Alternative Objectives, Rationale and Status of Other Coatings

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Research sponsored by the
Office of Fusion Energy Sciences
U. S. Department of Energy (DOE)
contract DE-AC05-00OR22725 with UT-Battelle, LLC.

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 electrical 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

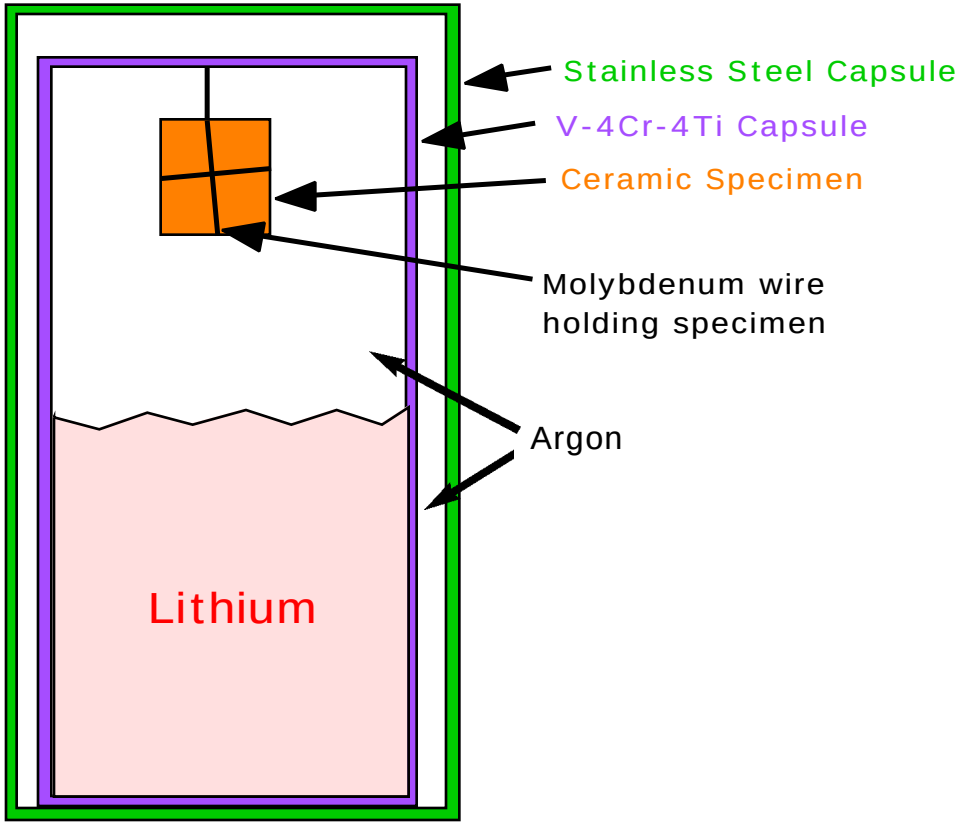
MHD Coating Metrics

Proposed by U.S. and adopted this year:

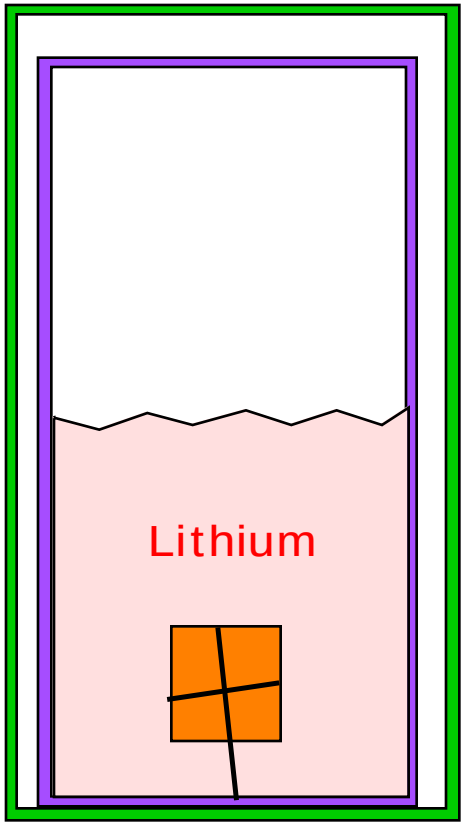
- Isothermal Li exposure:
  - coating: 5-15µm thick
  - duration: ≥1000h
  - temperature: 700°C or 50°C above max. T
  - less than 10%solute additions to Li
- Post exposure performance:
  - less than 10% dissolution/reaction
  - maintain electrical resistivity (≥10^5 Ω-cm)
- Cyclic Li exposure
  - heat 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 beginning Li loop testing

Lithium Capsule Testing at ORNL



before/after test



during test

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

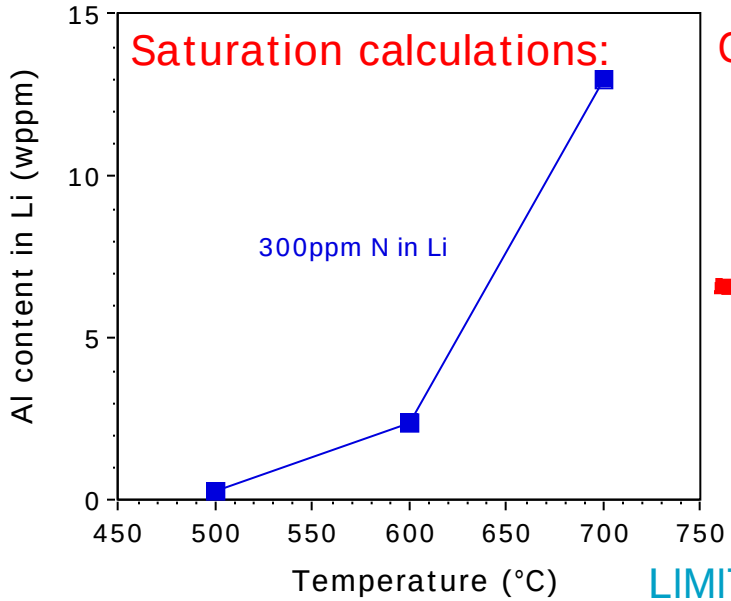
AlN -> requires Mo inner capsule to avoid N gettering from Li

Type 316 capsule protects the V or Mo capsule from oxidation

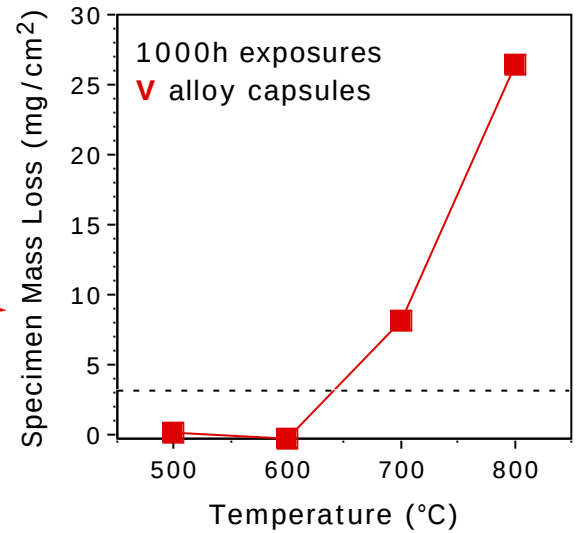
Inverting the capsule allows the lithium to drain from specimen

AlN: thermodynamics & experiments

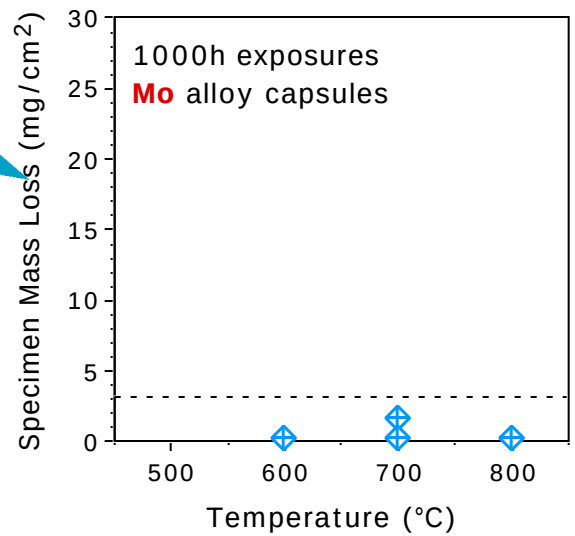
ThermoCalc using AlN = (Al)Li + (N)Li



Capsule getters N
No Saturation
of Al, N:
DISSOLUTION



Saturate
Al and N:
LIMITED DISSOLUTION



Al solubility increases with temperature

- but still relatively low levels

Limited dissolution when Al and N saturate

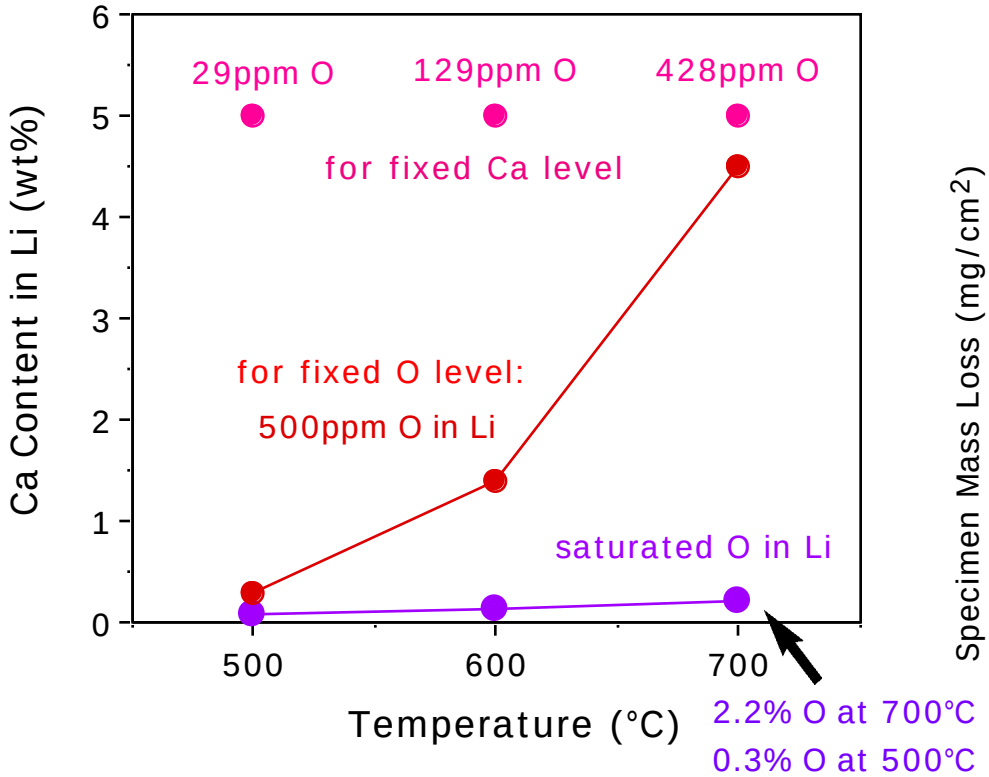
Critical issue may be V-Cr-Ti compatibility:

e.g. $2AlN + 2(\underline{Ti})V + 3(\underline{O})V \rightarrow Al_2O_3 + 2TiN$

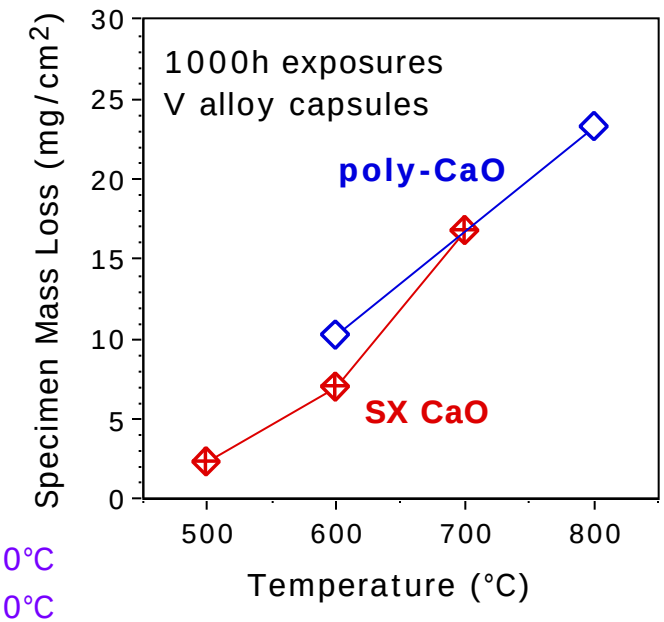
Al_2O_3 dissolves in Li, so need high purity coating for testing program

CaO: thermodynamics & experiments

ThermoCalc using CaO = (Ca)Li + (O)Li



Experimental results with V alloy capsule:



Calculated Ca values are 0.1-5wt%; for AlN, Al values in ppm

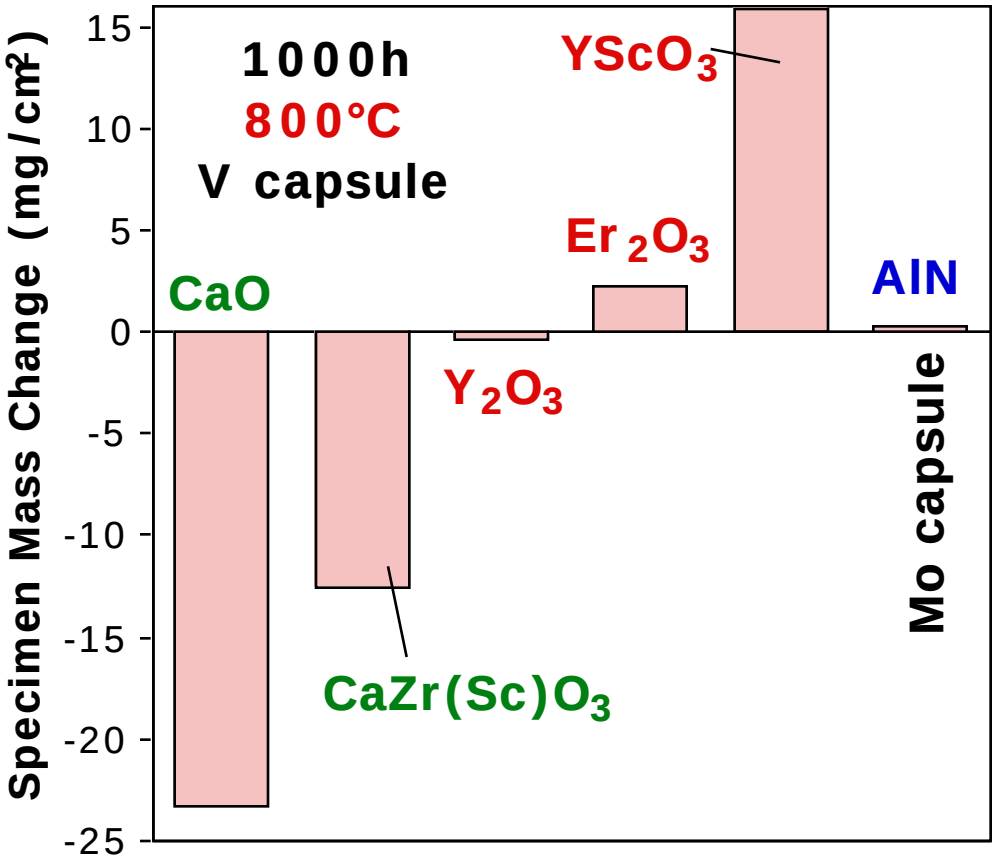
Calculations suggest dissolution possible; confirmed by experiments

High Ca and O could plug flow in cold leg or inhibit breeding

These results suggest that an oxide with a cation which has a low solubility in Li should have better compatibility

Other high temperature candidates

screening of bulk ceramics in Li at 800°C



Several show promise at 800°C in static testing

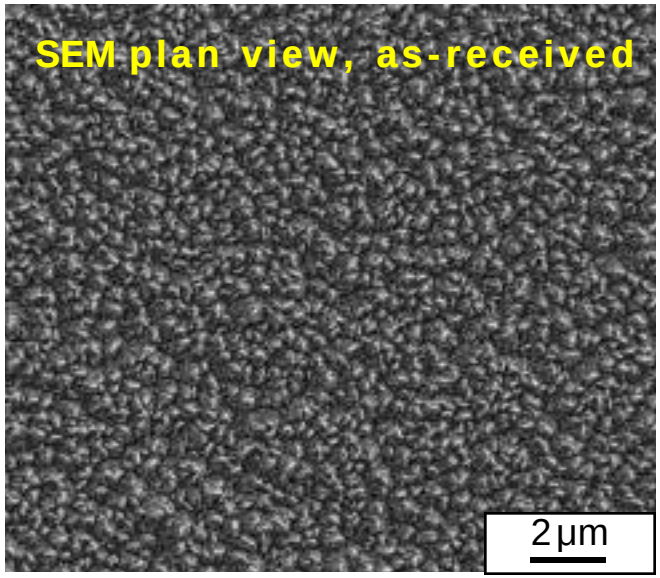
Er_2O_3 and $YScO_3$ mass gains due to specimen porosity

Suzuki: adding Zr and Sc to CaO reduced mass losses

Y_2O_3 showed most promise and was pursued first

Y_2O_3 coatings

- made at LLNL (A. Jankowski) using EB-PVD
  deposited on polished V-4Cr-4Ti 13mm disk
  measured thickness of 12.5µm (laser profilometry)
  fine grain size (0.5µm):



Li exposures:
  100h at 700°C
  1000h at 700°C
  100h at 800°C
  1000h at 800°C
  3 x 100h cycles at 800°C (cool to 25°C between cycles)

In progress:
  1000h at 700°C (first specimen damaged)
  3 x 100h at 700°C
  2000h at 800°C

Y_2O_3 coatings

After exposure:

1000h 700°C 0.59mg/cm^2 increase (+0.2%)

1000h 800°C 0.51mg/cm^2 increase (+0.2%)

Characterization:

Auger: 800°C/1000h specimen

Li observe to be mobile on surface

nodules nucleate and grow under beam

Ti-rich surface oxides

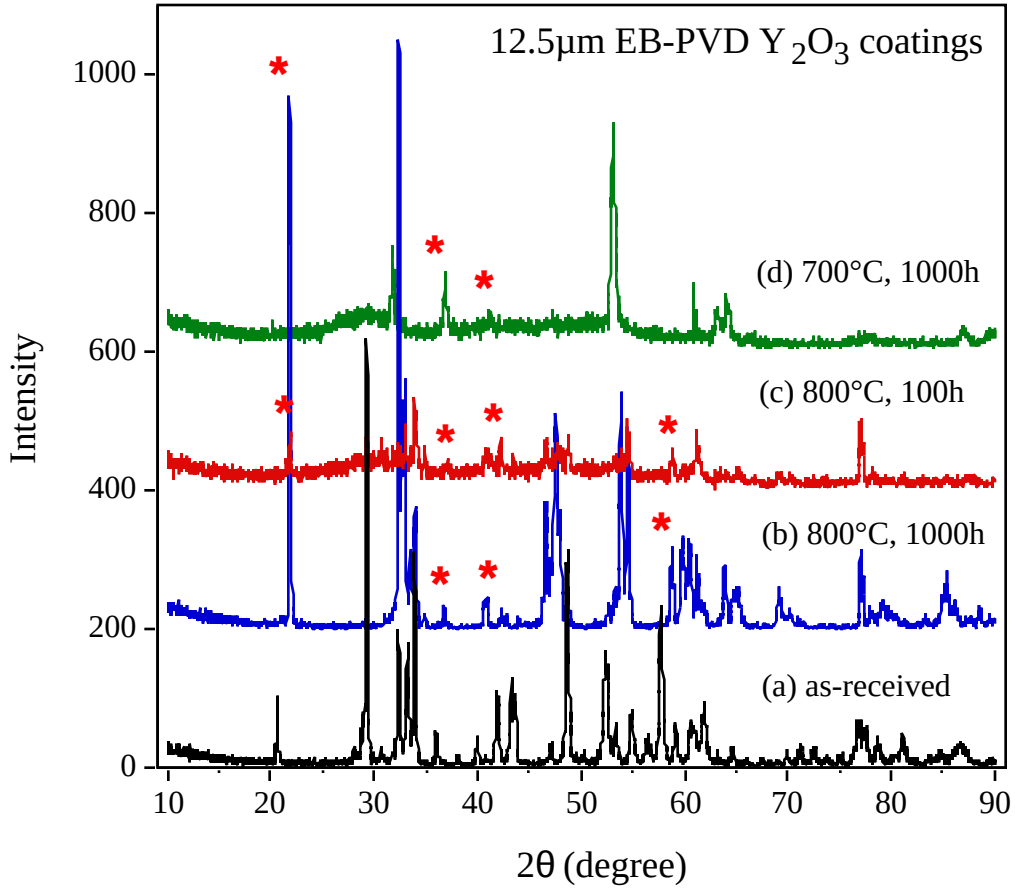
not present on as-received coating

Presence of Li and Ti may explain mass gain

Specimen will be cross-sectioned at later stage

Y_2O_3 coatings: XRD results

before and after Li exposures



* $LiYO_2$

As-received coating shows perfect match with Y_2O_3

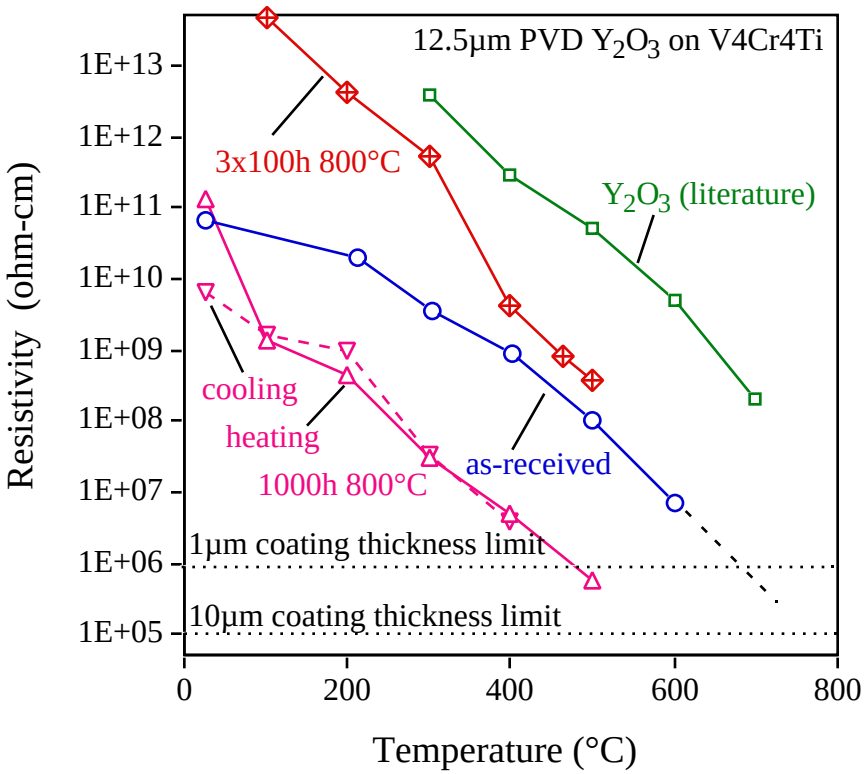
After exposure to Li, coatings show a few Y_2O_3 peaks + many others

$LiYO_2$ peaks increase in intensity with 800°C exposure time

Several unidentified peaks, possible Y-O or Y-Ti-O compounds

Y_2O_3 coatings: resistivity results

before and after Li exposures



vacuum: 10^{-6} Torr or less
- limit V-4Cr-4Ti oxidation

limited to 500-600°C:
- improved apparatus for +700°C being designed

Au electrode + guard
- 5.1mm diameter
- guard ring to limit leakage

Constant voltage: 5-30V

Current: measure to 10^{-12} A

As-received coating showed lower resistivity than literature values
- possibly due to Au in cracks/pores (2 other specimens shorted)

1000h/800°C lower resistance: Au electrode was attacked by Li
- lower resistivity measured at 25°C after heating cycle

Cycled specimen (800°C/3x100h): showed no degradation
- higher values using constant 5V to limit dielectric breakdown

Have we met the metrics?

Optimistically: Spirit has been met

- coated specimen survived 3, 100h cycles at 800°C and retained high resistivity
- reaction metric assumed resistivity drop
- 1000h test was at 800°C, metric was 700°C
- as-received coating had low resistivity

Pessimistically: More data are needed

- resistivity not measured to 700°C
- 800°C/1000h specimen resistivity too low
- apparently little Y_2O_3 left after 800°C tests
- $LiYO_2$ has low resistivity (<1000 Ω-cm at 400°C)
- early stage of understanding these results
- EB-PVD not appropriate for complex parts

Additional factors to consider

MHD coatings are critical to V/Li blanket concept

JUPITER-II funding is available

Loop construction will require ≥1 year to complete
- limited progress can be made without it
- continue collecting data on coatings
- allow time for coating development
- first loop tests will be on bulk ceramics

Importance of a U.S. loop test facility:
- several attractive liquid blanket concepts
  all require ΔT compatibility testing
- issue for ferritics &SiC as well as vanadium
- "tacit" knowledge is fading away in U.S.
  need to maintain this capability
  educate next generation of corrosion scientists
- address fundamental corrosion science issues

Summary

Based on bulk ceramic exposures in Li, Y_2O_3 was selected as a promising coating material

EB-PVD Y_2O_3 coatings have been exposed to Li at 700° and 800°C for up to 1000h

All coated specimens survived the exposure and were characterized

- small mass gains attributed to Li and Ti on coating
- reaction with Li resulted in new phases formed
- coating resistivity was measured after 800°C exposures
  - 3x100h: no change
  - 1000h: lower, some degradation due to Au-Li reaction

It is recommended in FY03 that coating testing and development continue and that construction begin on a U.S. loop testing facility

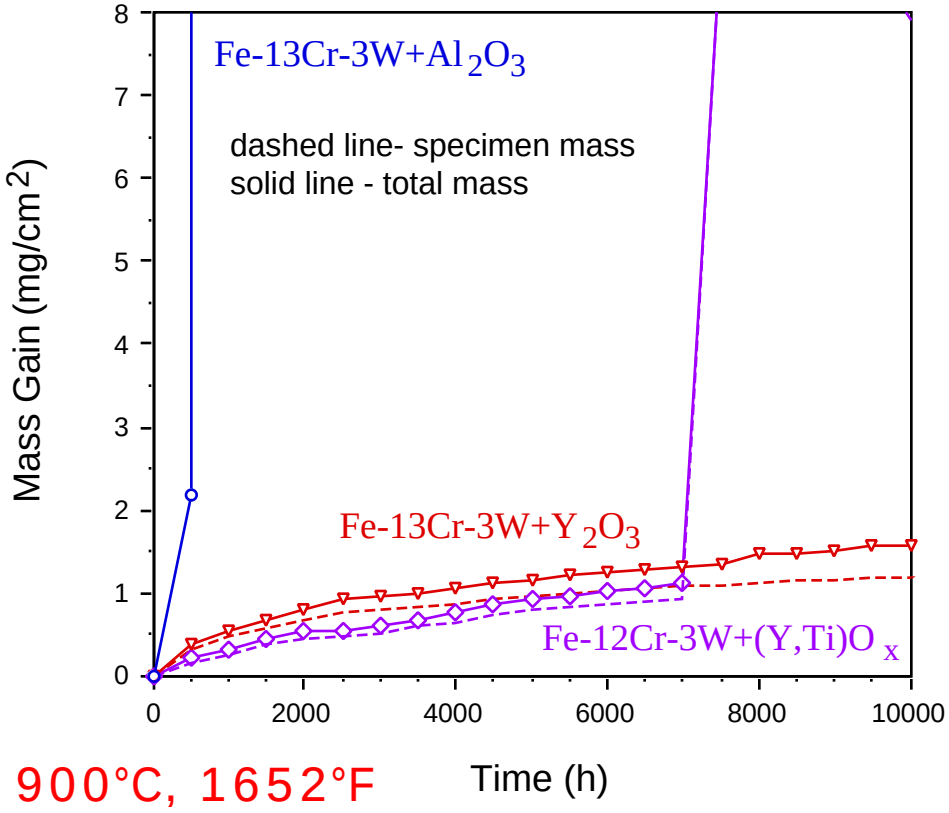
MHD future objectives

- better characterization of Y_2O_3-Li interactions
  microstructure (phases, Li penetration...)
  resistivity
- need coating experts
  bring state of the art thinking to problem
- need ΔT information from loop
  no substitute for experimental result
  no viable coating until passes this test
  Example: Nb-1Zr with Bi (100ppm Nb solubility)
    static capsule testing showed good results
    700°C loop plugged in 24h due to mass transfer
  testing facility could be designed for other systems
- continue development of other candidates
  AlN, Er_2O_3, $YScO_3$
- need to maintain U.S. expertise

ODS Fe-Cr Air Oxidation: 900°C

500h cycle, specimens held in alumina crucible

May 1999: thought that 900°C was no problem...



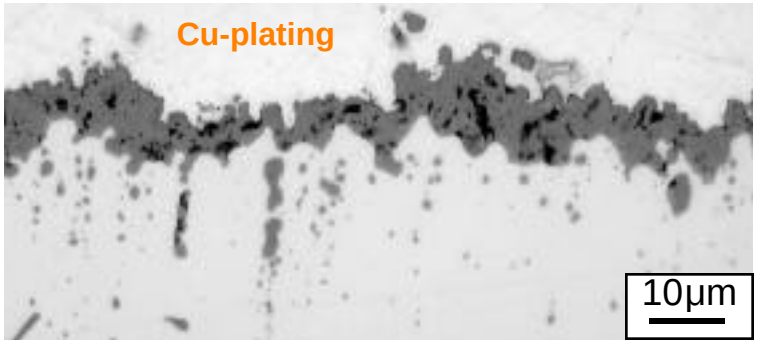
900°C, 1652°F

Fe13Cr3W+Al_2O_3 (No Y)

- faster Cr consumption
- alloy Cr depleted
- breakaway FeO oxidation

Y Benefit -

- reduces Cr_2O_3 growth rate by >10X
- convoluted oxide and some internal attack:



Fe-**12**Cr-3W+(Y,Ti)O_x

Breakaway oxidation after 7000h

Apparent effect of lower Cr content

ODS FeCr compatibility objectives

- liquid metals
  - behave the same as conventional alloys?
  - can MHD coating inhibit dissolution?
- O, H, He environments
  - any O-H-He embrittlement problem?
  - CrO_3 volatility problem?
  - any effect on oxide particles?
  - develop oxidation-limited lifetime model
- improved corrosion resistance
  - Cr: low for Pb-Li, high for oxidation
  - doping to improve performance
- great opportunity to interact with Fossil Energy

Refractory metal future objectives

- Vanadium alloys
  - fundamental difference from Ta and Nb(no getter)
  - no microstructural understanding of O embrittlement
    - no proven mechanism to explain O effect
    - where does O go?
    - grain boundaries vs. bulk effects
    - previously addressed by internal friction work
    - outcome: strategies for minimizing effect
  - thicker specimens - no confirmation of predictions
  - DBTT experiments - smaller specimens viable
- need to maintain U.S. expertise
  - refractory metal oxidation different problem
  - Wagner model not applicable
  - virtually non-existent research community