Research Program on the Development of Electrically Insulating Coatings for the Self-cooled Lithium/Vanadium System

Presented by

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Fusion Materials Program Review

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Research Program on the Development of Electrically Insulating Coatings for the Self-cooled Lithium/Vanadium System

BACKGROUND

- **Focus on electrically insulating coatings to mitigate MHD effects**
- **Coatings probably required for most systems**
- **Relatively new task of US fusion materials program**

APPROACHES of RESEARCH PROGRAM

- **Integrated program including theory, modeling and experiment**
- **Define requirements and identify candidate coating materials**
- **Develop approach for coating Research Program**

HIGHLIGHTS OF RESEARCH PROGRAM

- **Theory and modeling**
- **In-situ formation of coatings/self-healing**
- **Conventional coating processes (PVD and CVD)**
- **Compatibility of bulk ceramics in lithium**

Background - Coating Research Program

The self-cooled lithium blanket concept with a vanadium alloy structure offers potential for high performance with attractive safety and environmental features.

- Development of electrically insulating walls for the coolant channels is key feasibility issue for liquid-metal, self-cooled first-wall/blanket systems for magnetic fusion power applications.
  - Mitigate MHD pressure drop in flowing liquid metal
  - Electrically insulating coating on V-alloy channel walls is proposed approach for Li/V system
  - In-situ formation for large complex channel configuration
  - Self-healing coatings are proposed for reliability

Background - Coating Research Program

- **Coatings (or claddings) are probably required for almost all fusion first-wall/blanket concepts**
  - **Electrical insulators to mitigate MHD effects in liquid metal concepts**
  - **Tritium barriers in H_2O/PbLi concepts (EU)**
  - **He-cooled and flibe concepts for tritium containment**
  - **SiC/He to prevent He leakage into plasma chamber**
  - **To mitigate corrosion constraints in some concepts**
- **Coating research program offers significant benefits for non-fusion applications, e.g., hydrogen, petroleum**
- **Relatively new task of US fusion materials program**
- **Coating program involved extensive international interactions/collaborations (RF, J, EU)**

Approach for Coating Research Program

- Design Studies
  - Assessment of design performance
- Theory and modeling
  - Insulator effects on MHD flow characteristics
  - Preliminary evaluation of candidate coatings
  - Evaluation of potential coating methods
  - Evaluation of potential for self-healing
- Theory, Modeling, Experiment
  - Scoping tests on performance of candidate coatings in static lithium at elevated temperatures
- *Future:*
  - *Dynamic testing in Li with active chemistry control*

Considerations/Requirements for Insulator Coatings

- Electrical resistivity X thickness > 100 Ω-cm^2
  - For $\rho = 10^6$ Ω-cm, t > 1 μm
- Chemical stability/compatibility with lithium at elevated temperatures (to ~ 700^{o}C)
- Potential for coating complex geometries
- Potential for in-situ self-healing of defects that might occur
- Thermal expansion match/bonding with V-alloy
- Safety/environmental characteristics; e.g. low activation
- Materials availability/cost
- Acceptable neutronic properties
- Radiation damage resistance

Candidate Coating Materials

- Only a limited number of materials offer a potential for meeting the most basic requirements, viz., electrical resistivity and chemical compatibility
  - Carbides: most exhibit low electrical resistivity
  - Nitrides: Many exhibit low electrical resistivity
  - Oxides: Limited number are stable in lithium
- Early assessments identified CaO and AlN as leading candidates based on criteria
- Other candidate materials considered as alternates

  -*Y_2O_3, BeO, MgO, Er_2O_3, Sc_2O_3*

  -*$CaZrO_3$, $YScO_3$*

  -*BN, Si_3N_4*

Coating Research Program

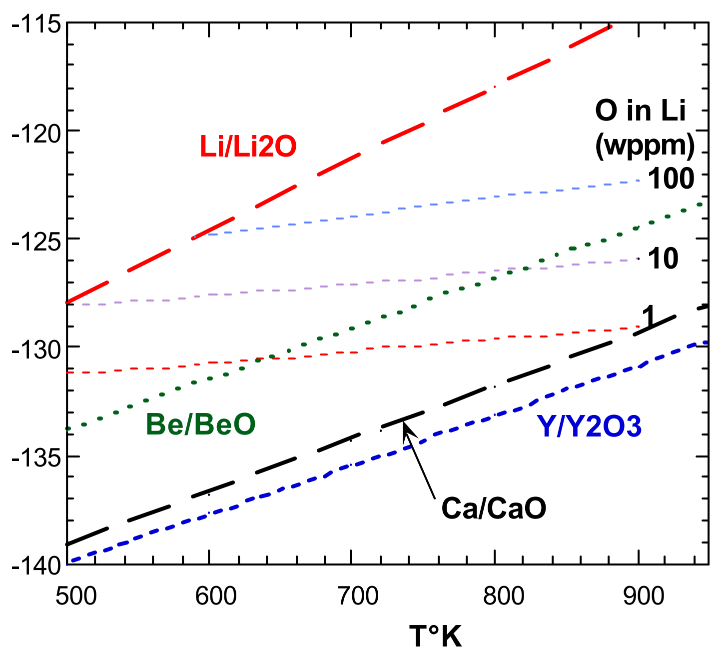
- Relatively new program with modest funding
  - ANL program initiated in 1992 (ITER)
  - ORNL program initiated in 1999
  - Integrated research program involving theory, modeling, and experiment
  - Major international collaborations (RF, Japan, EU)
- Theory and modeling
  - Define requirements
  - Identify candidate coating materials
  - Preliminary evaluation of performance

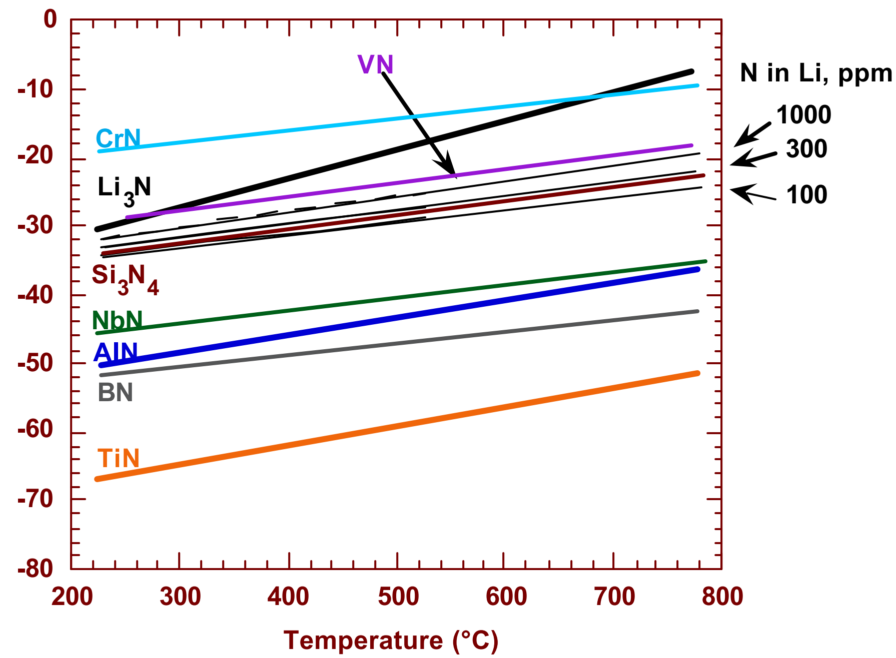
Coating Research Program (cont)

- In-situ formation of coatings on V-alloys by exposure to Li with controlled chemistry
  - Focus on CaO coating in LiCa alloy
  - Includes self-healing considerations
  - Chemistry control, microstructure, electrical properties
- Development of coatings by Thermal/Chemical Vapor Deposition and CVD processes
  - Focus on AlN and CaO coatings
  - Primary effort on thermal/chemical vapor deposition
  - Electrical property,microstructure and Li compatibility
- Investigations of compatibility of bulk ceramic materials in Li
  - Assess long-term, high temperature compatibility in Li
  - Evaluate compatibility of alternate bulk ceramics

Thermodynamic Stability of Oxides and Nitrides

ANL

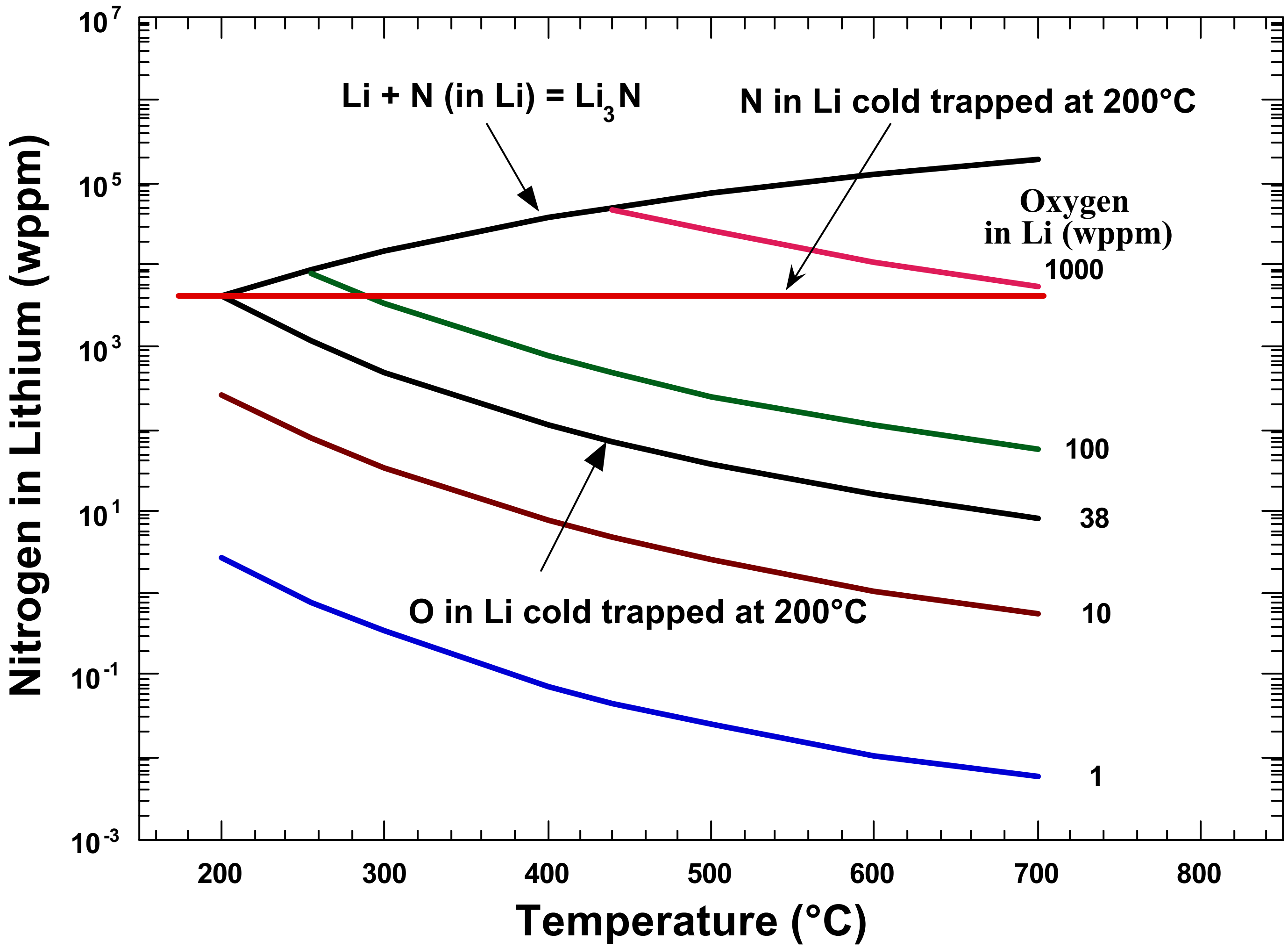




- Only few oxides are more stable than Li_2O
- CaO is stable in Li with very low oxygen content
- Ca is highly soluble in Li

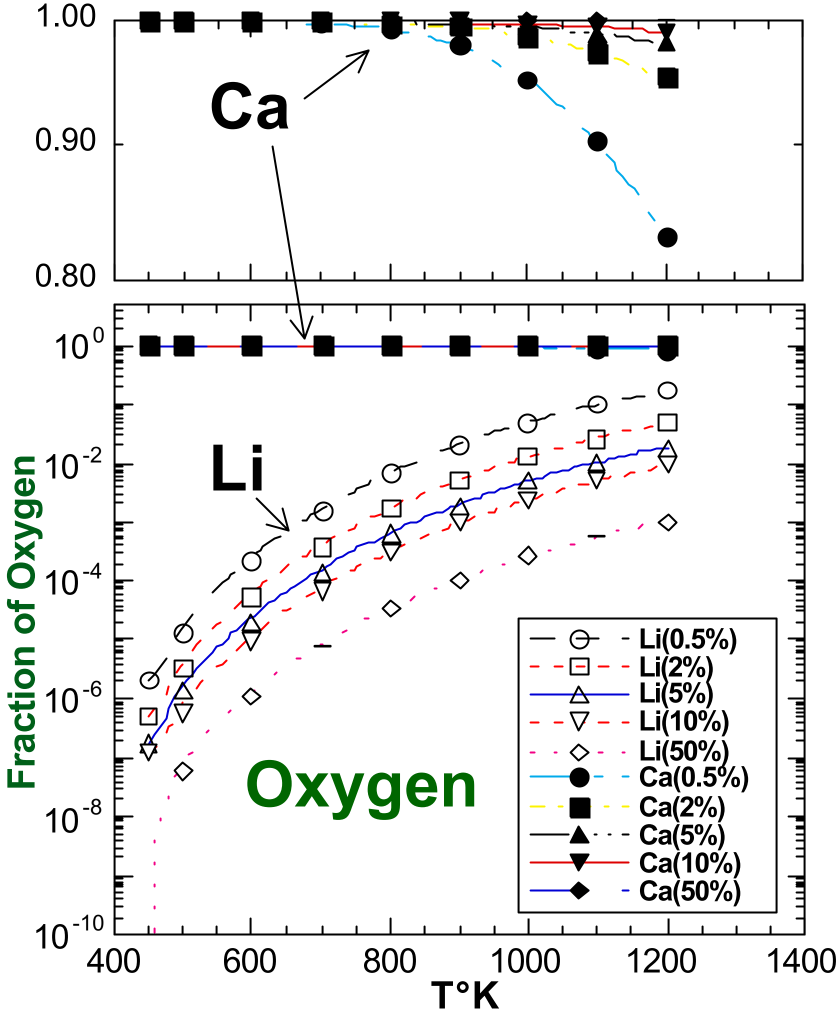
- Several Nitrides are more stable than Li_3N
- AlN is stable in Li with low nitrogen content
- Both N and Al have significant solubility in Li

Regions of Stability for AlN and $LiAlO_2$

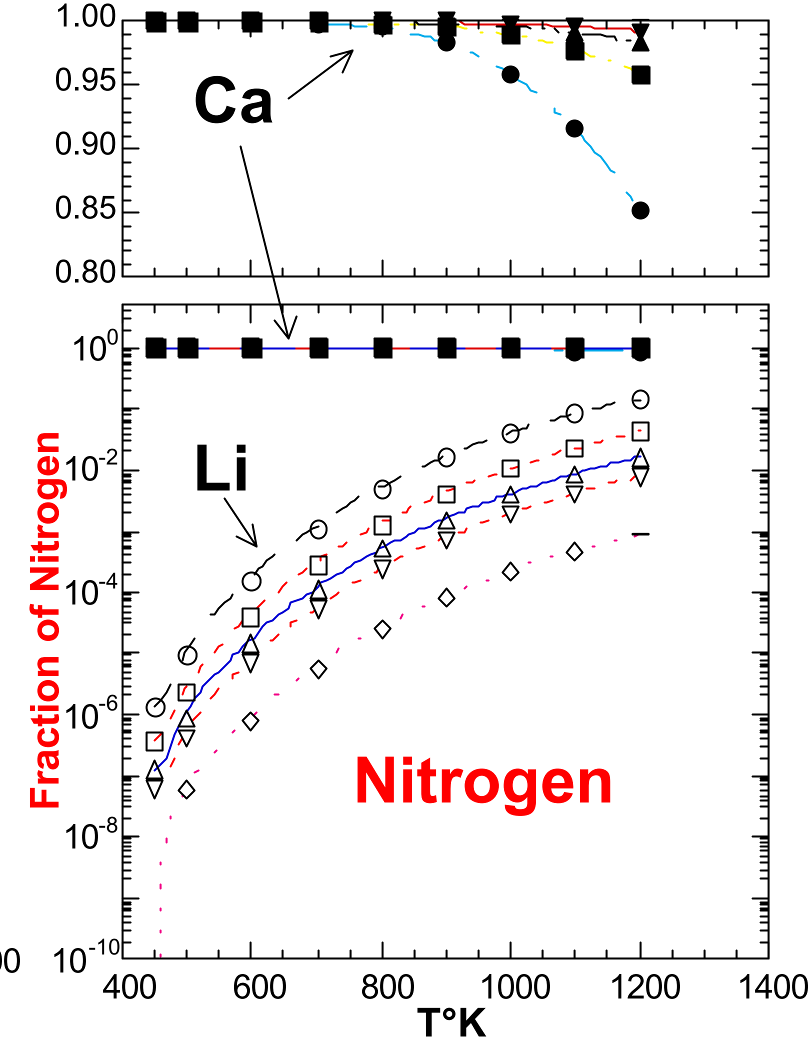


$$AlN + O\ (in\ Li) + Li = LiAlO_2 + N\ (in\ Li)$$

Calculated Distribution of O and N in LiCa Alloy



Distribution of oxygen between Ca and Li in LiCa alloy as a function of temperature



Distribution of nitrogen between Ca and Li in LiCa alloy as a function of temperature

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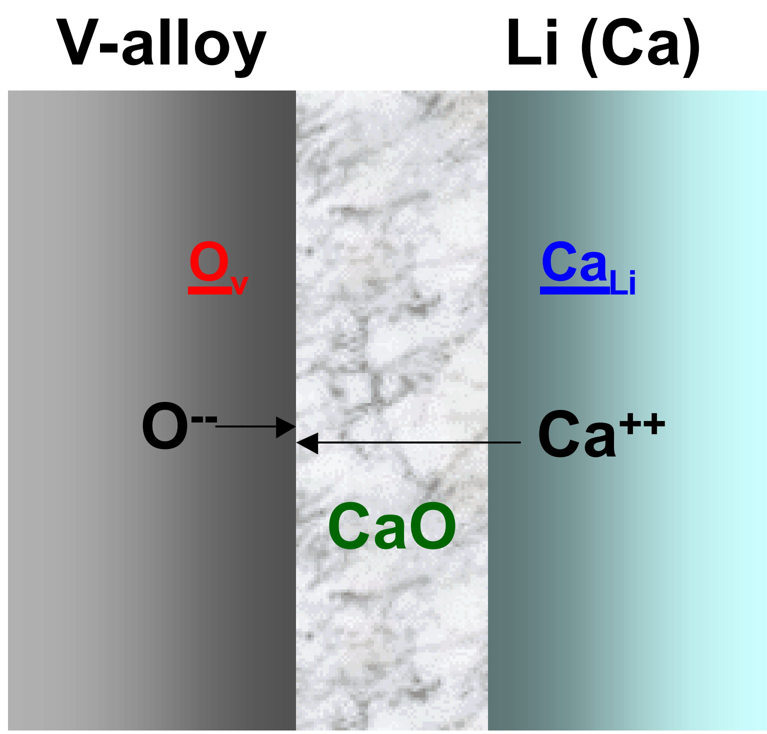
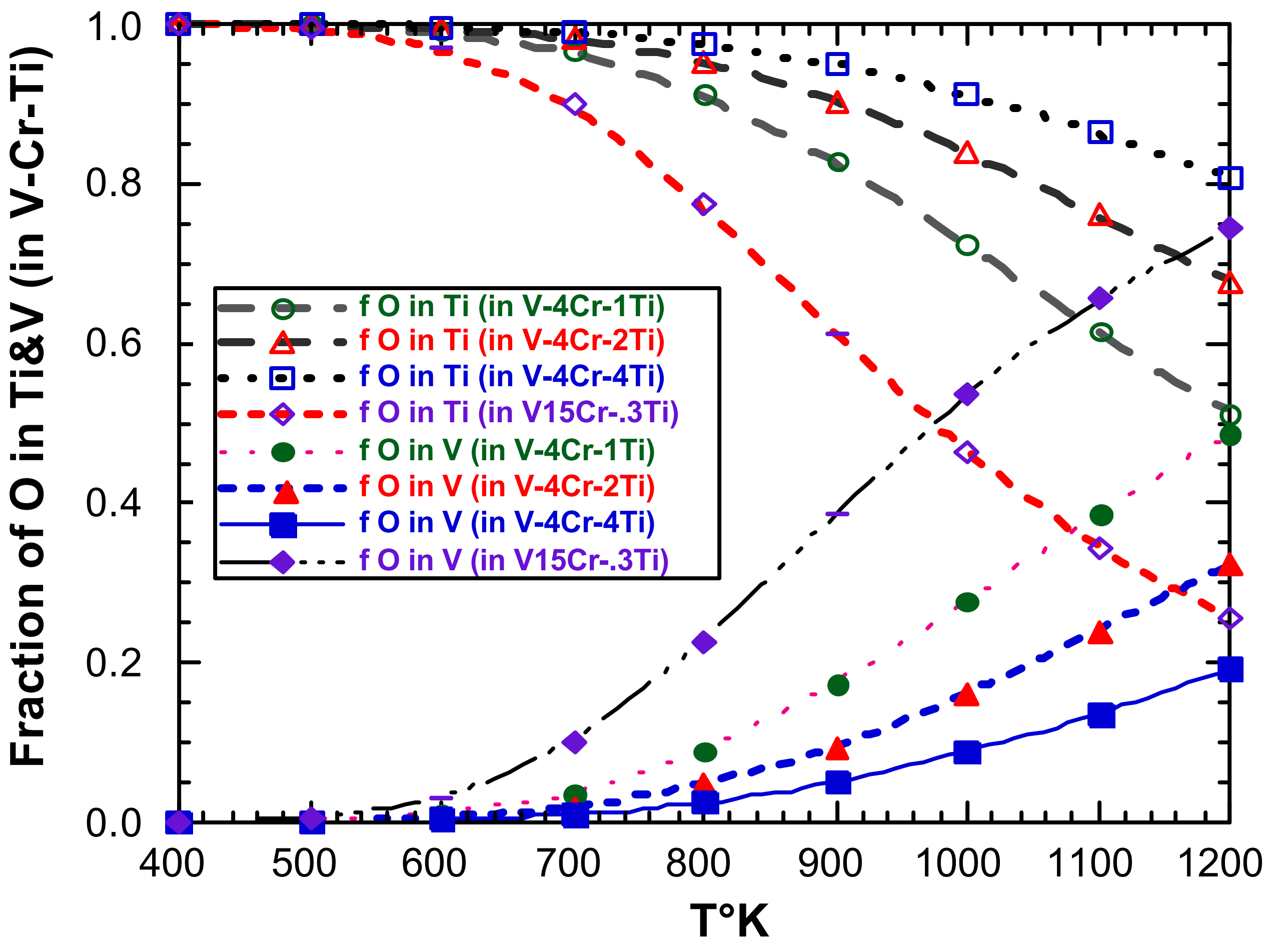
CaO Stability

- Ca in Li reacts with O in V-alloy at interface
  $\underline{Ca}_{Li} + \underline{O}_V \rightarrow \underline{CaO}$
- Add $\underline{O}$ to V-alloy surface
- Control Ca in Li
- If VO is formed on V-alloy
  $VO + \underline{Ca}_{Li} \rightarrow Ca\text{-}V\text{-}O$
  Ca-V-O has low resistivity



a) Diffusion of Ca in CaO is higher than O in CaO
b) Reaction controlled by Ca diffusion

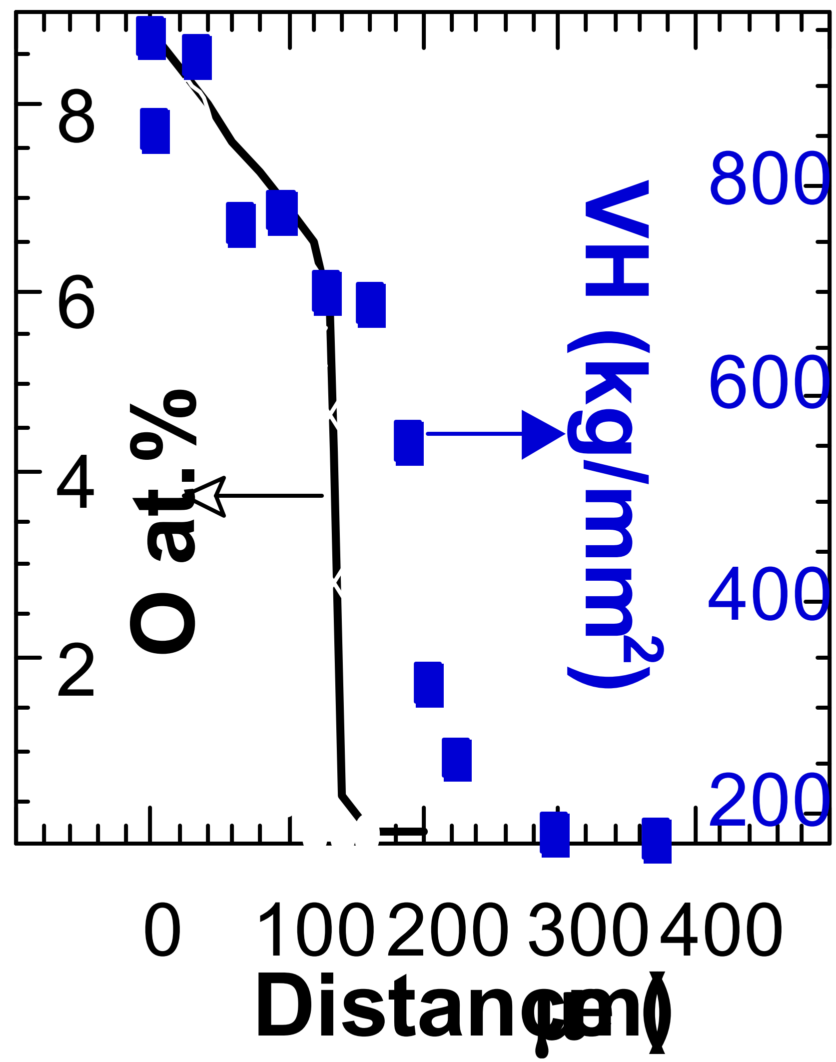
Calculated distribution of O between V and Ti in V-alloys



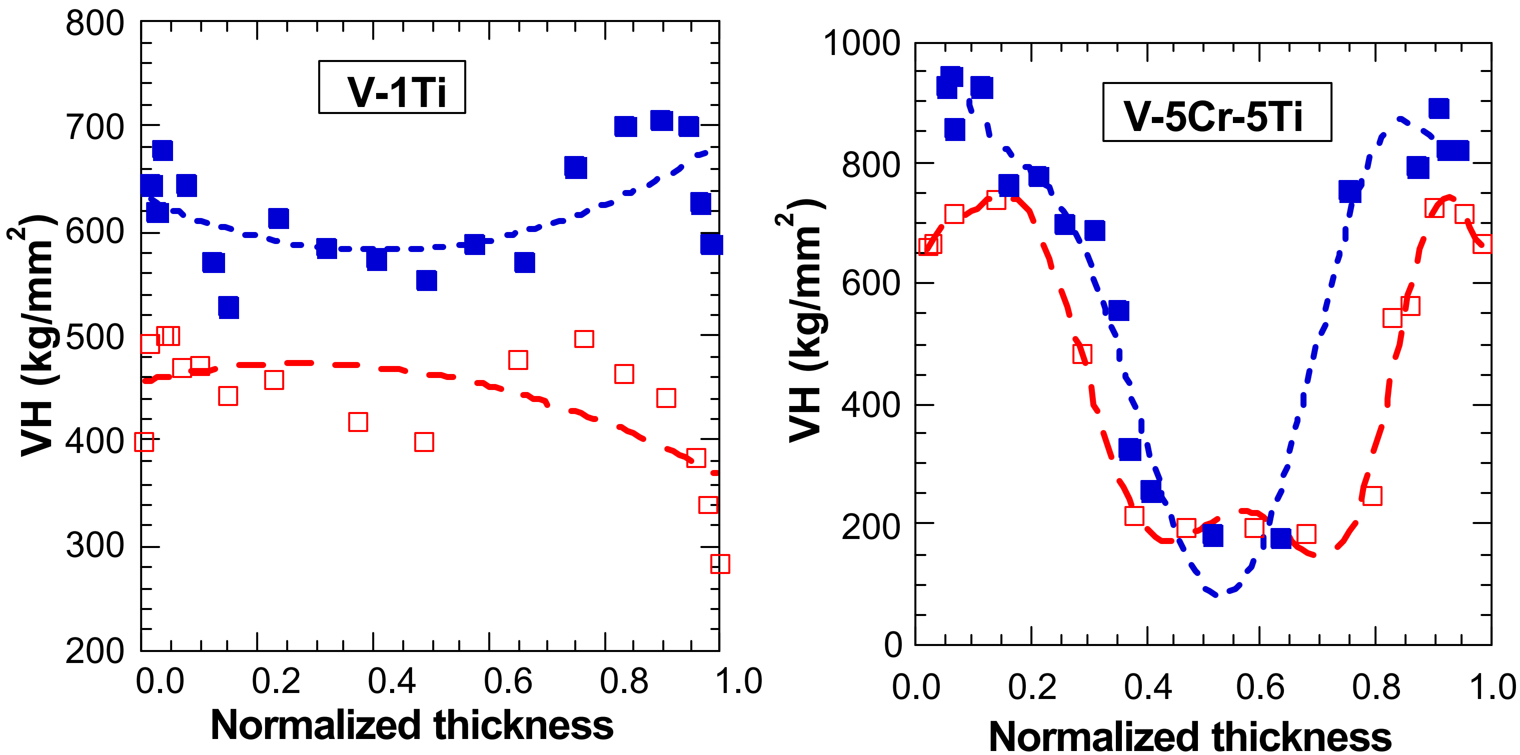
- Investigate range of alloy compositions
  - V, V-1Ti, V-10Cr, V-4Cr-4Ti

In-Situ formation of CaO on V-Alloy Exposed to Li(Ca)

- **Precharge V-alloy surface with <u>O</u> to provide source for initial formation**
- **Homogenize (~750°C) to dissolve any surface oxide (control $CaVO_2$ formation)**
- **Characterize <u>O</u> profile in V-alloy (Internal oxid'n of Ti)**
- **Compositional effects (V, V-1Ti, V-10Cr, V-4Cr-4Ti)**
- **Figure: V-4Cr-4Ti**
  - **Calculated <u>O</u> (750°C - 20 hr)**
  - **Experimental (750°C - 17 hr)**



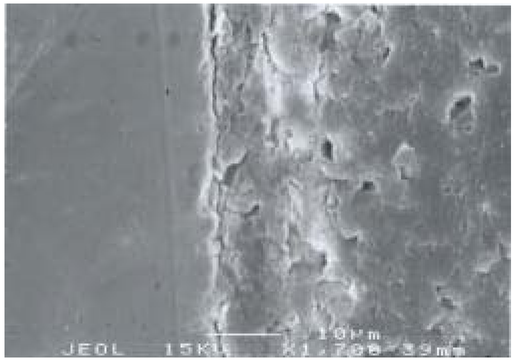
Vickers Hardness vs. Normalized Thickness



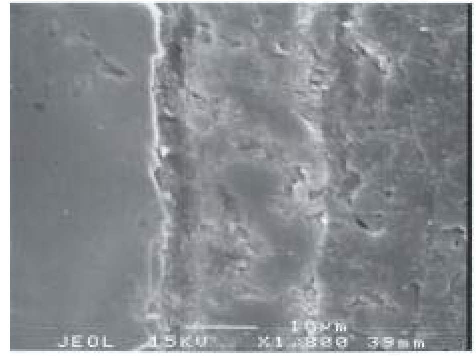
Before (closed square) and after (open square) exposure in 2.8 at. % Ca-Li at 600°C for 120 h

ANL

In-situ Formation of CaO Coating in LiCa Alloy

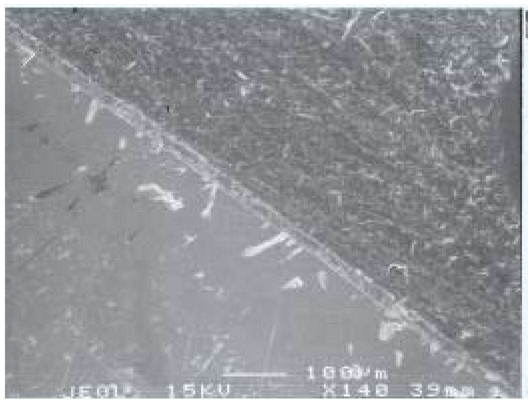


V   CaO mount

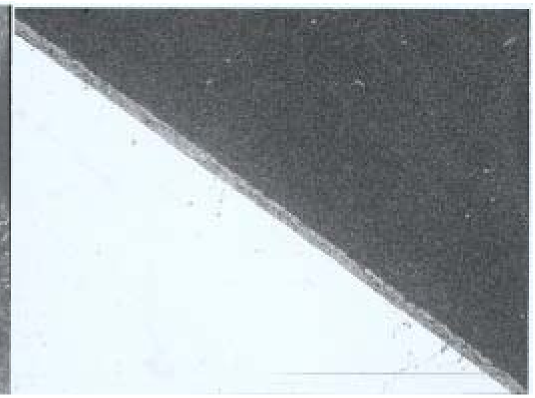


V-55 CaO mount

SEM of in-situ formed coating of CaO at 600 C on V and V-5Cr-5Ti alloy



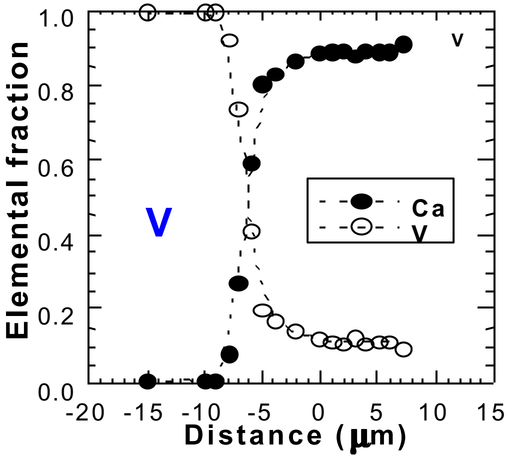
SEM V-55/CaO



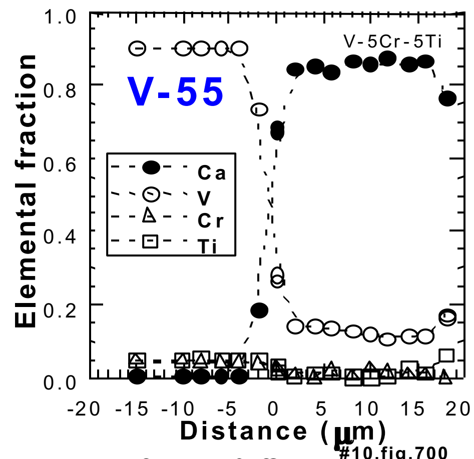
BEI V55/CaO

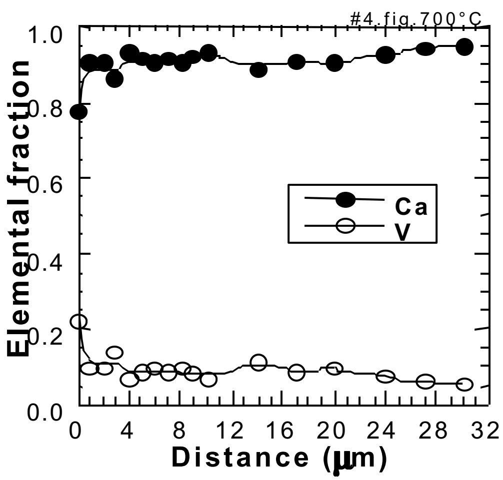
Low magnification of an in-situ formed coating on V-55 at 600 C

EDS Analysis of Coatings Formed on V-alloys

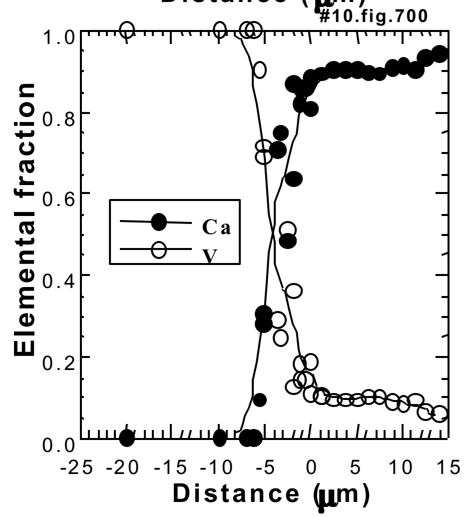


600°C
Li-2.8at.%Ca
120h





700°C
Li-2.8at.%Ca
50 h



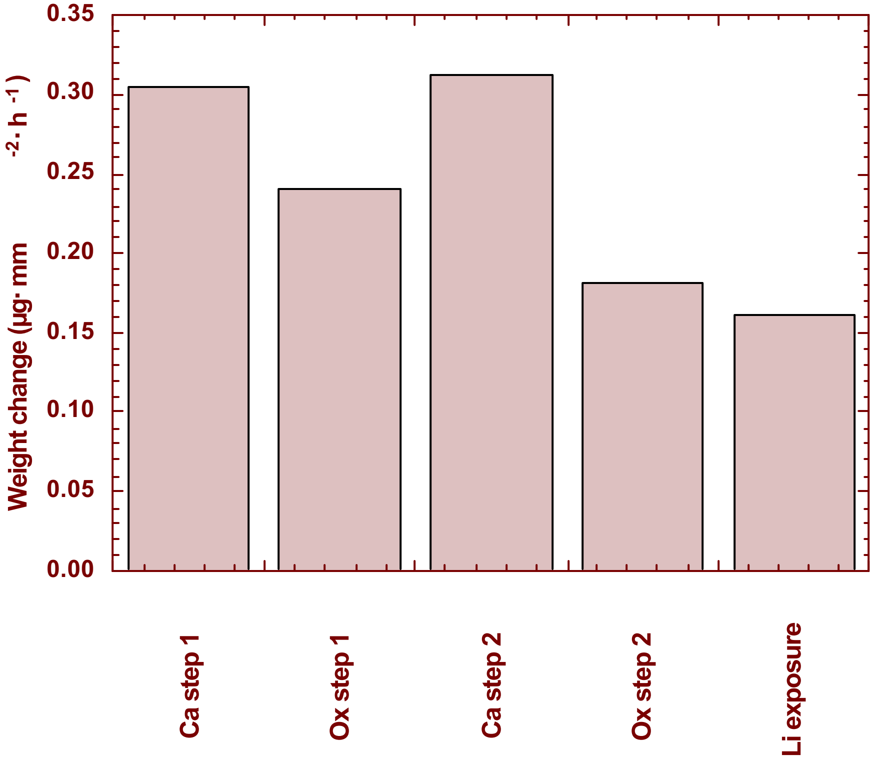
~9,000 wppm <u>O</u> in V44

~5,000 wppm <u>O</u> in V44

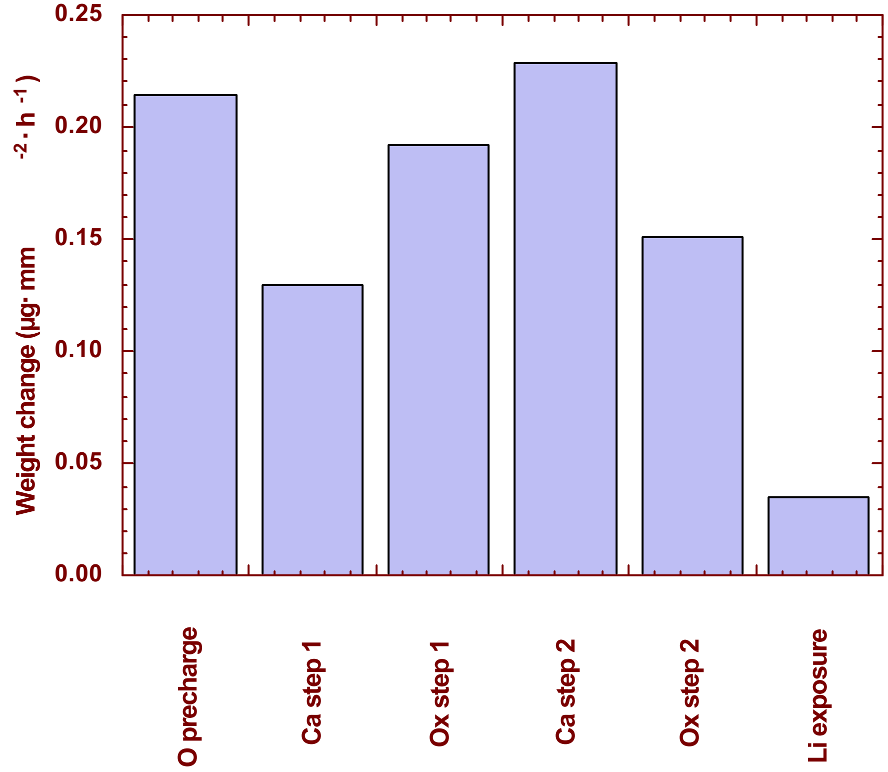
Development of AlN and CaO coatings by thermal/chemical vapor deposition and CVD

- Establish the thermodynamic conditions and kinetics of the coating processes
- Characterize the chemistries and microstructures of the coatings
- Evaluate the chemical compatibility of coatings in Li with controlled chemistry
- Evaluate the electrical resistance of the coating before and after Li exposure
- Evaluate the mechanical integrity of the coating/substrate bond
- Assess the development of alternate coatings

CaO coatings by He-Flow Process

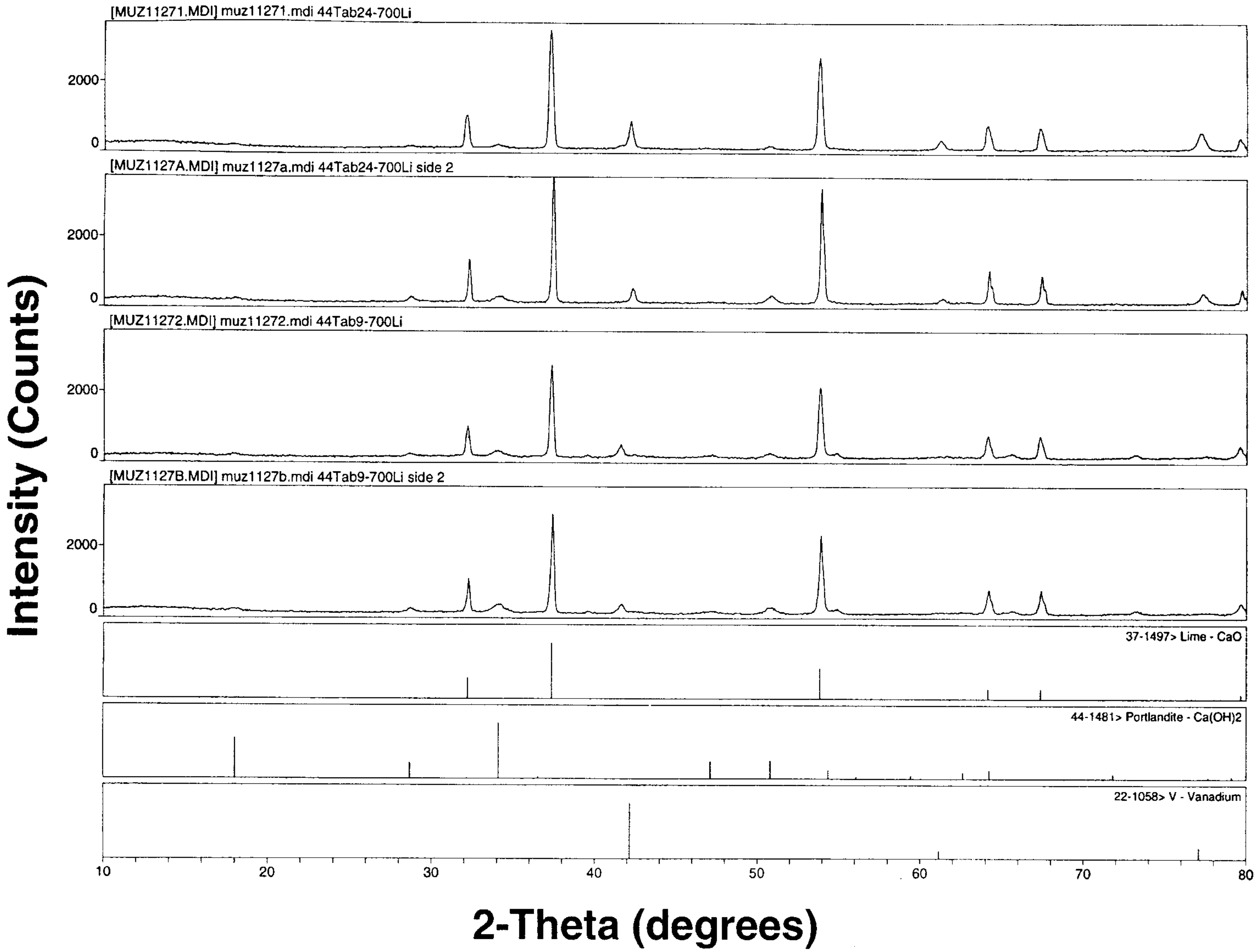


Li Exposure at 600°C for 137 h

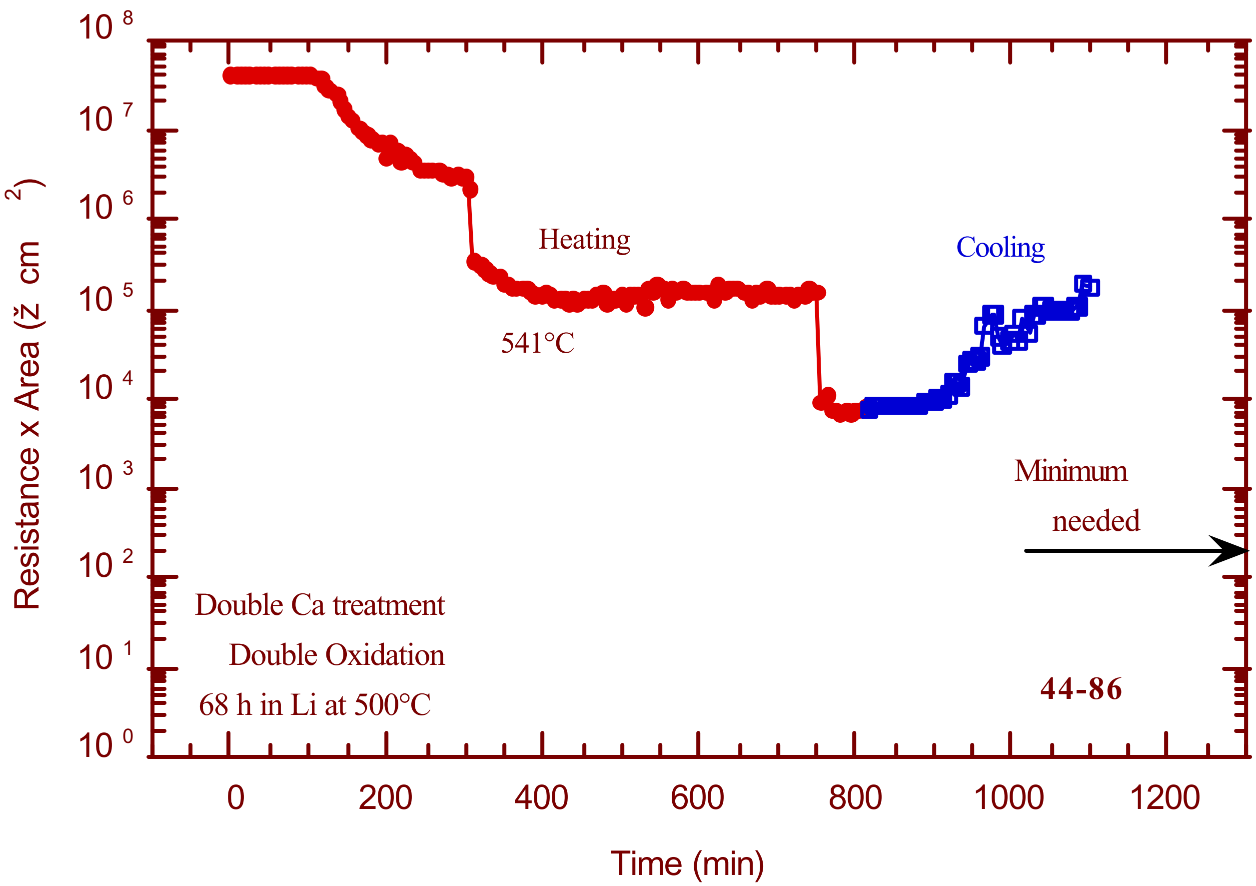


Li Exposure at 700°C for 145 h

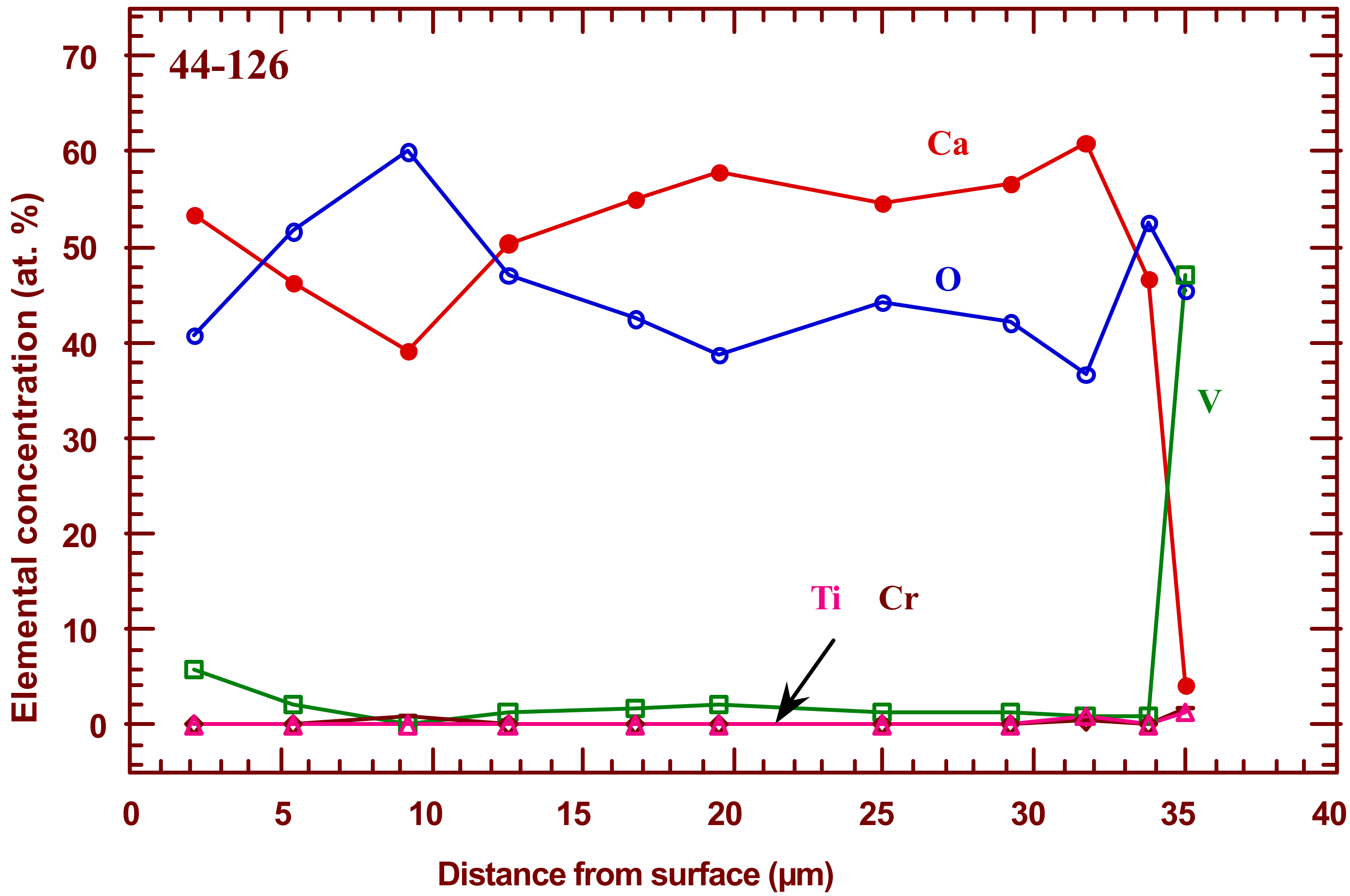
XRD of CaO Coating after Li-Ca Exposure at 700°C



Electrical Resistance of Thermally deposited CaO after Exposure to Li-2.8 at.% Ca



Elemental Profile in a Coating of CaO Developed by Thermal/Chemical Vapor Deposition



Experimental Procedure for Compatibility Testing

- 1000 h exposures at 500°-800°C in V-4Cr-4Ti or Mo capsules
- Specimens distilled in vacuum at 550-600°C to remove remaining Li

Characterization

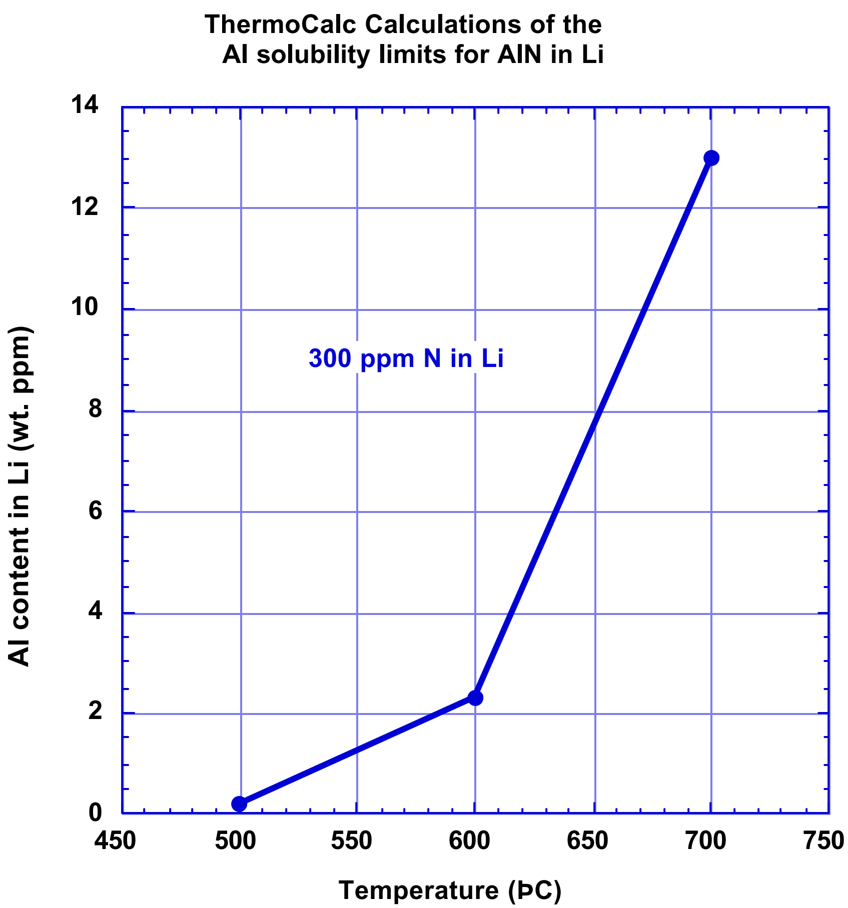
- Mass Change (0.01mg/cm^2 accuracy) and dimensional changes
- Spectrographic post-exposure analysis of the lithium
- Auger Electron Spectroscopy (AES)
  - able to detect Li
  - Ar sputter depth profiles
- Metallography

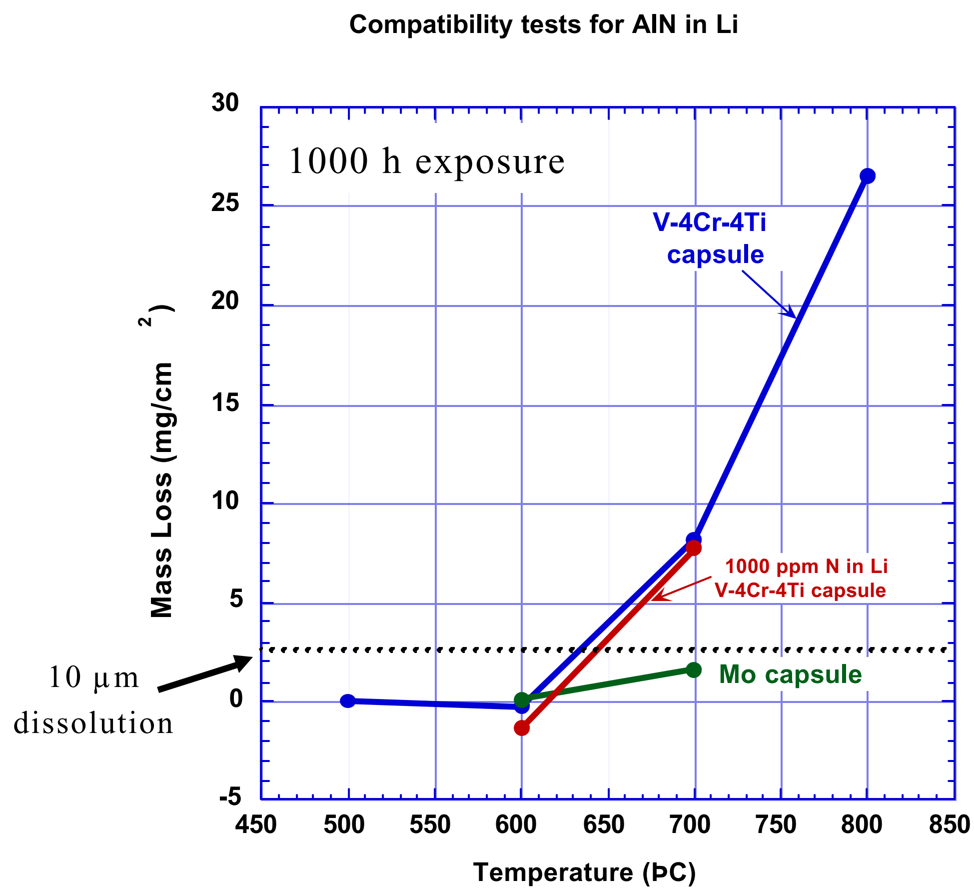
Analysis

- Examine reaction energy (e.g., CaO + 2Li <-> Ca + Li_2O) and solution chemistry [e.g., CaO = ($\underline{Ca}$)Li + ($\underline{O}$)Li]
  - ThermoCalc calculations

Dissolution of AlN in Lithium is Controlled by Li(Al,N) Chemistry

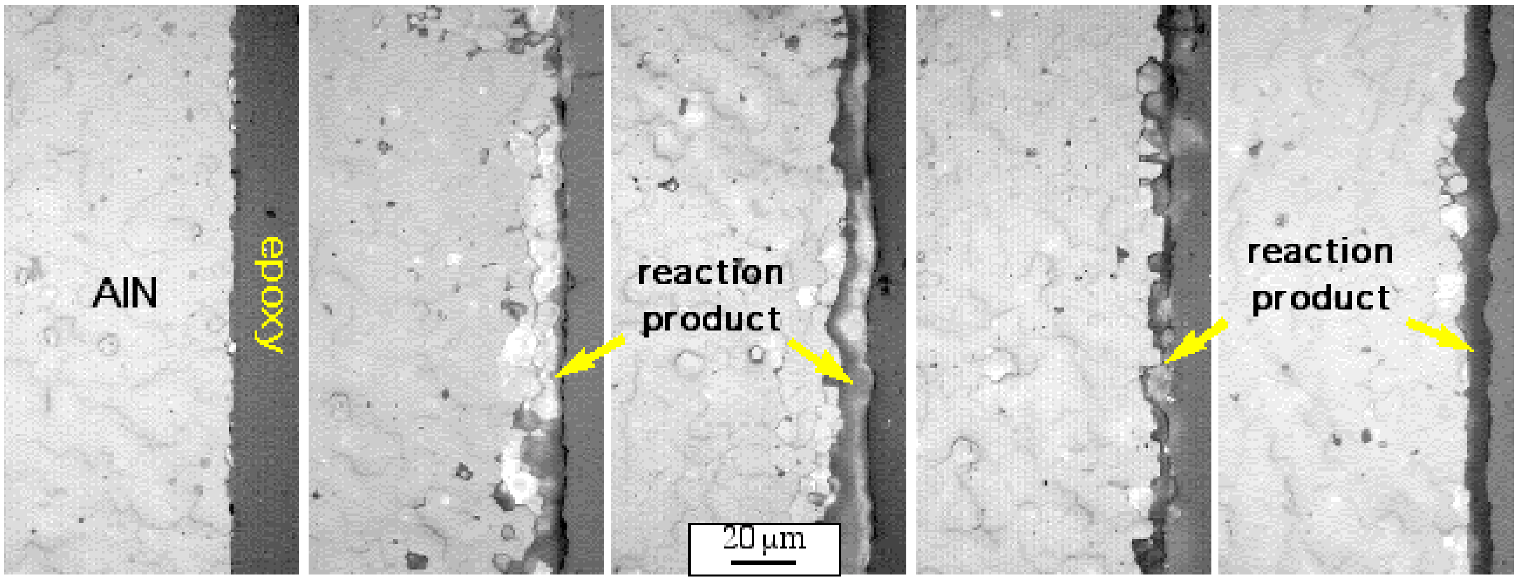
- **Higher dissolution rates occur in V capsules (vs. Mo capsules), due to N gettering by V capsule walls**





600°C: AlN+0.04Y+0.9O

changing capsule (V vs. Mo) and adding 1000wppm N



unexposed	V can	V can + N	Mo can	Mo can + N
	+0.26mg/cm²	+1.36mg/cm²	-0.10mg/cm²	-0.17mg/cm²

Using Mo capsule - mass losses instead of mass gains with V capsule

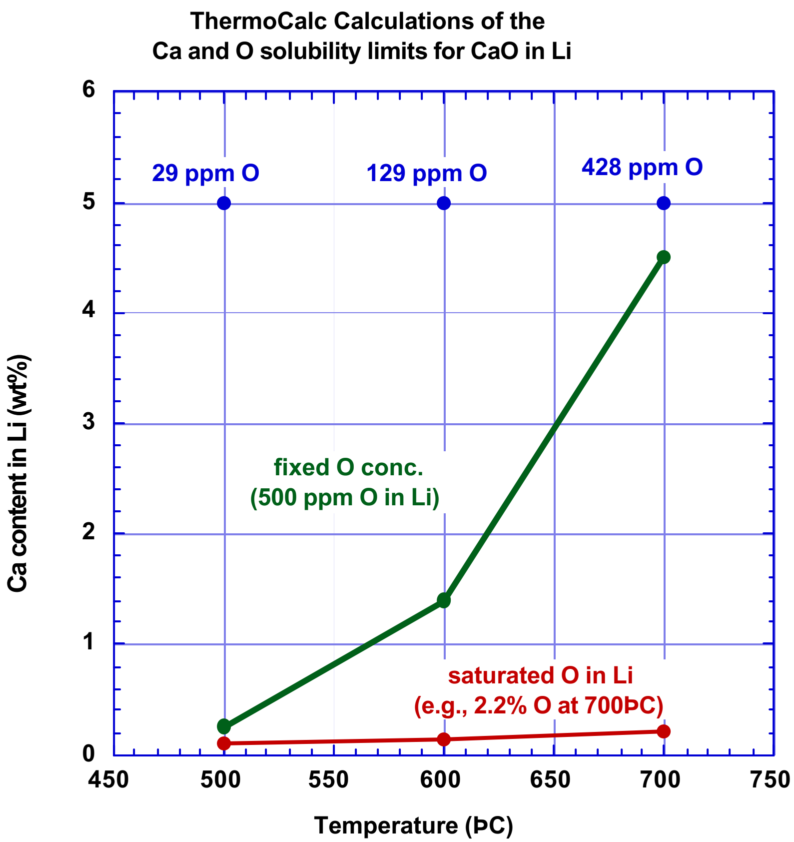
possible N reaction with V-4Cr-4Ti capsule wall (effect?)

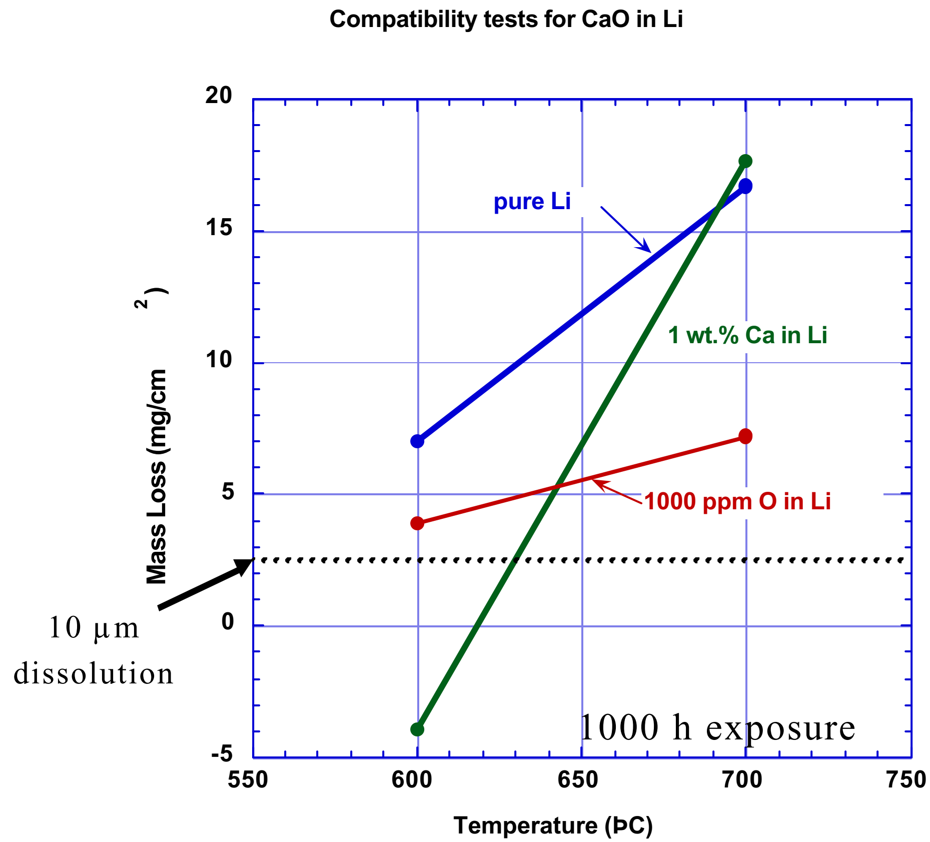
Adding N to Li - thicker reaction layer in both cases

Slight changes in mass not easily understood

High Solubility of Ca and O in Lithium Produces High Dissolution Rates of CaO at T>600 C

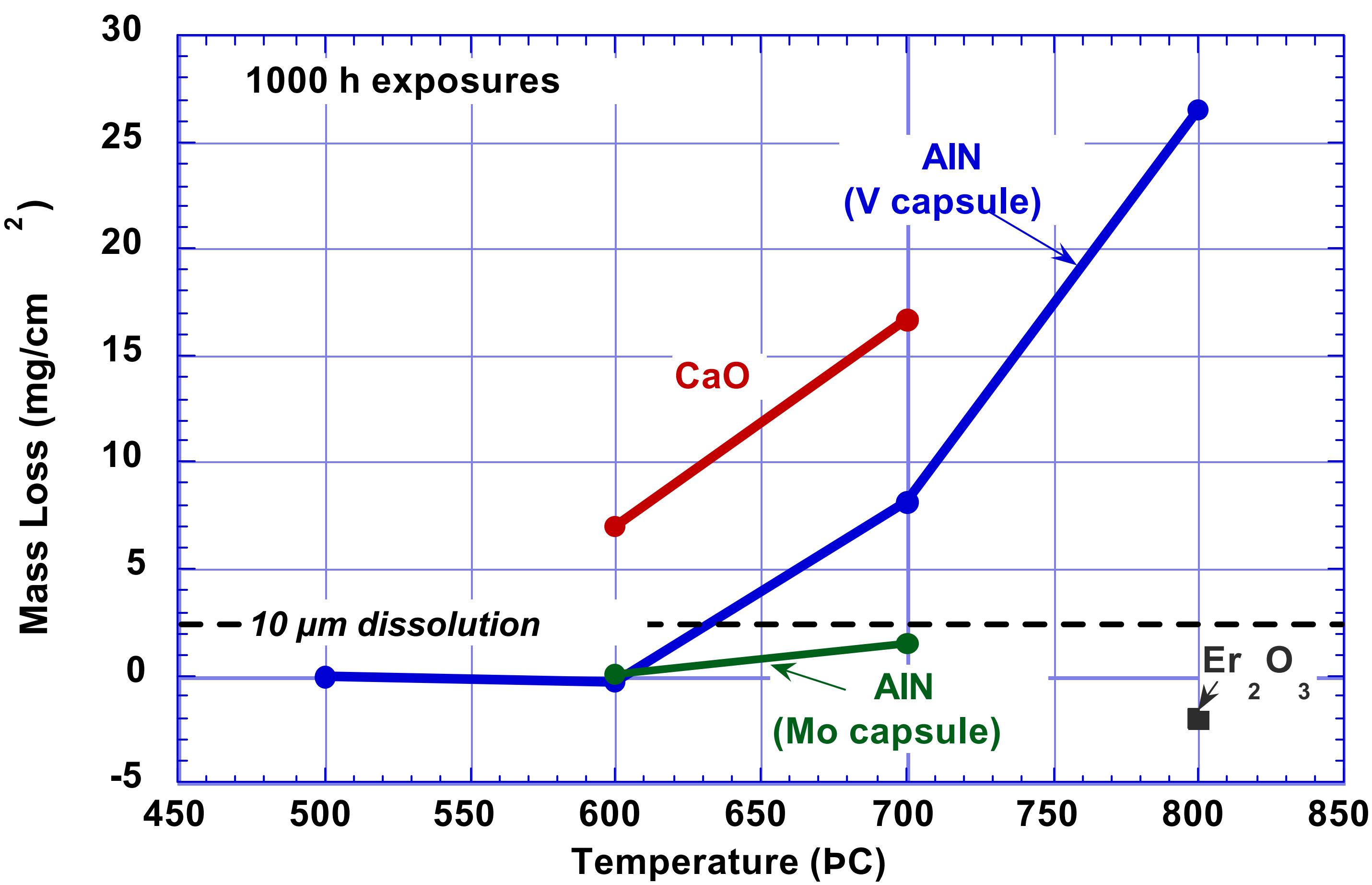
- Dissolution may be minimized by controlling the Li(Ca,O) chemistry





Alternative MHD Insulators are Being Examined

- **Selection based on thermodynamic stability and solubility in Li**
- **Er_2O_3, Y_2O_3, Sc_2O_3 and $YScO_3$ appear to be attractive candidates**



Conclusions - Insulator Coating Research

- Considerable progress has been made on the development of electrically insulating coatings for the Li/V system
- The experimental results are generally consistent with thermodynamic and kinetic modeling of the underlying mechanisms and processes
- Stable CaO coatings were formed on several V-alloys in situ in Li-2.8 at.% Ca contained in static test vessels at 600-700°C
- CaO and AlN coatings formed by thermal/chemical vapor deposition exhibit good compatibility in Li with controlled chemistry and high resistivity after exposure at 600-700°C
- Bulk AlN and CaO ceramics exhibit substantial weight loss after exposure to Li at 600 and 700°C in capsule tests
- Several alternate ceramic materials are under consideration
- Considerable effort on coating research is still required
- This coating research may have implications outside fusion