Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

Irradiation Testing in Support of the Tritium Production Enterprise

DJ SENOR

Pacific Northwest National Laboratory
NUEN 481/681, Texas A&M University

PNNL Roles in the Tritium Program

- TPBAR Design Authority
- TPBAR and lead use rod design and analysis
- WBN1 coolant tritium analysis and operations support
- TPBAR component development and testing
- TPBAR component procurement and assembly support
- Tritium extraction development and support
- Basic and applied research and development
    - Post-irradiation examination (PIE)
    - Ex-reactor testing
    - In-reactor testing (design, fabrication, PIE)
    - TPBAR performance model development

Tritium Production Enterprise: Background

- Tritium is required for US nuclear weapons stockpile
- Tritium has a 12.3 year half-life and must be replenished
- 1988: DOE ceased production of tritium at SRS
- 1988-1992: The US considered the use of dedicated reactors for tritium production
  - Heavy water reactors (HWRs)
  - High temperature gas-cooled reactors (HTGRs)
  - Light water reactors (LWRs)
- 1995-1998: The US considered dual-use facilities
  - Commercial LWRs
  - Accelerators
- 1995: PNNL selected by DOE to be Design Authority for Commercial Light Water Reactor irradiation demonstration

L Reactor at SRS

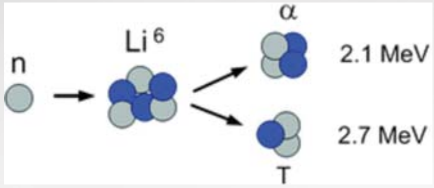
Tritium Production Enterprise: Background

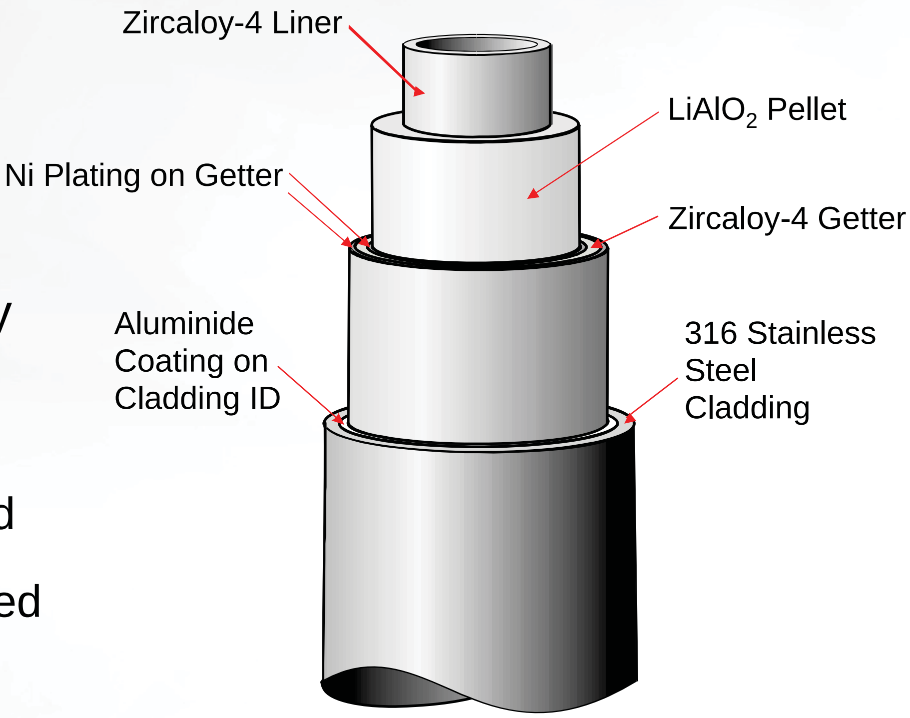
- 1995 – 1997: Lead Test Assembly (32 Tritium-Producing Burnable Absorber Rods, TPBARs) designed and built at PNNL for irradiation in TVA Watts Bar Nuclear Unit 1
- 1999: Post-irradiation examination of LTA
- 2000: The current Commercial Light Water Reactor tritium program was selected by DOE over accelerators for production
- 2001 – 2003: Design and manufacturing scale-up for production TPBARs
- 2003: First production core (240 TPBARs) irradiated at WBN1
- 2005 – 2008: TPBAR design modifications
- 2008: Modified TPBARs (Mark 9.2) first irradiated at WBN1

Watts Bar Nuclear Plant
Spring City, TN

Tritium Target Current Technology

- TPBARs replace burnable absorber rods normally used in Westinghouse PWRs (WABAs)
  - WABA reaction:
    - $^{10}B + {}^{1}n_{th} \rightarrow {}^{4}He + {}^{7}Li$
  - TPBAR reaction:
    - $^{6}Li + {}^{1}n_{th} \rightarrow {}^{3}H + {}^{4}He$
- Reactivity worth of TPBARs is slightly greater than WABAs
- Because TPBARs provide reactivity hold-down, they are considered a safety-related component by the NRC
  - All irradiation testing work governed by QA requirements in 10 CFR 50, Appendix B so results can be applied to TPBAR modeling and design




Zircaloy-4 Liner

$LiAlO_2$ Pellet

Ni Plating on Getter

Zircaloy-4 Getter

Aluminide Coating on Cladding ID

316 Stainless Steel Cladding

Not to scale

TPBAR Irradiation Performance

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

- In 2004, during the first production cycle at WBN1, it was determined that TPBAR tritium permeation was higher than predicted by performance models
  - Predicted ≈ 0.5 Ci/TPBAR/cycle
  - Actual ≈ 4 Ci/TPBAR/cycle
- Even 4 Ci/TPBAR/cycle represents only about 0.04% of the tritium produced
- TVA limited the number of TPBARs that could be irradiated because of current license limits on tritium release
- Subsequent irradiations have continued, but quantities are limited to <704 TPBARs/cycle
- An irradiation testing program was implemented in 2006 to provide a scientific basis for improving performance models and providing systematic, long-term TPBAR design evolution

Irradiation Testing Program Objectives

- Overall goal is risk reduction through fundamental understanding of TPBAR performance
  - Accurately explain and predict existing permeation performance
  - Provide confidence in performance predictions to support
    - Operating condition changes
    - Supplier changes
    - Manufacturing process changes
  - Provide basis for evolutionary design changes
- The testing program was tailored to address these objectives in support of the tritium production mission

Irradiation Testing Program

Cladding Permeation
TMIST-2
2006-2012

Getter Performance
TMED-4
2008-2010

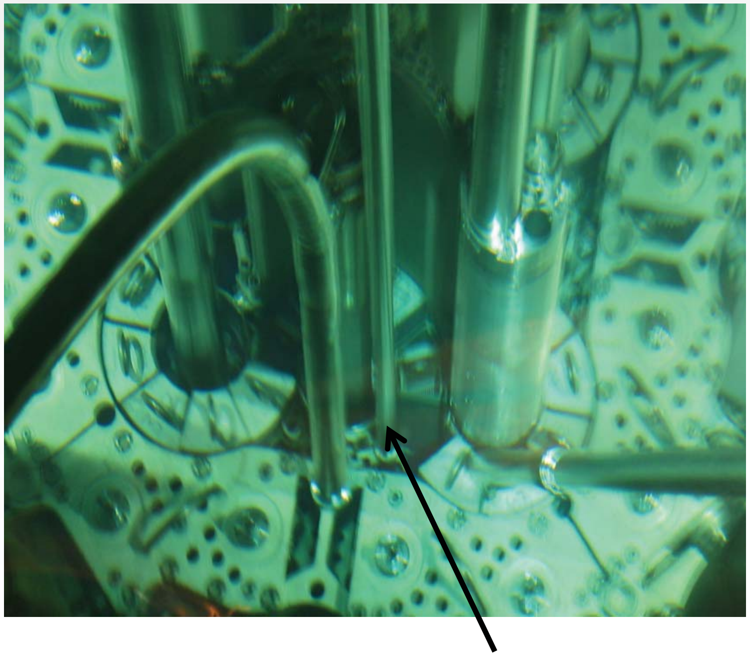
Pellet Performance
TMIST-3
2009-2019

Liner Oxidation
TMIST-1
TMED-1
2006-2010

Advanced Pellet Mfg
TMED-3
2008-2011

Motivation

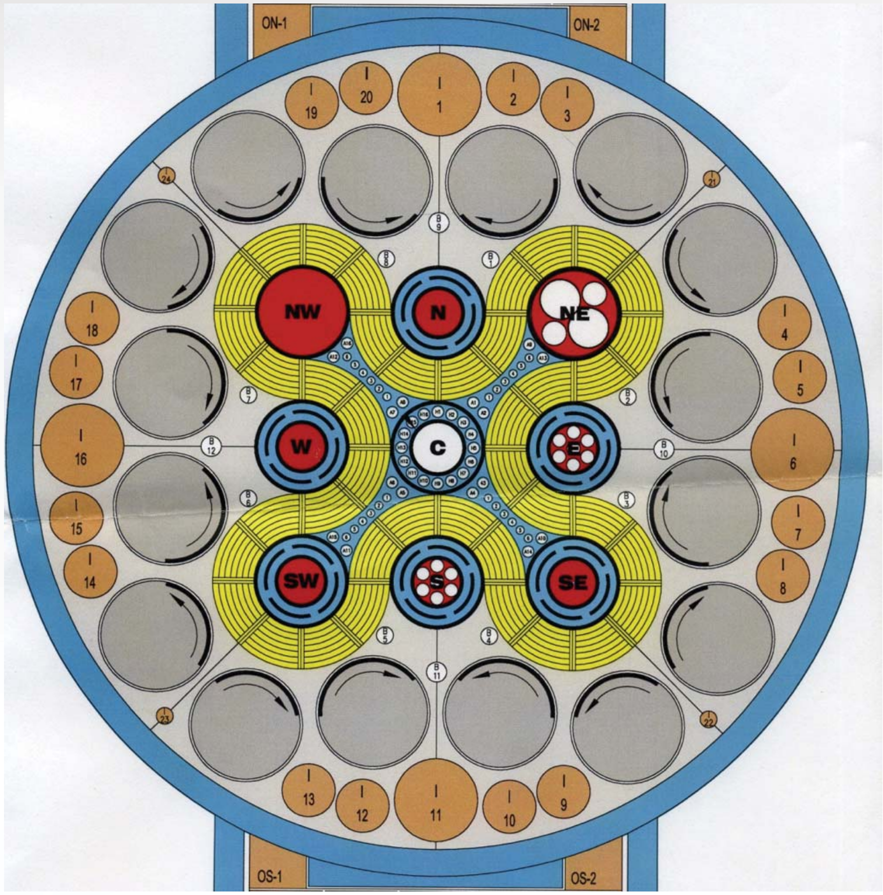
- TMIST-1/TMED-1
  - TPBAR liners are responsible for reducing T_2O released by pellets so that T_2 can be captured by getters
  - Nascent tritium uptake in liners is beneficial
  - In-reactor oxidation rates of liner materials at low water partial pressure needed for improved TPBAR performance modeling
  - Materials with higher oxidation rates may be needed to improve TPBAR performance
- TMIST-2
  - Hydrogen isotope permeation through stainless steel is enhanced by irradiation (Irradiation Enhancement Factor, IEF)
  - Ex-reactor permeation may have different rate-controlling mechanism than in-reactor permeation at very low pressures (i.e. surface decomposition versus diffusion)
  - In-situ measurements support TPBAR performance modeling



TMIST-1 leadout in the Advanced Test Reactor, Idaho National Laboratory

Objectives

- TMIST-1/TMED-1
  - Quantify temperature and pressure dependence of in-reactor oxidation for liner materials
  - Quantify nascent fraction of hydrogen isotopes deposited in test specimens during oxidation
  - Evaluate irradiation performance of advanced liner materials
- TMIST-2
  - Quantify irradiation enhancement factor
  - Determine temperature/pressure dependence of tritium permeation through stainless steel
  - Estimate permeation contribution from triton recoil resulting from He-3 conversion

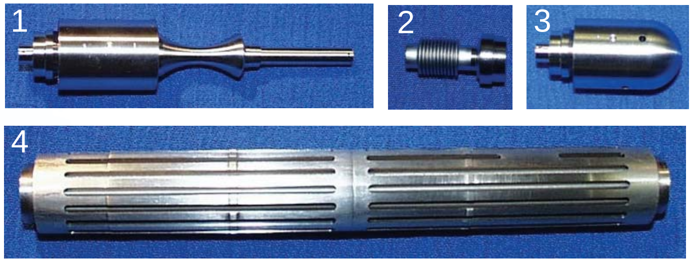


ATR Core Map

Test Specimens and Conditions TMIST-1/TMED-1

- Test Specimens
  - Zircaloy-4 (radial and uniform texture)
  - Zircaloy-2
  - Surface-Modified Zircaloy-4 with four different OD Ni plating thicknesses
    - 2.5, 5, 7.5, and 10 μm
  - Seamless tubing
    - 5.3 mm OD x 0.1 mm wall x 25 mm long
- Irradiation Conditions
  - Temperatures of 330 and 370˚C
  - He carrier gas at ~1 atm and 30 sccm
  - D_2O partial pressures of 300 and 1000 Pa
  - Irradiated for ~138 effective days at temperature (peak fast fluence, E>0.1 MeV, $\sim 2 \times 10^{21}$ n/cm^2)

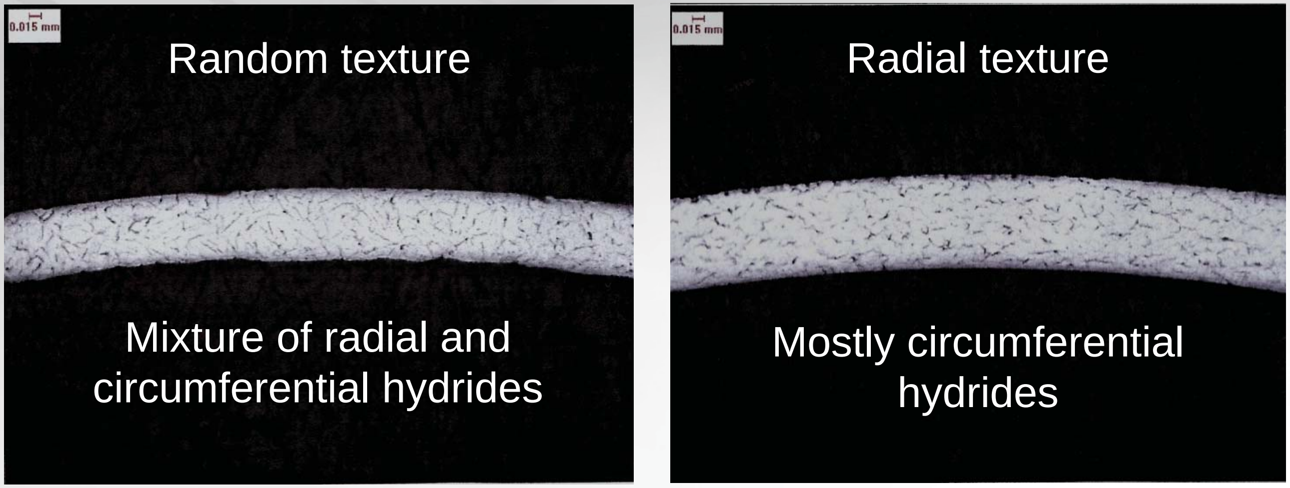

Several TMIST-1 samples with fixturing



Selected capsule components showing (1) bulkhead, (2) bellows, (3) bottom end plug, and (4) capsule body

Materials for TMIST-1/TMED-1

As-fabricated Zry-4 liners subjected to hydride orientation test

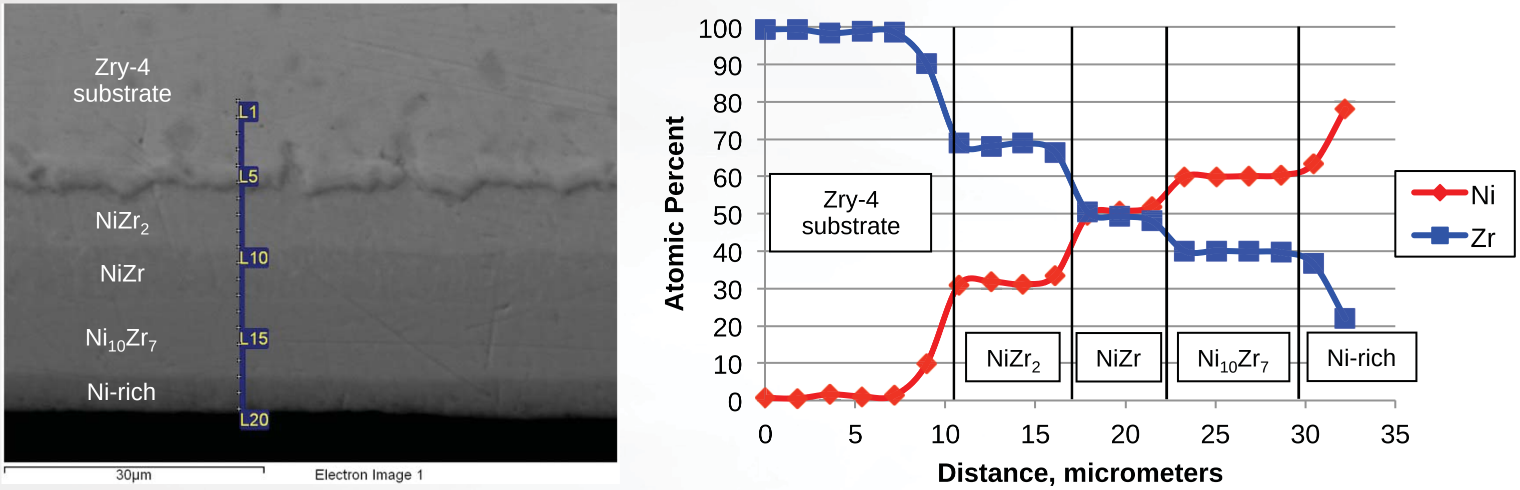


Random texture

Mixture of radial and circumferential hydrides

Radial texture

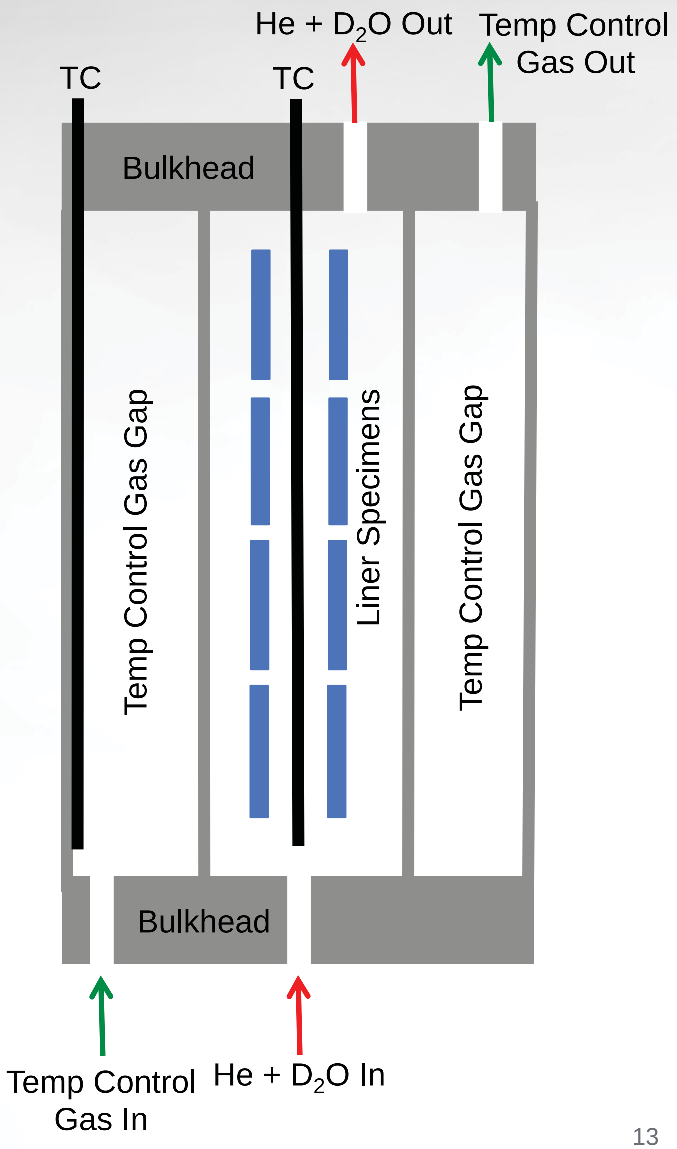
Mostly circumferential hydrides



Post heat treatment microstructure of
Surface-Modified Zry-4 with initial 10 µm Ni coating

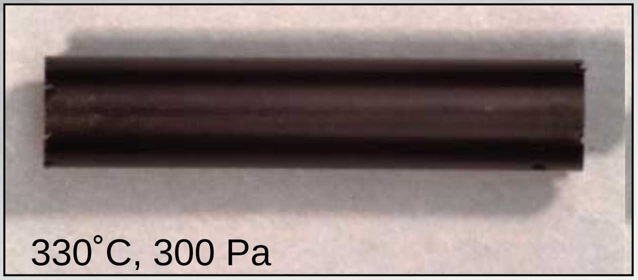
Capsule Design
TMIST-1/TMED-1

- Four specimens per capsule
- Four capsules with individual temperature control gas
  - Each specimen had unique gas gap dimensions within capsule
- Active temperature control using Type K thermocouples and He-Ne mixture in gas gap
- Fixturing to center specimens in capsule, minimize axial temperature gradients, and accommodate adjacent specimen degradation



Post-Exposure Specimen Condition

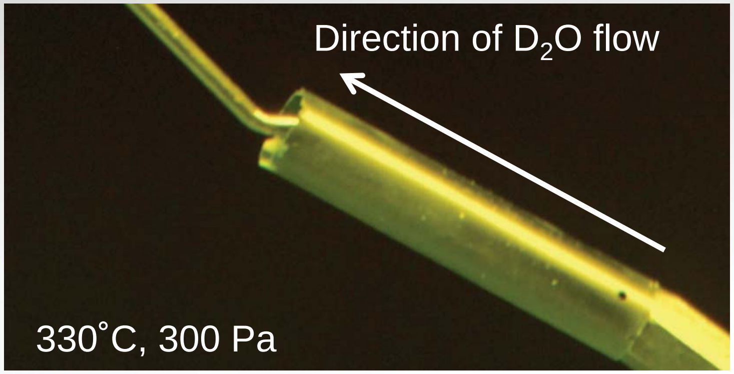
Ex-Reactor Exposure



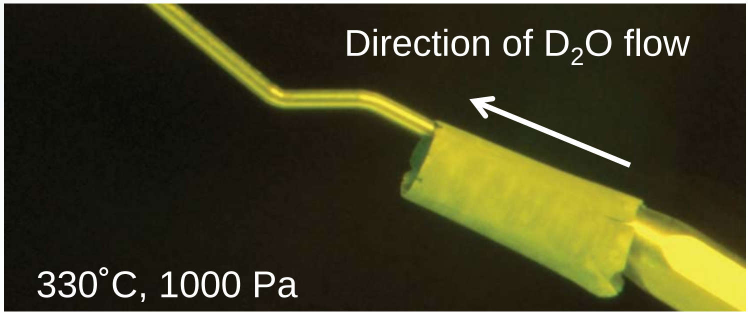
Zircaloy-4 – Fully Intact

SM-10 – Some Distortion and Cracking

In-Reactor Exposure



Zircaloy-4 – Fully Intact

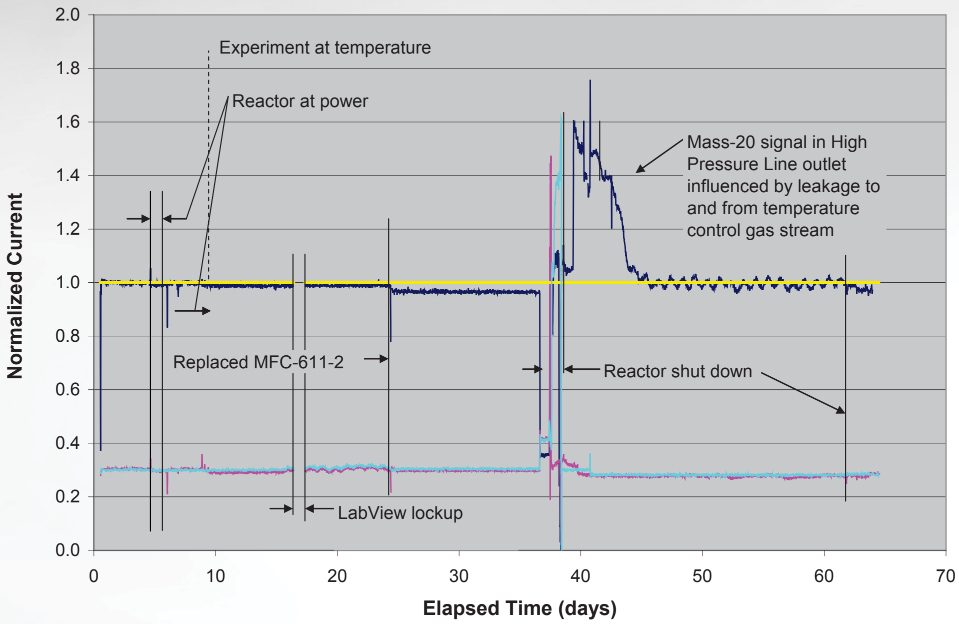


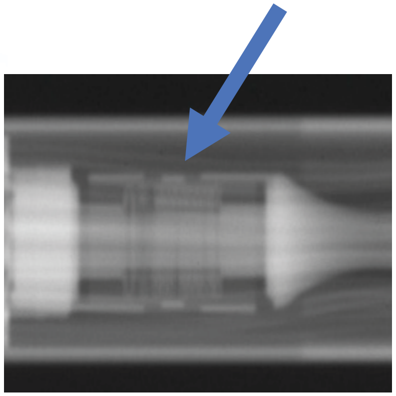
SM-10 – Partially Consumed

Because of SM specimen degradation, mass measurements were only useful for the Zircaloy samples

Experiment Performance TMIST-1/TMED-1

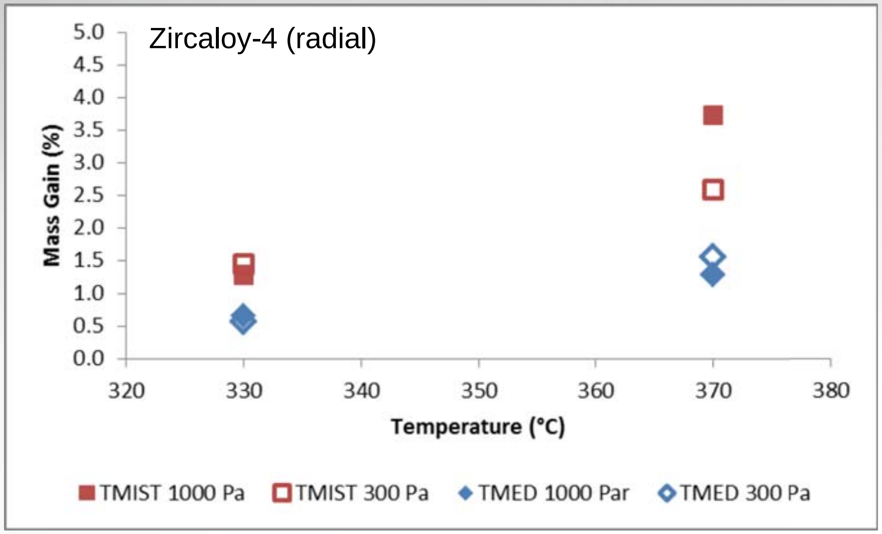
- No significant depletion of D_2O at either supply pressure
- D_2O leak observed during second ATR cycle in 1000 Pa/370°C capsule
  - Leak mitigated by differential pressure control in temperature control gas
  - Post-irradiation neutron radiography revealed a tear in the bellows as the cause of the leak
- Capsule temperature setpoints maintained to within ±5°C
- Four thermocouples failed during irradiation (one per capsule)
  - Temperature control maintained with redundant thermocouples

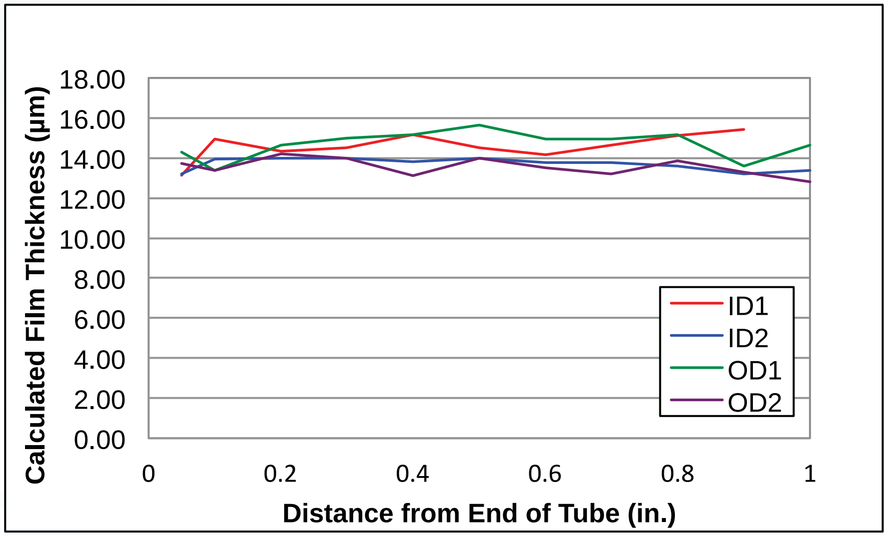




Results
TMIST-1/TMED-1

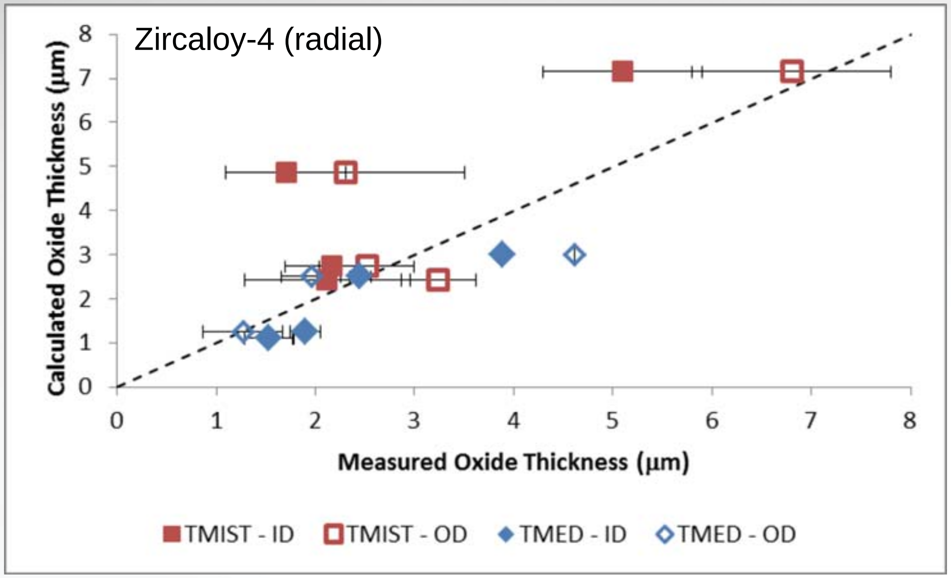
- Mass Gain - Zircaloy
  - Increased with temperature both ex-reactor and in-reactor
  - No obvious dependence on D_2O partial pressure
  - Irradiation enhancement by a factor of ~2-3X at both temperatures for Zircaloy specimens
- Fourier Transform Infrared Spectroscopy
  - FTIR oxide thickness measurements unreliable due to fine structure patterns in the diffraction spectra
  - FTIR data showed uniform oxidation along sample length on both inner and outer surfaces

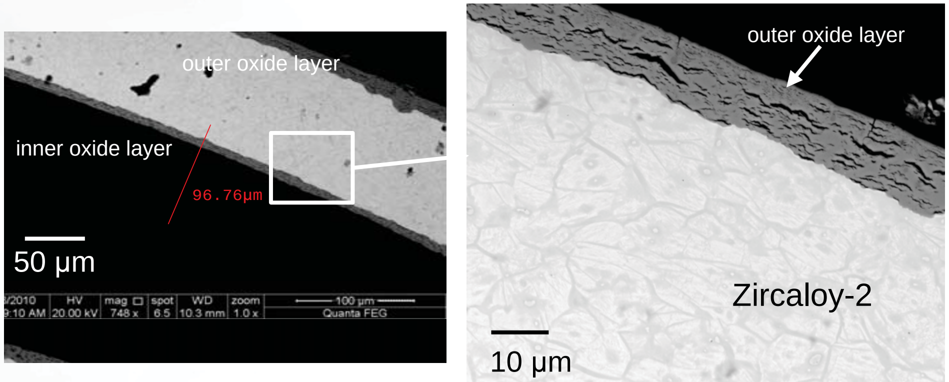




Results
TMIST-1/TMED-1

- Oxide Thickness - Zircaloy
  - Measured via optical and scanning electron microscopy
  - Mass gain measurements used to compare measured and calculated oxide thickness assuming uniform growth of tetragonal zirconia
  - In Zr-base alloys, a transition from dense tetragonal to porous tetragonal + monoclinic oxides occurs around 2 µm
    - Care must be taken when comparing pre- and post-transition oxides

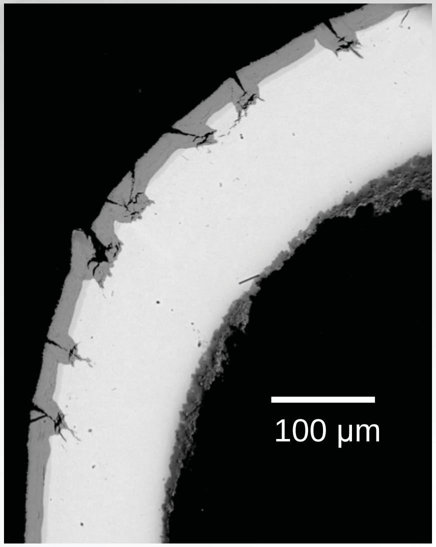




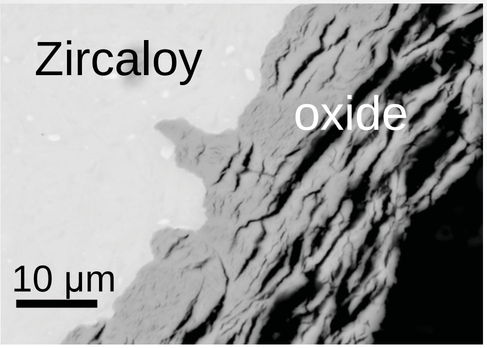
Zircaloy-2
Irradiated at 370°C and 1000 Pa

Results
TMIST-1/TMED-1

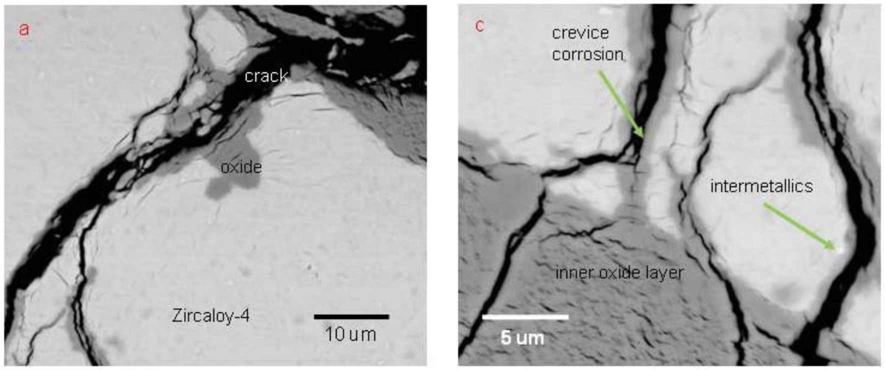
- Oxide Thickness – Surface Modified
  - Little irradiation enhancement is evident with thicker SM layers
  - Thicker SM layers were very prone to spalling
  - Dependence on both temperature and pressure
  - Inner surface of SM samples exhibited significantly more oxidation than Zry-4 specimens, indicating heat treatment affected corrosion resistance of substrate
- Large radial cracks observed in SM samples extending into substrate
- Prevalence of cracks higher for thicker SM samples
- SM layers thicker than 2.5 µm are probably not desirable due to extent of oxidation and deleterious impact on Zircaloy substrate



SM-7.5 specimen showing severe bending



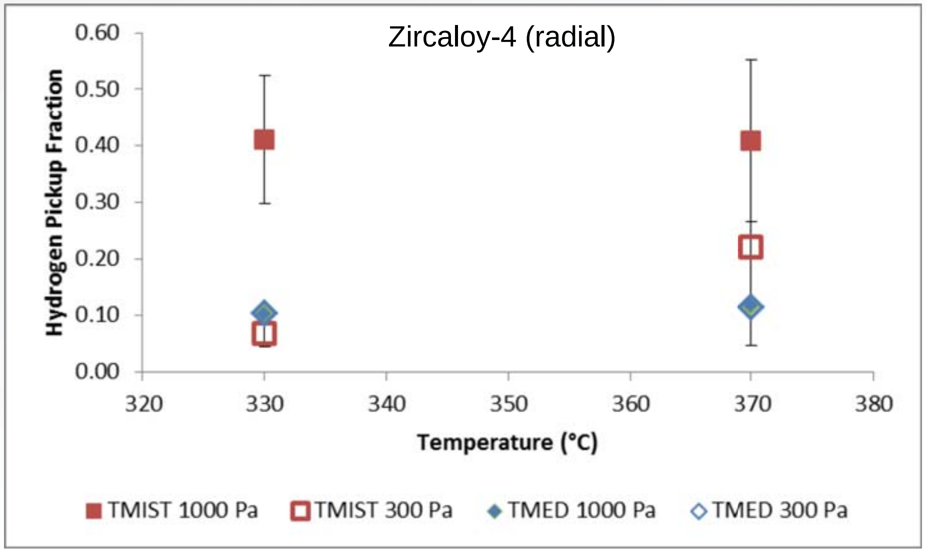
SM-10 specimen showing significant delamination within oxide layer



SM-5 specimen showing cracks extending from oxide into substrate with substrate oxidation confirming that cracks formed during irradiation

Results
TMIST-1/TMED-1

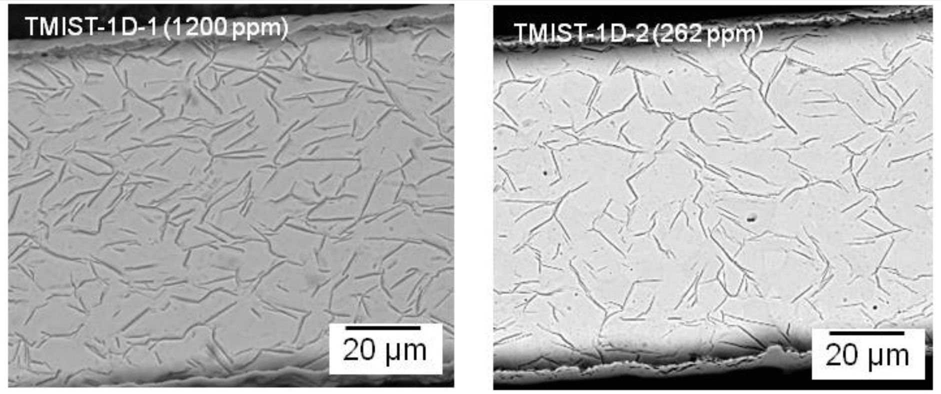
- Nascent Hydrogen Uptake - Zircaloy
  - Ex-reactor results appear insensitive to temperature and pressure
  - Temperature and pressure dependence of in-reactor results is unclear
  - Hydrogen uptake can be significantly enhanced by irradiation (1-4X)
- Nascent hydrogen Uptake – Surface Modified
  - Significantly more uptake than Zircaloy samples at same conditions
    - 2,000-30,000 ppm D
  - Irradiation enhancement of uptake (1-6X) is greater than irradiation enhancement in oxide thickness
  - Temperature and pressure trends are inconsistent
  - No significant dependence in D_2 uptake on SM layer thickness
  - Thicker SM layers had higher H_2 uptake (up to 10% of D_2 uptake)



Results
TMIST-1/TMED-1

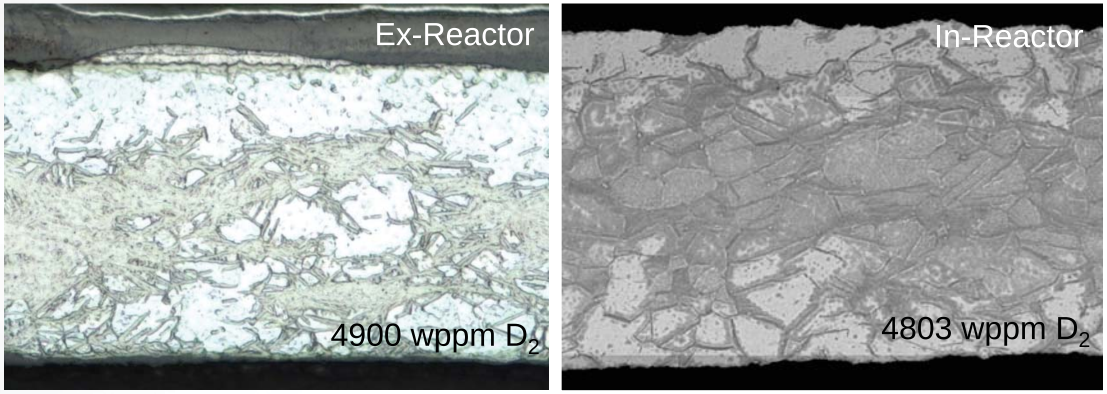
- Hydride Morphology
  - Appears to be similar for in-reactor and ex-reactor exposure
  - Irradiation does not seem to affect hydride morphology
  - Hydride morphology dictated by Zircaloy texture
    - Hydrides form parallel to basal planes

Hydride Orientation in Zry-4 Specimens Irradiated at 330˚C and 1000 Pa D_2O



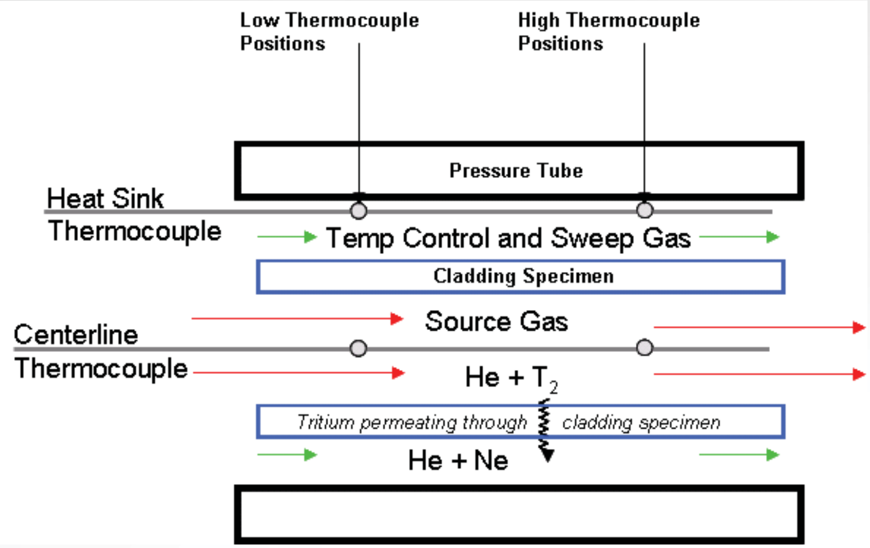
Radial Texture   Uniform Texture

Hydride Orientation in SM-5 Specimens Exposed at 330˚C and 300 Pa D_2O



Test Specimen and Conditions TMIST-2

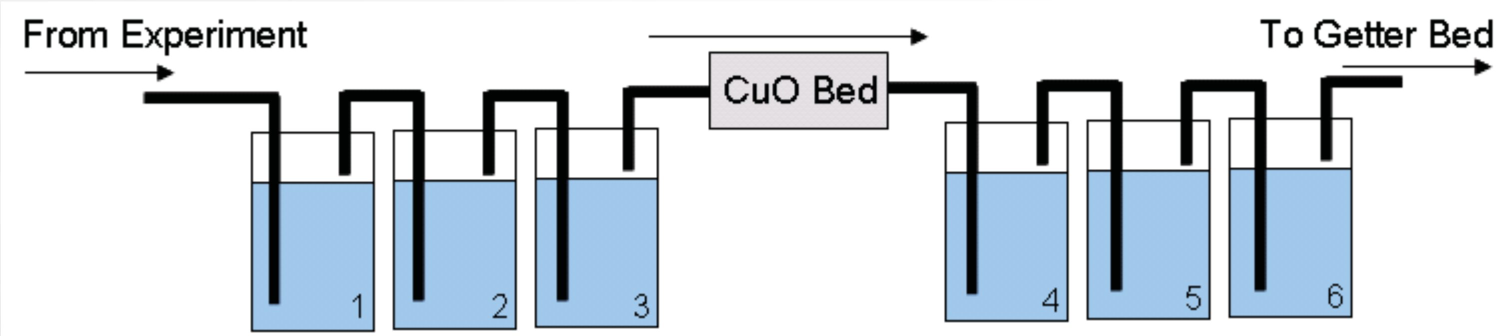
- Test Specimen
  - 316 stainless steel
  - 0.85 cm ID x 0.97 cm OD
- Irradiation Conditions
  - Temperatures of 292 and 330°C
  - He carrier gas at ~1 atm and 30 sccm
  - Tritium partial pressures of 0.1, 5, and 50 Pa, pre-mixed in carrier gas cylinders
  - Irradiated for ~200 effective days
    (peak fast fluence, E>0.1 MeV, est. ~3 x 10^{21} n/cm^2)
  - Temperature and pressure set points changed online after obtaining satisfactory permeation measurements on each experiment step
  - At least two separate measurements at each combination of temperature and pressure to evaluate possible fluence effects



TMIST-2 Test Capsule

Permeation Measurement System TMIST-2

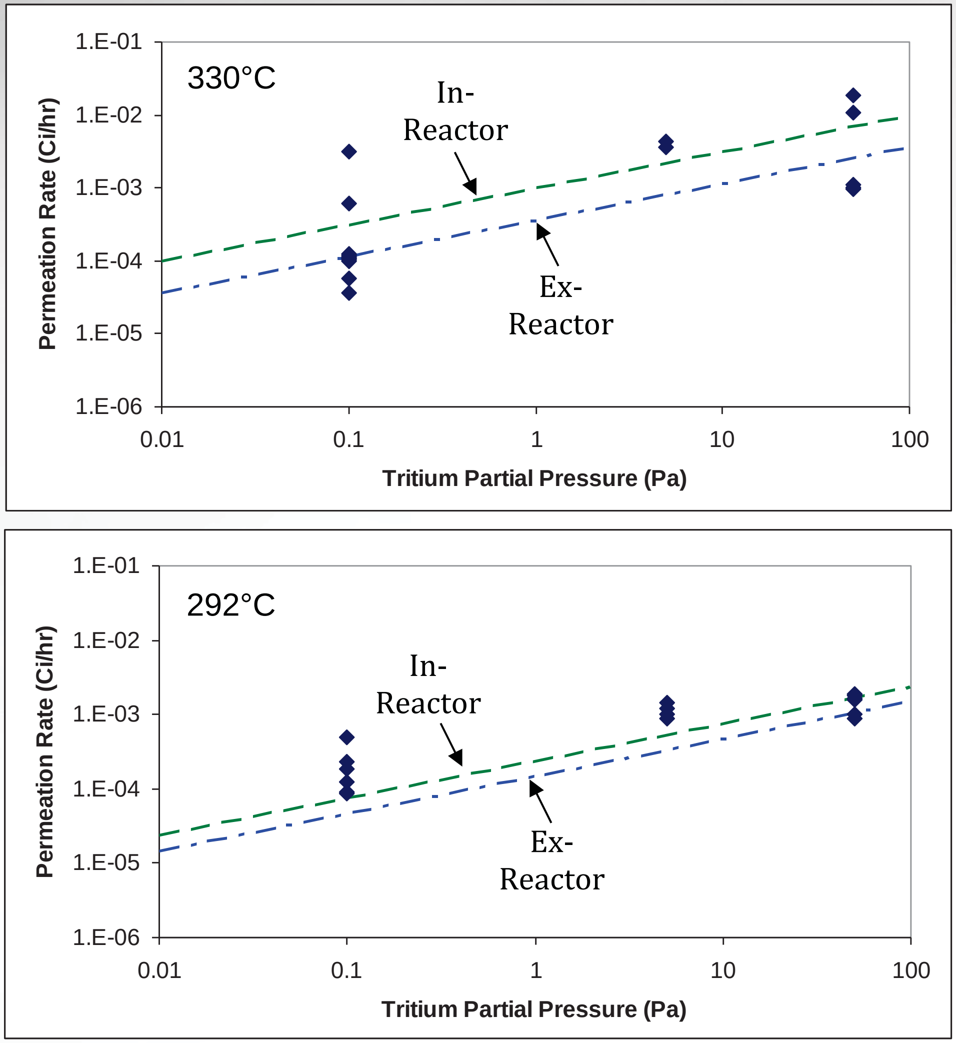
- Tritium Permeation Measurements
  - Real-time indication of tritium permeation rate provided by ion chambers
    - Used to determine when permeation reached steady-state (usually several days)
  - Quantitative tritium permeation results determined from periodic scintillation counter measurements of DI water bubbler vials
    - At least two collections of at least 24 hr each time a temperature/ pressure combination was tested
    - Two banks of three vials each to differentiate between T_2O/HTO and T_2/HT



Results
TMIST-2

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

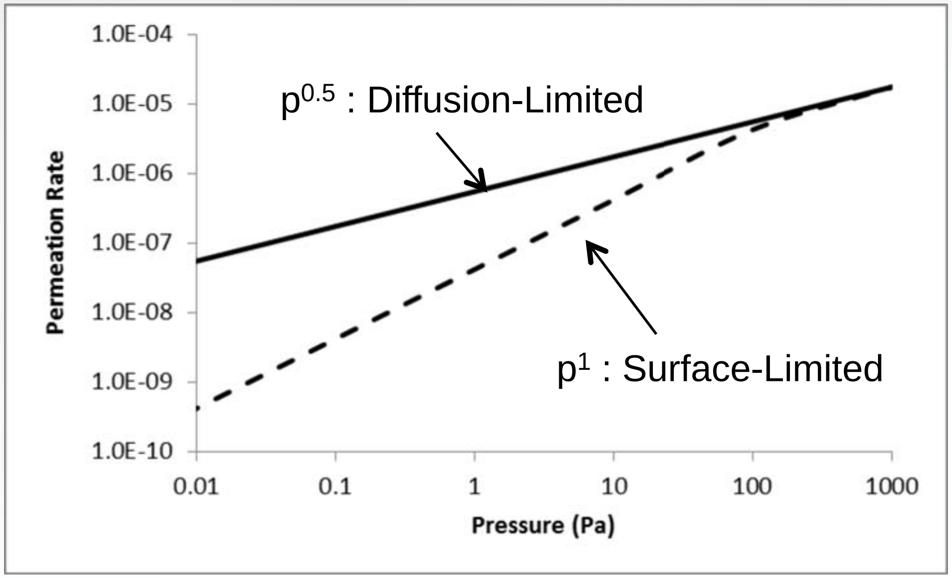
- In-reactor permeation rates through TPBAR cladding measured for the first time
- Permeation data show definite irradiation enhancement relative to ex-reactor behavior
  - Mechanism unclear
  - Currently evaluating microstructural evolution of TPBAR cladding during irradiation
- New TPBAR permeation model developed to address irradiation effect



TMIST-2 Data Showing Enhanced (~3X) In-Reactor Tritium Permeation Rate Through Uncoated Stainless Steel

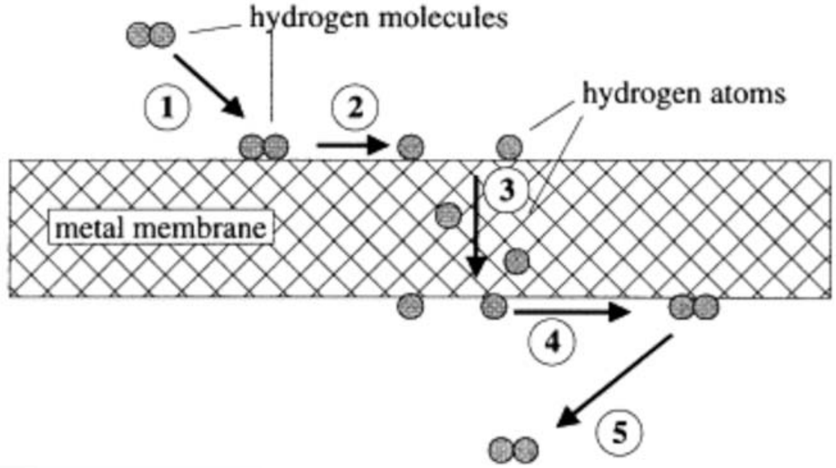
Rate-Limiting Permeation Mechanisms

- Ex-reactor permeation measurements
  - > 100 Pa → Diffusion-limited → $p^{0.5}$
  - < 100 Pa → Surface-limited → p^{1}
- In-reactor permeation mechanism uncertain
  - Direct dissociative chemisorption
    - Molecules adsorb and readily dissociate upon contact
    - Disrupted ex-reactor at low pressure by surface impurities or oxide films
  - Radiation-enhanced dissociation
    - Radiolysis of T_2 in gas phase
    - Physical or chemical changes in surface in-reactor



Results
TMIST-2

- Pressure dependence of $p^{0.5}$ observed
  - Suggests tritium permeation is rate-limited by diffusion, not surface decomposition (p^1)
- Temperature dependence consistent with diffusion
  - Scatter prevents determination of statistically significant trends in apparent activation energy
  - Nominal activation energies ~100 kJ/mol, consistent with diffusion-limited mechanism
  - Trend for increased permeation with temperature observed within the scatter, as expected

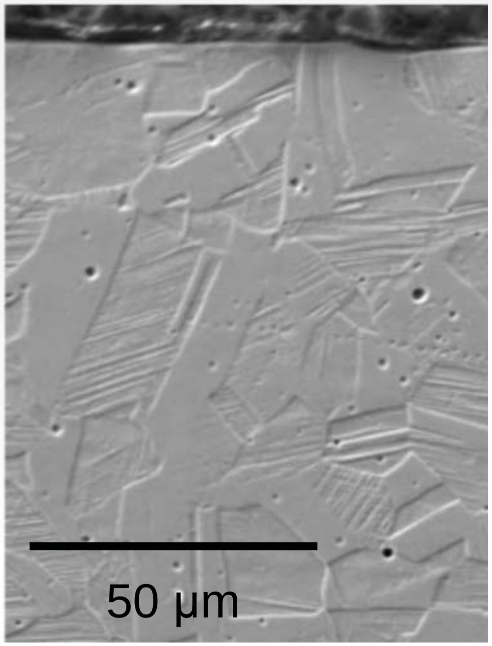


Processes involved in permeation of hydrogen through metals

Results
TMIST-2

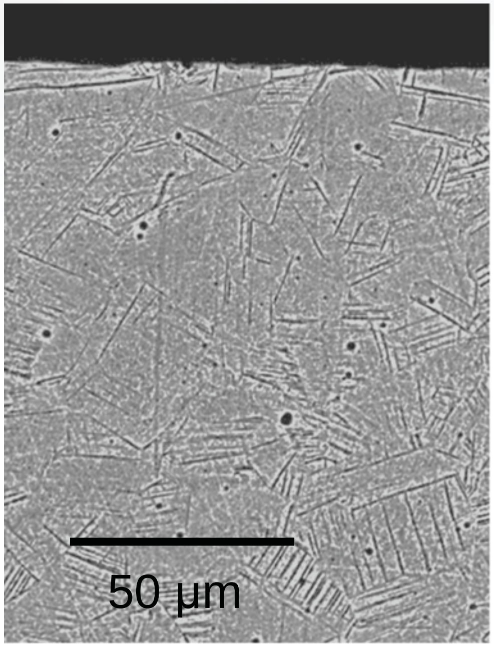
- Microscopy
  - After irradiation, grain boundaries are not as well defined
  - TEM necessary to evaluate extent of irradiation damage
- Auger Electron Spectroscopy
  - After irradiation, the inner surface of the specimen appears to be enriched in carbon and depleted in oxygen
    - Reducing atmosphere during test
    - Source of carbon?

Pre-Irradiation



SEM Image

Post-Irradiation



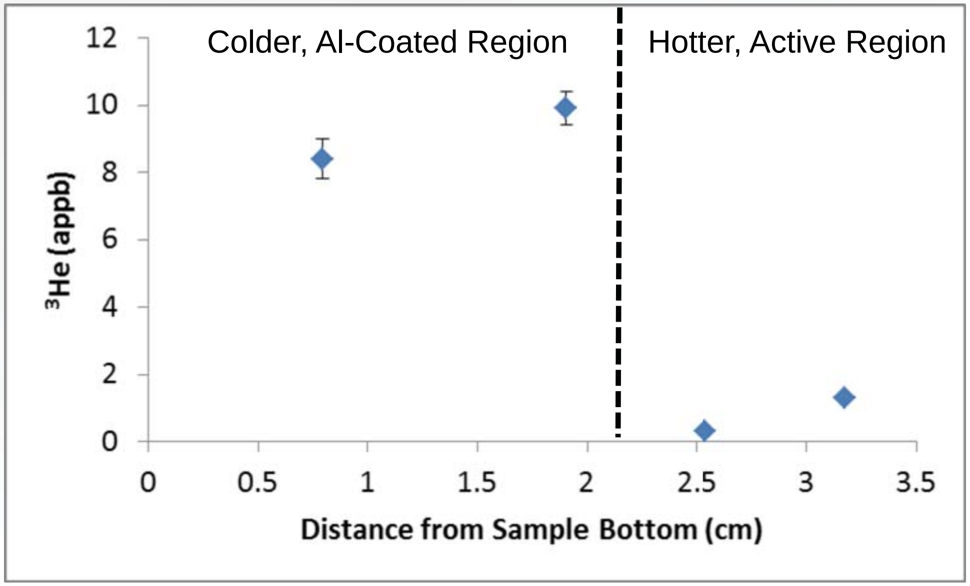
SEM Image

Results
TMIST-2

Pacific Northwest NATIONAL LABORATORY

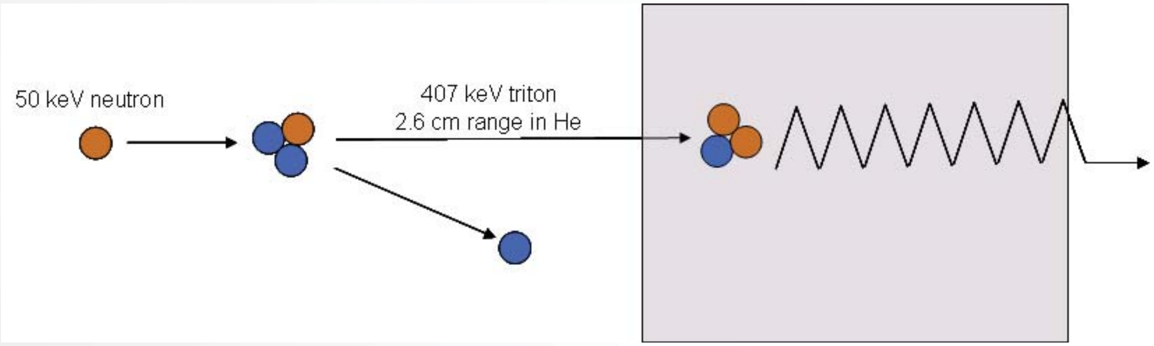
Proudly Operated by **Battelle** *Since 1965*

- Low-level ^{3}He Assay
  - Sample outer surface area below active region sputter-coated with Al to inhibit permeation
  - ^{3}He measurements made within and below active (hot) sample region
  - ^{3}He acts as a tracer for tritium
  - Higher concentration of ^{3}He in cold, sputter-coated region suggests slower tritium permeation



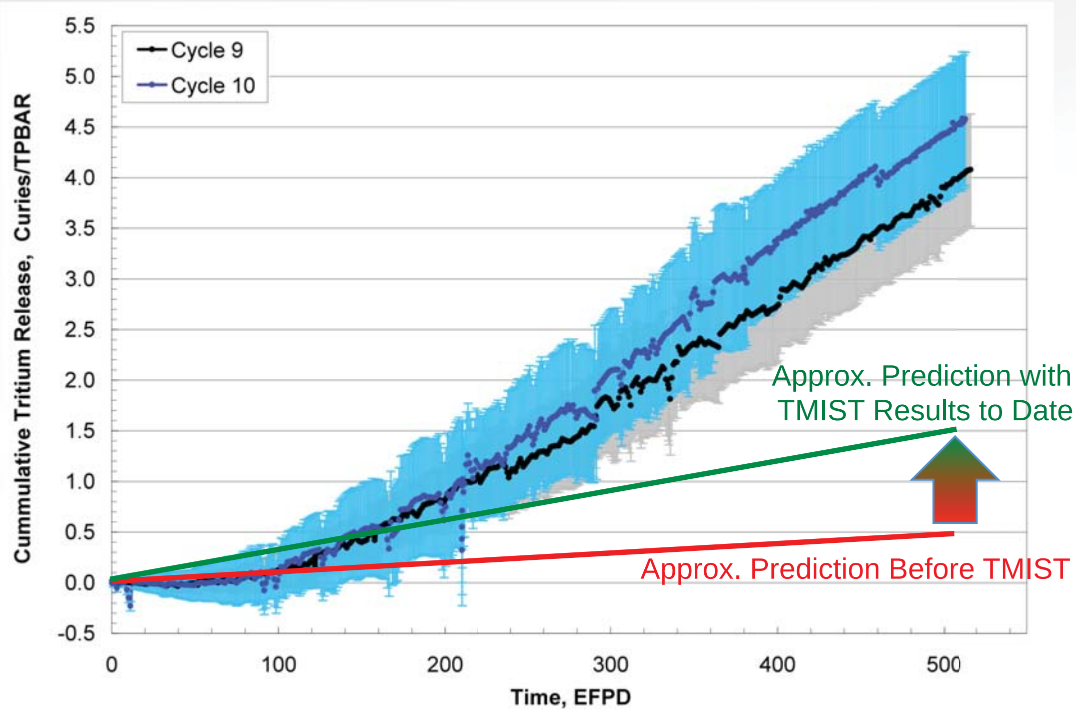
Results
TMIST-2

- Utilized source gas mixture of ^{4}He + 1% ^{3}He
- Calculations determined the conversion rate of He-3 to tritium
  - Used average neutron energy spectra for ATR
- Triton recoil distance large relative to inner diameter (2.6 vs. 0.85 cm)
- Implantation depth in stainless steel is ~ 2 μm
- Less than 4.1% (2σ confidence) of the tritium resulting from He-3 conversion permeated through the test specimen



Data from the Testing Program Has Improved TPBAR Performance Predictions

- TROD performance prediction code models updated with data from TMIST-1,TMED-1, TMIST-2, and TMED-4
- Discrepancy between predicted and observed permeation decreased by ~30%
- Time dependence still not correctly modeled
  - Will be improved by TMIST-3 data

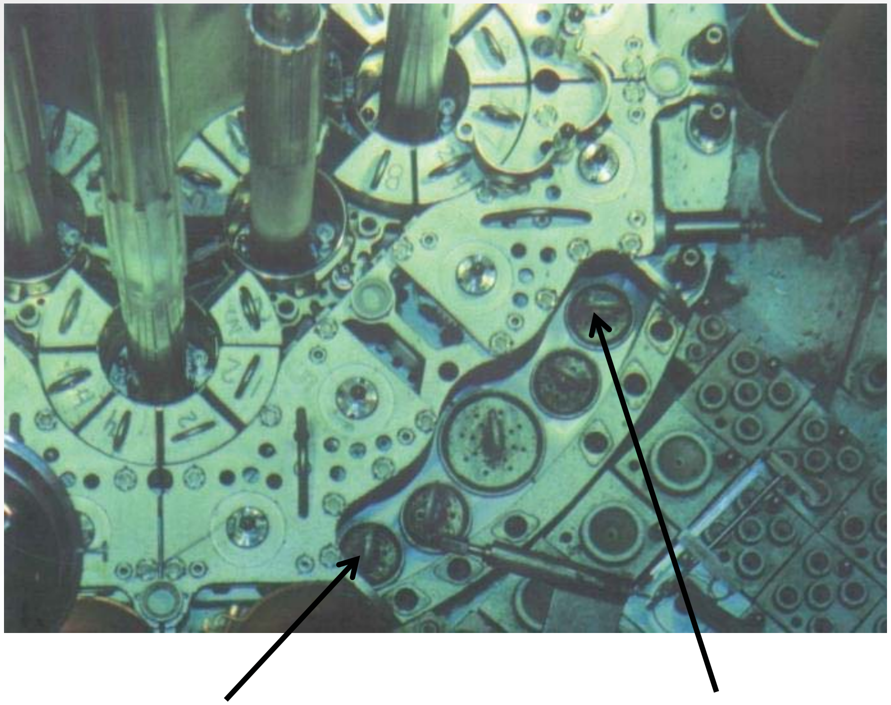


Approx. Prediction with TMIST Results to Date

Approx. Prediction Before TMIST

Pellet Performance Irradiation Experiment TMIST-3

- Data from TMIST-3 will
  - Explain time dependence of pellet tritium release and its relationship to TPBAR permeation
  - Evaluate the speciation of tritium release as a function of burnup, burnup rate, and time (T_2O versus T_2)
  - Define relationships between pellet burnup, burnup rate, and tritium release to help define an acceptable TPBAR operational envelope
  - Improve fundamental understanding of pellet microstructure and its effects on performance
  - Provide a better definition of the pellet burnup limit
  - Determine whether modifications to the pellets could improve TPBAR performance
    - Increased tritium retention
    - Increased TPBAR void volume

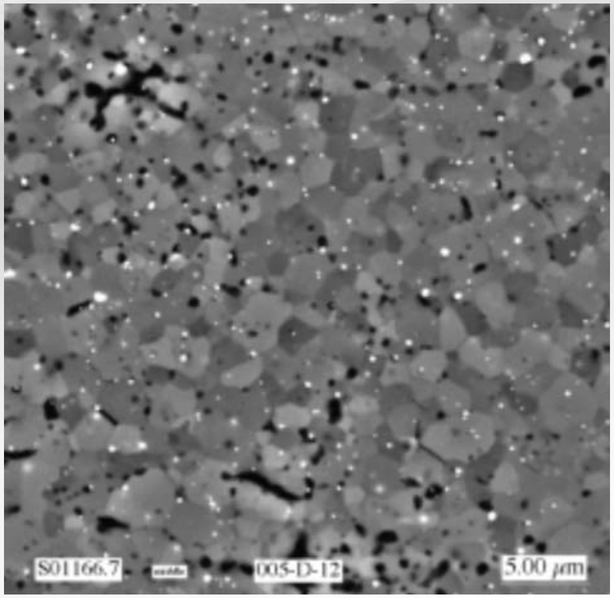


Location for the TMIST-3A low-burnup test train (I-13)

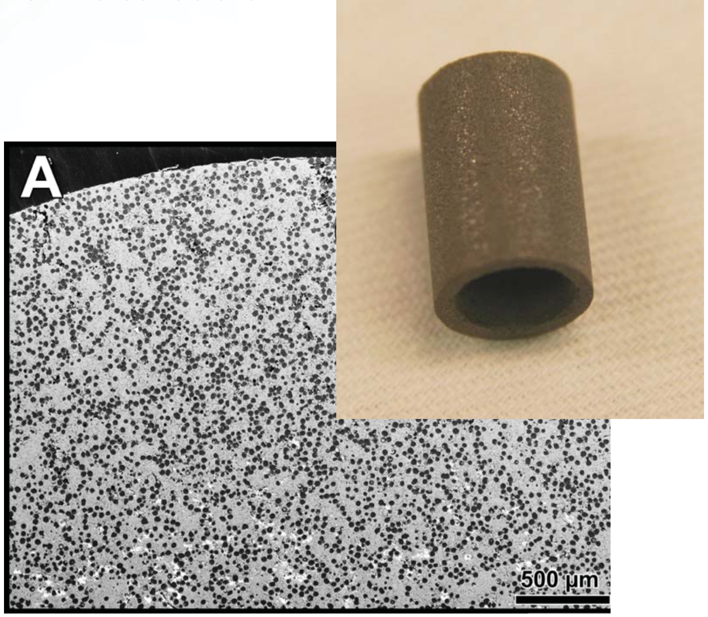
Location for the TMIST-3B high-burnup test train (I-9)

Test Specimens
TMIST-3

- Test specimens
  - Standard TPBAR $LiAlO_2$ pellets
    - 2 µm grain size
    - 97-98% TD
    - 1 mm wall thickness
  - Large grain $LiAlO_2$ pellets
    - 10 µm grain size
  - Porous $LiAlO_2$ pellets
    - Small pores (~90% TD)
    - Large pores (~85% TD)
  - Thin-wall $LiAlO_2$ pellets
    - 0.76 mm wall
  - Cermet pellets
    - $LiAlO_2$ particles in Zr matrix
    - Four ceramic particle loadings from 10-40 v/o



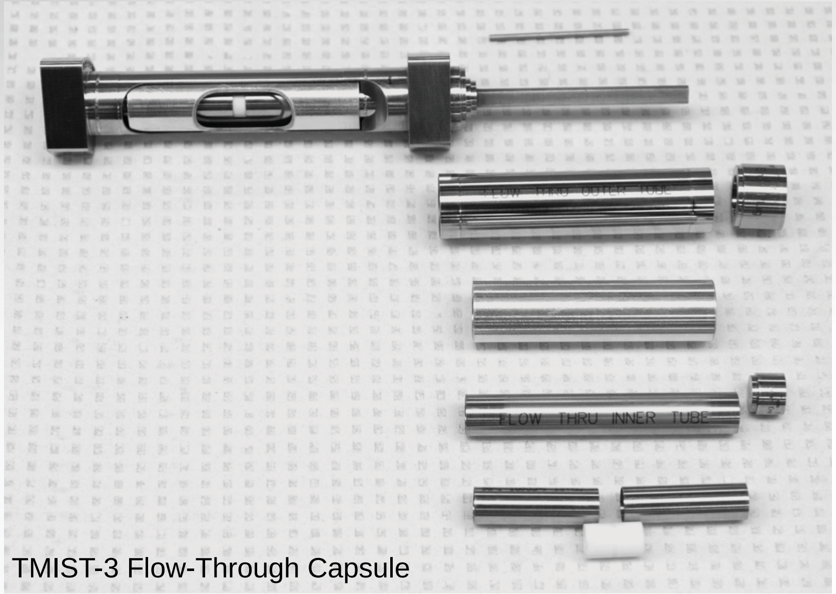
Standard $LiAlO_2$ pellet microstructure



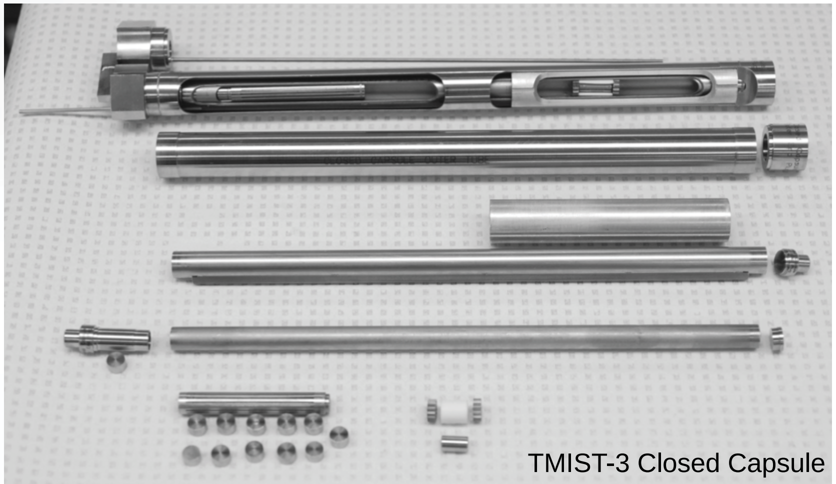
Cermet pellet with 40 v/o LiAlO2

Capsule Design
TMIST-3

- Two test trains
  - TMIST-3A – Irradiate for ~1.5 yr
  - TMIST-3B – Irradiate for ~2.5 yr
- Two capsule types in each test train (41 total)
  - Flow-through – 15 total
  - Closed – 26 total
- All capsules have active He-Ne temperature control gas
  - One capsule designed to operate over a wide temperature range to evaluate temperature effects
- Flow-through capsules have He sweep gas to remove tritium for ex-reactor sampling
- 106 total leads for both test trains



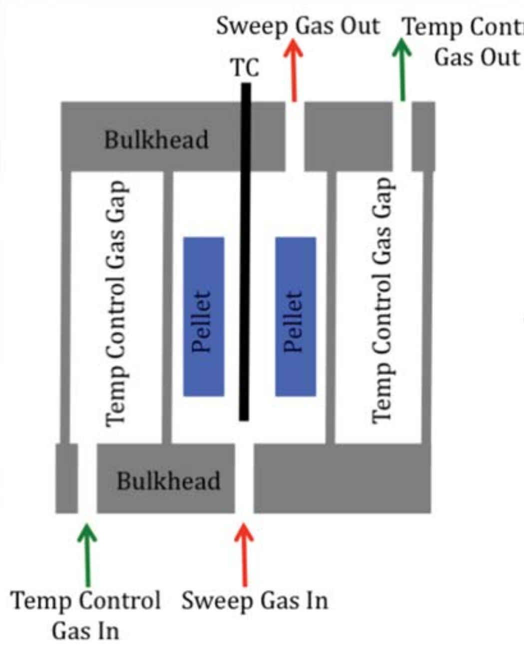
TMIST-3 Flow-Through Capsule



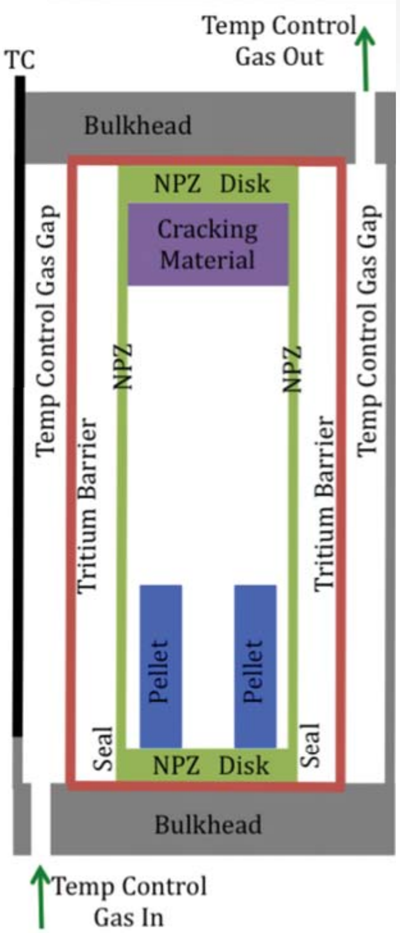
TMIST-3 Closed Capsule

Capsule Design
TMIST-3

- Flow-through capsules
  - Used for time, burnup, burnup rate, and temperature dependent tritium release measurements
  - Tritium released from pellets is carried to ex-reactor measurement system for analysis
  - Total tritium measurement only
- Closed capsules
  - Used for speciation measurements and pellet integrity/retention tests
  - Tritium released from pellets as T_2 and T_2O is spatially segregated and gettered in-situ
  - Speciation data inferred from post-irradiation examination tritium assays



Flow-Through Capsule



Closed Capsule