Zircaloy-4 for Low-Temperature Use with Hydrogen and Neutron Exposure

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Mo-99 Topical Meeting 2018

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

SHINE solution vessel

ORNL supports SHINE with materials research for the target solution vessel and support pipes

Conditions of the Target Solution Vessel:

- Neutron irradiation
- Hydrogen exposure
- Water exposure
- Uranyl sulfate solution corrosion
- Temperature <100°C
- Low pressure

Initially, several materials were surveyed:

- Stainless steels
- Zr2.5Nb
- Zircaloy-4

Solution Vessel

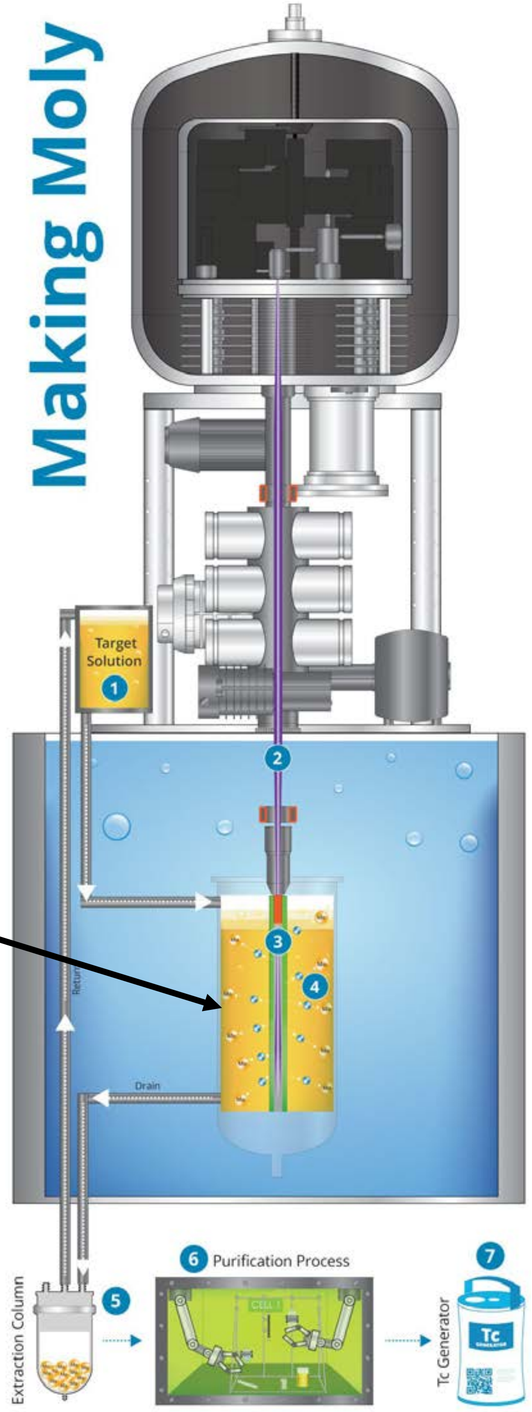


Image courtesy of SHINE http://shinemed.com/demonstrated-technology/

Zircaloy-4 Investigation

- Zircaloy-4 has a long history in the nuclear industry, but typically is used as cladding, ~200-400°C

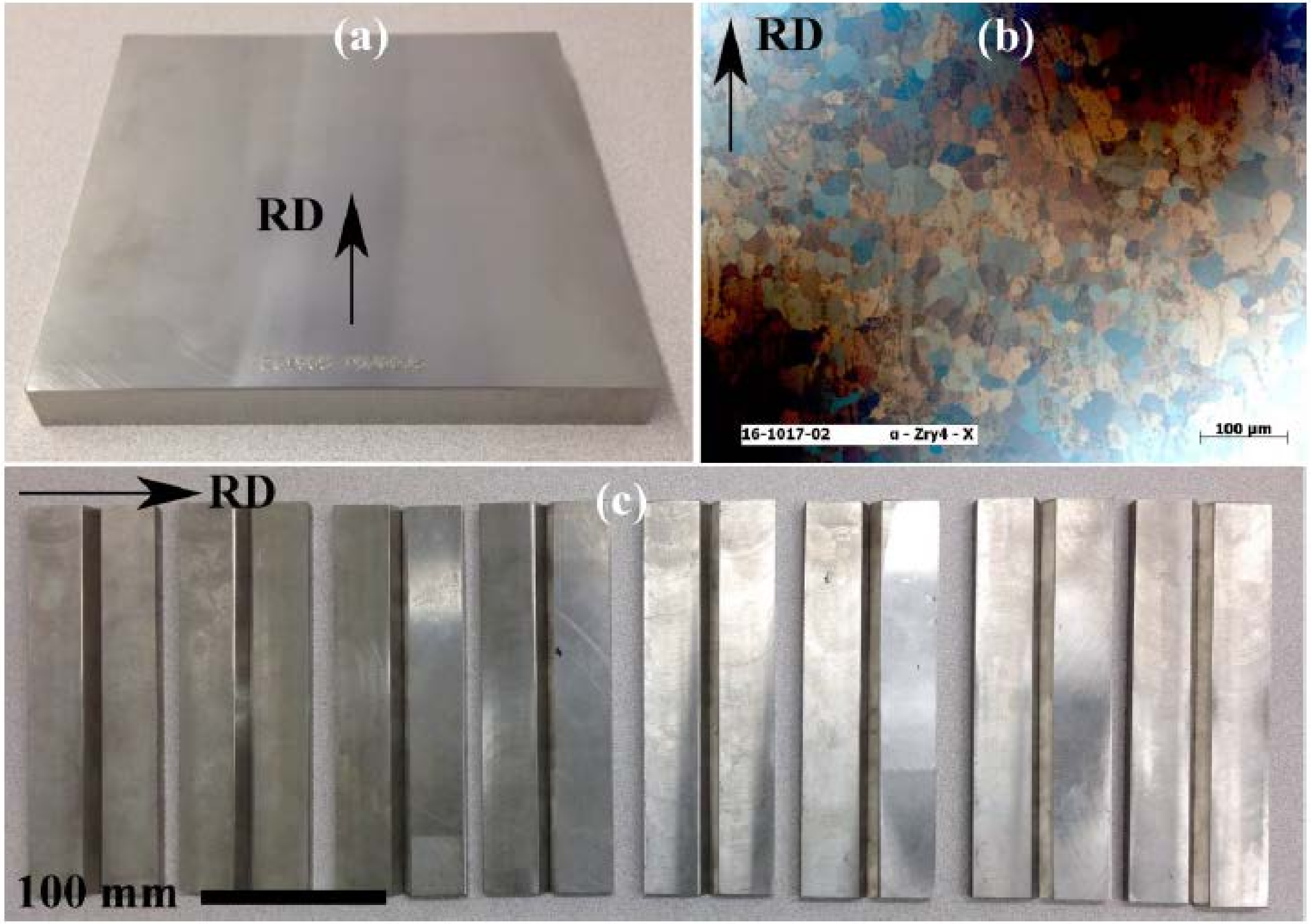
- Considerations for SHINE target solution vessel:
  - Neutron irradiation
  - <100 °C
  - Hydrogen, water, uranium solution
  - Welding

- Additional data is needed to confidently use this material for the unique application and to satisfy the NRC for licensing of the facility

Preparation of Material

Zircaloy-4 material

Machined bars for welding tests



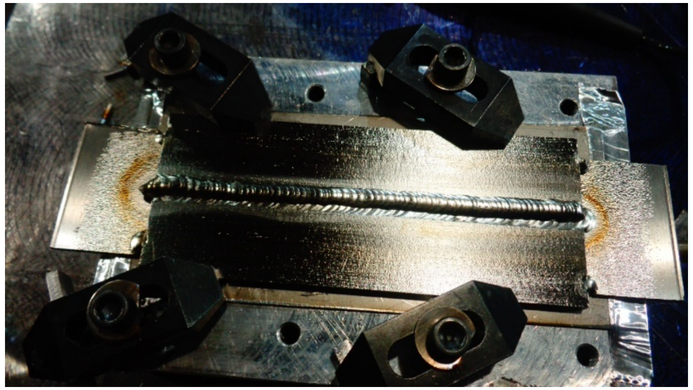
C. M. Silva, C. D. Bryan. “Evaluation of Zircaloy-4 as the structural material for the Target Solution Vessel and support lines of SHINE — Sample preparation for the third-round neutron irradiation” FY17 Report. ORNL/TM-2017/482

Tungsten Inert Gas Welding

- Welding tests performed at Major Tool& Machine Inc.
- ORNL developed a weld quality analysis procedure

Back of root pass

Cover pass 1



Final cover pass

Burn through on the root side

C. M. Silva, C. D. Bryan. “Evaluation of Zircaloy-4 as the structural material for the Target Solution Vessel and support lines of SHINE — Sample preparation for the third-round neutron irradiation” FY17 Report. ORNL/TM-2017/482

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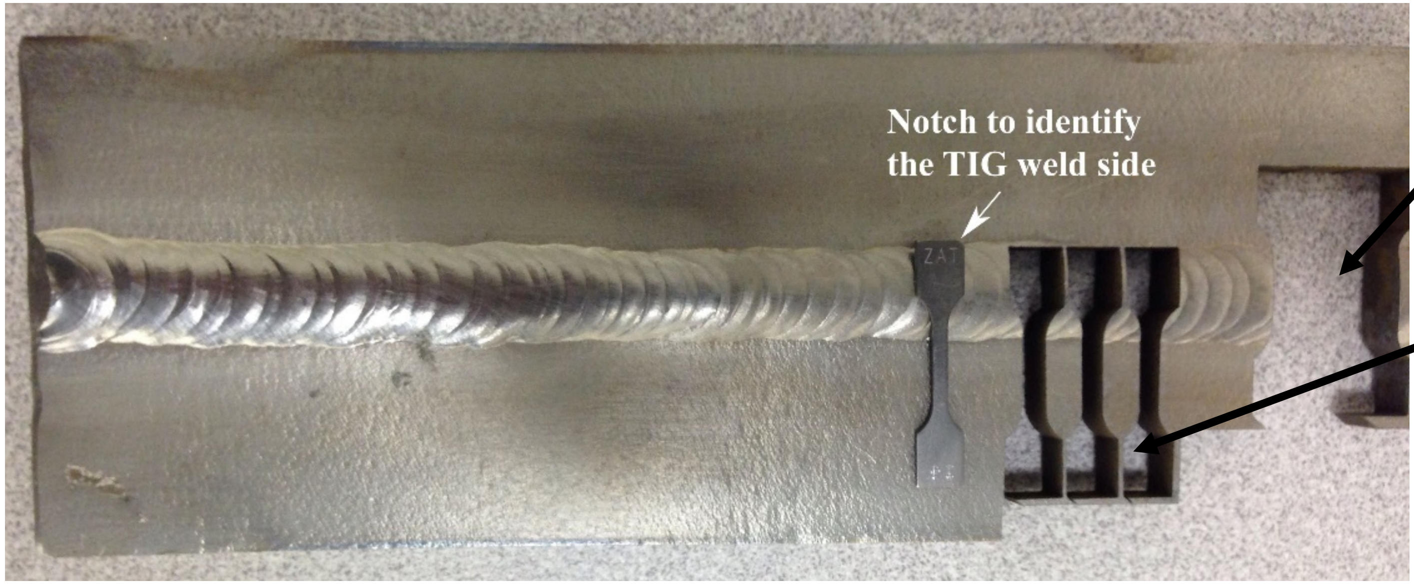
Post-weld heat treatment-Motivation

- **Base metal** total elongation is **~22-29%**
- **After TIG welding,** no post-weld heat treatment, total elongation is **similar to base metal for asymmetric samples (**one tab was in the weld and one tab reached the base metal)
- **After TIG welding**, no post-weld heat treatment, total elongation is **~10-13%** for symmetric weld samples



Symmetric weld sample cut location

Asymmetric weld sample cut location

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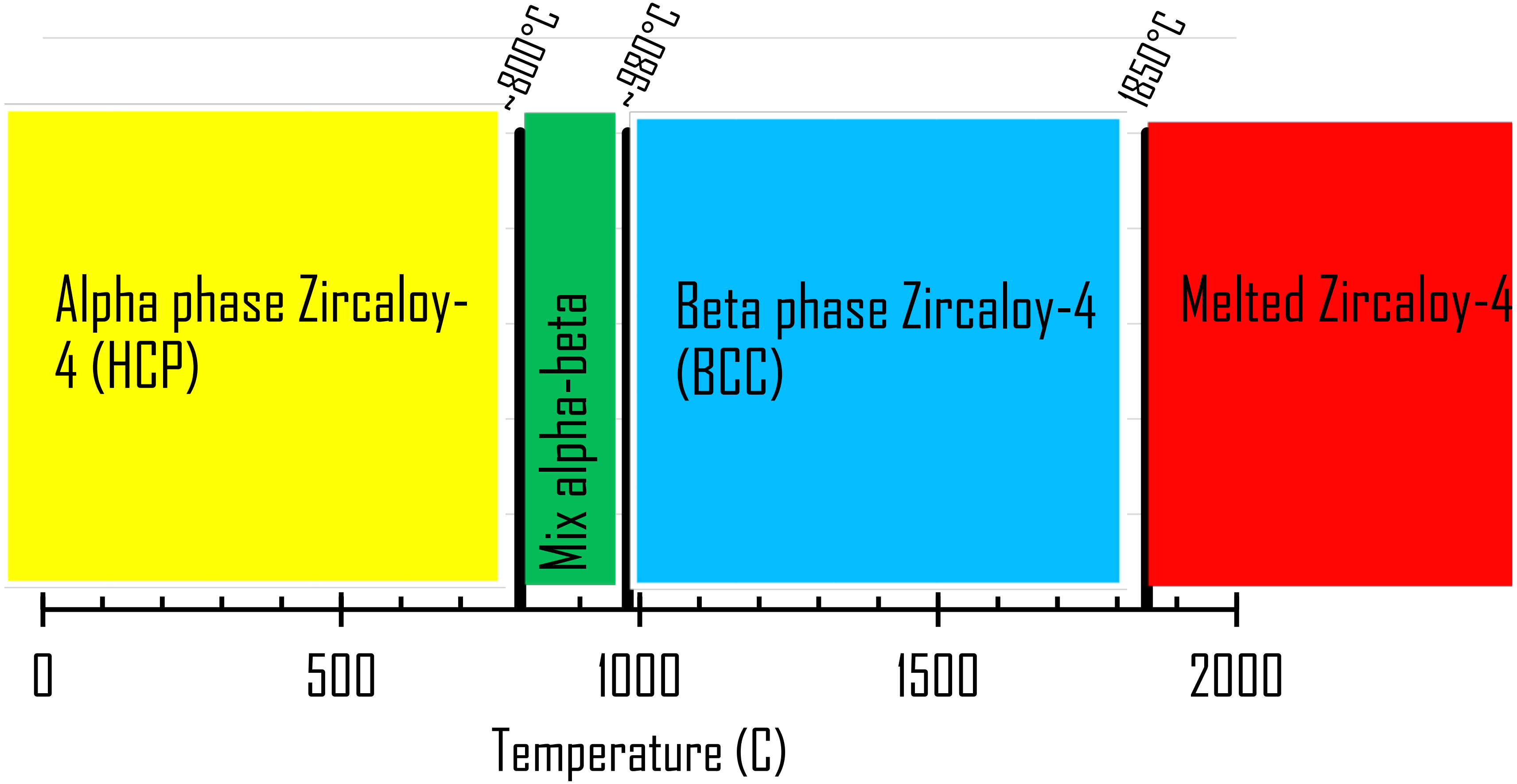
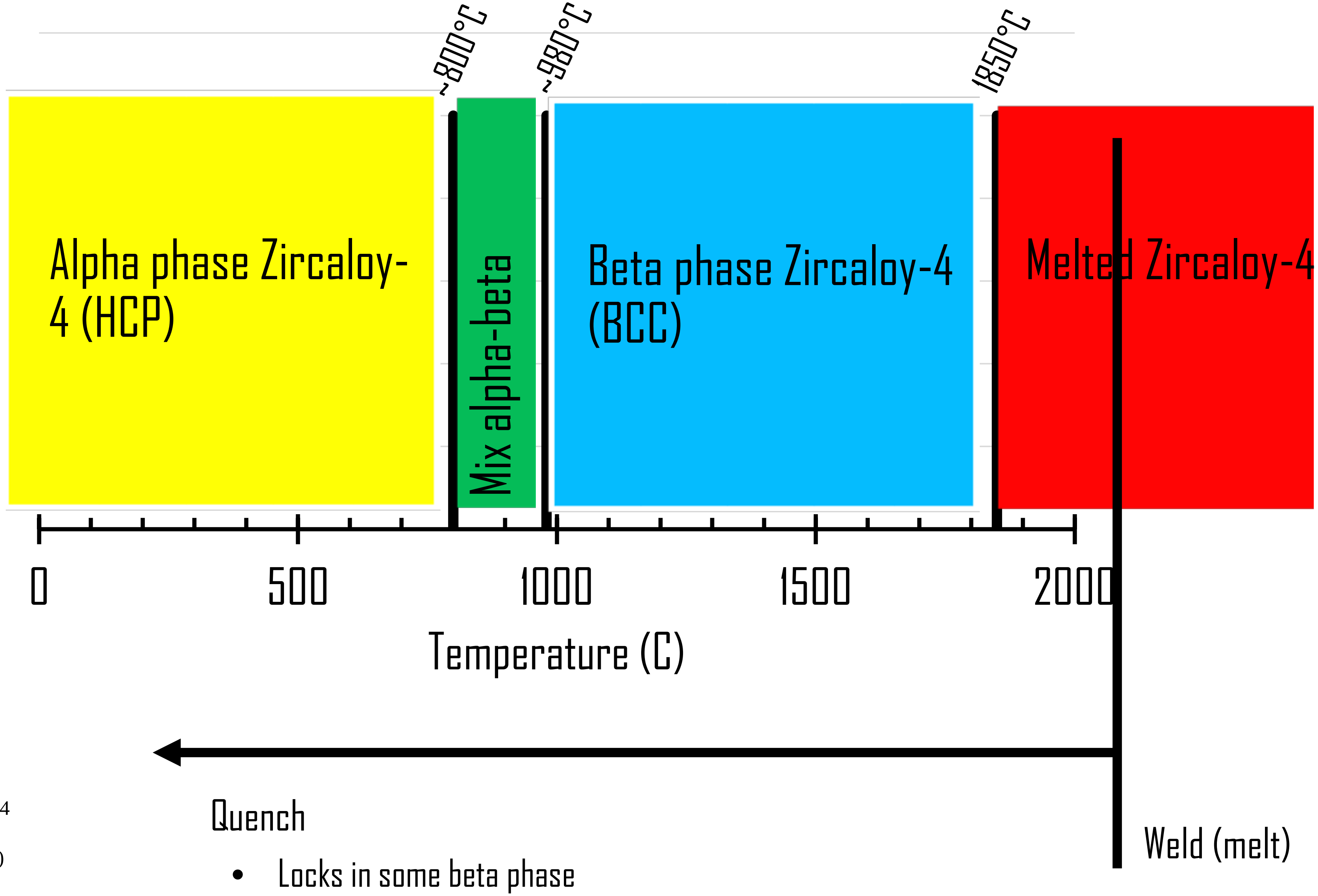
Zircaloy-4 Phases



“Reactor grade zirconium.” Technical Data Sheet. ATI (2015) https://www.atimetals.com/Products/Documents/datasheets/zirconium/alloy/Zr_nuke_waste_disposal_v1.pdf#search=zircaloy-4

Zircaloy-4 Phases

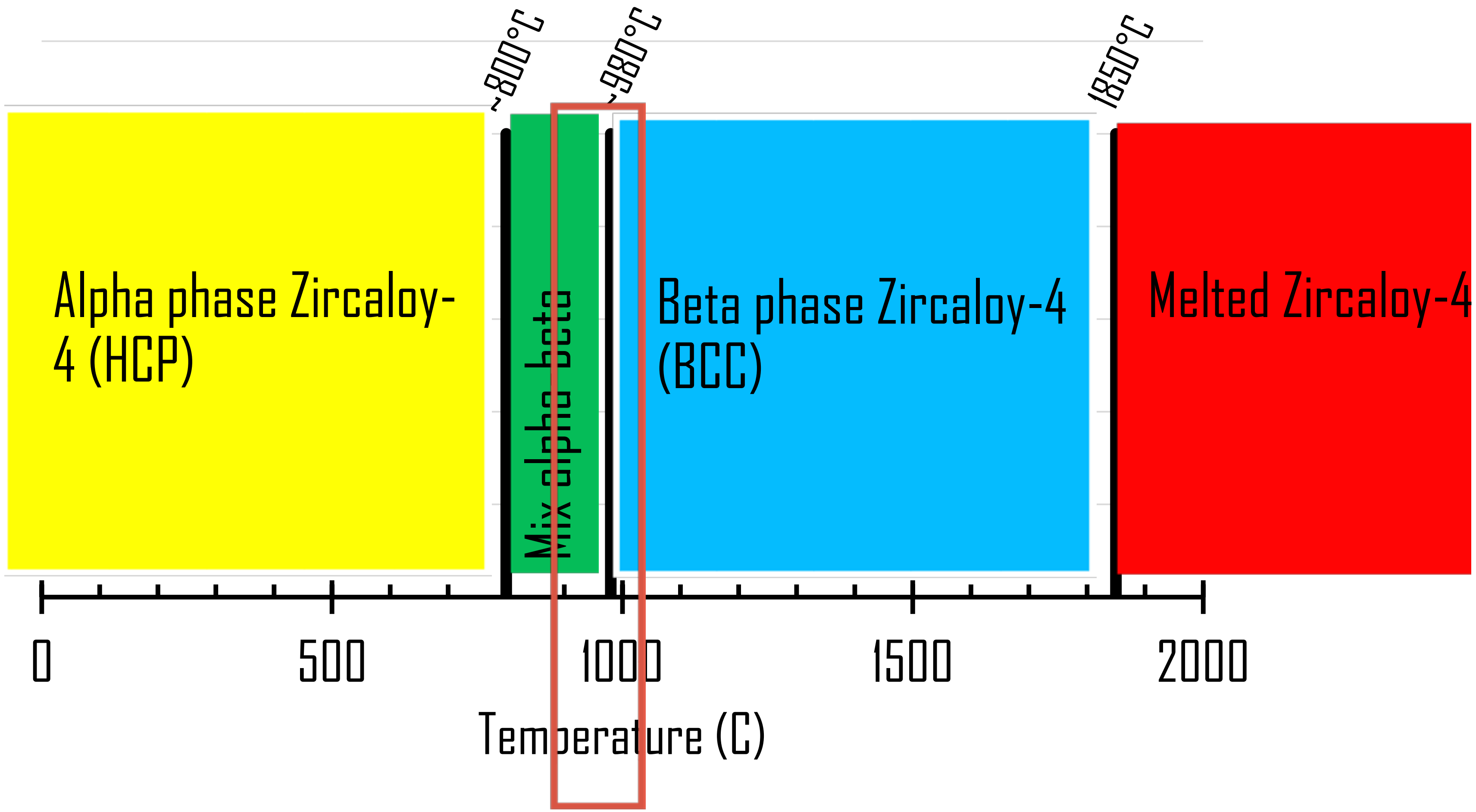
- How weld affects phases and properties
  - Ultimate tensile strength decreases
  - Yield strength increases
  - Total elongation decreases significantly



C.L. Whitmarsh, Review of Zircaloy-2 and Zircaloy-4 properties relevant to N.S. Savannah reactor design, Oak Ridge National Laboratory, ORNL-3281, (1962)

Zircaloy-4 Phases

- Annealing affects corrosion and mechanical properties



899-1010°C annealing

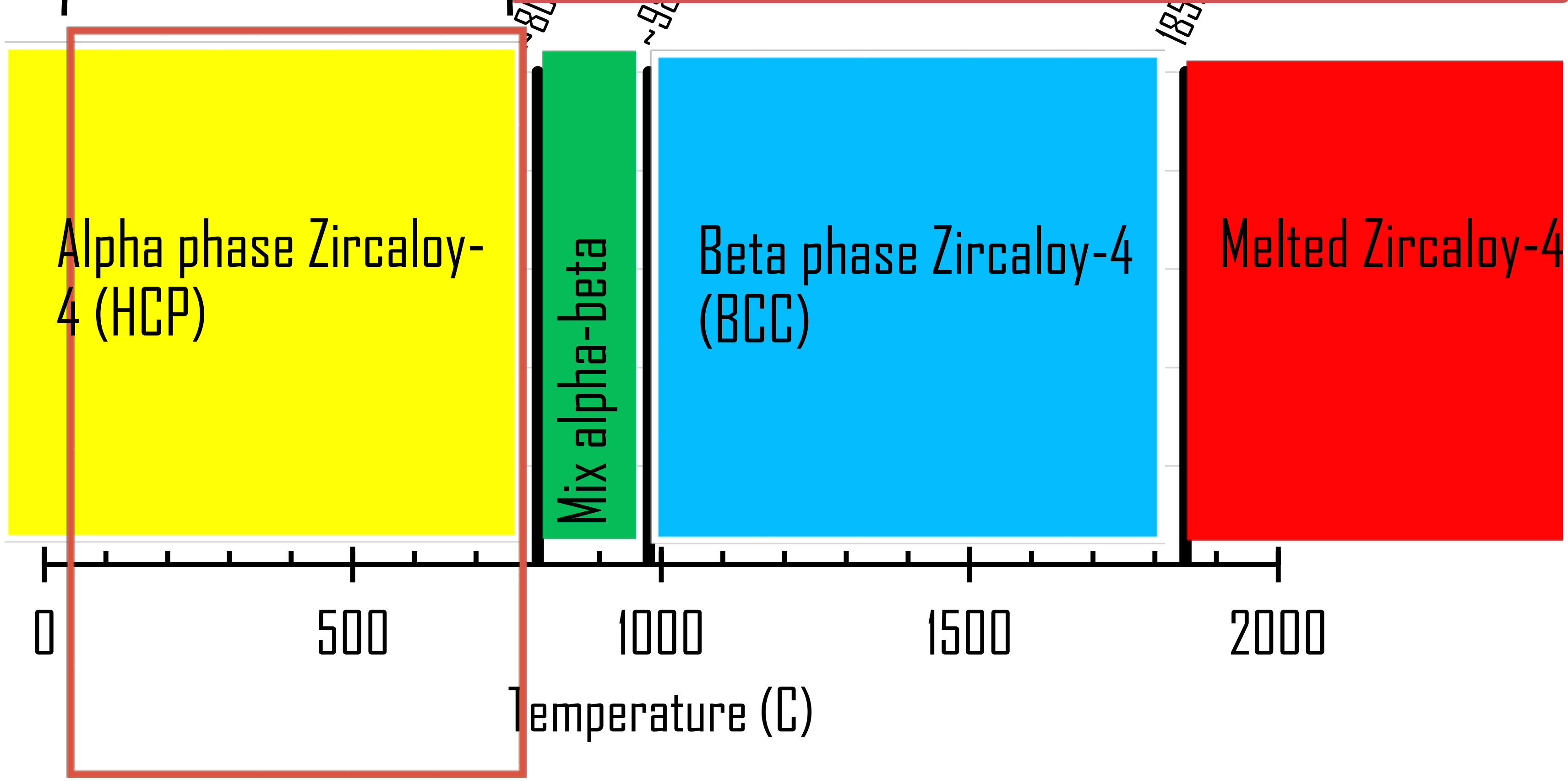
- Forms significant beta phase
- 20-80% increased corrosion in 350°C water or 750°C steam
- Tensile total elongation reduced

C.L. Whitmarsh, Review of Zircaloy-2 and Zircaloy-4 properties relevant to N.S. Savannah reactor design, Oak Ridge National Laboratory, ORNL-3281, (1962)

Zircaloy-4 Phases

What temperature to use for post weld heat treating?

- Annealing affects corrosion and mechanical properties



Annealing below ~800°C

- Stays in alpha phase
- No change to corrosion rate
- Tensile properties can be improved

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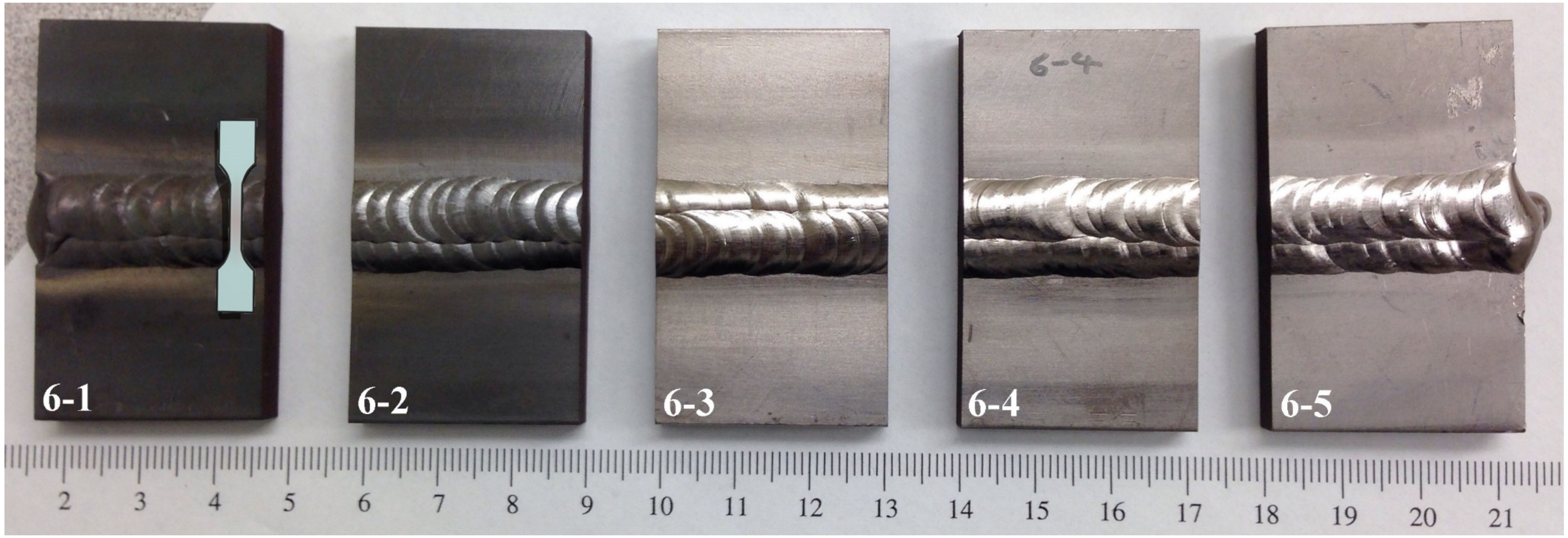
Post Weld Heat Treatment

Heat treatment parameters for Zry-4, weld-6 samples. **Holding time 1h.**

Sample	Target temperature (°C)	Ramping	Cooling
6-1	500	500 °C in 4.5 hours	Furnace cooling
6-2	600	600 °C in 5.0 hours	Furnace cooling
6-3	700	700 °C in 7.0 hours	Furnace cooling
6-4	750	750 °C in 7.0 hours	Furnace cooling
6-5	800	800 °C in 7.0 hours	Furnace cooling



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Post Weld Heat Treatment

Heat treatment parameters for Zry-4, weld-6 samples. **Holding time 1h.**

Sample name	Cut location	PWHT temp. (°C)	Layer from surface	Ultimate tensile strength (MPa)	Yield stress (MPa)	Total elongation* (%)
ZFA01	SW	500	1	571	442	18.5
ZFA02	SW		2	583	468	19.4
ZFA03	SW		3	586	468	19.3
Average	SW			580	459	19
ZFB01	SW	600	1	601	488	17.2
ZFB02	SW		2	597	489	15.9
ZFB03	SW		3	586	476	15.6
Average	SW			595	484	16
ZFC01	SW	700	1	611	504	20.3
ZFC02	SW		2	596	485	17.1
ZFC03	SW		3	589	480	20.6
Average	SW			599	490	19
ZFD01	SW	750	1	568	477	17
ZFD02	SW		2	583	485	16.2
ZFD03	SW		3	583	481	20.9
Average	SW			578	481	18
ZFE01	SW	800	1	578	473	21.5
ZFE02	SW		2	592	482	20.9
ZFE03	SW		3	583	481	19.7
Average	SW			584	479	21

600°C slightly lower elongation

800°C slightly higher elongation

*TE values are overestimated here from raw data

Post Weld Heat Treatment

Heat treatment parameters for Zry-4, weld-7 samples. 800 °C, varied holding times.

Sample	Layer from surface	Ultimate tensile strength (MPa)	Yield stress (MPa)	Total elongation (%)
ZGA01, 800C, 12h	1st of 4	588	487	18.1
ZGA02, 800C, 12h	2nd of 4	582	489	16.6
ZGA03, 800C, 12h	3rd of 4	584	476	17.2
ZGA04, 800C, 12h	4th of 4	572	474	17
Avg.		582	482	17.2
ZGB01, 800C, 24h	1st of 4	581	368	23.6
ZGB02, 800C, 24h	2nd of 4	495	428	9.1
ZGB03, 800C, 24h	3rd of 4	553	485	12.9
ZGB04, 800C, 24h	4th of 4	466	425	8.7
Avg.		524	427	13.6
ZGC01, 800C, 48h	1st of 4	351	346	17.8
ZGC02 800C, 48h	2nd of 4	366	358	10.9
ZGC03, 800C, 48h	3rd of 4	352	350	13.7
ZGC04, 800C, 48h	4th of 4	495	434	13.4
Avg.		391	372	14.0

consistent

erratic

erratic

Large elongation

Smaller elongation than no post weld heat treatment

*TE values are overestimated here from raw data

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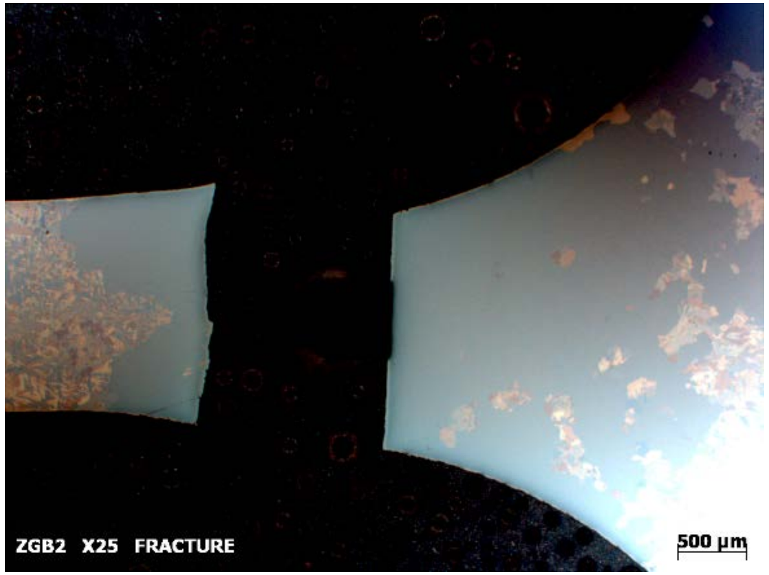
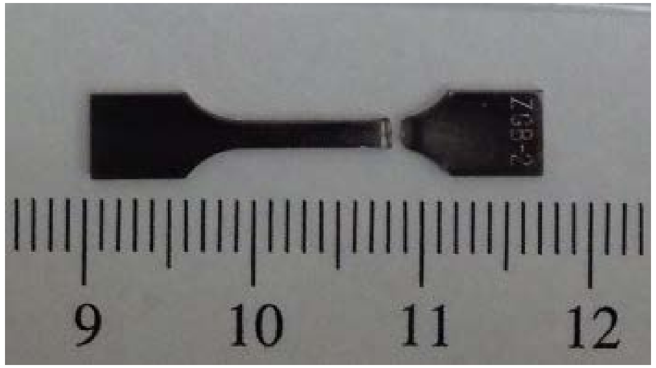
Large grain growth likely caused spread in tensile data for long hold 800C treatments

- **ZGB2, 9.1 % elongation**

Typical grain structure





Large grain boundary-free area corresponded to fracture location

- Long holds at 800°C cause large grain growth and scatter in tensile elongation
- Similar recoveries were measured for test temperatures below 800°C
- Future post weld heat treatments will be below 800°C

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Hydrogen in Zircaloy-4

- The most significant source of H in reactors is from water corrosion

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$$

- Radiolysis of water can also be a source

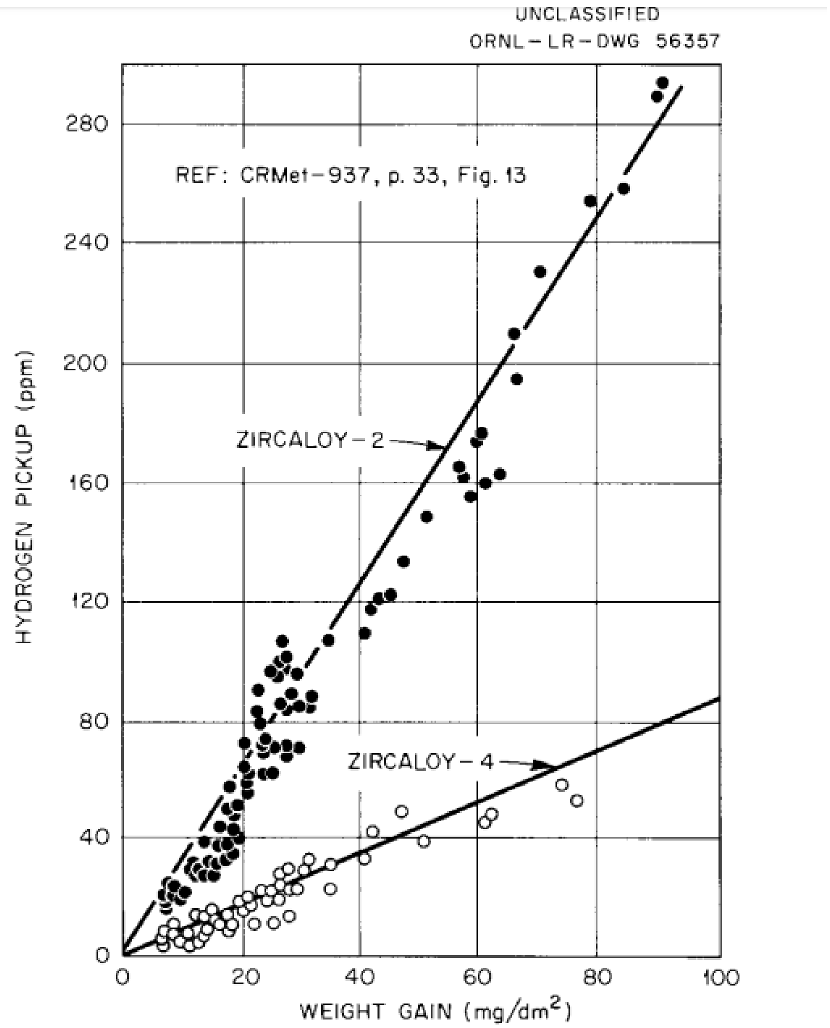
C.L. Whitmarsh, Review of Zircaloy-2 and Zircaloy-4 properties relevant to N.S. Savannah reactor design, Oak Ridge National Laboratory, ORNL-3281, (1962)

Zircaloy-4 has less H absorption than Zircaloy-2

- Zircaloy-2 (Grade R60802)
  - Zr
  - 1.5%Sn
  - 0.15%Fe
  - 0.1%Cr
  - 0.05%Ni

Responsible for significant H absorption

- Zircaloy-4
  - Zr
  - 1.5%Sn
  - 0.2%Fe
  - 0.1%Cr



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"Reactor grade zirconium." Technical Data Sheet. ATI (2015) https://www.atimetals.com/Products/Documents/datasheets/zirconium/alloy/Zr_nuke_waste_disposal_v1.pdf#search=zircaloy-4

Hydrogen effect on mechanical properties

- Hydrogen absorption in Zircaloy is expected to reduce the ductility
- Historical data for Zircaloy-2 shows severe effect above ~100 ppm H
- This must be tested for Zircaloy-4 under low temperature neutron irradiation

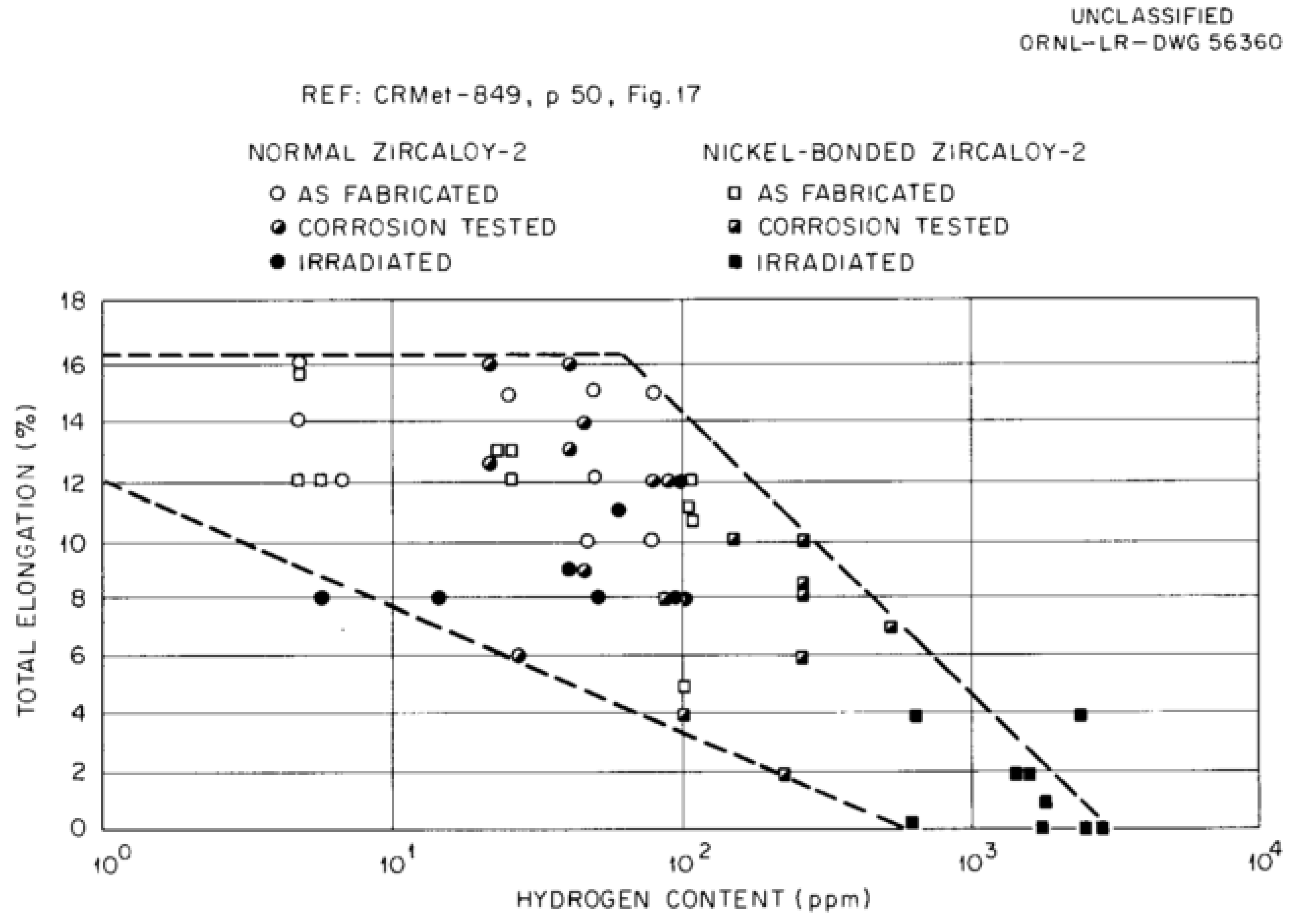

Fig. 10. Effect of Hydrogen on Elongation of Zircaloy-2.

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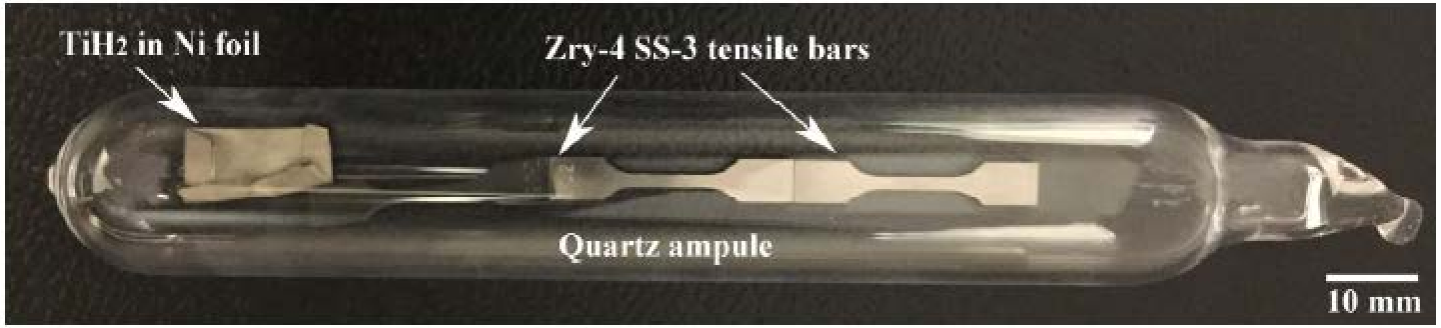
Hydrogen Charging



$$TiH_2\,(s) \rightarrow Ti\,(s) + H_2\,(g) \qquad [1]$$

$$(1\text{-}x/2)\,H_2\,(g) + Zr \rightarrow ZrH_{2\text{-}x}\,(s) \qquad [2]$$

- Controlled hydrogen charging is accomplished with heating TiH_2 powder in a sealed vacuum tube with Zircaloy-4 samples present
- Samples with different ppm amounts are being produced now for inclusion in the neutron irradiation capsules

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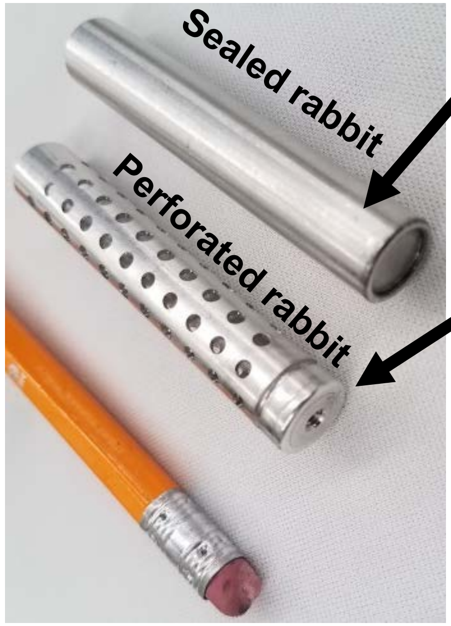
Neutron Irradiation of Zircaloy-4

- Samples are being prepared for neutron irradiation in HFIR at temperatures of 60 and 100°C and fluences of 1×10^{20} and 1×10^{21} n/cm^2 (E>0.1 MeV)

Testing plan for irradiated samples

- Tensile tests at room temperature
- Microhardness
- Microstructure

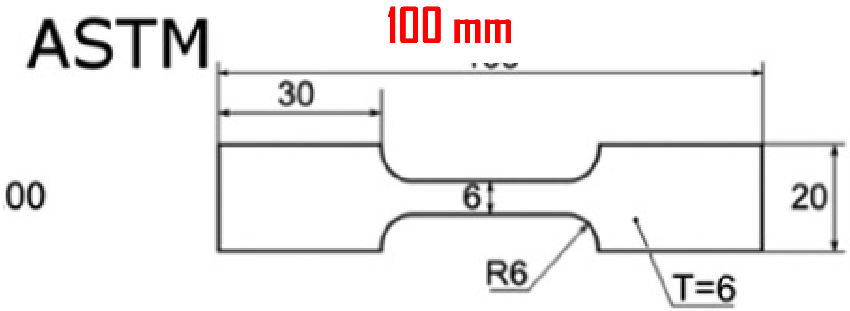


This style used to achieve ~100°C irradiation for this project

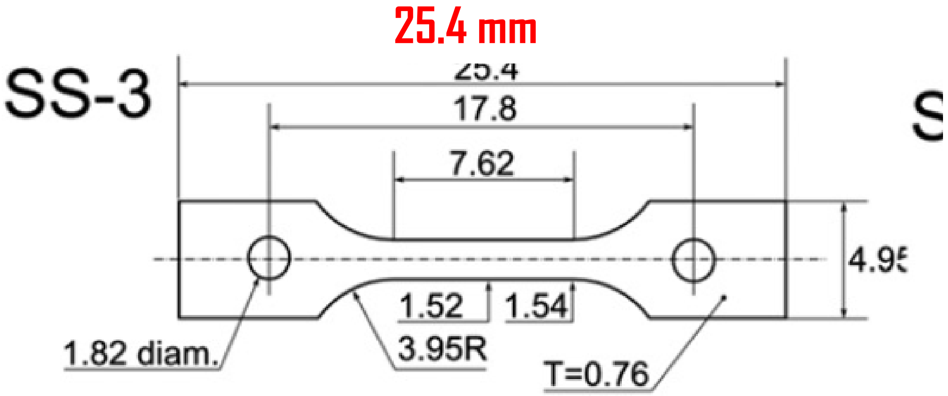
This style used to achieve ~60°C irradiation for this project

Rabbits inside target rod holder

Sub-size specimens for in-reactor irradiation

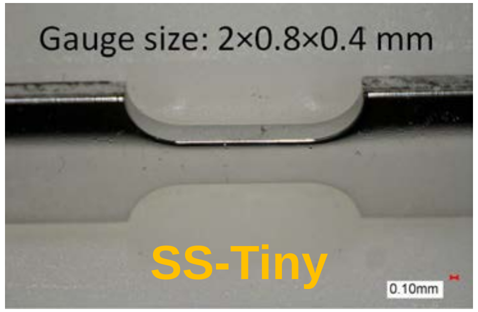


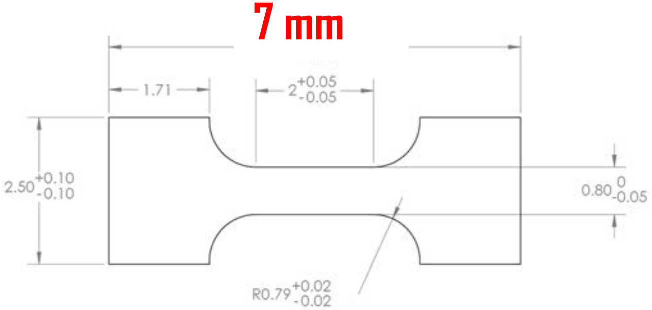
- Cannot fit in HFIR irradiation capsules
- Would have very high activity level after irradiation
- Cannot be used.



- Size and dose are significantly reduced with SS-3 samples
- End tabs used for microhardness measurements and microstructure characterization.

M.N. Gussev et al. / Nuclear Engineering and Design 320 (2017) 298–308



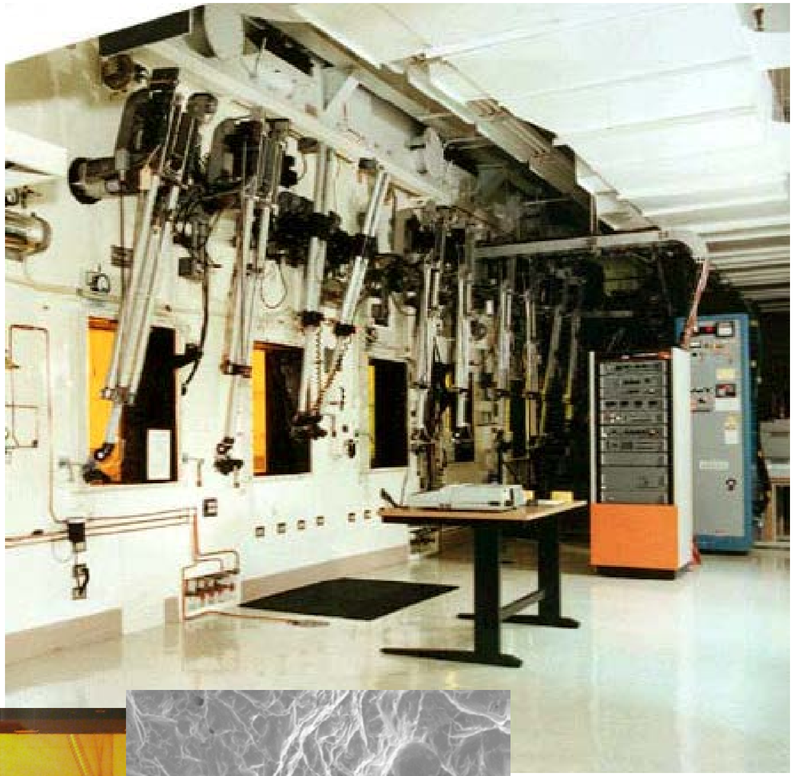


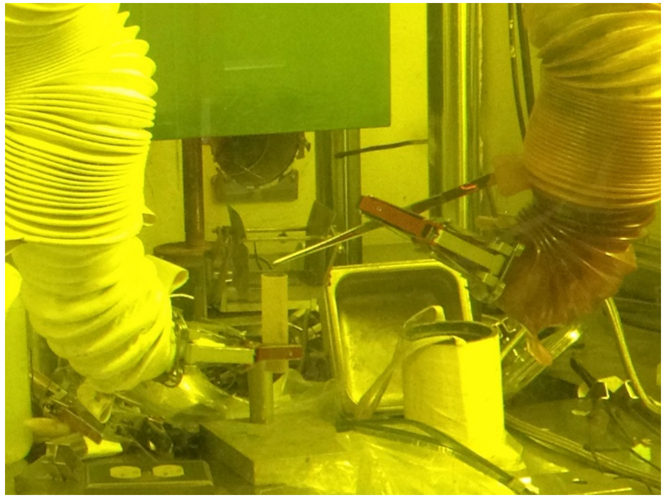
For certain applications, even smaller tensile samples can be used for neutron irradiated tests.

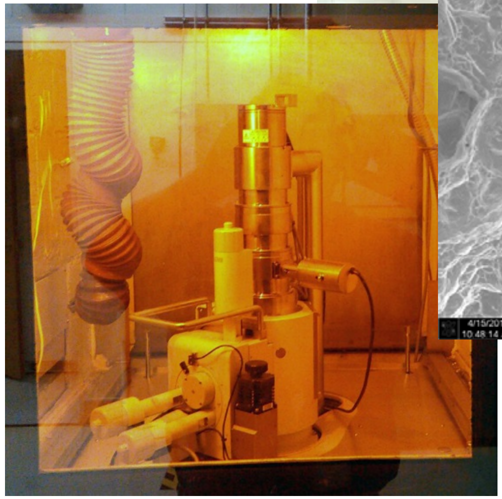
M. Gussev, et al. ORNL/TM/2017/507

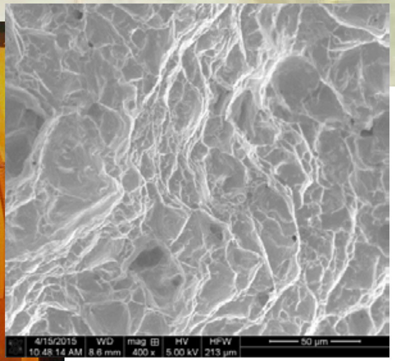
Overview of IMET

- Six interconnected steel-lined examination cells containing 30 m^2 of workspace.
- Cells 1~3 focusing on mechanical testing
- Low alpha contamination facility (<70 dpm / 100 cm^2).
- Irradiation capsule disassembly, mechanical testing (tensile, fracture testing, microhardness), density measurement, SEM, general characterization (optical, video documentation).





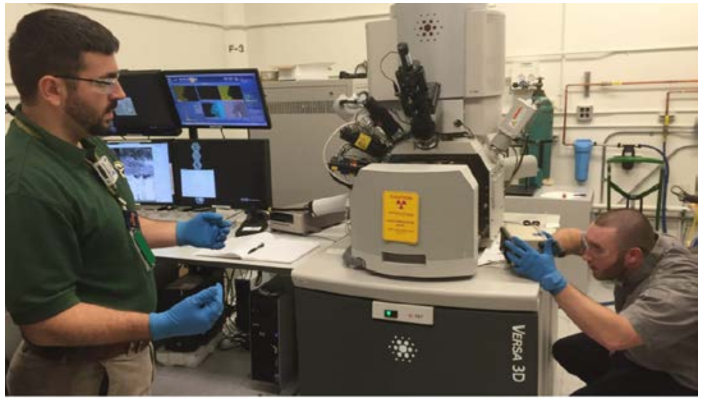




In-cell JEOL 6010LA and fractograph from irradiated tensile specimen

LAMDA: Low Activation Materials Development and Analysis

- **Overview**
  - Facility designated for the study of radiological materials by advanced characterization methods and instruments.
  - 4327 Sq. Ft of clean lab space and 2732 Sq. Ft of radiological contamination area
  - ~9000 specimens: fuels, metals, ceramics, graphite
- **Specimen acceptance criteria**
  - 100,000 dpm/100cm^2 beta/gamma
  - 2,000 dpm/100cm^2 alpha
  - 100 mR/hr @ 30cm
- **Core capabilities**
  - Microstructure characterization
  - Thermal/physical property
  - Mechanical testing
  - Machining irradiated materials
  - Various specialized instruments



Mechanical property testing instruments

- **Test Resource 160 series torsion test machine**
  - 125Nm torsion system
  - Adjustable speed to 8 rpm
- **Tinius Olsen Impact 104**
  - Pendulum impact tester; Charpy or Izod configuration
  - 30J capacity
  - Testing temperatures from -196 to 400°C
- **Creep test stands**
  - 1kN load capacity; Air environment
  - Temperature from -196 to 500°C
- **Buehler Wilson VH3100 microhardness tester (10 to 1000g load, programmable)**
- **Mituyoyo Vickers Microhardness (10 to 2500g load, programmable)**
- **Agilent Technologies G200 Nano Indentation system**
- **Sonic velocity measurement system**
  - Measure Young’s and shear moduli with the sonic velocity methodology according to ASTM C769 and C1419


Microscopes: TEM, FIBs, and SEM

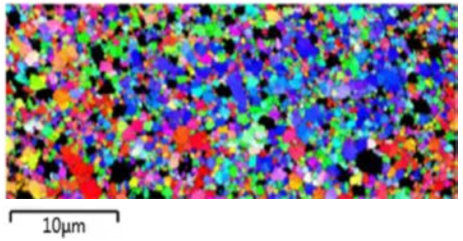
FIB with cryo-stage: Good for sensitive materials (i.e., prevent hydriding of Zr alloys)

FEI Quanta 3D 200i Dual Beam

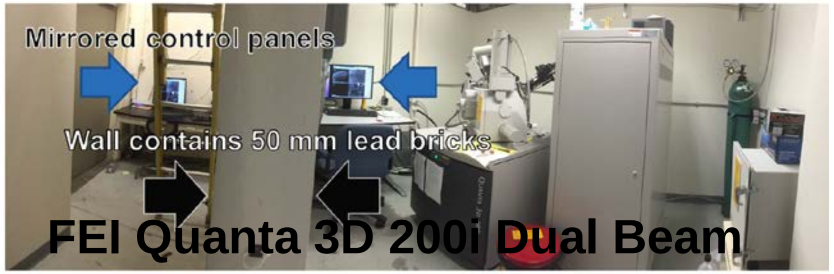
FEI Versa 3D Hi-Vac Dual Beam

High-Brightness FEG Electron Source
- 0.96 nm resolution

Available Detectors:
- Secondary electrons (ETD and in-column)
- Backscattered electrons (ETD & concentric)
- STEM
- Secondary ions



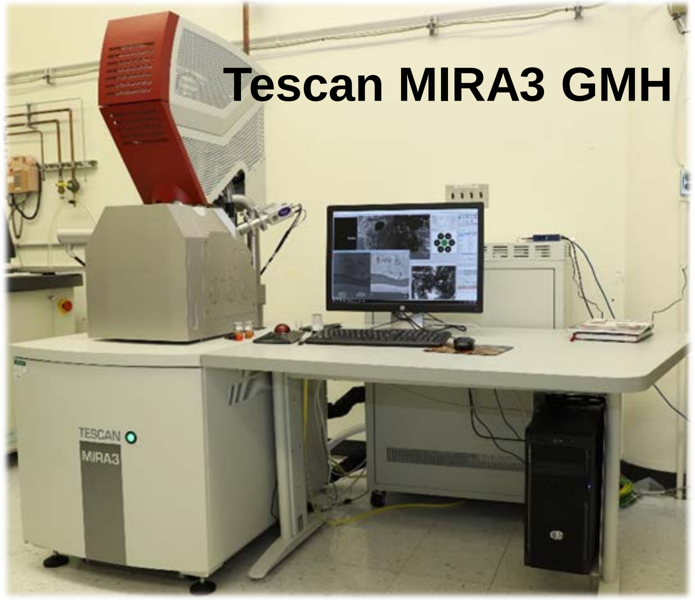
Shielded FIB: Control panel outside of 50 mm-thick lead envelope. Allows high-dose samples to be milled under ALARA conditions



FEI Quanta 3D 200i Dual Beam

High-Brightness FEG Electron Source
- <1.7 nm resolution

Available Detectors:
- Secondary electrons (ETD and In-Lens)
- Retractable annular Backscattered electron detector
- Extended wavelength cathodoluminescence (CL) detector



Tescan MIRA3 GMH

- JEOL JEM 2100F Transmission Electron Microscope (FEG, TEM/STEM, EDS, EELS)
- FEI Talos F200X Transmission Electron Microscope (X-FEG, TEM/STEM, super-X EDS)
- XRADIA X-ray Tomography
- Positron Annihilation Spectroscopy

Acknowledgements

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Thank you very much for your attention.

Questions ?

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