Insulator Coatings

J.-H. Park, K. Natesan, and R. Mattas

Argonne National Laboratory

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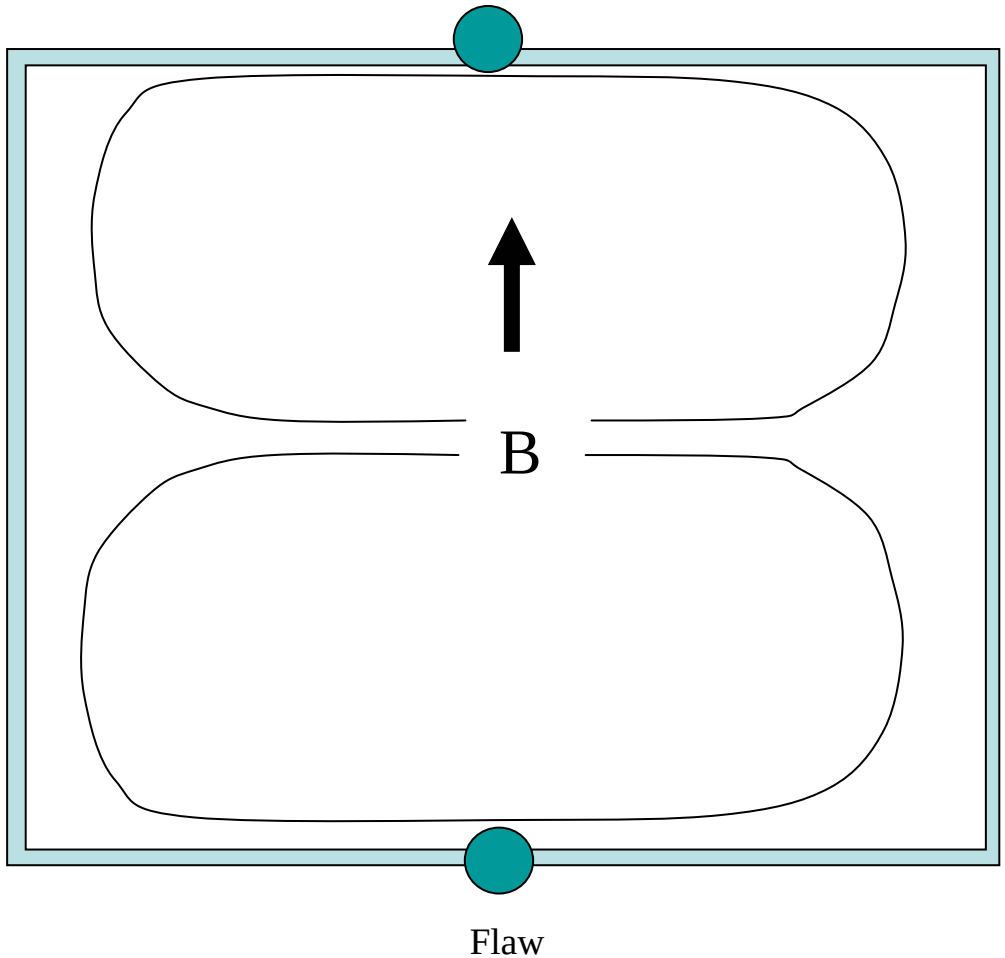
Background

- MHD pressure drop with bare walls with Li is unacceptable for design
  - Pumping power
  - Primary stress
- Insulator coatings reduce pressure drop by ~100.
  - Self-healing
    - Solves issues with coating lifetime
    - Requires sources of coating constituents during operation
    - Requires adequate formation kinetics
  - Highly failure resistant coatings
    - No constituent sources required during operation
    - Lifetime should be comparable to structure
    - Long term reliability?

MHD Considerations



Insulating requirement is modest at ~>10^2 Ω–cm^2

Coating Requirements

- Electrical resistivity x thickness > 100 Ω-cm^2
- Chemical stability/compatibility with lithium at elevated temperatures (to ~ 700°C)
- Potential for coating complex geometries
- Thermal expansion match/bonding with V-alloy
- Safety/environmental characteristics; e.g. low activation
- Materials availability/cost
- Acceptable neutronic properties
- Radiation damage resistance

Irradiation Effects

- Reduction in resistivity
- Dimensional change
  - Debonding
- Radiation induced precipitation formation affects interstitials in solid solution

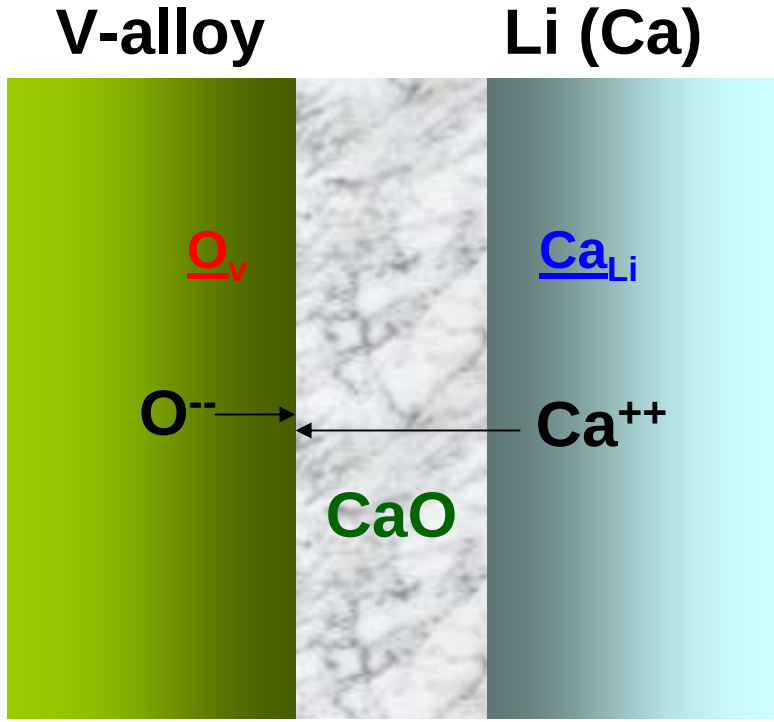
Approach

- Emphasize self-healing coatings
  - Potential for flaw formation is too high and flaw limit is too low to rely on flaw resistant coatings
  - Provides method for fabrication in large, complex shapes
  - Chemistry control and understanding (kinetics) is crucial
  - Modifies coolant and vanadium chemistry
  - Limited number of materials that meet requirements
  - 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

Emphasis on CaO coatings

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

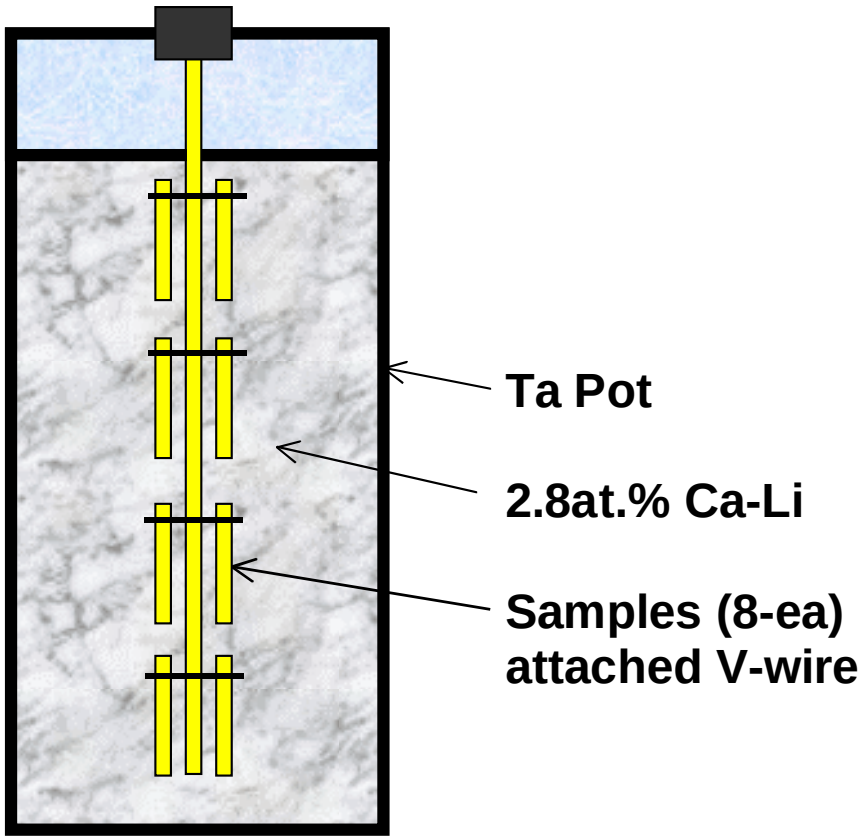


- a) Diffusion of <u>Ca</u> in CaO is higher than <u>O</u> in CaO
  b) Reaction controlled by Ca diffusion

Test Conditions

- Exposure at 600 C
  - 2.8 atomic percent Ca in Li
  - Exposure times to 747 h
  - Test coupons include both US and Japan heat
  - Extensive post exposure characterization
- Exposure at 700 C
  - 2.8 atomic percent Ca in Li
  - Exposure times to 425 h

Experimental Apparatus



Schematic for the Ca-Li pot made by Ta bucket inside the aluminized steel container. V-4Cr-4Ti samples attached on the V-4Cr-4Ti sample tree by V-wire and make space between sample tree and samples with small V-4Cr-4Ti spacers.

Test Procedures - 600 C

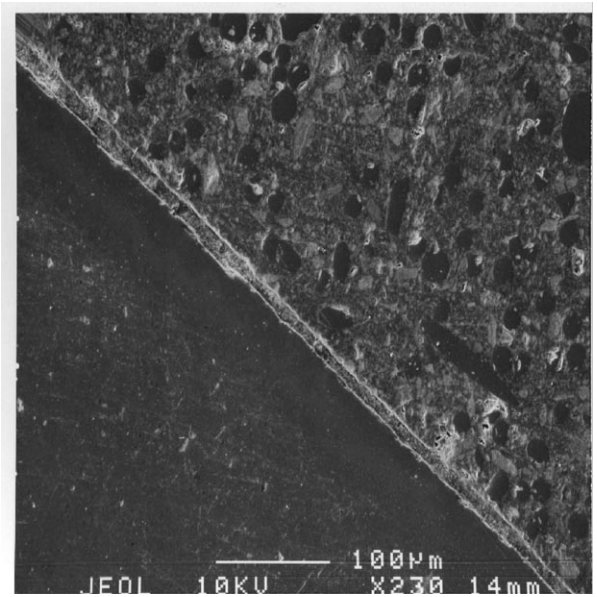
- Oxygen charging
  - Two methods -
    - Ar+10-100ppm O_2 @ 900-950C for 17 h
    - Cr/CrO exposure in sealed quartz tube @ 900-950C for 17 h
  - Oxygen content - 2000-10,000 wppm (6000 typ.)
- Exposure in LiCa
  - CaO coating forms in first 50-100 h
- Post exposure exams
  - SEM
  - EDS
  - Resistivity

Test Results - 600 C

- Uniform CaO coatings of 10-25 μm formed on both US and Japan heats.
- Extended exposures (625 h (J) and 747h(US)) showed intact coatings with very little change following the initial coating formation period.
- Resistance measurements in inert gas showed high resistivity to 700 C.
  - High resistance even after >10 thermal cycles

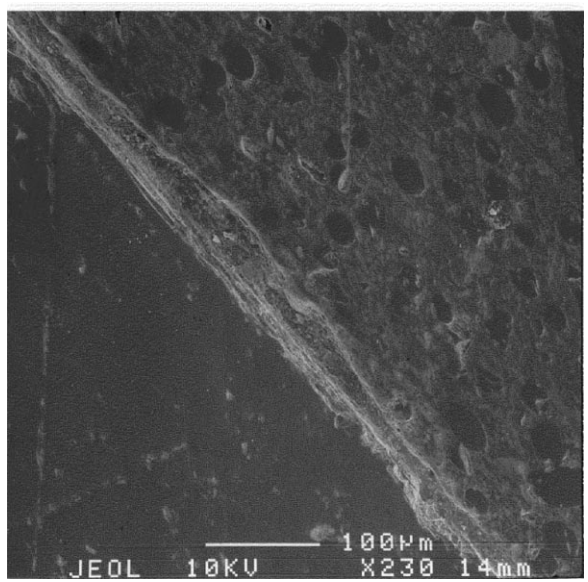
Coating Appearance after 747 h @ 600 C

Low oxygen in V



Sample # 29. Below 500 O-Wppm estimated. Left (or left down) is V-4Cr-4Ti, diagonal layer (~14 μm) is the in-situ formed scale, and right (or right top) is the sample mounting.

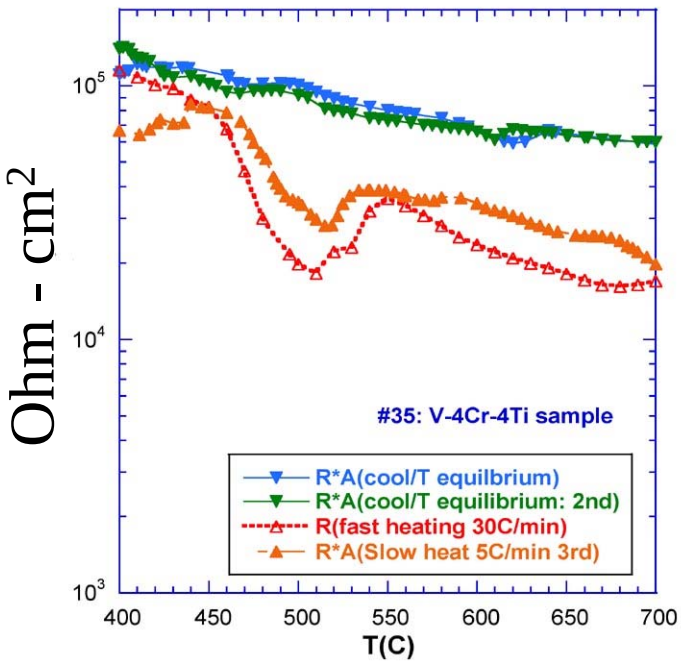
Typical oxygen in V



Sample # 46. 6,400 Wppm-O charged by Ar gas pursing at 700ºC for 18 h. Left down is V-4Cr-4Ti, diagonal layer (18 to ~33 μm) is the in-situ formed scale, and the right top is the mounting.

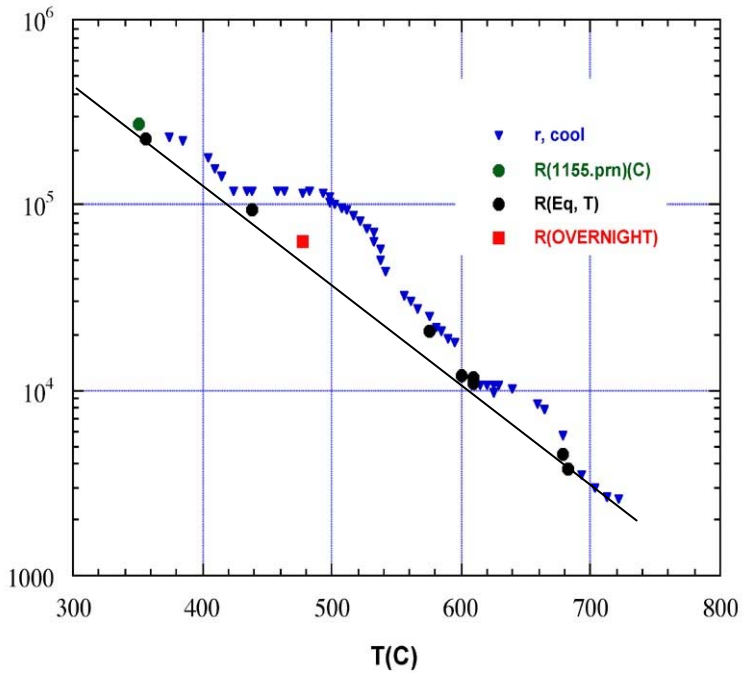
Resistance Following 600 C Exposure

US Heat



Electrical resistance times area vs. temperature in an inert atmosphere for the film formed on the V-4Cr-4Ti #35 (1431 O-wppm) after exposure in the 2.8at.%Ca-Li at 600C for 747.5 h.

Japan Heat



R*A vs. T in an inert atmosphere for the in-situ coated in 2.8at.%Ca-Li for 623 h to the O-charged 5347.6 wppm (7D3) V-4Cr-4Ti (NIFS-II heat).

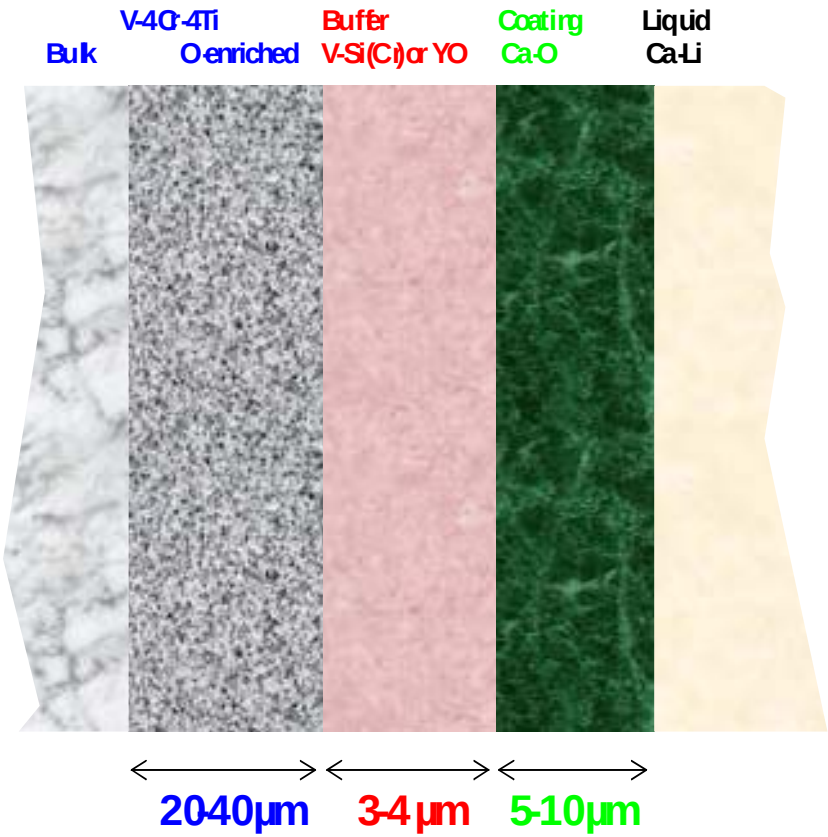
Test Results - 700 C

- Oxygen charging performed exactly as for 600 C tests.
- CaO coating forms in less time (~50 h) compared with 600 C tests.
- CaO coating is intact at 100 h, but dissolution of coating is observed after 425 h.
- Further work is required to understand kinetics of coating growth and dissolution plus effects of local chemistry at 700 C.

Initial Development of Yttrium Oxide Coating

- Vanadium samples were pre-charged with oxygen.
- A thin layer (~0.5 μm) of yttrium was vapor deposited on the vanadium.
- The samples were annealed at 750 C, forming yttrium oxide via a solid-state reaction.
- The resulting coating is extremely adherent.
- Samples were exposed to Li-2.8 at % Ca

Yttrium Oxide Coating



- Exposure to Li-2.8% Ca at 600 C resulted in formation of CaO over the Y_2O_3 film.
- The Y_2O_3 remained intact.
- Further work is planned

Issues

- CaO test results have not met 700 C metric
  - Results at 600 C look acceptable
- Oxygen source in vanadium
  - Potential effects on mechanical properties
  - Source may not be adequate for self-healing during operation
- Coating formation and response is complex
  - Local chemistry and kinetics
  - Coating structure and chemistry varies over entire thickness
- Program resources are limited

Recommendations

- Initiate coating modeling activity
  - Kinetic and thermodynamic models
    - Relate to MHD requirements
  - Not likely to accurately reflect experimental results, but can provide insight into important phenomena and help guide experiments
  - Apply to CaO, others
- Emphasize self-healing approach
  - Reliability of coatings, without self-healing, is not high enough
- Re-examine systems where O or N source is in Li and not vanadium
  - AlN
- Move forward with flow loop