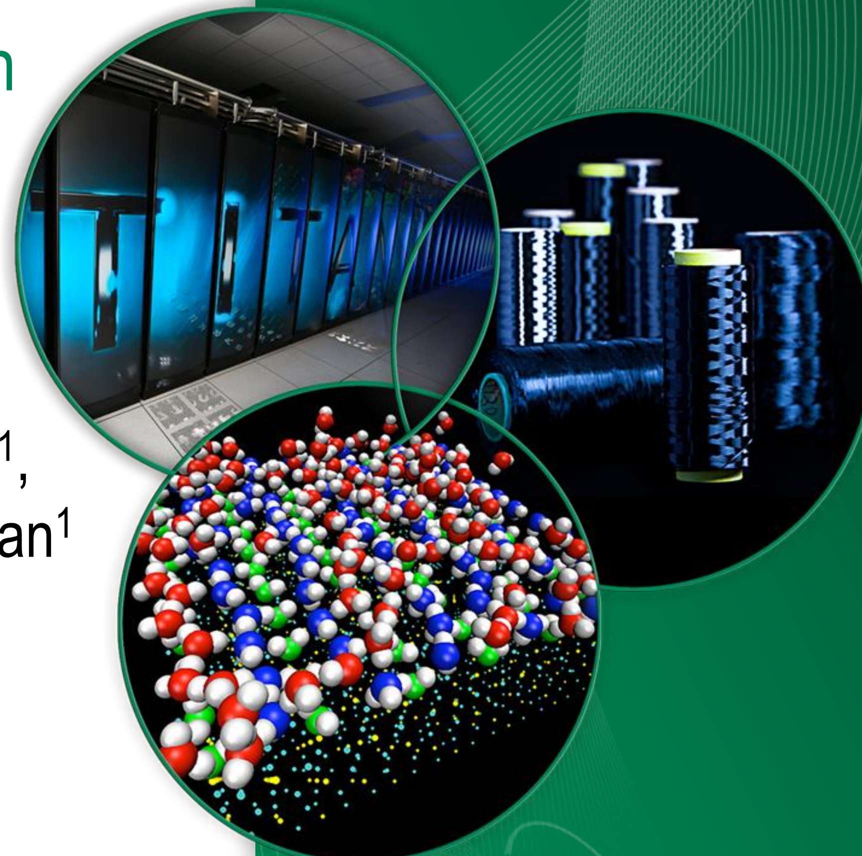
# Neutron Irradiation Testing of Structural Materials in Support of an Accelerator Driven Subcritical Assembly for the Production of Mo-99



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Boston, Massachusetts

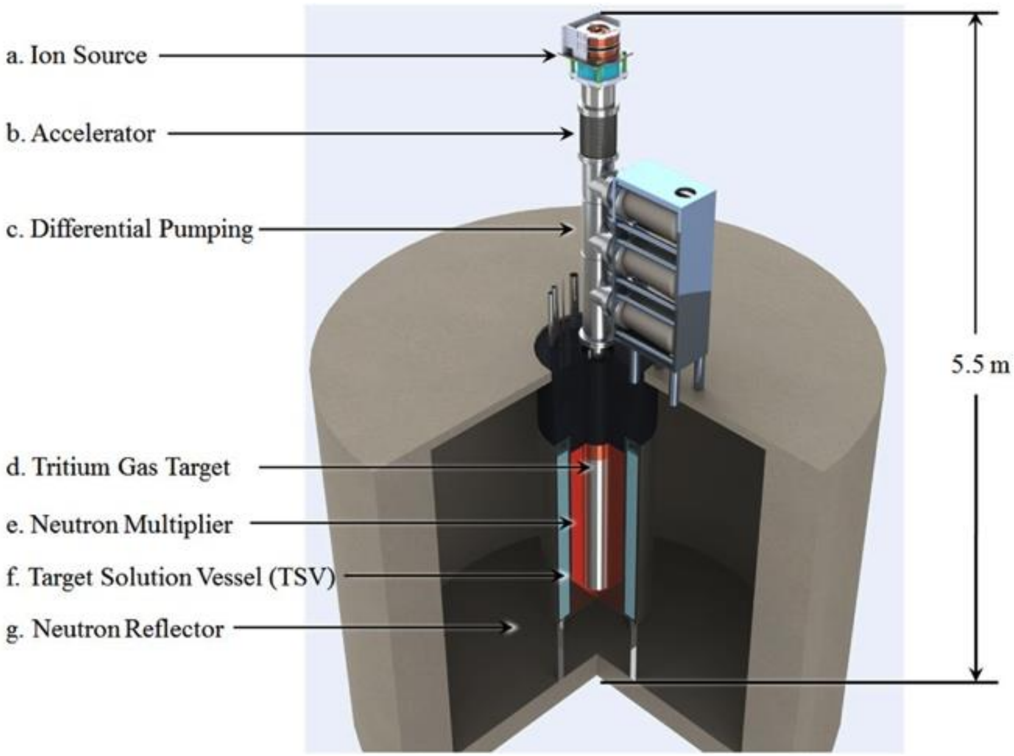
Sep 3rd, 2015

# Outline

- Importance of Material Selection
- Testing Needs
- Test Plans and
- Highlights of Current Results

# Materials Challenges

- Exposure to $H_2SO_4$ / Uranyl Sulfate
  - Solution pH ~1 : ensure uranium solubility
  - Corrosion behavior
  - Radiolytic decomposition of solution – changing corrosion rates: formation of H, OH, $H_2O_2$ and $H_2$
  - Oxidation / hydrogen uptake
- Irradiation damage
  - Reactor vessel, has 50/50 fast to thermal flux ratio at inner wall, 5/95 ratio at outer wall.
  - Stainless steel piping closest to the TSV is exposed to lower neutron fluxes.
  - Lower operating temperatures than commercial reactors: effects on irradiated mechanical properties.



# Past Materials Evaluations

- Significant amount of past research on aqueous fuel reactors.
- See ORNL report, "Aqueous Homogeneous Reactors, Part I", edited by James A. Lane, June 1958. In particular, chapters 3 and 5 (only Part I is of particular interest for us)
  – http://energyfromthorium.com/ornl-document-repository/
- Experimental corrosion / irradiation testing of materials, in-pile loop experiments.
- Initial evaluation of different austenitic and F/M steels, Ti, Ni and Zr-alloys (mainly pure Zr and Zry-2).
- In-pile irradiation/corrosion loop testing of Zry-2:
  – Radiation effect on corrosion by uranyl-sulfate not directly associated with radiolytic changes in chemistry.
  – Oxide growth in irradiated testing showed oxide break-up and reforming appears at a steady rate.

THE CORROSION RATES OF SEVERAL ALLOYS IN 0.17 *m* $UO_2SO_4$ AT 250° C

Pressurizing gas: 200 psi $O_2$.
Time: 200 hr. Flow rate: 10 to 15 fps.

| Metal or alloy | Range of avg. corrosion rates, mpy |
|---|---|
| *Austenitic stainless steels* | |
| 202, 302, 302B, 303, 304, 304L, 309SCb, 310S, 316, 316L, 318, 321, 347, Carpenter Alloys 10, 20, 20Cb, Croloy 1515N, Durimet, Incoloy, Multimet, Timken 16–25–6, Worthite | 14–65 |
| SRF 1132 | 190 |
| *Ferritic and martensitic stainless steels* | |
| Armco 17–4 PH (37 RC), Armco 17–7 PH (43 RC) | 3.1–4.9 |
| 322W, 322W (27–38 RC), 329, 430, 431, 431 (43 RC), 446, Armco 17–4 PH, CD4MCu, Allegheny 350, Allegheny 350 (38–43 RC), Croloy 16–1, Frogalloy | 6–35 |
| 410, 410 (43 RC), 414, 416, 416 (37 RC), 420, Armco 17–7 PH | 46–81 |
| 420 (52 RC), 440 C | 100–430 |
| *Titanium and zirconium alloys* | |
| 45A, 55A, 75A, 100A, 150A, AM, Titalloy X, Y, and Z | 0.01 |
| AC, AT, AV | 0.03–0.12 |
| Zircaloy-1 and -2, zirconium, zirconium-tin | <0.01 |
| *Nickel and cobalt alloys* | |
| Hastelloy R-235, Inconel X, Stellite 1 | 77–88 |
| Hastelloy C and X, Haynes Alloy 25, Inconel, Stellite 3, 6, and 98M2 | 120–340 |
| *Other materials* | |
| Gold, platinum | <0.1 |
| Niobium | 6.7 |
| Sapphire | 17 |
| Quartz | 58 |
| Pyrex glass | 730 |

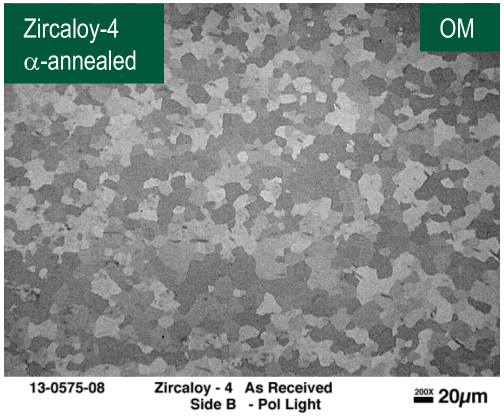
# Materials of Study

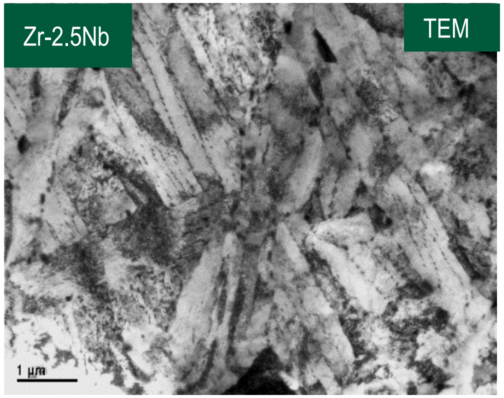
**Candidate alloys for the TSV:**

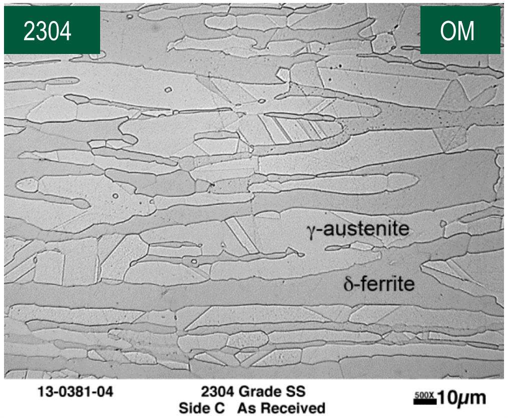
- <u>Zircaloy-4</u> in the *alpha annealed* and *beta quenched* conditions. The latter has been hypothesized as having better corrosion properties and less sensitivity to irradiation hardening – being evaluated.
- <u>Zr-2.5Nb</u> an alloy with improved aqueous (water) corrosion properties and more tolerant of higher hydrogen concentrations, but with a faster hydrogen pick-up rate.

**Candidate alloys for the support lines:**

- <u>316L</u> a low carbon grade of 316 with improved corrosion resistance over 304L due to the higher levels of Cr, Ni and Mo. The low carbon grade reduces sensitization of the grain boundaries by Cr-carbides. Well established materials database.
- Duplex <u>2304 grade</u> stainless steel, with improved sulfuric acid corrosion resistance, better toughness and greater stress corrosion crack resistance than 316L. This is a relatively low alloyed composition compared to other duplex grades to avoid forming unwanted phases through radiation induced solute segregation. Unknown radiation database.
- <u>17-4PH grade</u> (type 630) precipitate hardened stainless steel, investigated for use in the pipe connections between dissimilar metal components (instead of dissimilar metal welds). Used in annealed (soft) condition in application.



# Neutron Irradiation of Structural Materials: Questions

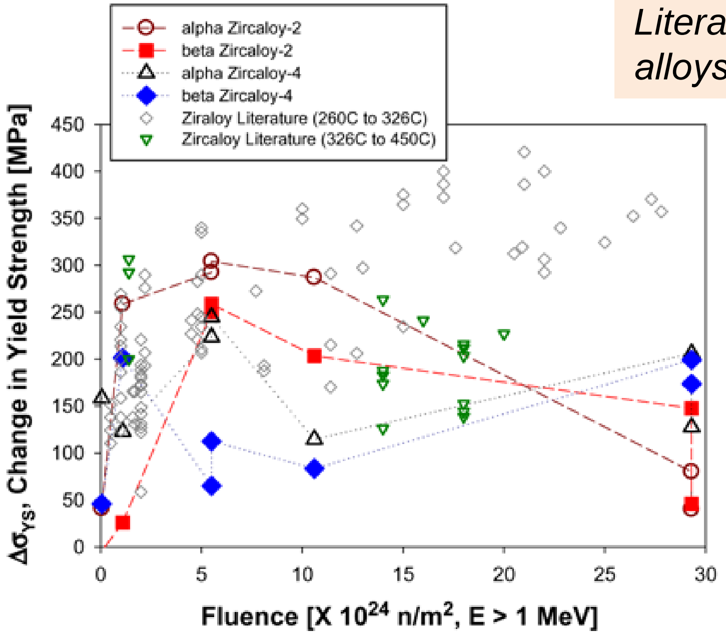
- Substantial irradiation database for Zircaloy-4 (Zry-4), Zr-2.5Nb and 316L: most of this data is for temperatures ~300°C or higher.
- Little to no available irradiation data on 2304 and 17-4PH grade steels.
- Effects of hydrogen pick-up in the zirconium base alloys?
- Performance of welded materials following radiation exposure?

# Radiation Effect on Materials

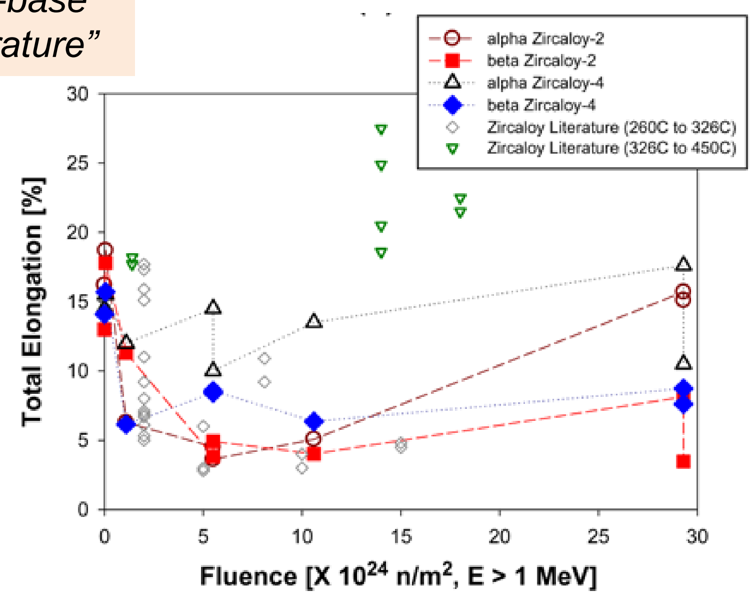
Exposure conditions of interest:

- Zr-base materials are evaluated for values up to $\sim 10^{21}$ n/cm$^2$, or ~2 displacements per atom (dpa).

Concerns regarding radiation-induced changes in Zr-base alloys?




*Literature data on Zr-base alloys at "low temperature"*



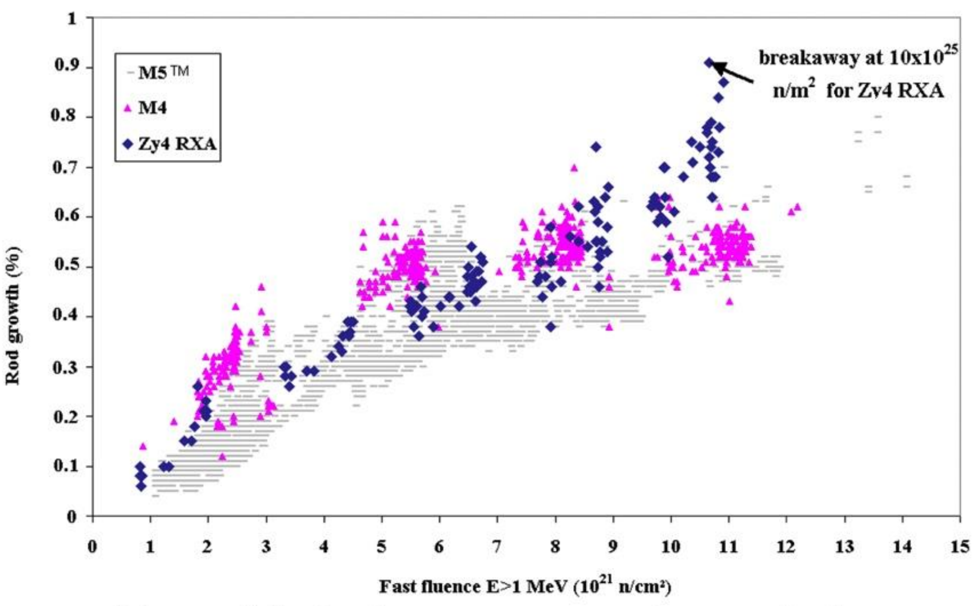

- Increased tensile hardening of 100 to 250 MPa with dose (~40% increase).
- Irradiation hardening occurs up to $\sim 5\times10^{20}$ n/cm$^2$, similar trends between $\alpha$-annealed and $\beta$-quenched conditions, slightly greater hardening in $\alpha$-annealed for the tested conditions.

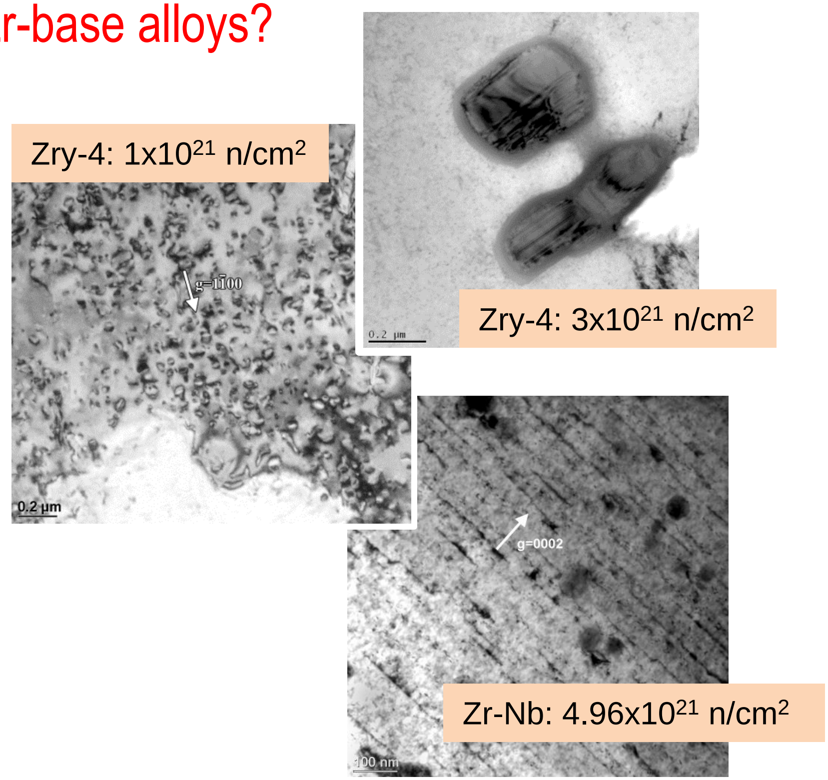
# Radiation Effect on Materials

Exposure conditions of interest:

- Zr-base materials are evaluated for values up to ~$10^{21}$ n/cm$^2$, or ~2 displacements per atom (dpa).

Concerns regarding radiation-induced changes in Zr-base alloys?




- "a"-type dislocation loop formation initiates around 3x$10^{19}$ n/cm$^2$ and reaches a saturation point at 1x$10^{21}$ n/cm$^2$ where "c"-type loop formation starts.
- Amorphization of the Laves phase with irradiation has been reported for fluences between 0.6 - 2.5x$10^{21}$ n/cm$^2$ at irradiation temperatures near 80°C.

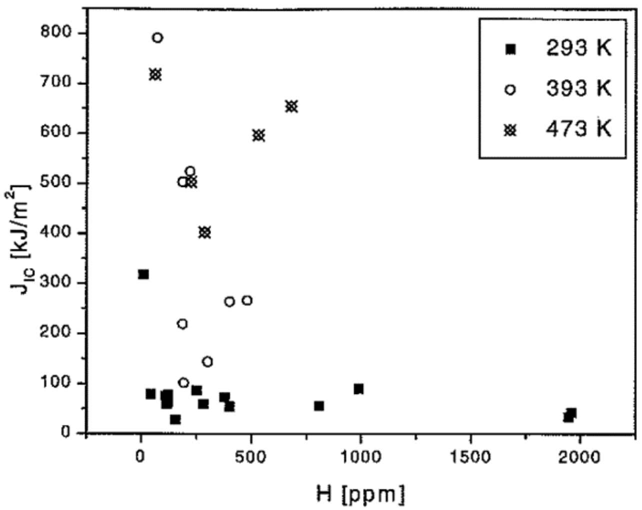
# Radiation Effect on Materials

Exposure conditions of interest:

- Zr-base materials are evaluated for values up to ~$10^{21}$ n/cm$^2$, or ~2 displacements per atom (dpa).

Concerns regarding radiation-induced changes in Zr-base alloys?

- Hydrogen pick up in the material from the uranyl-sulfate has not been fully evaluated.
- H solubility in Zr is very low at the temperature of the TSV.
- Hydrogen uptake and the development of hydrides can detrimentally impact properties.
- Literature: $T_{rm}$ tensile testing of unirradiated H-charged Zr-4, ductile-brittle transitions reported between 400 and 800 wppm H. Notched tensile samples have shown increased sensitivity.
- At this time, ORNL is working to determine hydrogen uptake.



# Radiation Effect on Materials

Exposure conditions of interest:

- Stainless steel support and piping are evaluated for fluences up to ~$10^{19}$ n/cm$^2$, or ~0.01 dpa.

Concerns regarding radiation-induced changes in steel?

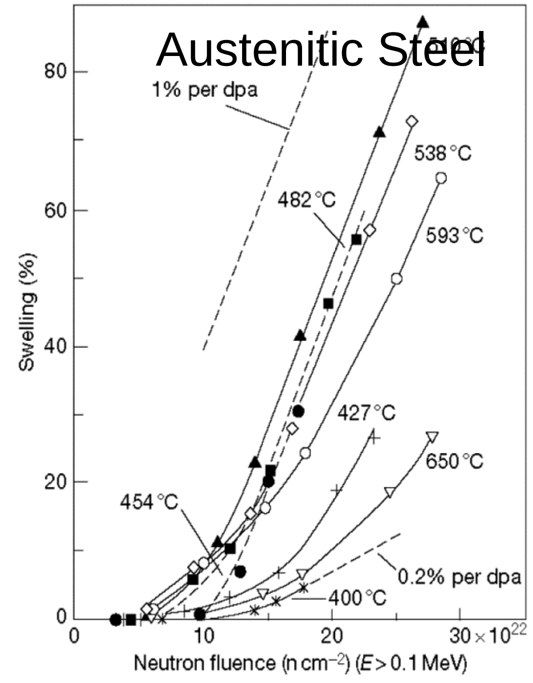
- Swelling?

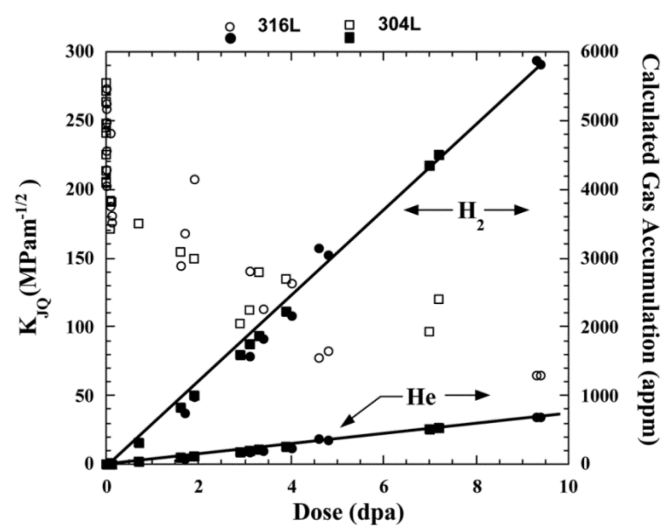
  No. For stainless steel radiation induced swelling would be a concern at much higher doses at temperatures between 400 and 600°C.

- He and H generation in steel?

  No, exposure dose too low.

  He(appm)/dpa ≈ 60 and H(appm)/dpa ≈ 400



# Radiation Effect on Materials

Exposure conditions of interest:

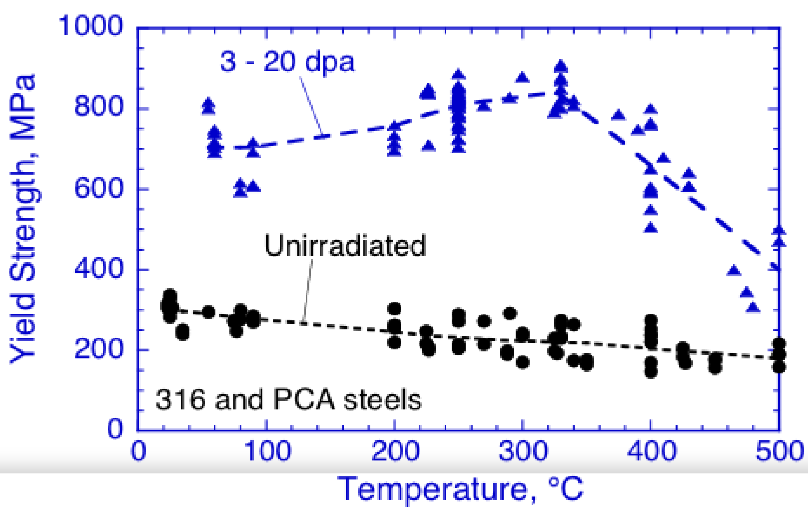
- Stainless steel support and piping are evaluated for fluences up to ~$10^{19}$ n/$cm^2$, or ~0.01 dpa.

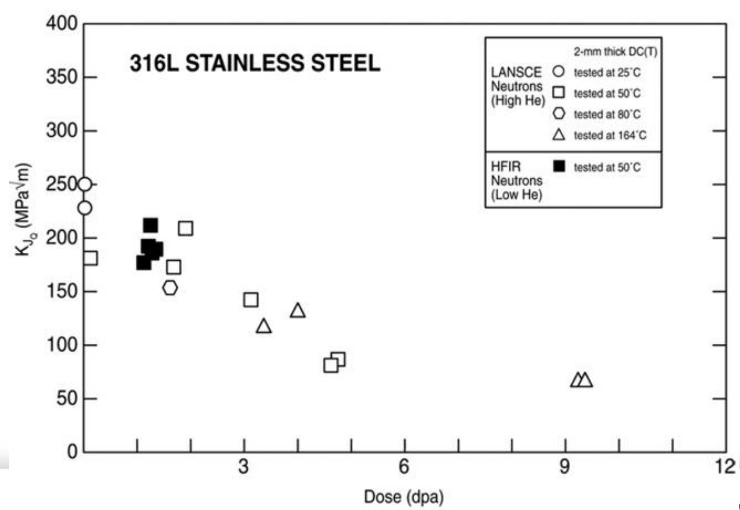
Concerns regarding radiation-induced changes in steel?

- Mechanical property changes?

  Yes. Expect increase in hardening some decrease in ductility - dose is small and should not be a detriment to ductility or fracture toughness.

  The irradiation temperature corresponds to a regime of vacancy motion onset, with limited ability of vacancy clusters formed within the damage cascades to become thermal unstable. Expect a high density of small (<5 nm) defect clusters.



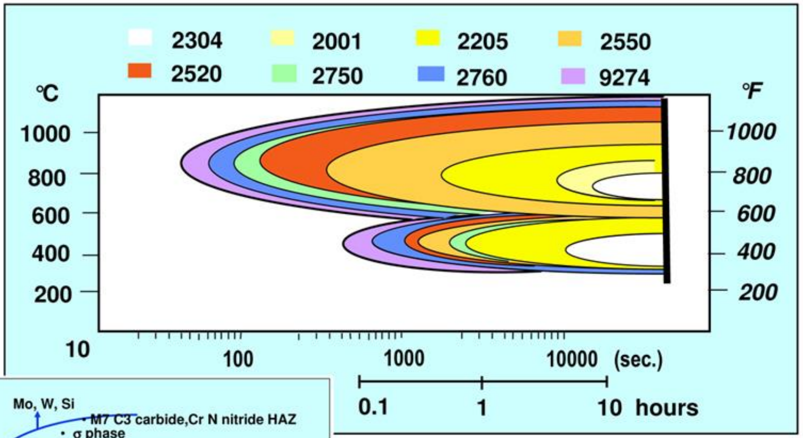
# Radiation Effect on Materials

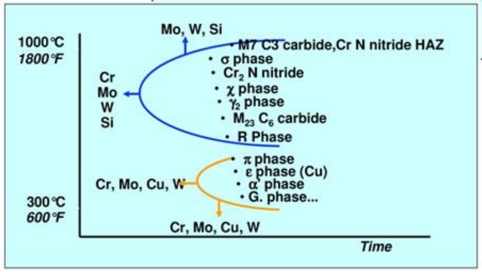
Exposure conditions of interest:

- Stainless steel support and piping are evaluated for fluences up to ~$10^{19}$ n/cm$^2$, or ~0.01 dpa.

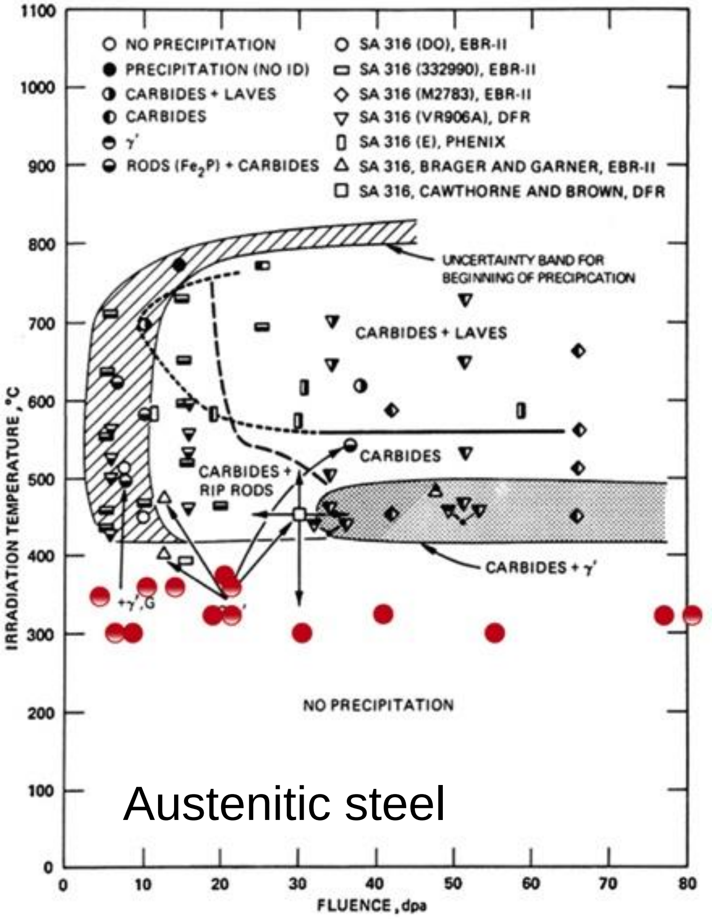
Concerns regarding radiation-induced changes in steel?

- Radiation-induced precipitation/solute segregation.
- Corrosion properties?




Duplex steel




Austenitic steel

# Materials Test Matrix

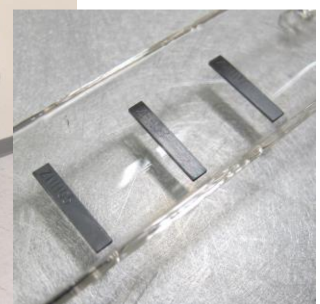
- Zircaloy-4 alpha-annealed and beta-quenched conditions, and Zr-2.5Nb:
    - Forms: base metal, e-beam welded and TIG welded.
    - Hydrogen charged: near 300 wppm and 500 wppm H
    - Neutron irradiated: $10^{20}$ to $10^{21}$ n/cm$^2$ (E>0.1MeV)

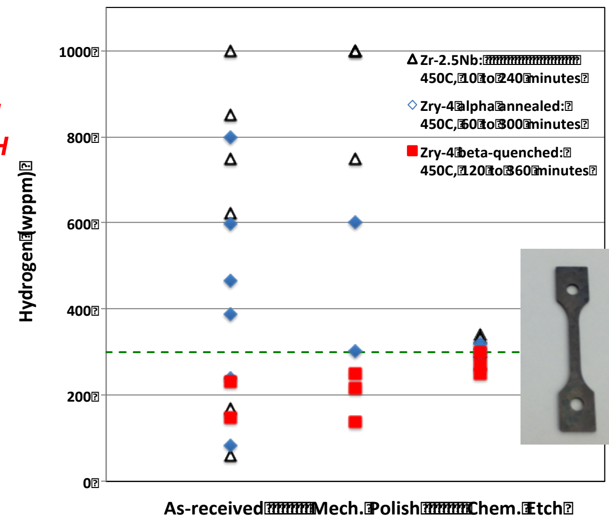
- 316L, 2304 and 17-4PH grade steels:
    - Longitudinal direction and transverse directions (2304 has “composite”-like microstructure)
    - Form: Base metal, e-beam welded, TIG welded (17-4PH only in base metal form)
    - Neutron irradiated: $10^{18}$ to $10^{19}$ n/cm$^2$ (E>0.1MeV)

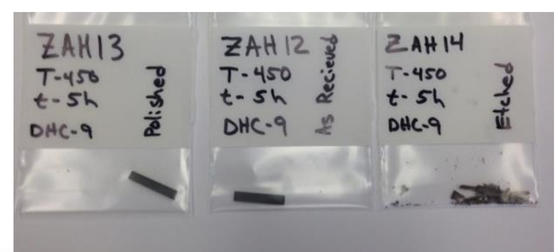
# Hydrogen Charging

- Dynamic hydrogen charging of materials.
- Evaluated for different temperatures, time, gas (Ar-4%H) flow rate, positioning of samples, etc.
- Test samples were rectangular pieces of the same thickness and volume of materials as SS-J3 tensile bars (0.75mm) used in the irradiation capsules.
- Small variations in the surface finish had a big impact in the sample pick-up rate of hydrogen, polishing and etching on sample preparation was required.

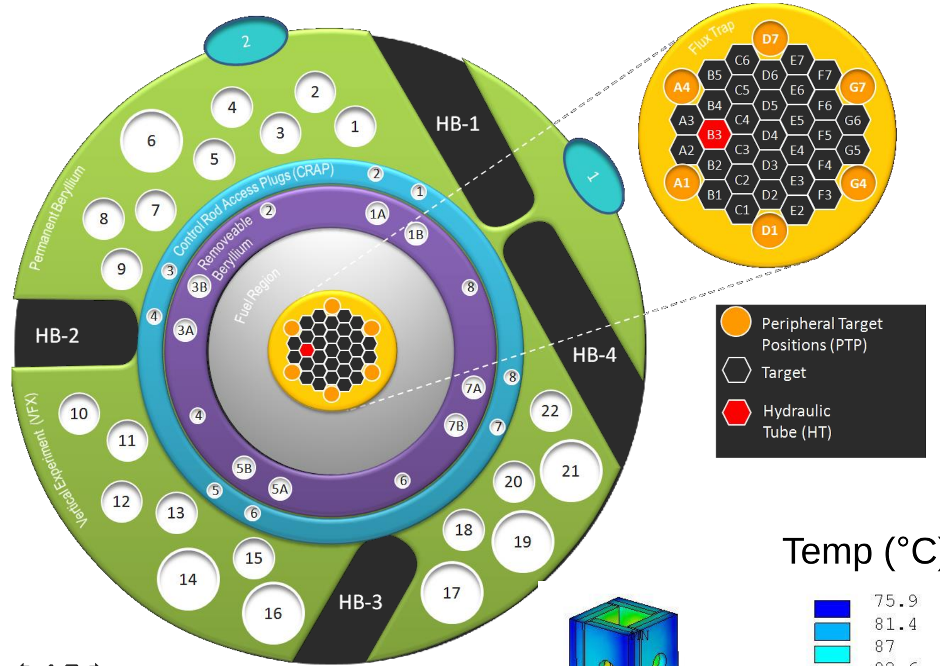

*Etched surface increased susceptibility of alloy to H charging – parameters were reset.*

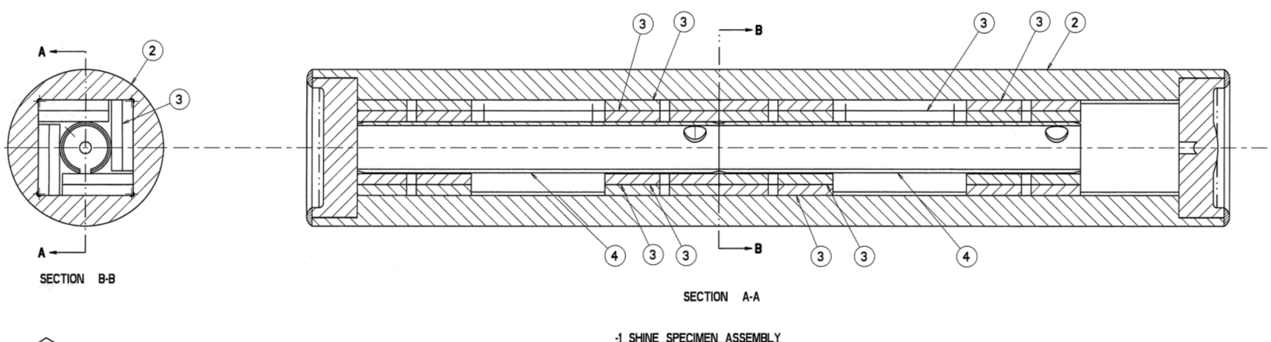


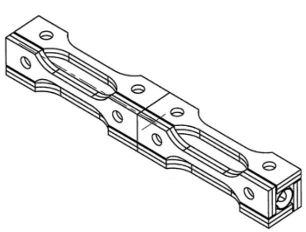


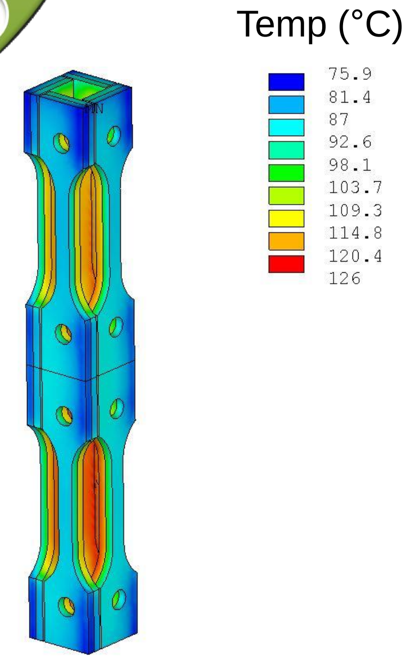



# High Flux Isotope Reactor: In Vessel Irradiations



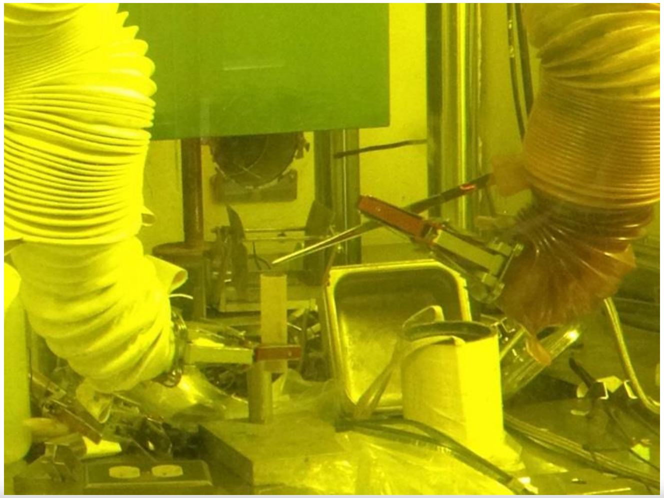





# Facilities for Post-Irradiation Examination (PIE)

***Irradiated Materials Examination and Testing (IMET)***

- Six interconnected steel-lined examination cells containing 30 $m^2$ of workspace.
- Low alpha contamination facility (<70 dpm / 100 $cm^2$).
- Irradiation capsule disassembly
- Mechanical testing
- Other capabilities include density measurement, SEM, general characterization (optical, video documentation).



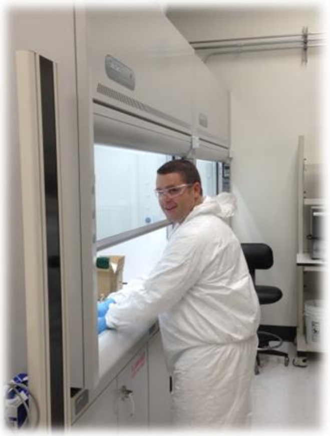
# Facilities for Post-Irradiation Examination (PIE)

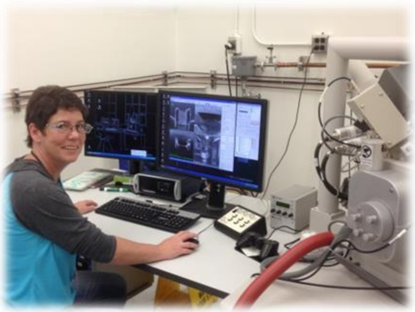
**Low Activation Materials Development and Analysis (LAMDA)**

- Facility designated for the study of radiological materials by advanced characterization methods and instruments.
- Small or subscale size samples.
- Sample limit: < 100 mrem/hr at 30 cm.

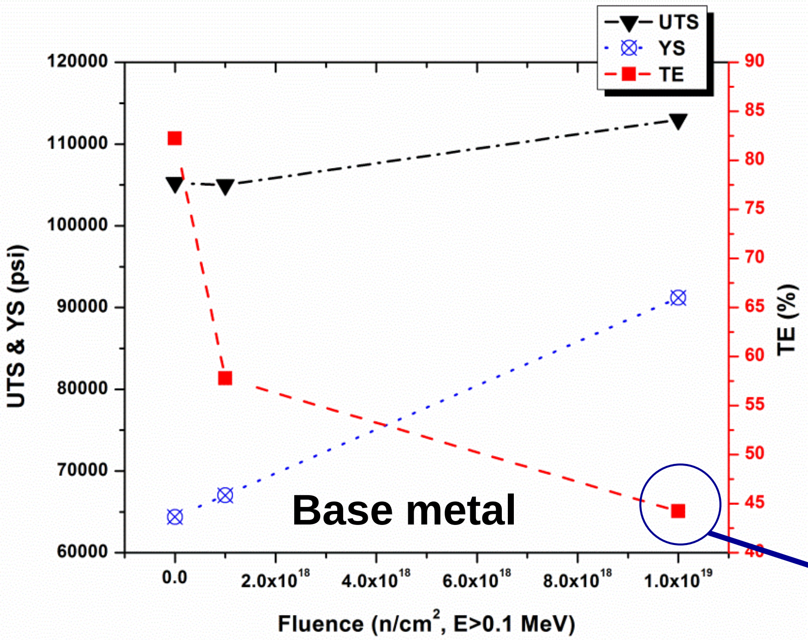
**Microstructural Characterization:**

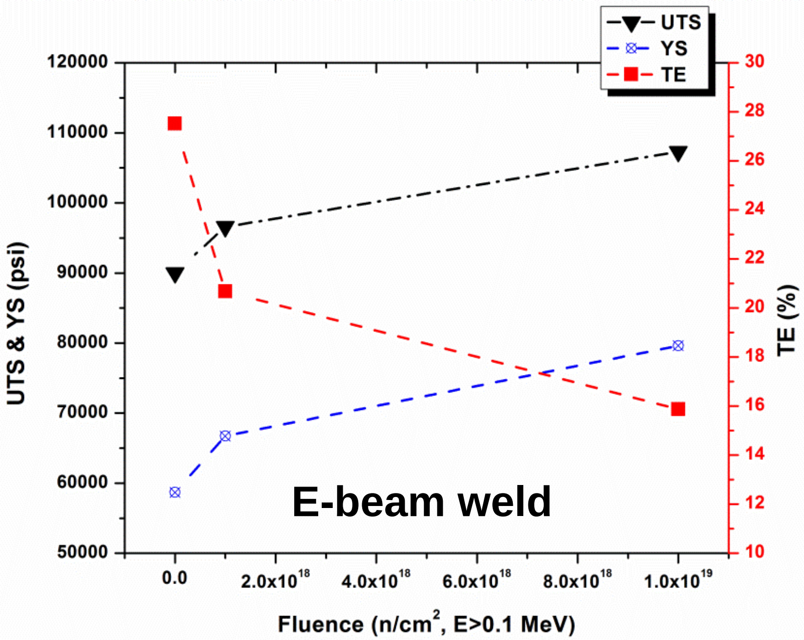
- Deformation behavior of hydrogen charged Zr-base alloys in the irradiated and non-irradiated conditions.
- Defect analysis of low temperature irradiated Zr- and stainless alloys.
- Radiation-induced phase precipitation in duplex 2304 grade steel.





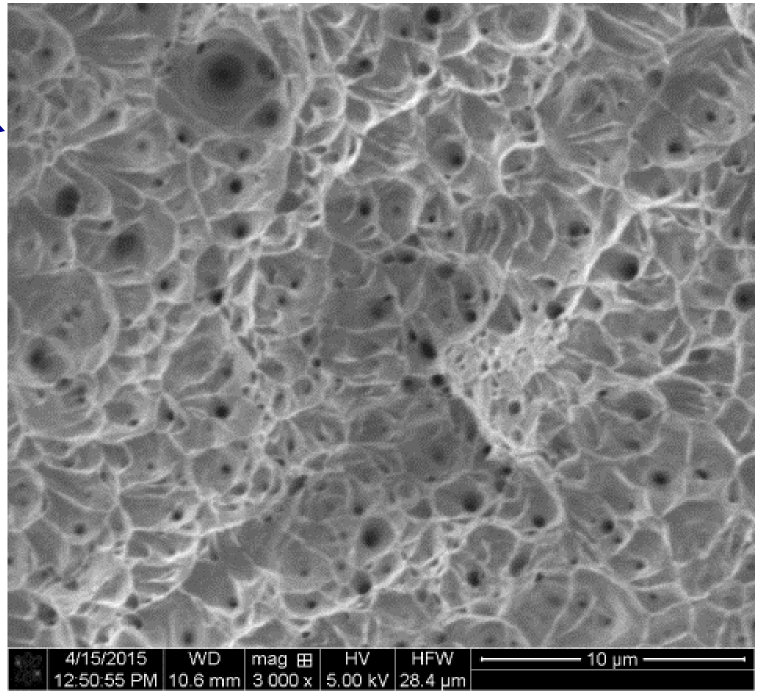

# Test Results: 316L Stainless



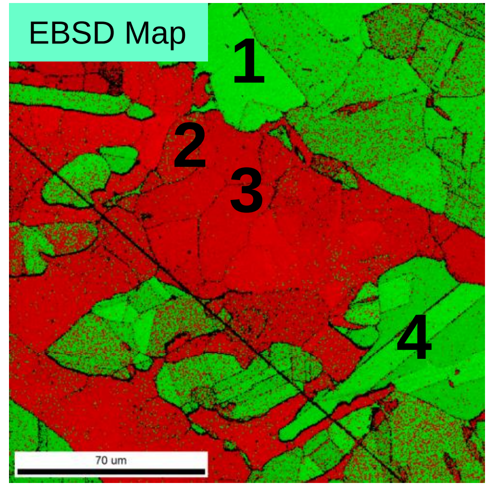

- Test data not unexpected, behavior for life exposure acceptable.
- Drop in elongation following irradiation
- Irradiated TIG-welded sample data forthcoming.

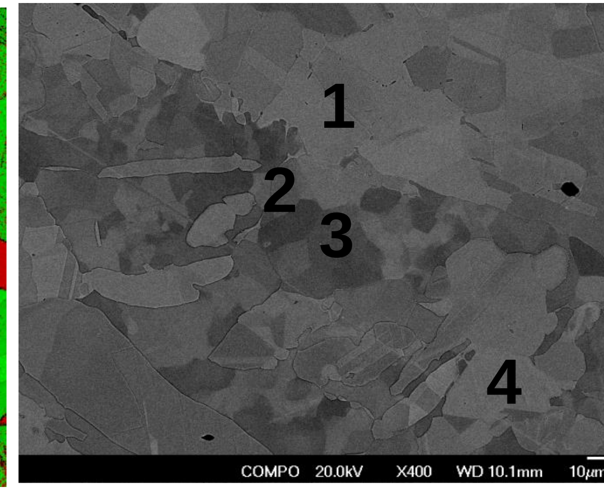
$1.0x10^{19}$ n/cm$^2$ (E>0.1MeV)

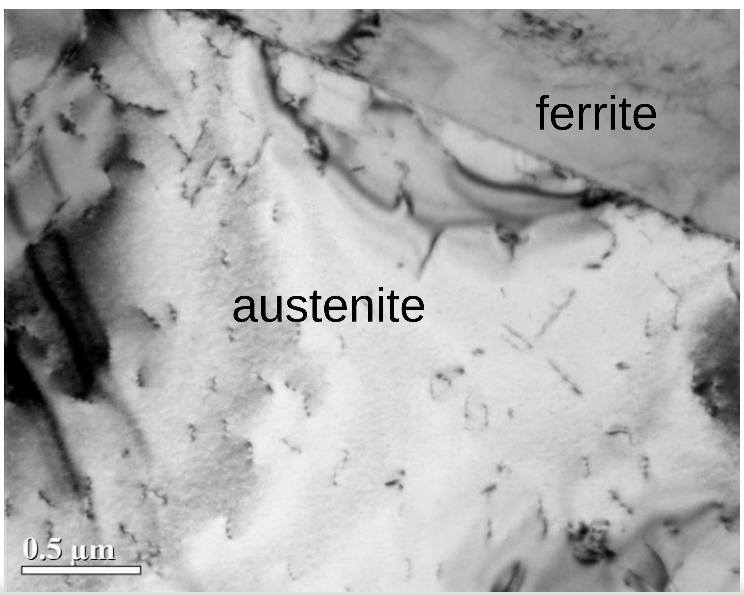


# 2304 Duplex Stainless Steel-Microstructural Characterization

- **Documenting the microstructure of the as-received material to later compare with irradiated samples.**
- Only ferrite and austenite observed in microstructure. No grain boundary phases (G-phase).
- Twinning in austenite, heavy defect structure in ferrite.



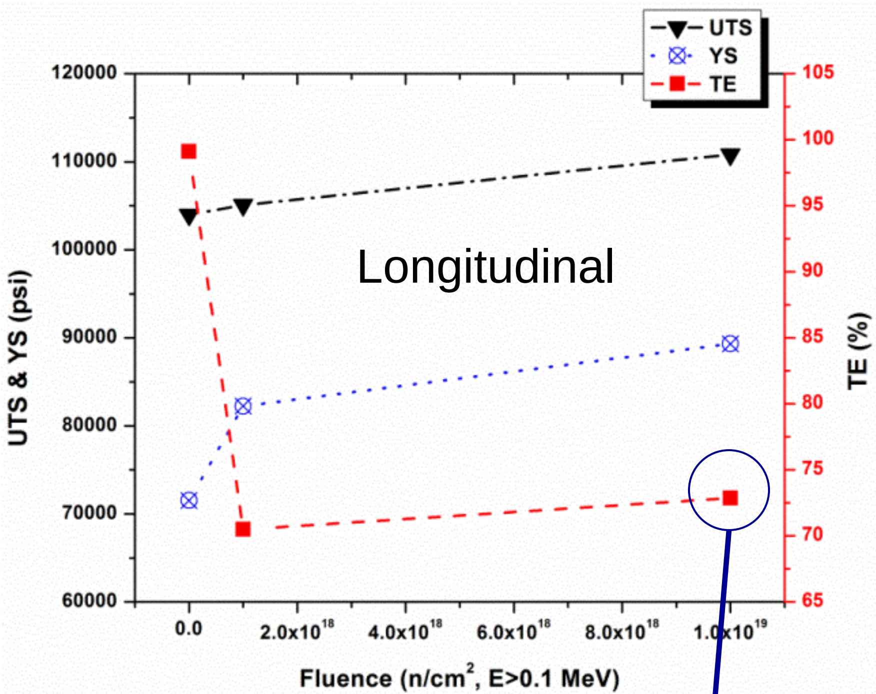



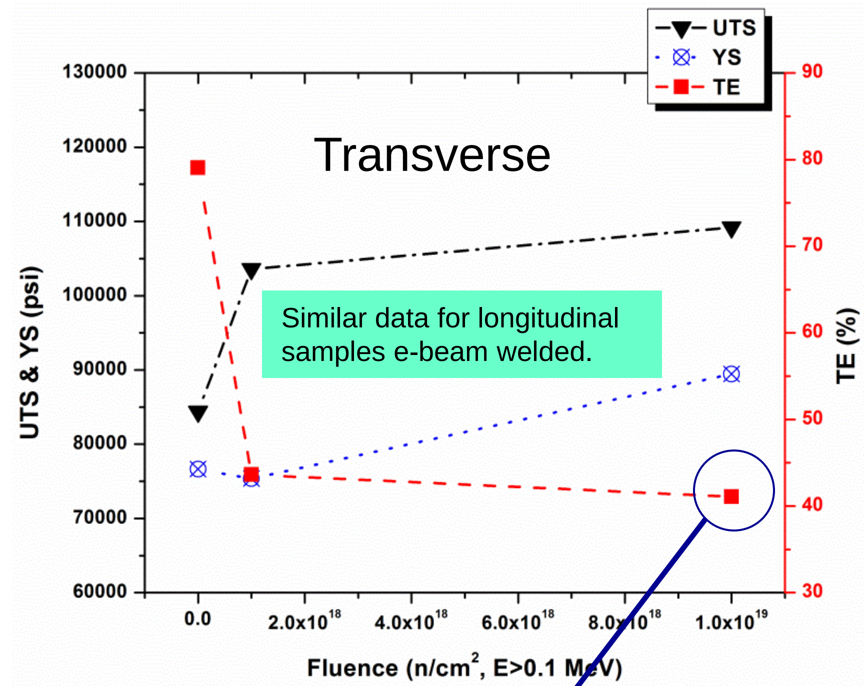

**Red: $\alpha$-ferrite**
**Green: $\gamma$-austenite**

| Spot # | Cr wt% | Fe wt% | Ni wt% |
|---|---|---|---|
| 1 | 21.6 | 73.9 | 4.5 |
| 2 | 25.5 | 71.9 | 2.6 |
| 3 | 25.1 | 72.2 | 2.7 |
| 4 | 21.1 | 74 | 4.9 |

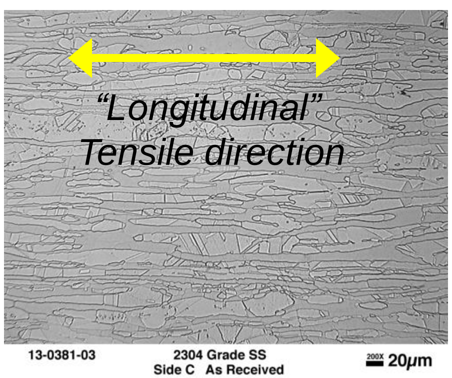
- As expected, austenite higher in Ni and lower in Cr.
- Nominal alloy composition: *Fe-22.4Cr-4.38Ni-1.3Mn-0.025C (wt.%)*
- XRD analysis: 34% ferrite and 66% austenite.

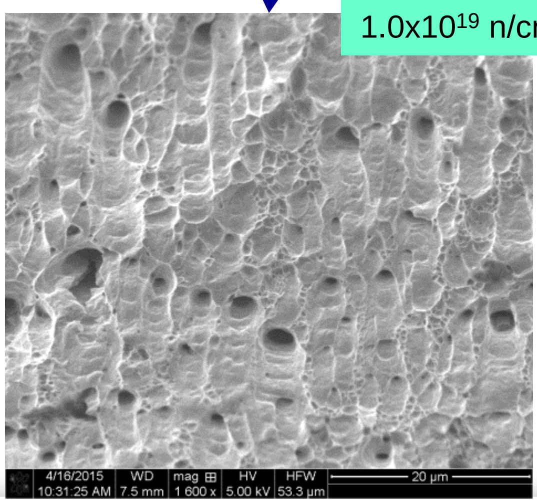
# Test Results: 2304 Duplex Stainless Steel

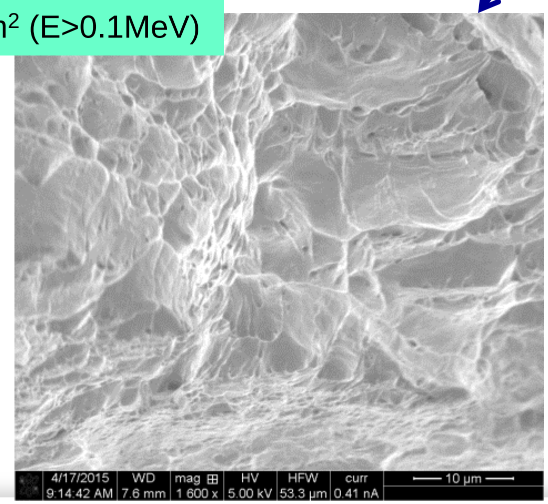


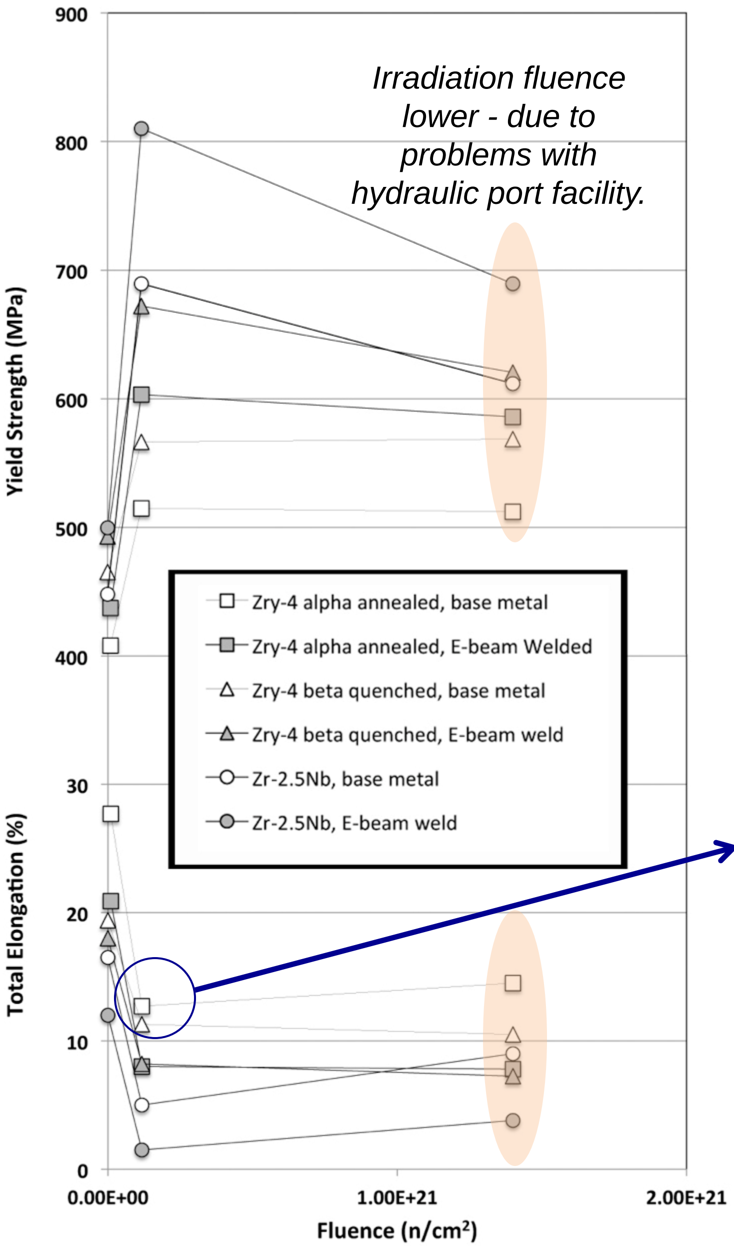

1.0x10$^{19}$ n/cm$^2$ (E>0.1MeV)



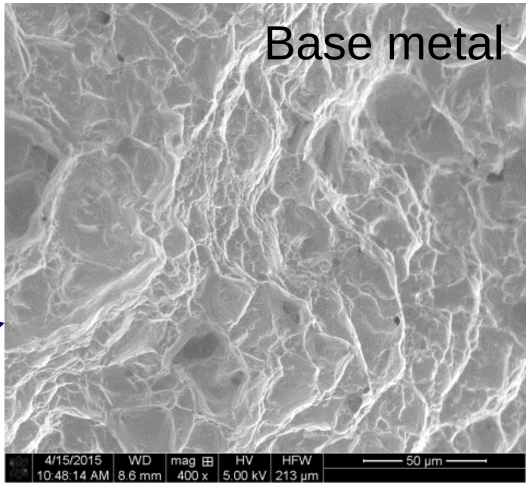



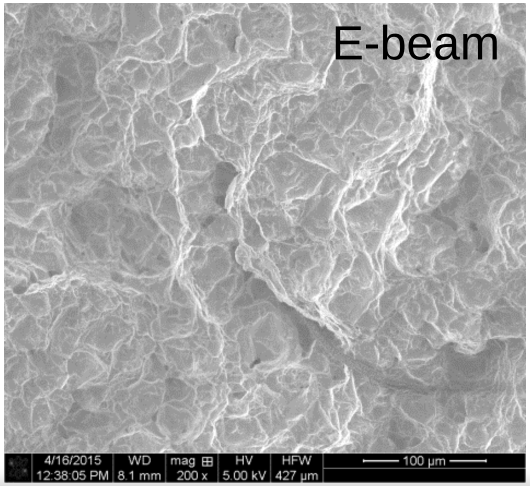
# Comparison of α-Zry-4, β-Zry-4 and Zr-2.5Nb



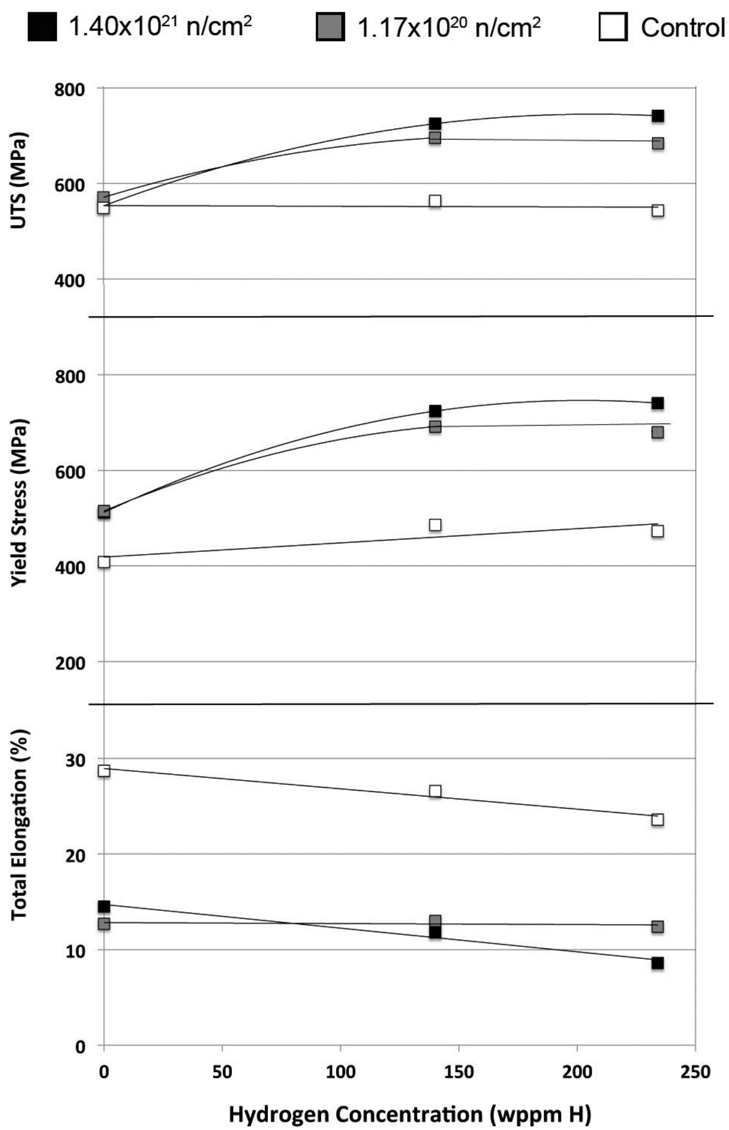

- High fluence data is being repeated (test results to be updated) - HFIR capsule insertion problems.
- Data still being collected to examine sensitivities to hydrogen between the two Zry-4 forms.
- High levels of hardening in Zr-2.5Nb and loss in ductility considerable in weld material.




Alpha-annealed
$1.17 \times 10^{20}$ n/cm$^2$

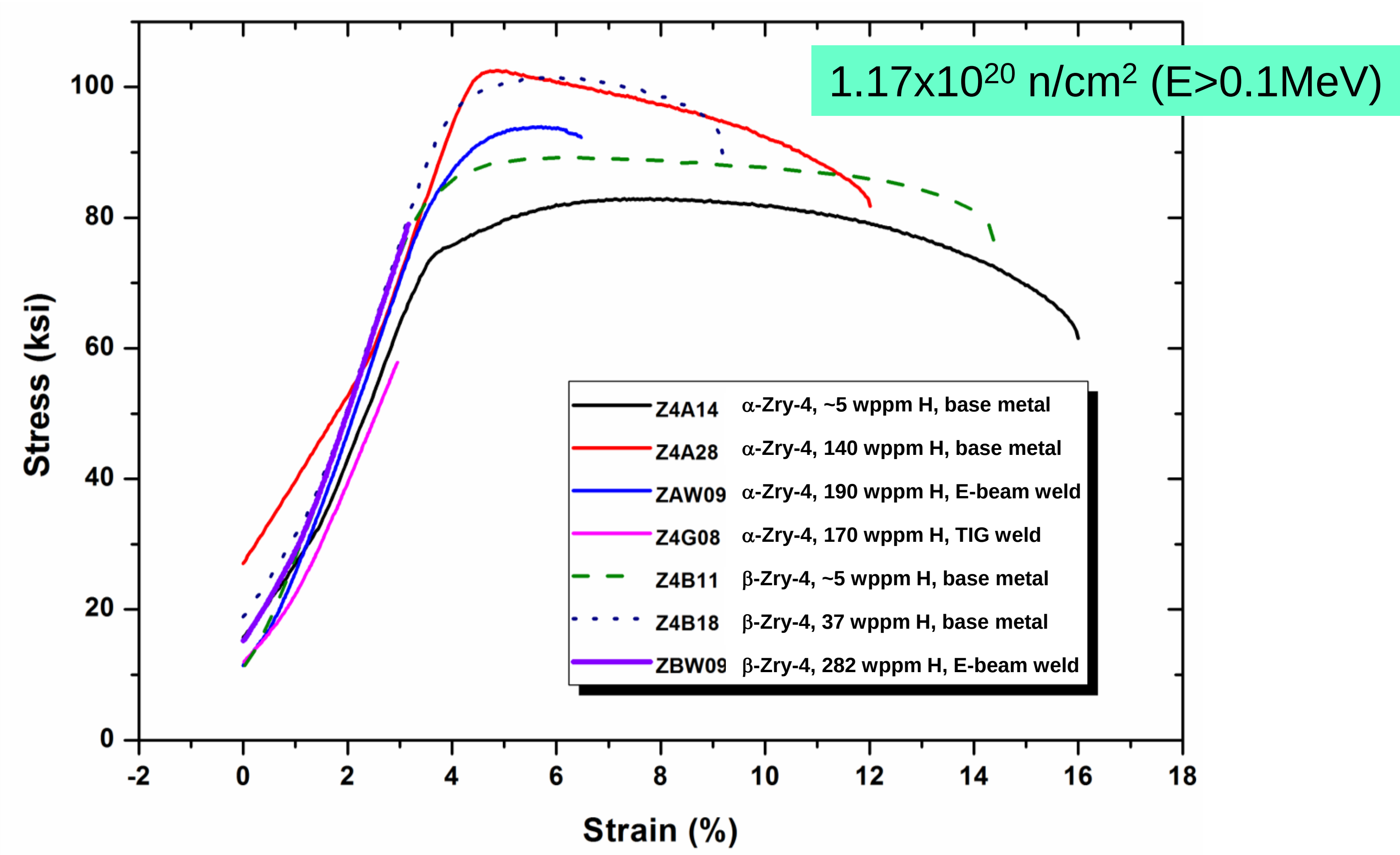


# Test Results: Zircaloy-4 (alpha annealed) Hydrogen Charged



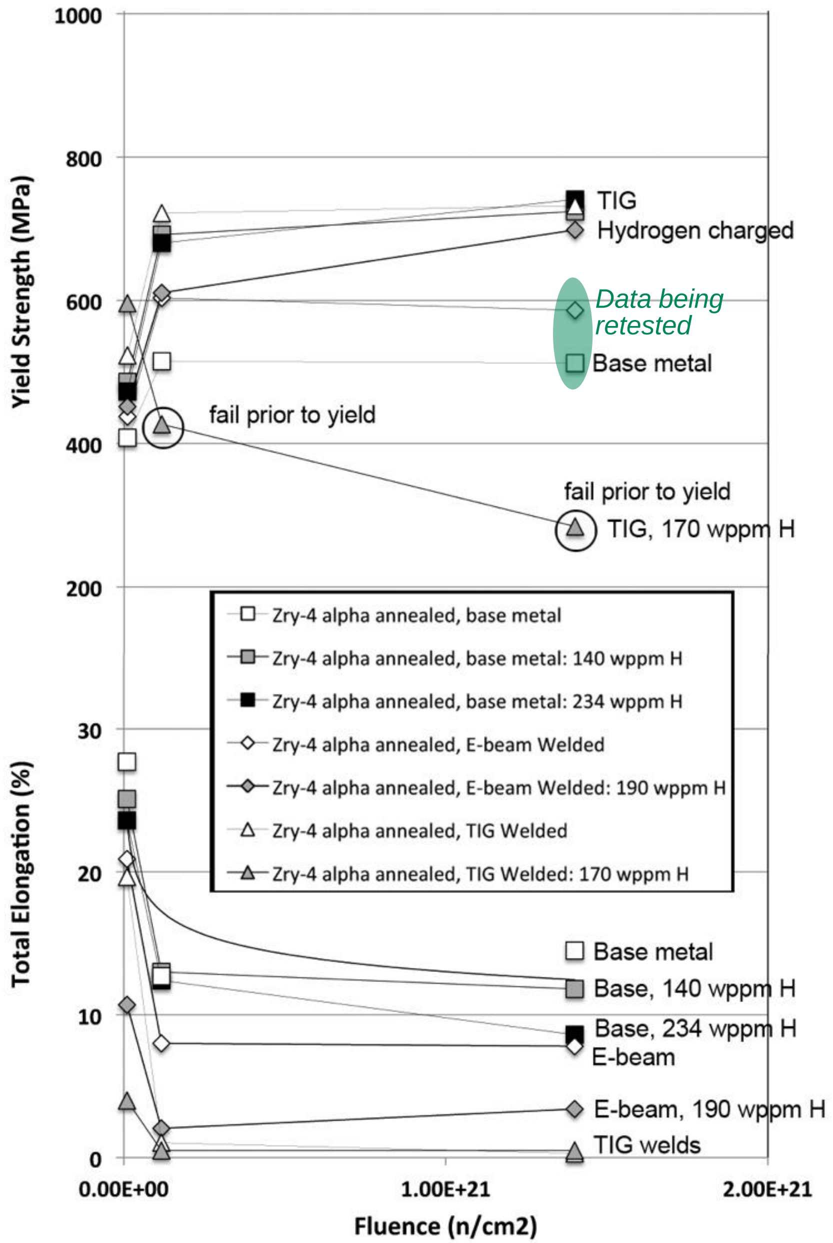

- Level of hydrogen charging lower than that targeted. Concentration determined from the average witness sample concentration. Samples shown from the two charging batches.
- Hydrogen concentration up to 234 wppm H has little influence on mechanical strength on non-irradiated (control) samples.
- Large change in mechanical properties-increased hardness, decreased ductility - when radiation-induced defects and hydrides interact.
- Possible mechanism: dislocation channeling of the deformation dislocation (resulting from the radiation-induced defects) are impeded by the presence of the hydrides - *microstructural analysis is required.*

# Test Results Zircaloy-4: Influence of Hydrogen




- Increased hardening of irradiated material when hydrogen level is increased.
- Failure of material prior to or following yielding of hydrogen charged, welded Zry-4.

# Zircaloy-4 (alpha annealed) Weld and Hydrogen Charged




- Data comparing the "base metal" (non-welded) Zry-4 in the alpha annealed condition to that of the E-beam and TIG welded material as a function of neutron fluence and hydrogen concentration.
- Hydrogen charged base metal shows increase in hardness and decrease in ductility - more severe in welded conditions.
- Hydrogen charged TIG welded material failed prior to yielding.
- Greater sensitivity to hydrogen uptake in the weld area - microstructure similar to $\beta$-quenched material, which had a faster rate of hydrogen absorption.

*Data is preliminary: additional data analysis and collection being performed.*