Recent Progress Addressing Compatibility Issues Relevant to Fusion Environments

B. A. Pint, K. L. More, H. M. Meyer, J. R. DiStefano
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156

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Introduction

Compatibility (corrosion) critical durability concern
in any high temperature system

Fusion reactors:

- Specific concerns determined by:
  - structural materials (ferritics, austenitics, V, SiC...)
  - blanket concept (cooling, breeding, etc.)
  - coolant (He, Li, PbLi, FLiBe...)
  - temperature, pressure, etc.

Currently active U.S. priorities:

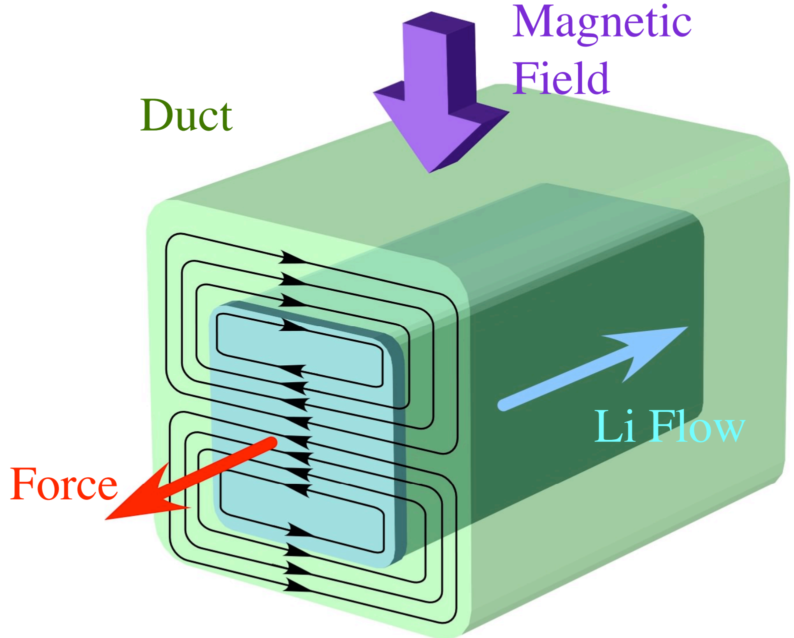
- Insulating coatings for V-4Cr-4Ti/Li blanket
- SiC composites / Pb-Li

Recently concluded:

- V-4Cr-4Ti / vacuum (O, H impurities) or He

The magneto hydrodynamic problem

For self-cooled liquid metal blanket and magnetic field



MHD force causes:

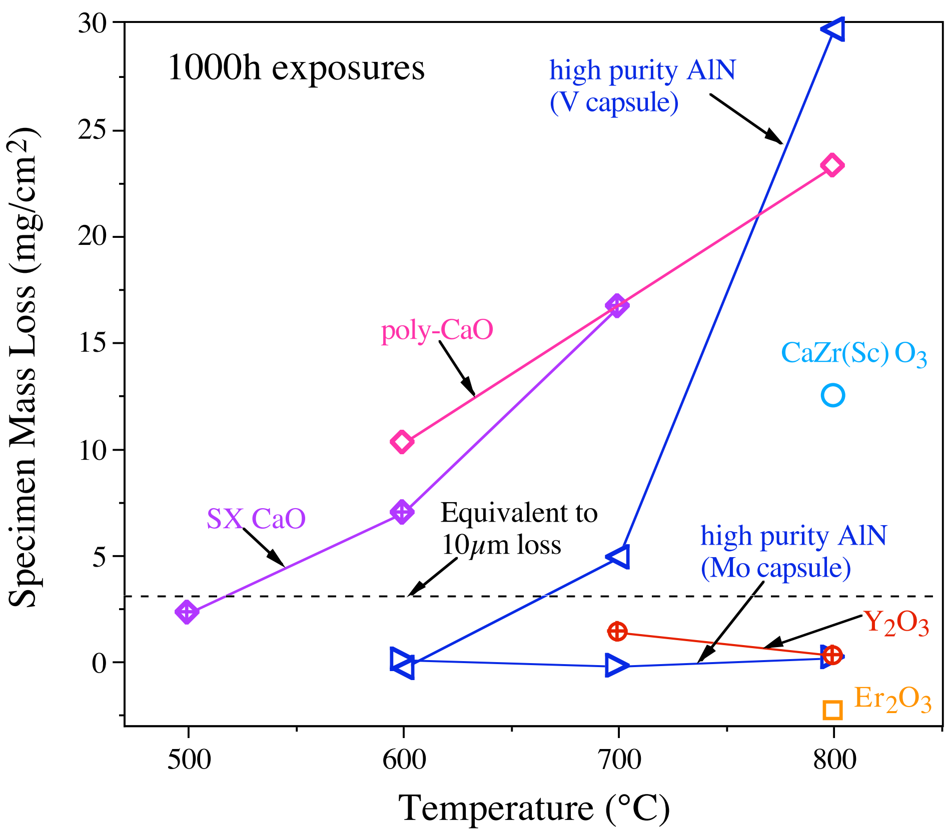
- a load to the pumping system
- additional stress on structures

A solution is required for this concept to be viable

Change in research emphasis

Recent reviews focused on CaO and AlN as the best candidates

However, Li compatibility results showed problems



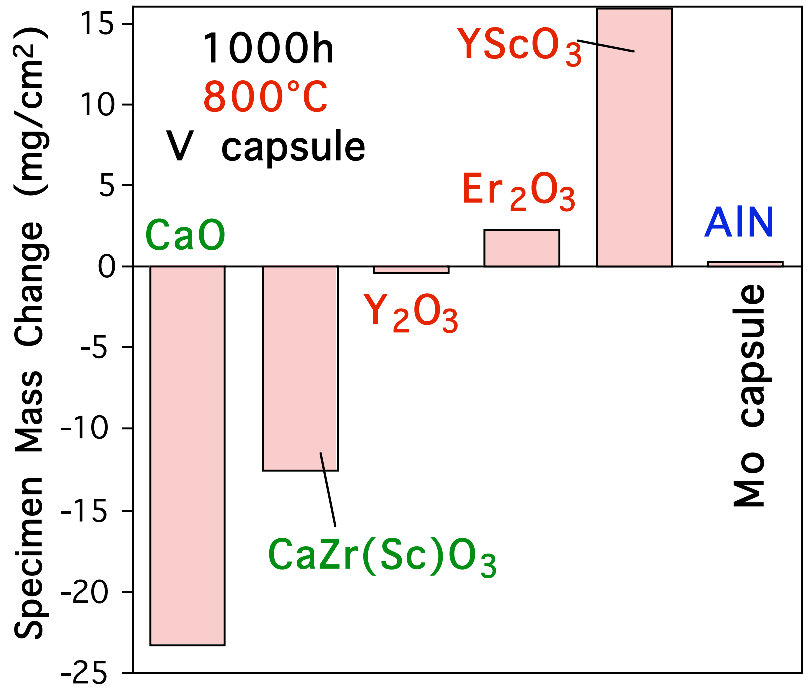
CaO dissolved:
Polycrystalline CaO
and single crystals

AlN dissolved:
when tested with V alloy capsule (not with Mo capsule)
issue of N gettering
(also need low O coatings)

What is left?

Few materials are compatible with Li
Screening of bulk ceramics in Li at 800°C

Materials	ΔG_f° (kJ/mol O_2)
CeO_2	-1025
Al_2O_3	-1045
Li_2O	-1122
Er_2O_3	**-1206**
CaO	-1207
Y_2O_3	**-1211**
Sc_2O_3	-1213



Several show promise at 800°C in static Li testing

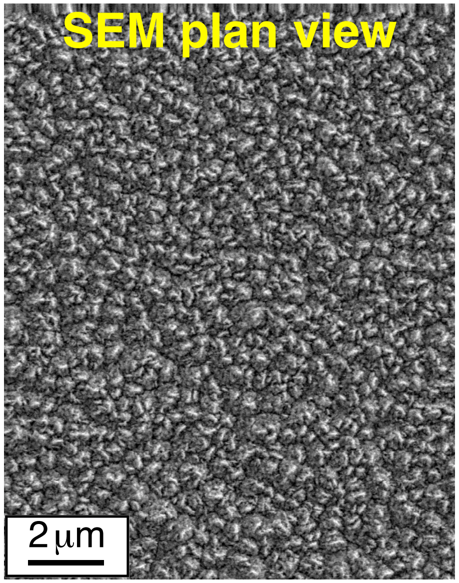
Er_2O_3 and $(Y,Sc)O_3$ mass gains due to specimen porosity

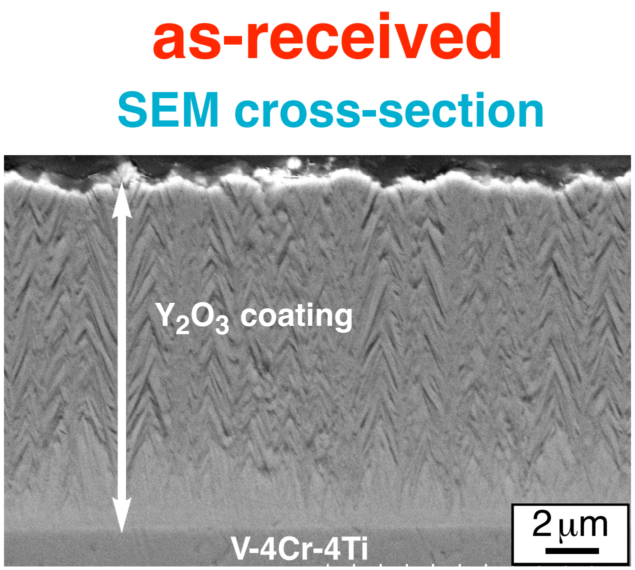
Y_2O_3 showed most promise and pursued first by U.S.

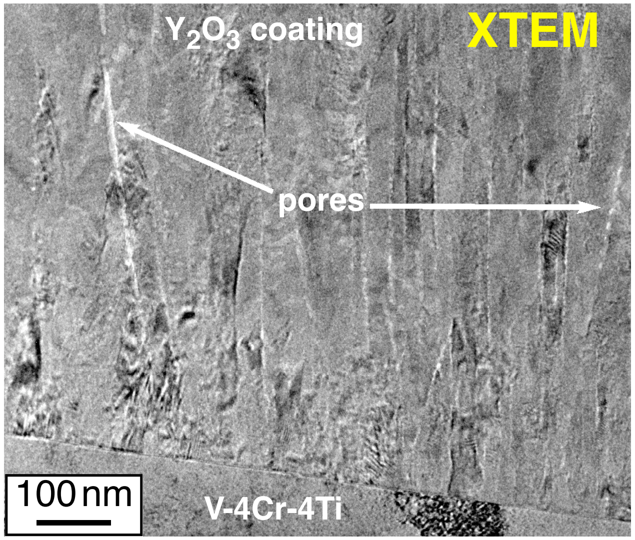
Er_2O_3 coatings now being fabricated at LLNL

Y_2O_3 coatings by EB-PVD

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



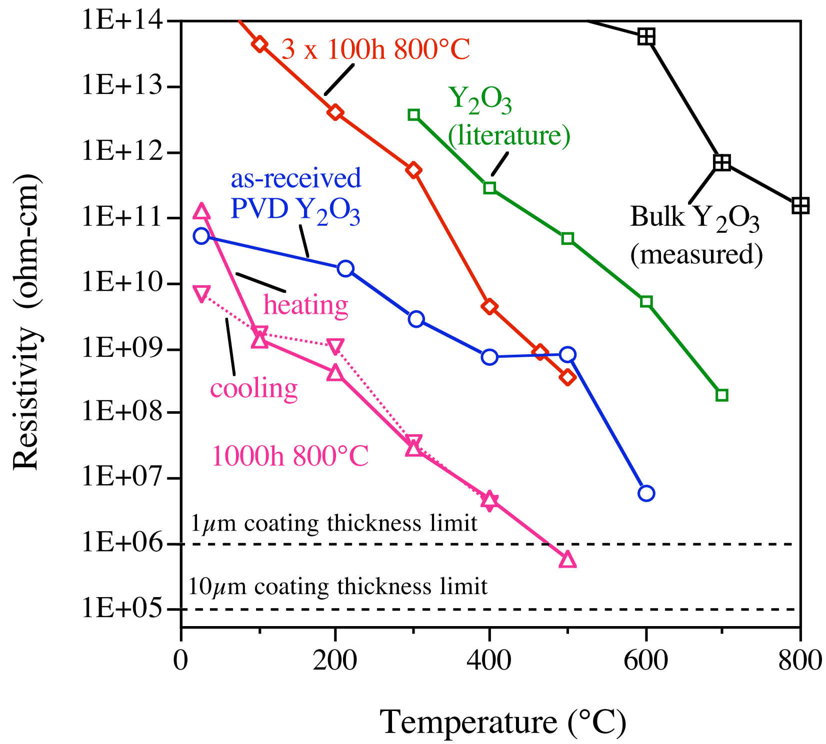


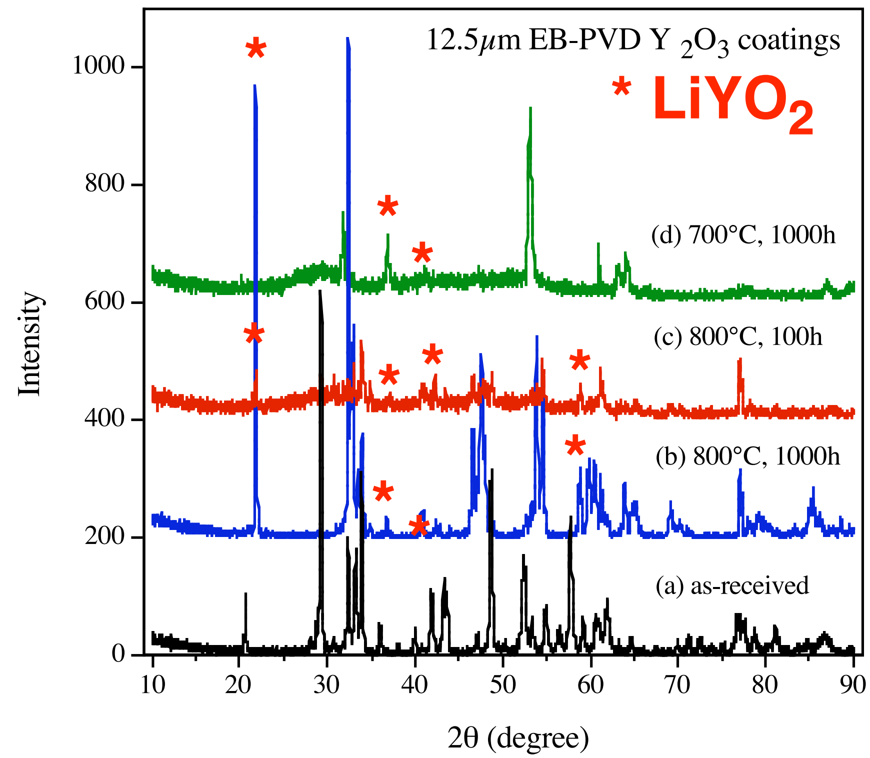


Exposures:

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

Y_2O_3 coatings: initial results
before and after Li exposures





As-received coating showed lower resistivity than literature values and much lower than measurements on sintered, bulk Y_2O_3

1000h/800°C lower resistance: likely degradation by $LiYO_2$
$LiYO_2$ has much higher conductivity and is not acceptable

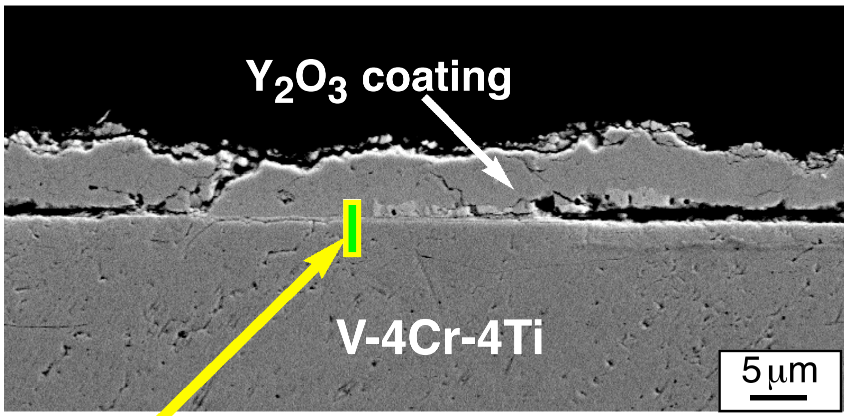
Cycled specimen (800°C/3x100h): showed no degradation

Surface morphology changed, Ti-rich oxides by Auger

Characterization: after 100h at 800°C

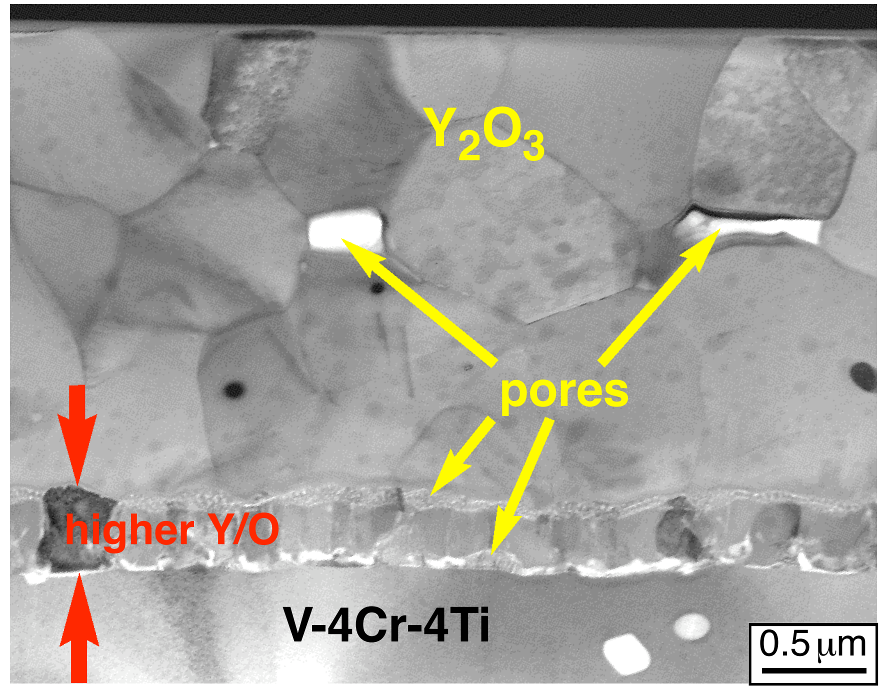
EB-PVD Y_2O_3 coatings exposed to Li in Mo capsule

SEM polished cross-section



Focused ion beam section cut from mounting to make TEM sample

TEM cross-section near interface



Substrate-coating separation observed in cross-section

XTEM specimen from intact region

Columnar grains -> coarser, equiaxed Y_2O_3 (same d spacing)

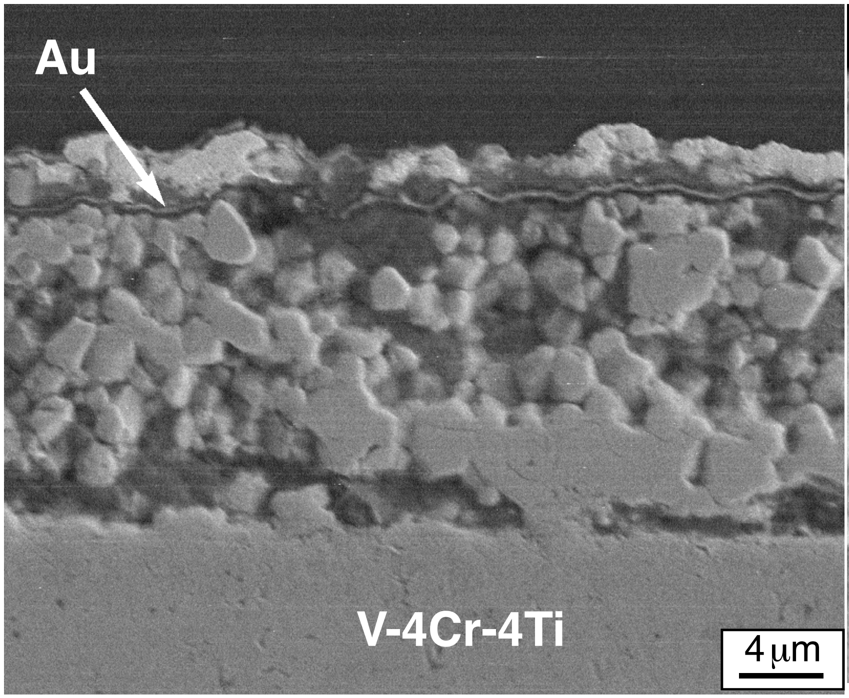
Interlayer: higher Y/O ratio (O loss to substrate, no Li?)

Fine pores above and below interlayer

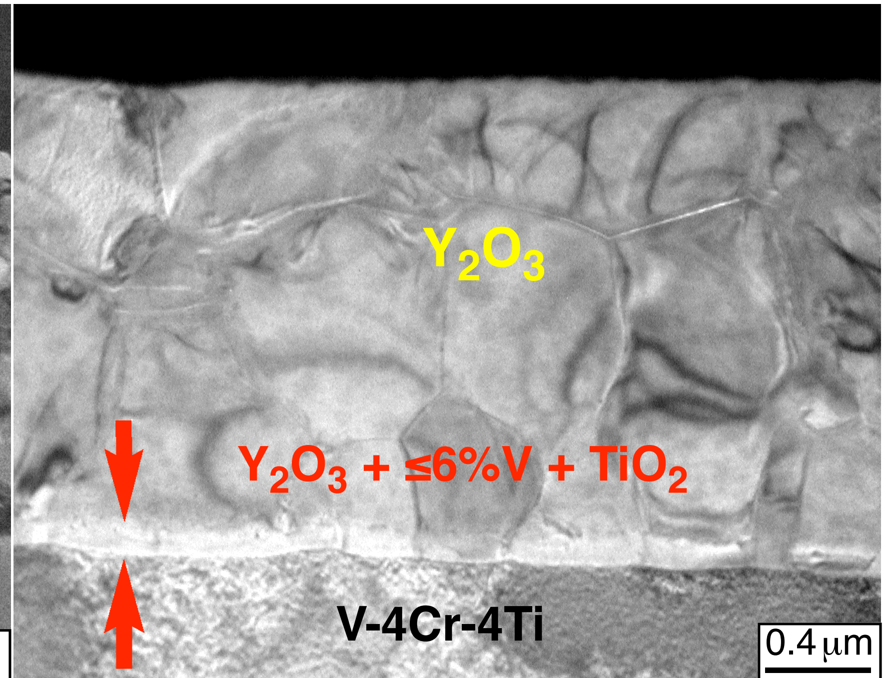
Characterization: after 1000h at 800°C

EB-PVD Y_2O_3 coatings exposed to Li in Mo capsule

SEM polished cross-section



TEM cross-section near interface



Coating crumbled during sectioning
Similar equiaxed grain structure as after 100h
Interlayer not present
Near V-4Cr-4Ti substrate - fine Ti-rich oxide particles
up to 6at.%V in oxide

Current MHD coating strategy

(1) Ceramic - Li contact is a major problem

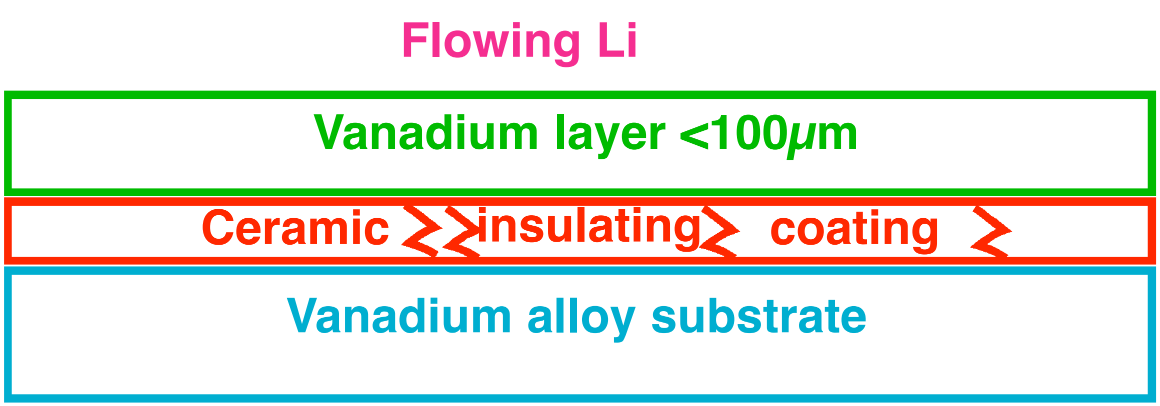
(2) Cracks in coating may short it

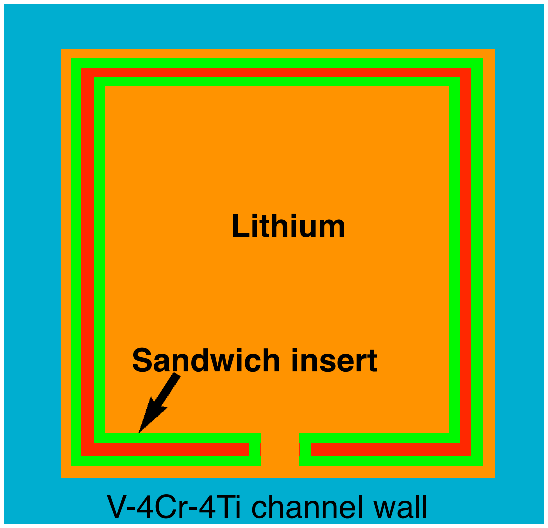
- There will be defects in the ceramic coatings
  Either as-deposited or due to tensile cracking
- Reasonable assumption that Li will wet cracks
  (Once Li in crack how could crack heal?)

Therefore, a metallic layer is needed

Vanadium is the logical choice for this layer

Compatibility now an issue for both layers





Vanadium alloy - Li Compatibility

Thin vanadium coating needs good compatibility

"Textbook" response - good compatibility to >700°C

Low V solubility, Li removes O without dissolution

From thermodynamics:

ΔMass = [Carbon + Nitrogen](gain) - [Oxygen](loss)

Literature - loop experiments on V alloys

mixed results (mass gains and losses)

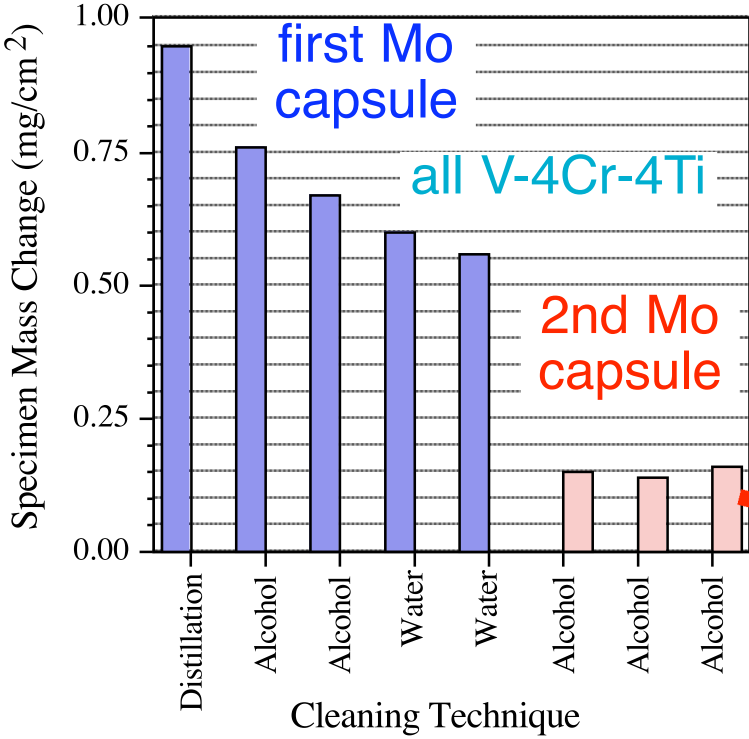
losses with ferritic steel loops - bi-metal issue

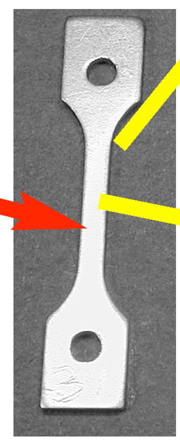
Does Cr and/or Ti change V compatibility?

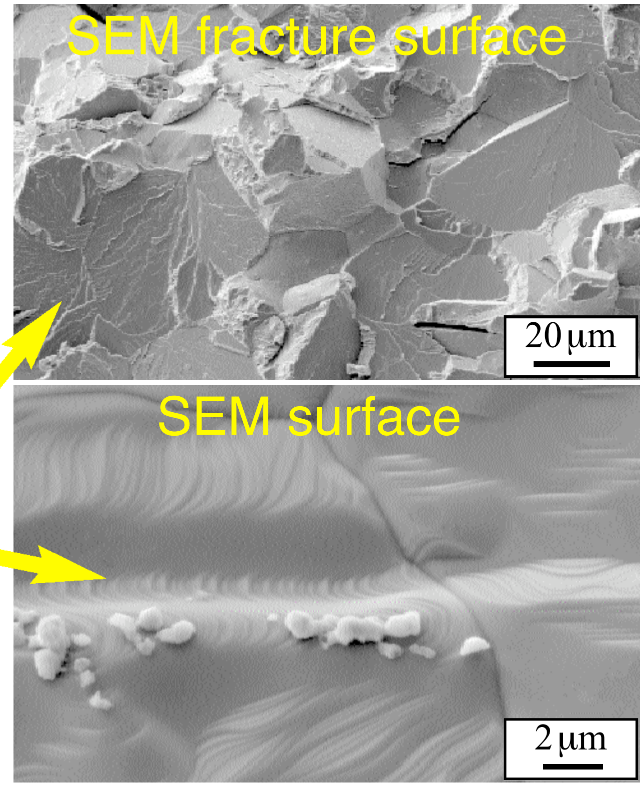
Issue needs to be revisited with a monometallic loop

Recent results of V alloys in Li

V-4Cr-4Ti samples - 800°C, 1000h Mo capsules at ORNL







1st capsule test - high mass gains (different cleaning methods)

2nd capsule test with SS-3 specimens - still small gains

- Nominal Li contamination of 65 ppmw N (manuf. spec.)
- One specimen broke during cleaning (transgranular)
- Mass gain + fracture: indicate very brittle metal
- Auger - surface: little Mo, some Ca, N in native oxide

SiC Composites / Pb-17Li

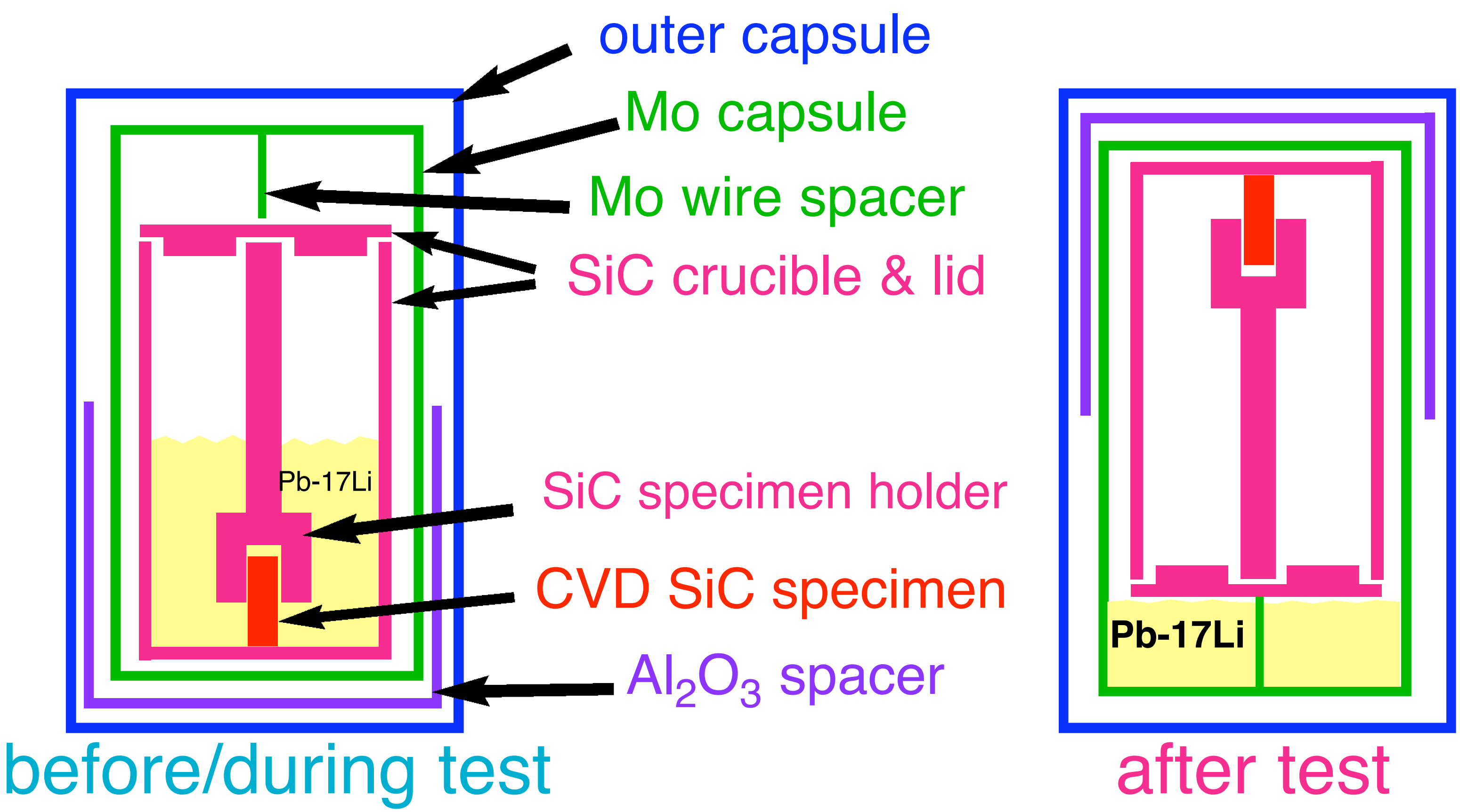
TAURO and ARIES-AT - reactor concepts using SiC_f/SiC composites and a self-cooled Pb-17Li blanket design at temperatures up to 1100°C.

Kleykamp, Terai et al. and Barbier et al. have studied compatibility of SiC and SiC_f/SiC composites at 500°C-1000°C. Generally found good static compatibility to 800°C. Experiment at 1000°C by Kleykamp gave uncertain result.

Need to determine upper temperature limit for compatibility of SiC_f/SiC composites with Pb-Li.

Begin with testing on monolithic high-purity SiC

Capsule testing at ORNL



Inner SiC capsule used to avoid potential Mo-C formation

SiC + Li-Pb + Mo -> Li-Si + MoC_2 (or $PbMo_xC_y$)

Outer capsule: 304SS at 800°; Inconel 600 at 1100°C

Al_2O_3 spacer added at 1100°C to prevent reaction w/Mo

Mo wire welded in place to hold SiC lid shut

Inverting capsule after test allows Pb-Li to drain away from SiC

Test results

- SiC capsule prevented unwanted reactions
- 800°C: no wetting, Pb-Li flowed out after test

  No mass change (±0.02mg precision)

  Black residue: no Pb, Li by AES

  XPS: 54C-26O-10Si-9Li-0.2Pb-0.5N-0.1Na

- 1100°C: limited wetting

  no mass change when PbLi removed

- No wetting, no corrosion
- Pb-Li chemistry (inductively coupled plasma & combustion)

  Kleykamp found 350ppmw Si in PbLi after 800°C test

Test	Li	Si	C	O	N	Al	Cr	Fe	Mo	Ni	Y
800°C	17.49%	<300	1850	4090	98	6	<30	33	<10	<30	<2
1100°C	16.27%	<300	1160	3550	87	193	<30	21	<10	<30	<2

Compatibility testing in liquid metals not complete without a loop test!

Systems reach equilibrium in static tests

Dissolution flux of element X: $J \propto k(C^o - C_x)$

k = rate constant

C^o = solubility limit of X in Li

C_X = actual concentration of X in Li

Static (capsule) testing: no driving force at equilibrium

C_X increases with time -> J decreases to zero

Dynamic (loop) testing: continuous driving force

$C^o = f(T)$, C_X constant (due to precipitation in cold leg)

Value of C^o is not a reliable indicator of compatibility

Example: liquid Bi - capsule tests showed Nb good compatibility, loops showed rapid dissolution

Summary

Solid state reaction between Y_2O_3 and Li at 800°C: $LiYO_2$ formation, reduced resistivity and grain growth were observed

Cracks and compatibility questions have led to a focus on durable multi-layer MHD coatings

Mass gain of V-4Cr-4Ti in Li has raised questions More work needed to assess role of Cr and Ti

Good compatibility was observed between monolithic SiC and Pb-17Li at 800° and 1100°C in a static capsule test

Pb-Li did not wet SiC at 800°C with only limited wetting after 1000h at 1100°C

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MHD Coating Metrics

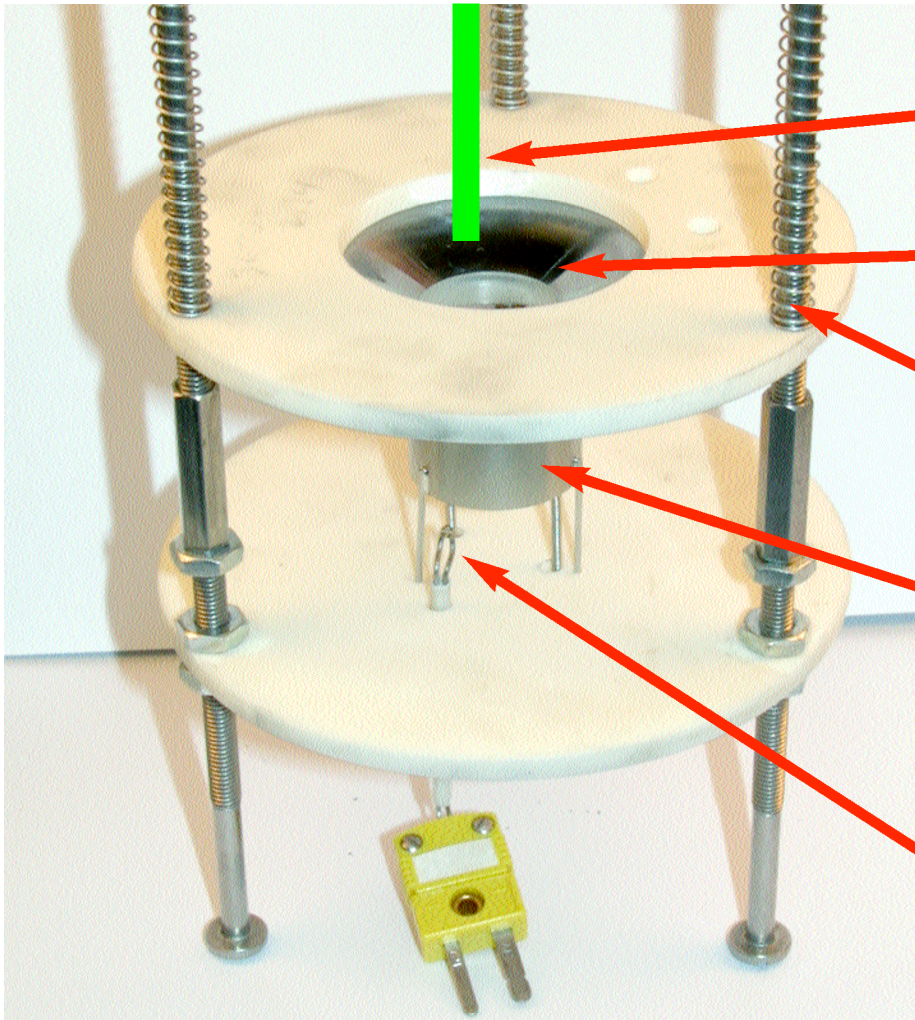
Proposed by U.S. and adopted in 2002:

- 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

“in-situ” coating test

measure resistance of coating in contact with Li

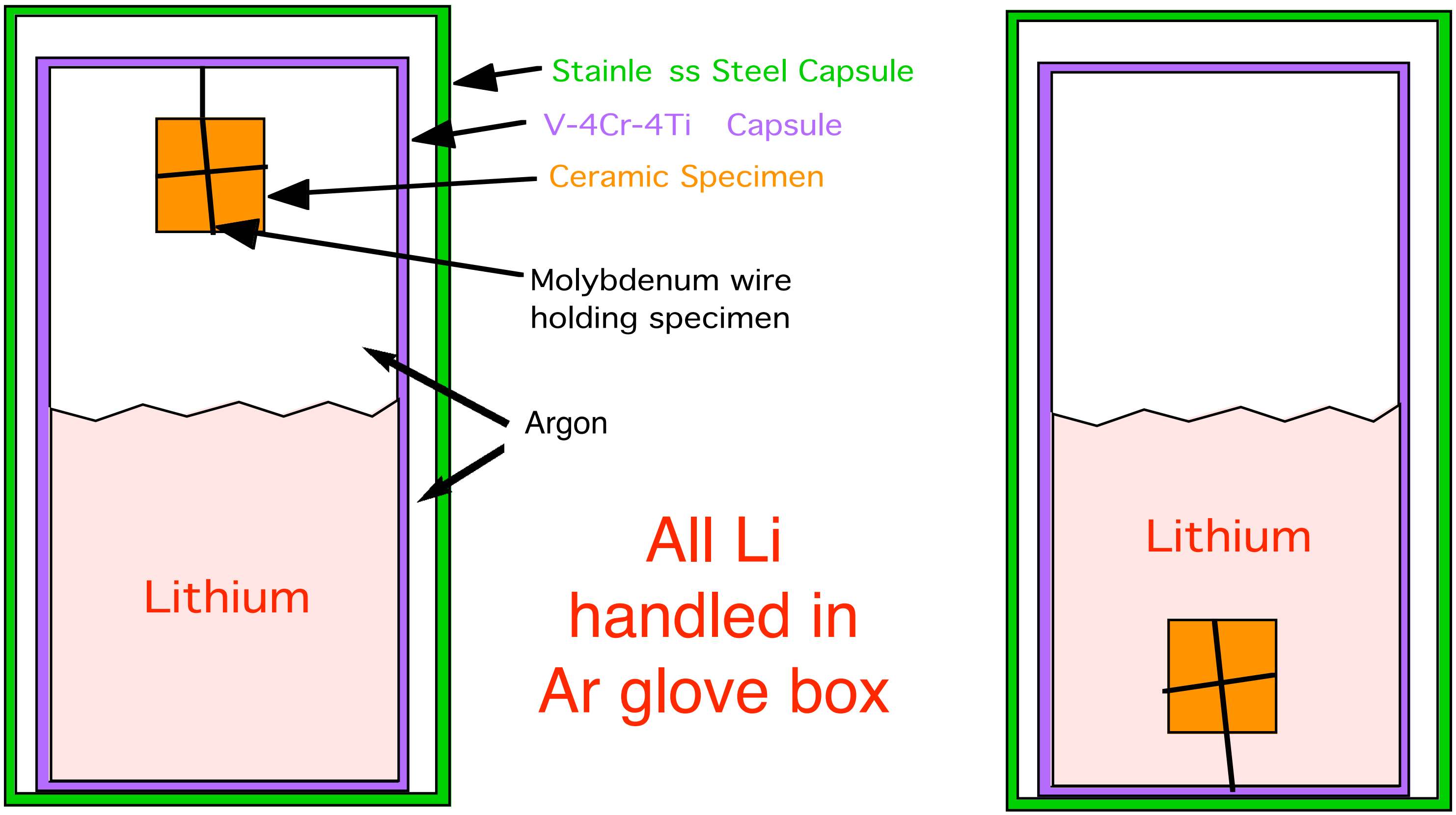


All contained in large Ar glove box to minimize reaction

Additional plexiglass containment to capture Li vapor

high vapor pressure above 400°C could limit experiment

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

Previous work: Vanadium in Li

1964 ORNL report on Li corrosion (only static tests)

Oxygen content can affect corrosion susceptibility of Nb

No O effect for unalloyed vanadium specimens:

Oxygen Content (ppmw) Before Test (dissolved O)	After Li exposure (100h, 816°C)	Mass Loss (mg/cm^2)
400	80	0.08
800	110	0.20
1200	30	0.25
2200	180	0.52

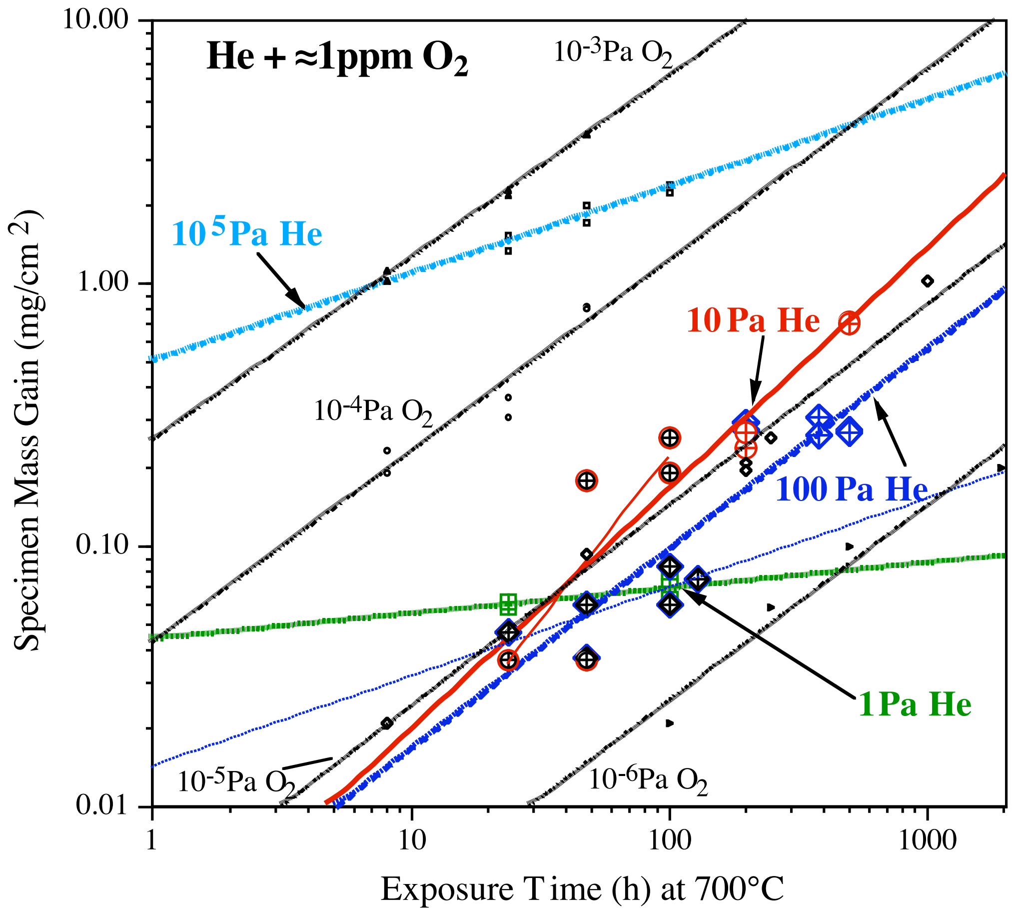
O dissolved in specimens by 850°C, 9×10^{-5} Torr exposures
Li removal from specimens by distillation

Li removed O from vanadium - i.e. mass loss!

No dissolution or attack of vanadium specimens

Oxygen Uptake Kinetics of V-4Cr-4Ti

Effect of Total He Pressure



700°C

Thin line - old data fit

Thick line - fit with 500h data

Near linear kinetics for 10 and 100Pa He - similar to low P_{O_2} data

Lower uptake with higher He pressure

Similar surface oxide thickness formed in each case: 20-40nm

Beginning to collect data at 1Pa and 1000Pa

V-4Cr-4Ti / Helium or Vacuum

Prior Work

Disagreement: parabolic vs. linear kinetics