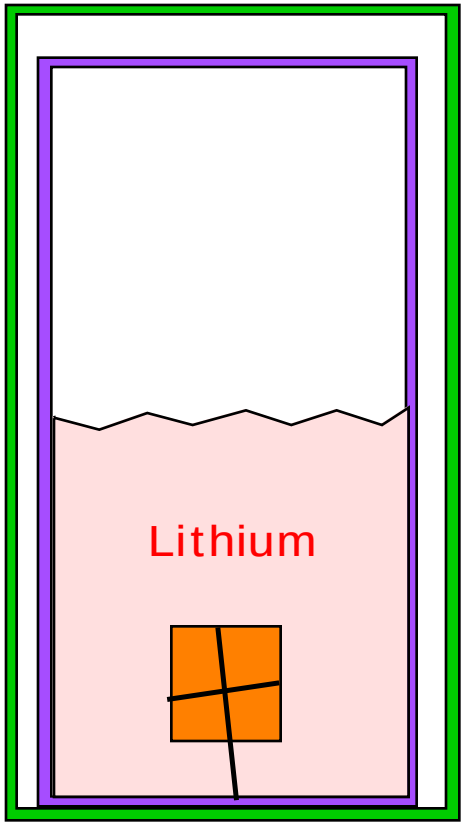
Correlation between Thermocalc calculations & experiments

- Opposite result is found for metals: especially Na or N in Li with ferritic steels

Lithium Capsule Testing at ORNL



before/after test



during test

CaO-> V-Cr-Ti inner capsule

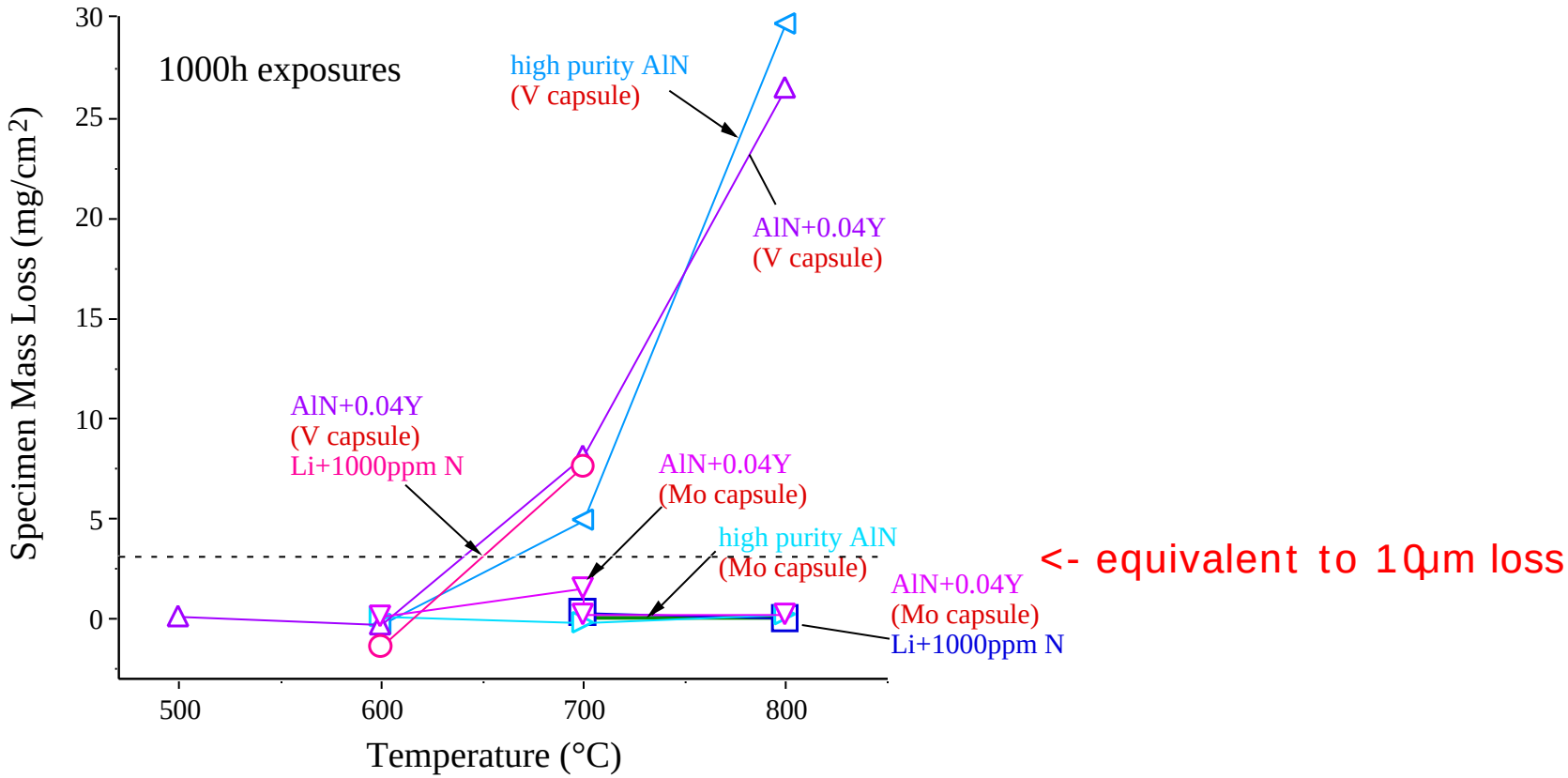
AlN -> V alloy or Mo inner capsule

Type 316 capsule protects the V or Mo capsule from oxidation

Inverting the capsule allows the lithium to drain from specimen

AlN: bulk AlN + Y, O impurities

Sensitive to container: good compatibility with Mo, not V



Tests on AlN+0.04Y and higher purity AlN from Tokuyama Corp.

Both show high mass losses above 600°C in V alloy containers

but small mass changes up to 800°C in Mo containers

Addition of 1000ppma N to Li has little effect in either case

Post-test Li chemistry indicates only V alloy capsule getters N

AlN coatings

Concerns

Critical issue may be compatibility with V-Cr-Ti

e.g. AlN + (Ti)V + (O)V -> Al_2O_3 + TiN

- require coating on all high T metal surfaces?

Delicate fabrication for coating

- Any residual O will be gettered by Li
- adhesion problem at metal-AlN interface ?

Status

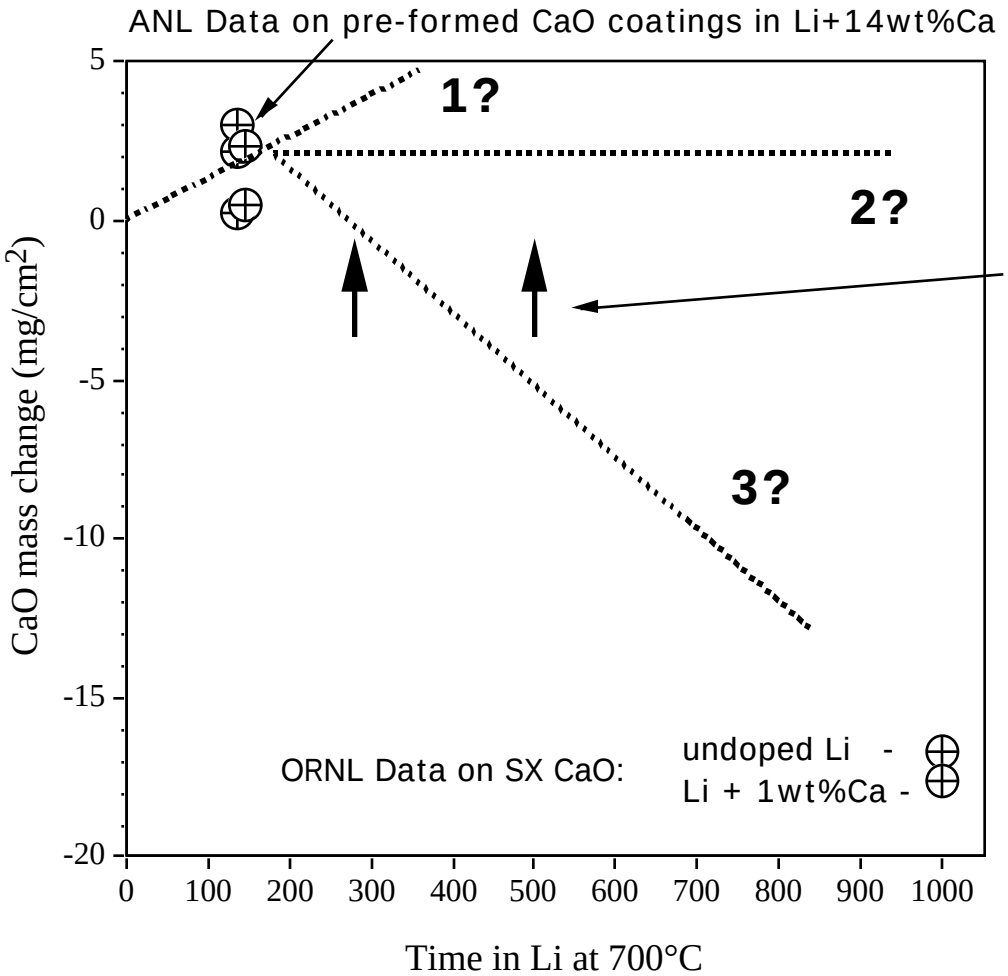
Bulk testing concluded

Initial AlN coatings made by PNNL are being characterized at ORNL prior to Li exposure deposited on 15mm polished V-4Cr-4Ti disk

Difficult to find high purity AlN coating process

CaO: ORNL/ANL differences

Results are not necessarily inconsistent



137h and 145h ANL experiments
- 3 of 5 specimens showed mass gains equivalent to 10µm thickness increase

282h and 500h ANL experiments
- no data reported in papers
- these data points are critical for analysis

<u>3 options for longer time:</u>
1. continued mass gains
- not possible, V will run out of O
- thick coating, heat transfer problem
2. no additional mass gain - CaO stable
3. mass loss at longer times
- CaO initially grows, then dissolves
- consistent with ORNL result

Differences in experiment:
ANL
- same Li used for many experiments
  oxygen% = f(t)?
- cleaned residual Li off with alcohol
ORNL
- new Li for each test (needs O analysis)
- vacuum distillation to remove Li
- lower Ca content in Li

CaO coatings

Concerns

Dissolution rate too high at 700°C

restricted to lower temperatures

High solubility of Ca and Oin Li may be detrimental

potential problems with breeding if above 10at%

precipitation at lower T could cause flow problems

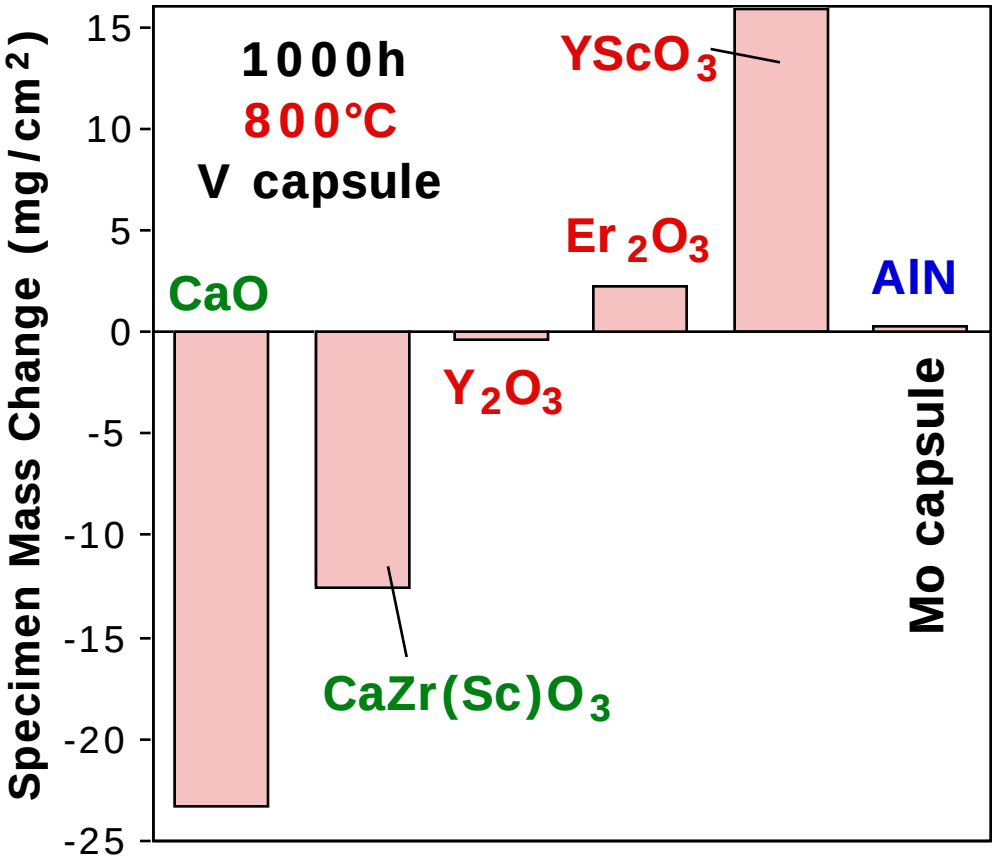
Delicate coating - can't be exposed to air

Status

Long-term testing continuing at ANL

Other high temperature candidates

screening of bulk ceramics in Li at 800°C



Several show promise at 800°C in static testing

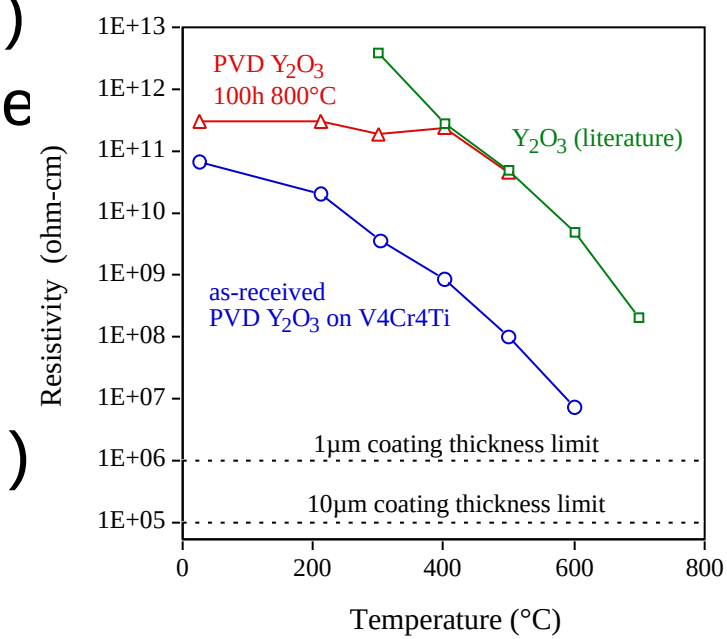
Er_2O_3 and $YScO_3$ mass gains due to specimen porosity

Adding Zr and Sc to CaO reduced mass losses

Y_2O_3 coatings are being developed

Y_2O_3 coatings

- 10µm thick, made by LLNL using PVD process deposited on polished V-4Cr-4Ti 13mm disk
- Tested 100h and 1000h at 700° and 800°C
  1000h 700°C 0.59mg/cm^2 increase (+0.2%)
  1000h 800°C 0.51mg/cm^2 increase (+0.2%)
- Post test characterization
  XRD: weak/no Y_2O_3 peaks, $YLiO_2$ + other? peaks
  (consistent with mass gain)
  AES: Li, mobile on surface
  Ti-rich surface oxides
  Resistance: (in progress)
  vacuum 10^{-6} Torr
  (prevent V oxidation)
  heated to 600°C:



Y_2O_3 coatings

Concerns

Is resistance high enough at 700°C?

Formation of $YLiO_2$ or other compounds

- degrades resistance ?
- first step in dissolution ?
- interaction with Ti in V ?
- Li on surface: why not removed by alcohol?

Adhesion - 1000h/700°C coating spalled on handling

Need coating technique for complex shapes

Status

Continuing characterization

Resistance is primary figure of merit

XTEM to examine microstructure

Close to meeting metrics for coating

Other candidates

less progress due to focus on Y_2O_3

Er_2O_3

- suggested candidate from prior work
- no commercial source of material
- recently produced 97% dense bulk specimen
- repeat Li capsule testing at 600°-800°C

$YScO_3$

- suggestion of Suzuki
- both Sc and Y oxides should be stable in Li
- different crystal structure

  "open" Y_2O_3 structure may allow Li to enter

  smaller Sc ion may fill lattice
- attempting high temperature sinter and/or

  hot pressing to get density above 80%

Summary

Several candidate materials show progress

- Y_2O_3 - close to meeting metrics
- AlN - need high purity coatings for testing
  - evaluating PNNL coatings at ORNL
- CaO - need long-term data
  - only candidate that can in situ "heal"
- $Er_2O_3/YScO_3$ - need better bulk specimens

Need to add coating fabrication experts to team

Li loop proposals submitted to US DOE & Japan

- ANL - pumped loop
  - V alloy construction
- ORNL - thermal convection loop
  - Mo construction (able to test AlN or oxide)
- Start date based on meeting metrics and $