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Recent Results at Argonne on Post-Quench Ductility of High- Burnup Cladding

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Introduction

■ Research Sponsored by U.S. NRC Office of Nuclear Regulatory Research (RES)

■ Purpose

- Determine post-LOCA embrittlement-threshold oxidation level (calculated ECR) as a function of hydrogen content
- Determine breakaway oxidation time for as-fabricated alloys

■ Review of Results Reported in NUREG/CR-6967

■ New Results Generated Since July 2008

- Isothermal (ZIRLO, M5) and transient (ZIRLO) breakaway oxidation
- High-burnup ZIRLO (300-340 wppm H) embrittlement threshold
- Prehydrided ZIRLO (200-250 wppm H) embrittlement threshold.
- Development and documentation of procedures for conducting performance-based tests and for assessing test data

Executive Summary for NUREG/CR-6967

- **Testing Performed at $\leq 2200^{\circ}\text{F}$ ($\leq 1204^{\circ}\text{C}$)**
 - As-fabricated cladding (800-1204°C)
 - Pre-hydrided cladding (1180-1204°C)
 - High-burnup cladding (1100-1200°C); note: $< 1200^{\circ}\text{C}$ during heating ramp

- **Determine Ductile-to-Brittle Transition in Terms of:**
 - Calculated oxidation level at high cladding temperature (1000-1200°C)
 - *Use Cathcart-Pawel (CP) weight-gain correlation to calculate CP-ECR*
 - Time at lower temperatures for breakaway oxidation (800-1000°C)

- **Quantify Decrease in Embrittlement Threshold with**
 - Temperature: CP-ECR $> 20\%$ for 1000-1100°C; CP-ECR = 16-20% for 1200°C
 - Increase in hydrogen content due to: in-reactor corrosion, breakaway oxidation, and secondary hydriding following burst

- **Results for Fresh, Pre-hydrided, and High-Burnup Cladding**
 - Fresh: Zry-2, Zry-4 (3 types), ZIRLO, and M5
 - Pre-hydrided nonirradiated: Zry-4
 - High-burnup: Zry-4, ZIRLO and M5

Summary for NUREG/CR-6967 (Cont'd)

■ Notes on Embrittlement Data Shown in Executive Summary

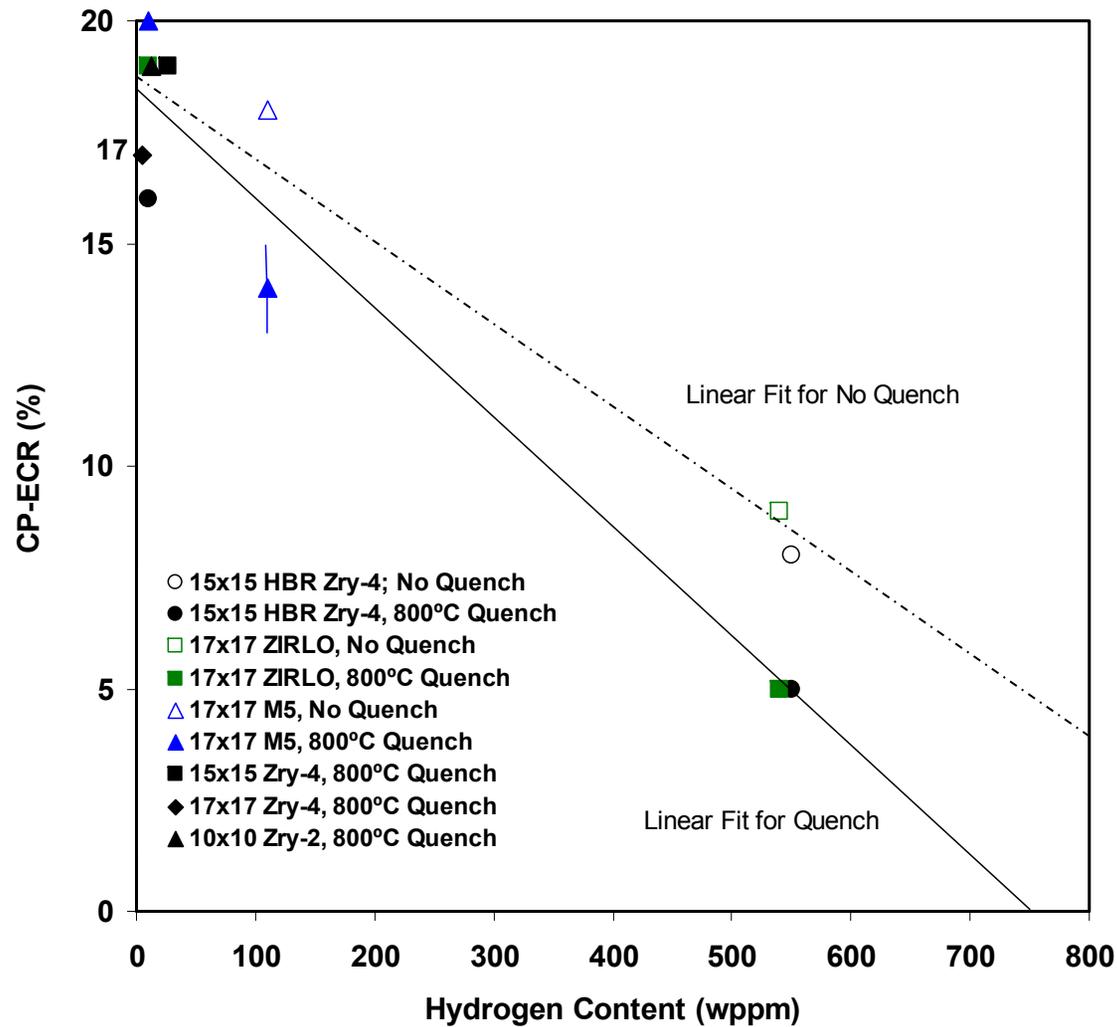
- Oxidation threshold is nearest % oxidation level (CP-ECR) for which cladding retains marginal ductility ($\geq 1\%$ permanent strain)
- Peak oxidation temperature is $< 1200^\circ\text{C}$ for $> 5\text{-}8\%$ CP-ECR
- Ductility is based on ring-compression tests conducted at 275°F (135°C)
- Pre-test hydrogen measured for corroded high-burnup ZIRLO was ≈ 80 wppm higher than hydrogen measured after oxidation tests
- High-burnup Zry-4 and ZIRLO exhibit significant circumferential variation (± 100 wppm) in hydrogen concentration; both pre-test and post-test

■ Embrittlement Threshold vs. High-Burnup ZIRLO Post-Test Hydrogen ($\approx 40 \mu\text{m}$ corrosion layer)

- Quenched: 620 ± 140 wppm \rightarrow 540 ± 100 wppm (post-test corrected for Wg)
- Need better method to determine metal hydrogen content (H_M/M_M) than current method: $L_H = (H_C + H_M + H_B)/(M_C + M_M + M_B)$,
where subscripts C = Corrosion, M = Metal, and B = fuel-cladding Bond
(Method described in backup slides.)

Summary for NUREG/CR-6967 (Cont'd)

Embrittlement Threshold vs. Post-Test Hydrogen Content



High-Burnup M5 and ZIRLO Cladding for PQD Tests

Cladding	Reactor (Discharge)	Burnup GWd/MTU	Corrosion Layer microns	Pre-test Hydrogen Content in Cladding Metal, wppm
17x17 ZIRLO	North Anna (Mar. 2001)	70	26±1	300-340
			43±2	540-590
17x17 M5	Ringhals (Jul. 2003)	63	12±1	90-150
	North Anna (May 2004)	68, 72	(≈10-20)	(≈100±30)

Experimental Approach

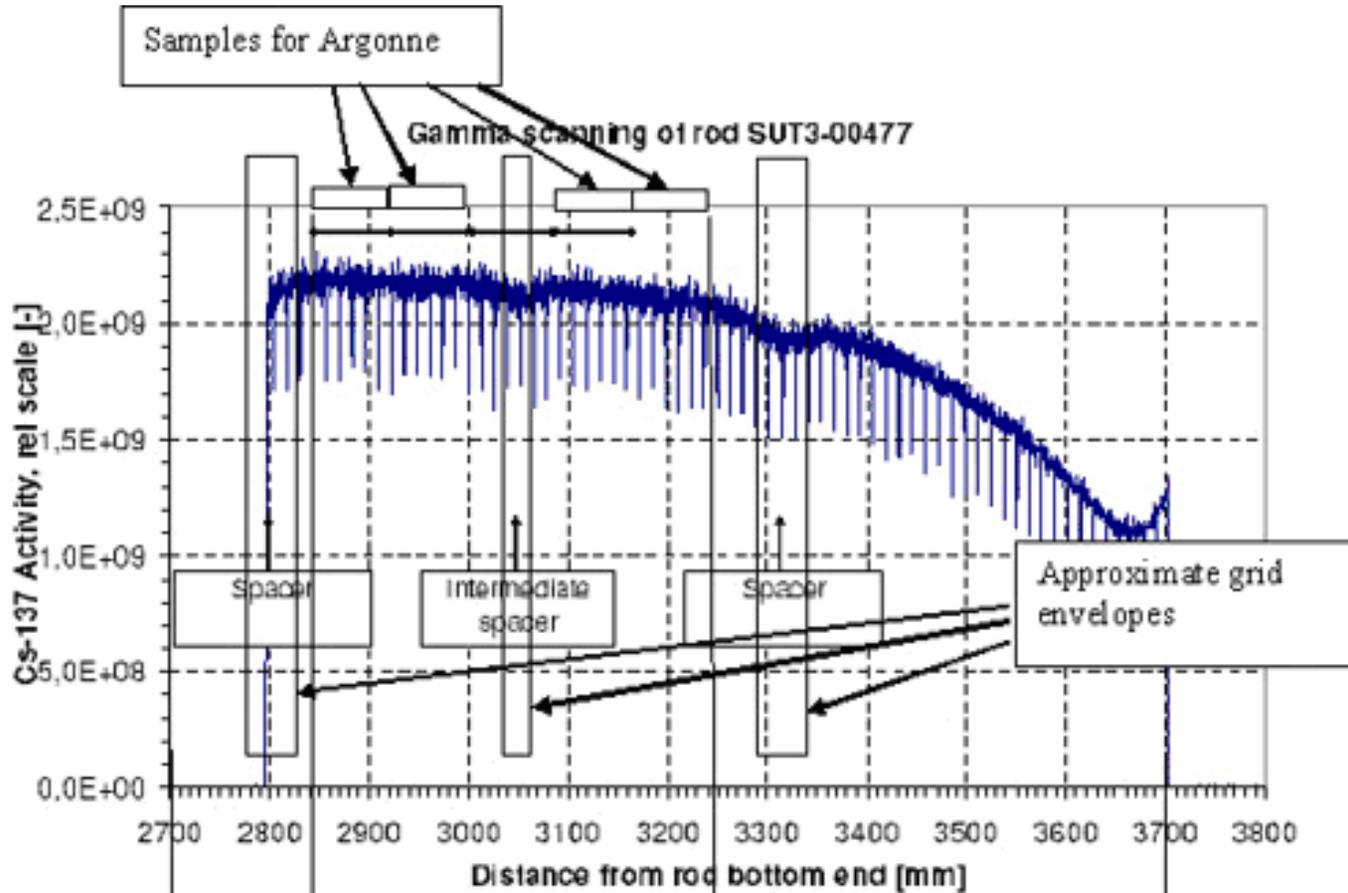
■ LOCA Oxidation and Quench Apparatus

- All alloys are steam-oxidized and quenched in same apparatus
- Temperature is carefully controlled and monitored

■ Ring-Compression Ductility Tests

- Performed at RT and 135°C and 2 mm/min. with 8-mm-long rings
- Failure = through-wall crack along length of ring
- Ductility = plastic decrease in diameter just prior to failure
 - *Offset strain from load-displacement curve*
<2% offset strain implies brittle response (this has been revised)
 - *Permanent strain from pre- and post-test micrometer measurements*
<1% permanent strain implies brittle response (from error analysis)

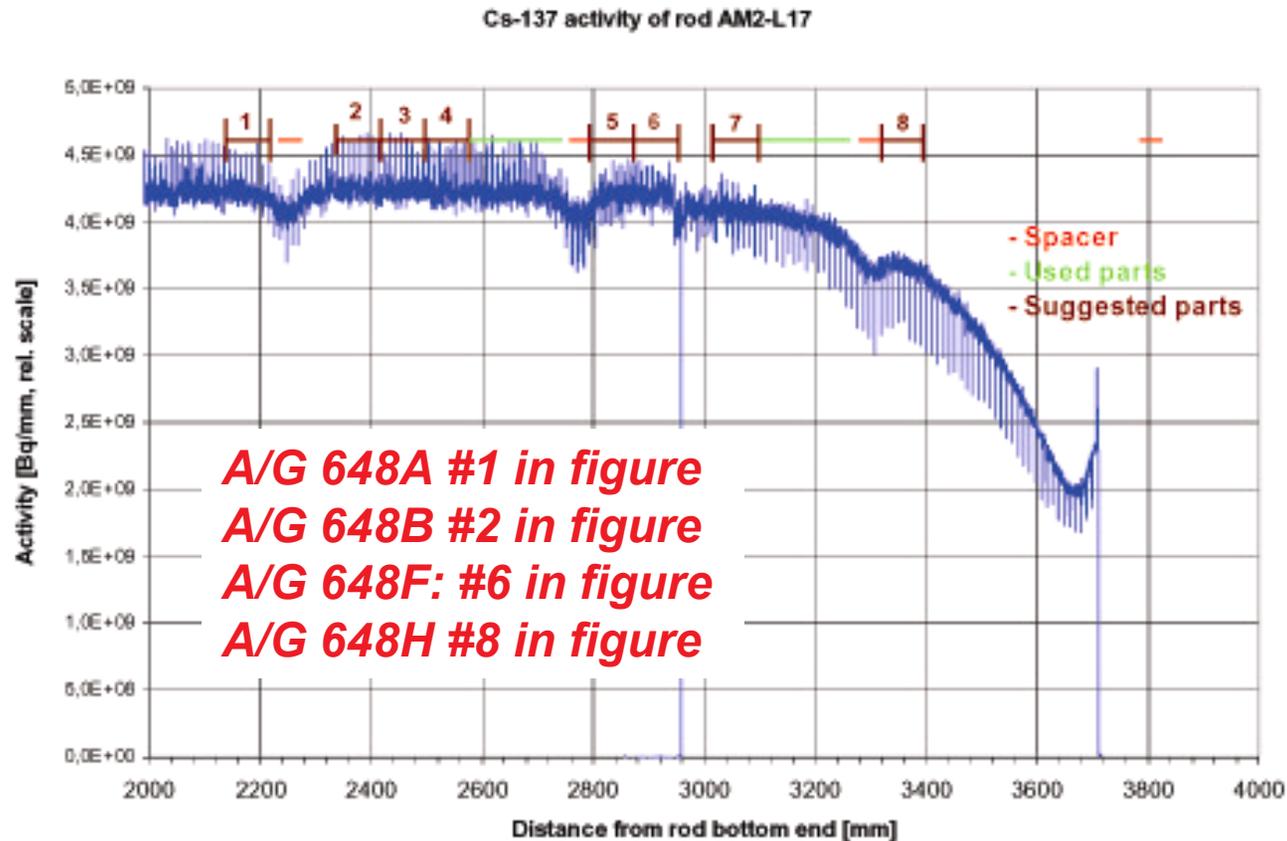
Gamma Scan Profile and Location along Ringhals Rod SUT3-00477 of M5 Samples for ANL LOCA Testing



High-Burnup M5 Characterization Results

- Corrosion layer: Thin and uniform azimuthally ($\approx 12 \pm 1 \mu\text{m}$ avg.)
- Metal layer: Very uniform azimuthally ($554 \pm 2 \mu\text{m}$)
- Bond layer: $8 \pm 3 \mu\text{m}$
- Low Cladding Hydrogen Consistent with Thin Corrosion Layer
 - ≈ 110 wppm in corroded cladding (corrosion-layer + metal + bond)
 - 90-150 wppm in cladding metal
 - Note: metal hydrogen content (H_M/M_M) could be higher or lower than the hydrogen content measured for a corroded cladding sample with a fuel-cladding bond, especially if samples are not well defueled

Gamma Scan Profile and Locations along North Anna Rod AM2-L17 of ZIRLO Samples for ANL LOCA Testing



North Anna ZIRLO Characterization Results for Rod AM2-L17

Sample ID # W (ANL)	Corrosion Layer from Eddy Current, μm	Corrosion Layer from Met., μm	Metal Layer from Met., μm	Fuel-Clad Bond Layer from Met., μm	Hydrogen in Corroded Cladding, wppm	Hydrogen in Cladding Metal, wppm
1 (648A)	25-28	26 \pm 1	551 \pm 5	7 \pm 1	310 \pm 32	296 \pm 33
6 (648F)	43-48	43 \pm 2	544 \pm 2	7 \pm 2	620 \pm 140	540 \pm 114

- Hydrides in ZIRLO Sample 648F3
 - *Hydride-rim thickness varied circumferentially, consistent with H content variation*
- Hydrides in ZIRLO Sample 648A
 - *Both circumferential and radial hydrides at one of eight circumferential locations.*

Hydrogen Concentration Variations in High-Burnup ZIRLO

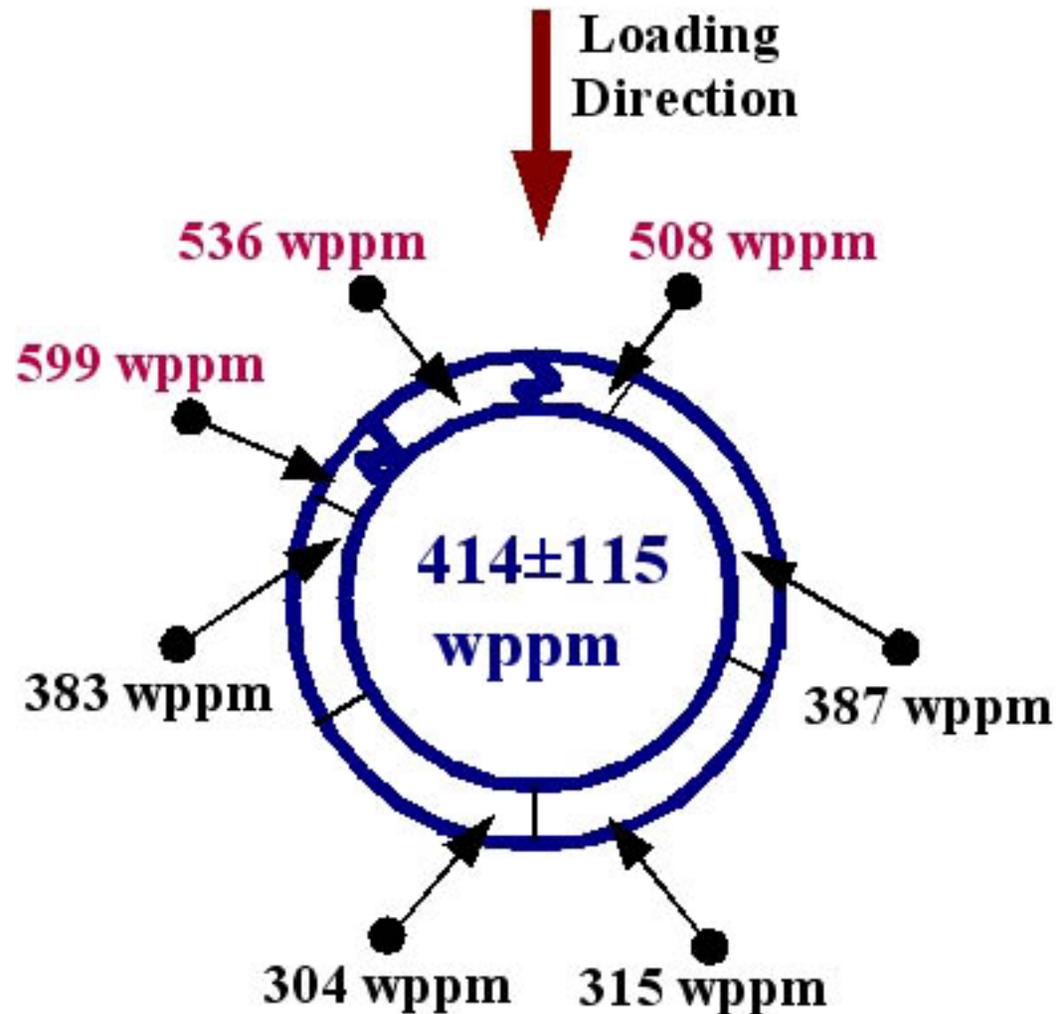
■ Pre-Test vs. Post Test Values

- Pre-test measurements performed routinely in hot cells
 - *Small sample length (1-2 mm) and mass (0.1-0.2 g)*
 - *Sample includes corrosion layer and bond layer*
- Post-test measurements performed by ANL
 - *Larger sample length (2-16 mm) and mass (0.2-1.0 g)*
 - *Some of corrosion layer flakes off during LOCA test cooling*
 - *Change in sample weight for <7% CP-ECR is small (-1 to 0.3%)*
- Higher pretest values due to hydrogen content in corrosion layer
 - *ANL improved technique to determine hydrogen in metal*

■ Large Circumferential Variations for High-Burnup Zry-4 & ZIRLO

- Supported by metallographic images of hydride distribution
- Dense hydride rim in ZIRLO varies systematically from ≈ 40 to $70 \mu\text{m}$ for $43 \pm 2 \mu\text{m}$ corrosion layer and 660 ± 150 wppm pre-test hydrogen

Hydrogen Distribution in a High-Burnup ZIRLO Ring after 5.1% CP-ECR, 1162°C Peak Oxidation Temperature and 800°C Quench



Oxidation Levels and Times for LOCA Embrittlement Tests with High-Burnup M5 and ZIRLO Samples

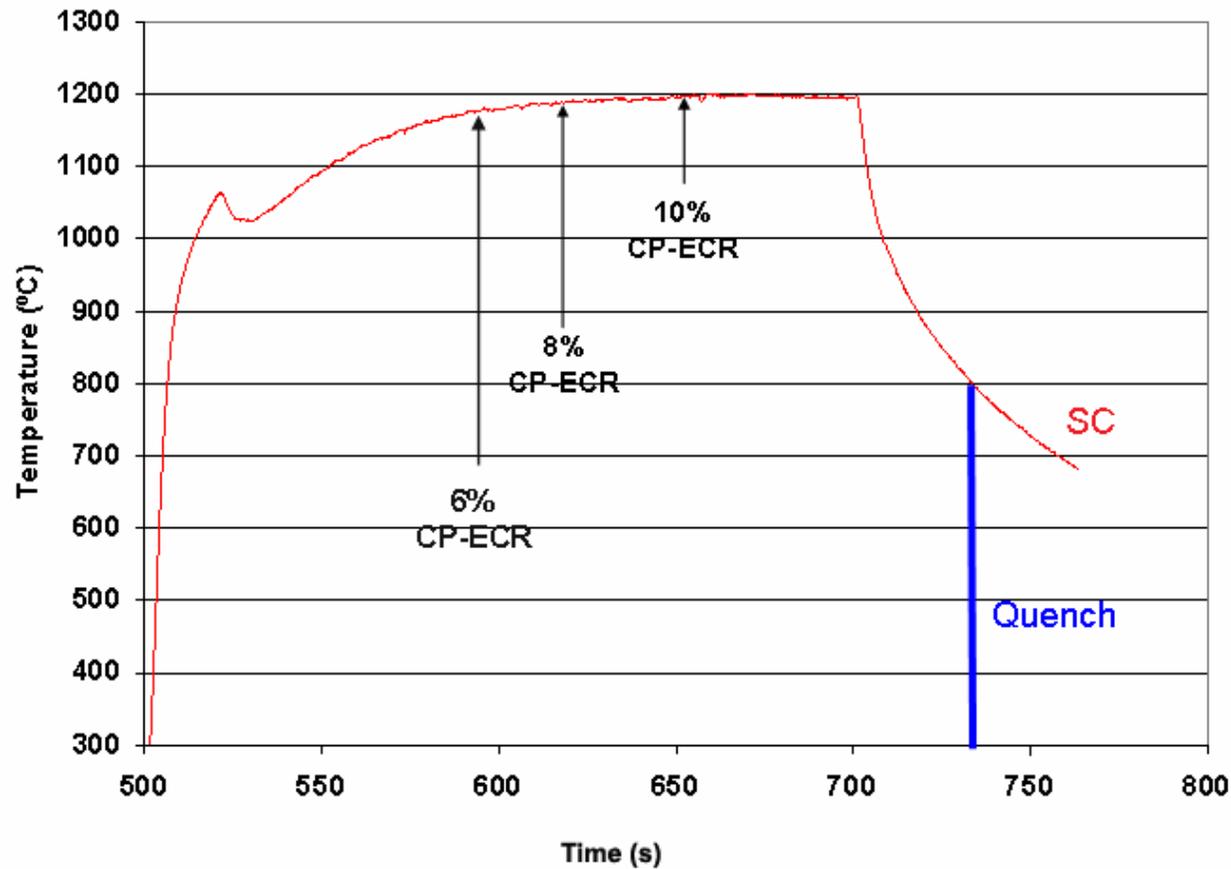
■ High-Burnup M5 Oxidation Levels

- CEA data: prehydrided (120-130 wppm) M5 oxidized/quenched at 1200°C
 - *Low ductility (6% offset strain) at 11% CP-ECR*
 - *Very Brittle at 18% CP-ECR*
- ANL Oxidation levels
 - *13 to 18% for slow cooled samples*
 - *13 to 16% for samples quenched at 800°C*

■ High-Burnup ZIRLO Oxidation Levels

- ANL data for prehydrided and high-burnup Zry-4 used as guide
- Oxidation levels for tests without quench: 6-10% CP-ECR
- Oxidation levels for tests with quench: 4-10% CP-ECR depending on hydrogen concentration

Temperature History for High-Burnup 17x17 ZIRLO Tests with Mid-Range Hydrogen Content of 300 and 340 wppm



Recent Post-Test Ductility Results for High-Burnup North Anna ZIRLO Cladding Oxidized at $\leq 1200^{\circ}\text{C}$

Test #	Pre-test Hydrogen Content, wppm		Test Time s	Peak T, $^{\circ}\text{C}$	CP-ECR, %	Strain, %	
	Cladding	Metal				Offset	Perm.
ZLI#7 SC	366 \pm 30	340 \pm 34	153	1200	10	9.9 13.4	5.0 9.4
ZLI#8 Quench at 800 $^{\circ}\text{C}$	310 \pm 32	294 \pm 37	153	1200	10	0.7 2.2	--- ---
ZLI#9 Quench at 800 $^{\circ}\text{C}$	310 \pm 32	296 \pm 35	118	1190	8	2.9 4.6 >2.0	--- --- >1.2
ZLI#11 Quench at 800 $^{\circ}\text{C}$	366 \pm 30	340 \pm 34	118	1190	8	0.6 1.0	--- ---

- **Post-Quenched Embrittlement CP-ECR is 9% based on 1 ductile ring at 10% and 3 at 8%**
- SC= slow cooled without quench

Embrittlement Oxidation Level as a Function of Pre-test Hydrogen Content for High-burnup Cladding Materials Oxidized at $\leq 1200^{\circ}\text{C}$ and Quenched at 800°C

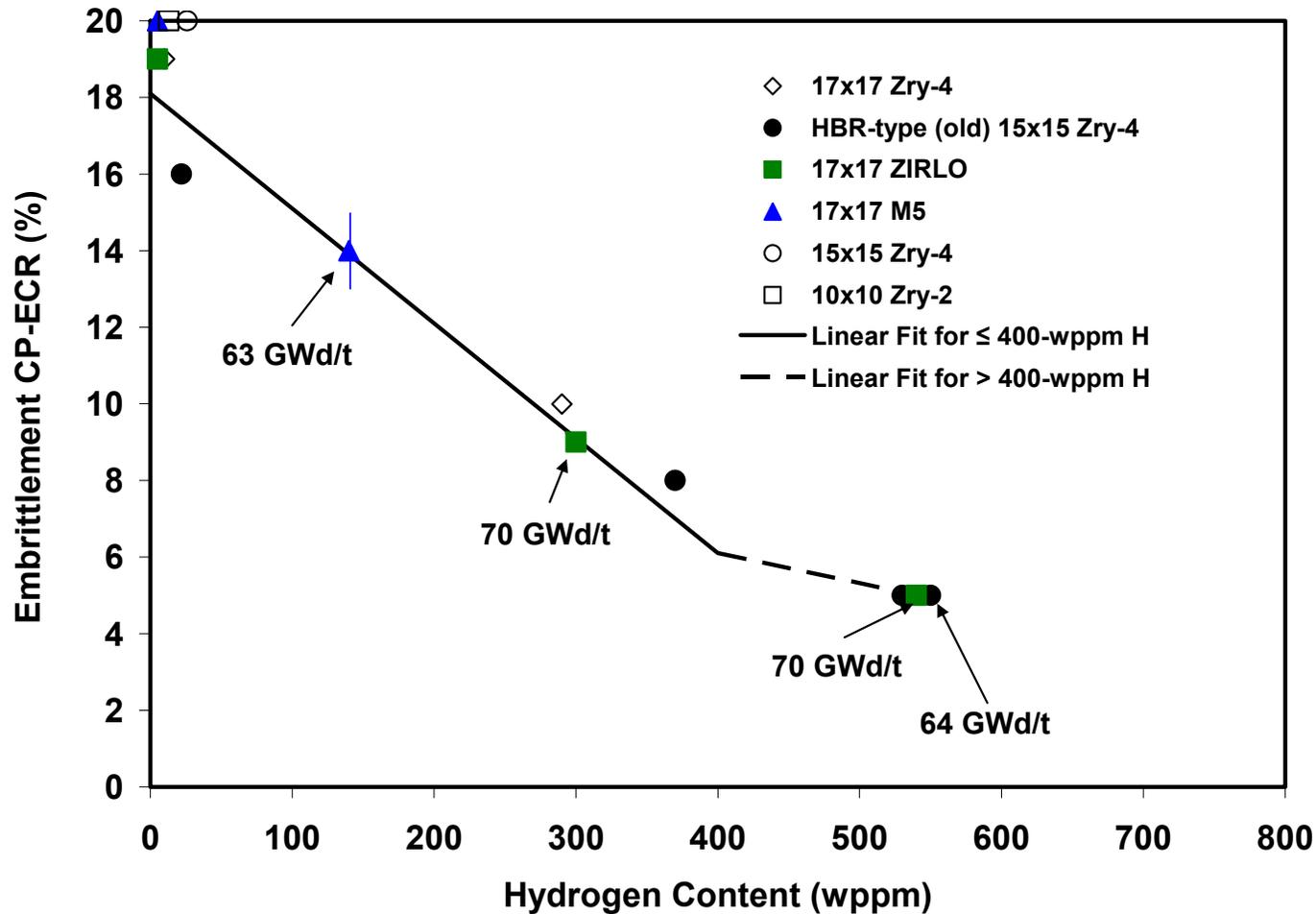
Material	Hydrogen Content, in Metal wppm	Peak Temp. $^{\circ}\text{C}$	CP-ECR %	Strain %		Embrittlement CP-ECR
				Offset	Perm.	
Ringhals 17x17 M5	137±16	1200	15.1 13.4	2.8±0.7 4.2±0.2 (or 3.4±1.3)	---	14±1% at 140-wppm H
NA 17x17 ZIRLO	296±33	1200 1190	10 8	1.5±1.1 3.8±1.2	---	9% at 300-wppm H
HBR 15x15 Zry-4	≈550±100	1180	5	---	---	5% at 550-wppm H
NA 17x17 ZIRLO	540±114 448±104 592±115	1176 1162 1132	6.3 5.1 4.0	0.8±0.5 10-60% >43	0.2 >50 >43	5% at 540-wppm H

Ductility criteria documented in "Procedure for Conducting Oxidation and Post-Quench Ductility Tests with Zirconium-based Cladding Alloys," Argonne National Laboratory, Mar. 31, 2009.

Ductile-to-brittle Transition Oxidation Level (Embrittlement CP-ECR) vs. Pre-test Hydrogen in Cladding Metal for As-fabricated (AF), Prehydrided (PH) and High-burnup Cladding Materials; HBR= H.B. Robinson; NA= North Anna

Cladding Material	Pre-test Hydrogen Content in Metal, wppm	Peak Oxidation Temperature, °C	Embrittlement CP-ECR, %
AF 17×17 M5	5	1200	20
AF 15×15 Zry-4	26	1200	20
AF 17×17 ZIRLO	5	1200	19
AF 10×10 Zry-2	13	1200	20
AF 17×17 Zry-4	5	1200	19
AF HBR-type 15×15 Zry-4 (Old Vintage Cladding)	22	1200	16
Ringhals High-burnup 17×17 M5	140	1200	14±1
PH 17×17 Zry-4	290	1200	10
NA High-burnup 17×17 ZIRLO	300	1200	9
NA High-burnup 17×17 ZIRLO	340	1190	<8
PH HBR-type 15×15 Zry-4	370	1200	8
NA High-burnup 17×17 ZIRLO	450	1160	>5
PH HBR-type 15×15 Zry-4	530	1190	5
HBR High-burnup 15×15 Zry-4	550	1180	5
NA High-burnup 17×17 ZIRLO	540	1160	5
NA High-burnup 17×17 ZIRLO	590	1130	>4

Ductile-to-Brittle Transition Oxidation Level (CP-ECR) as a Function of Pre-test Hydrogen in Cladding Metal for AF, PH, and High-burnup Cladding Materials



Correlations for the Embrittlement Oxidation Level (CP-ECR) as a Function of Pre-test Hydrogen in Cladding Metal

For $C_H \leq 400$ wppm H and peak oxidation temperature = 1190-1200°C

$$\mathbf{CP-ECR = 18.1 - 0.030 C_H}$$

For $C_H > 400$ wppm H and peak oxidation temperature < 1190°C

$$\mathbf{CP-ECR = 6.1 - 0.0078 (C_H - 400 \text{ wppm})}$$

C_H is the pre-test hydrogen content in the cladding metal (in wppm)

CP-ECR is the oxidation level (in %)

High-burnup Zry-4, M5, and ZIRLO data were assigned weighting factor of 2

Prehydrided Zry-4 data were assigned a weighting factor of 1

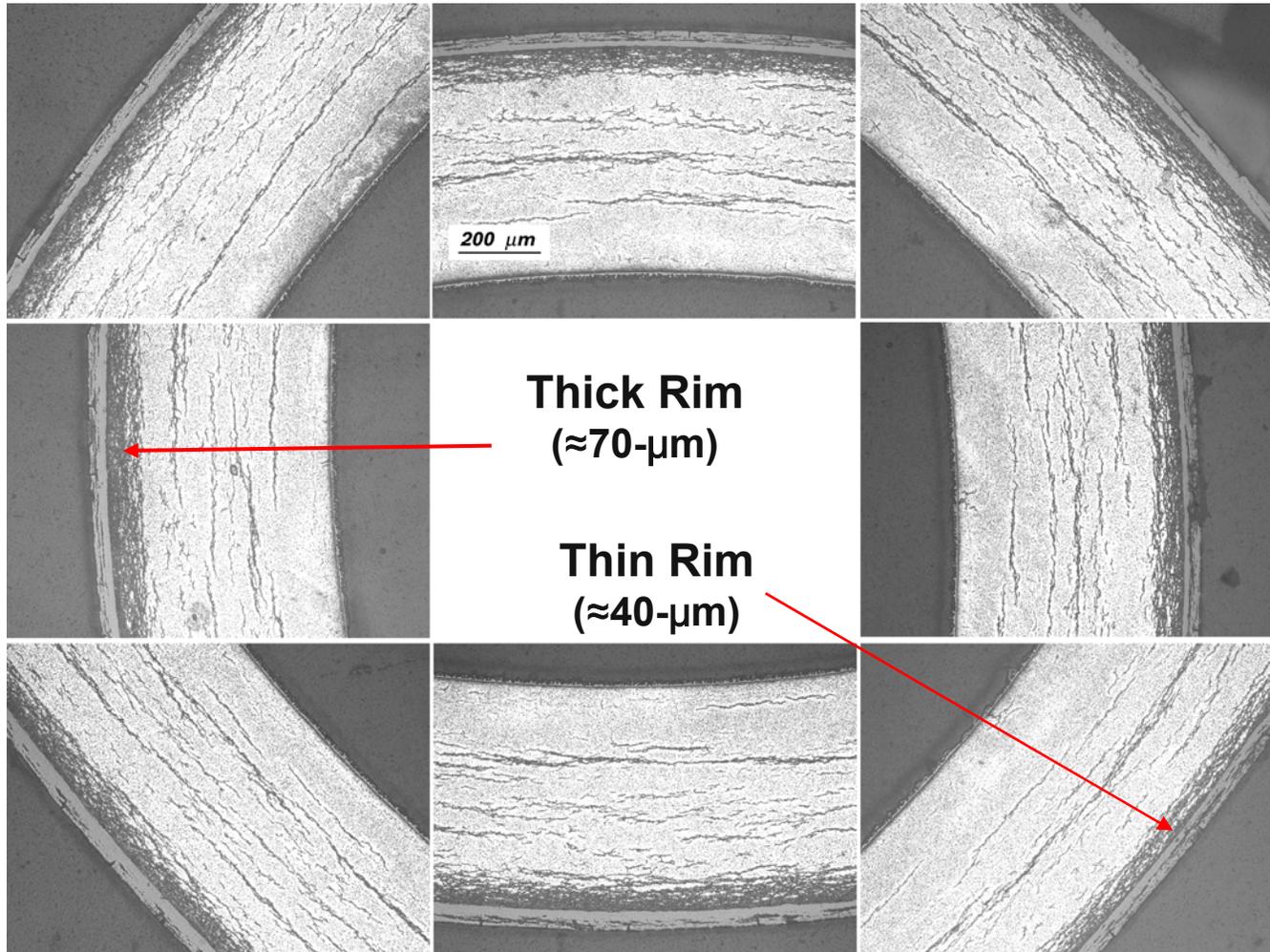
Backup slides

- Metallographic Results for As-Irradiated High-Burnup Cladding
- Determination of Metal Hydrogen Content for Corroded Cladding
- New Ductility Criterion for Offset Strain

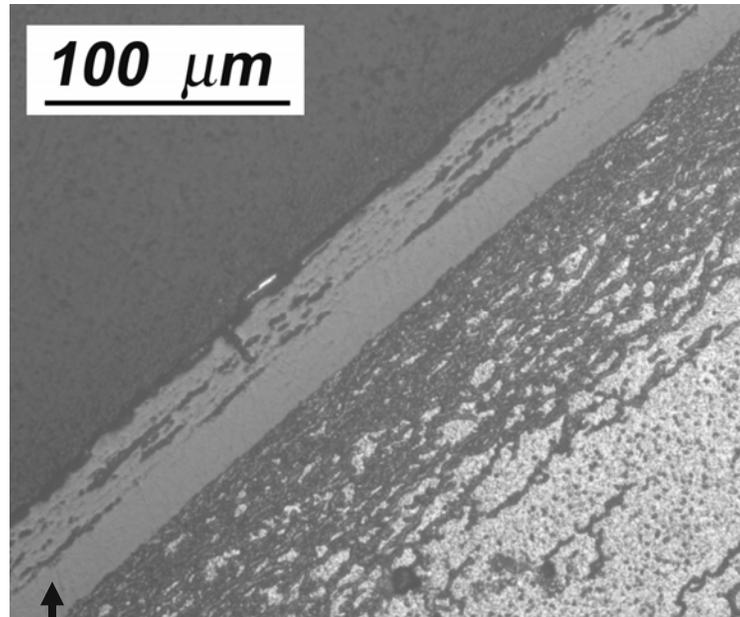
Metallographic Results for As-Irradiated High-Burnup Cladding

- North Anna ZIRLO at 70 GWd/MTU
- Ringhals M5 at 63 GWd/MTU

Hydrides in ZIRLO Sample 648F with $43 \pm 2 \mu\text{m}$ Corrosion Layer and 660 ± 150 wppm Pre-Test H in Corroded Cladding

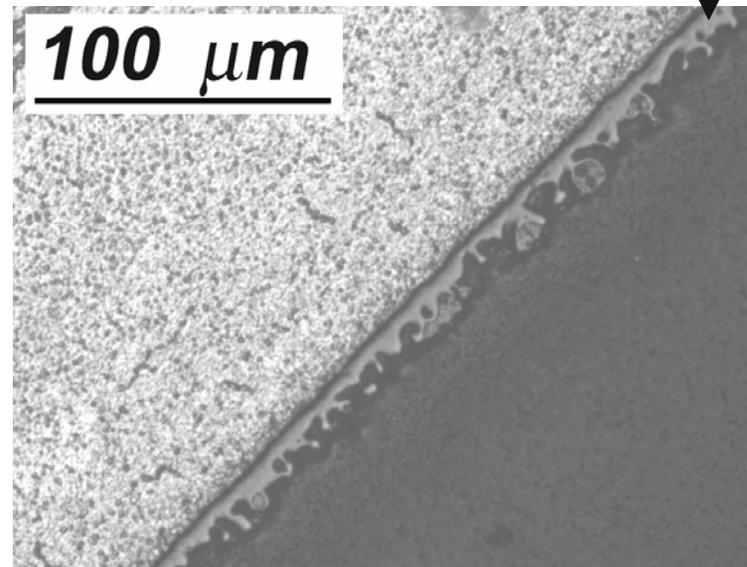


High Magnification Micrographs of ZIRLO Sample 648F3 OD and ID with 660 ± 150 wppm Pre-Test H

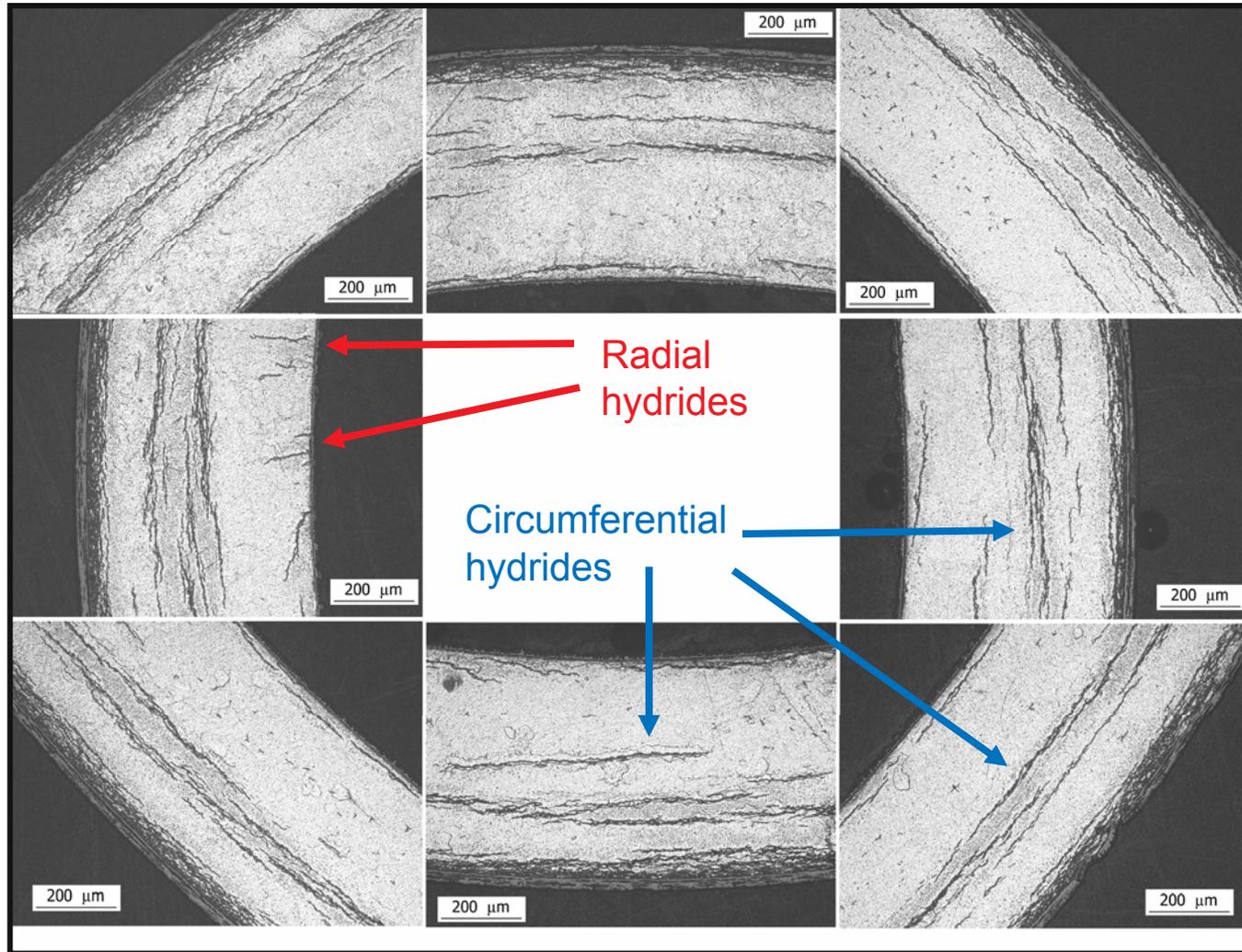


Corrosion layer

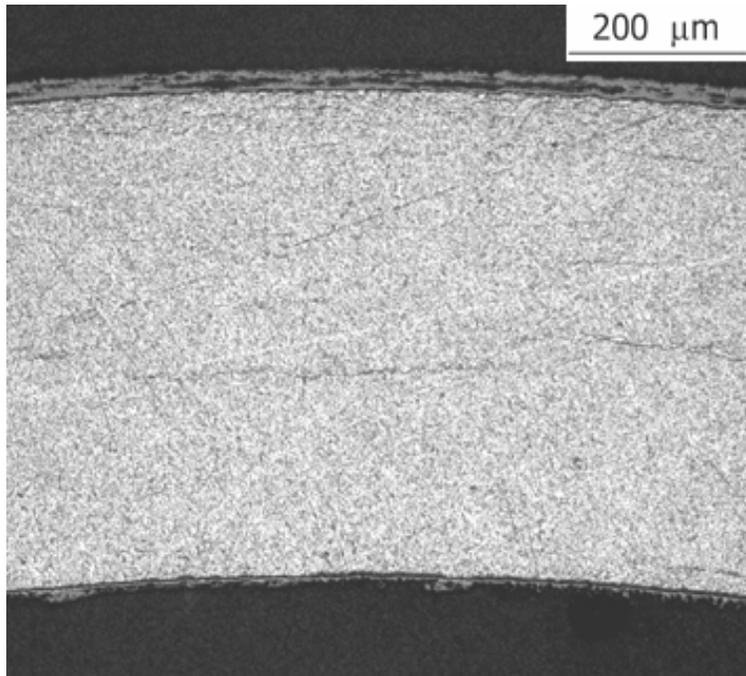
Fuel-cladding bond layer



Hydride Morphology for 648A Sample with 318 ± 30 wppm Hydrogen in Corroded Cladding

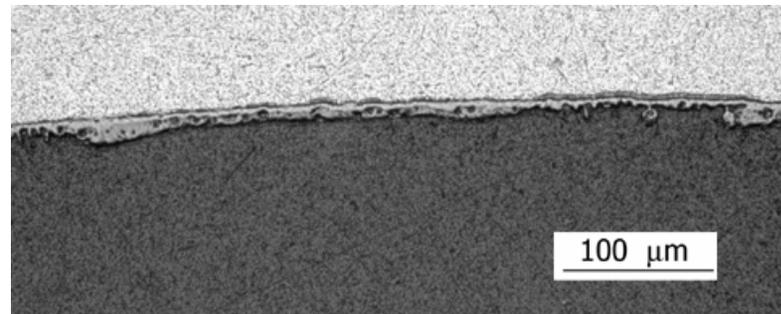
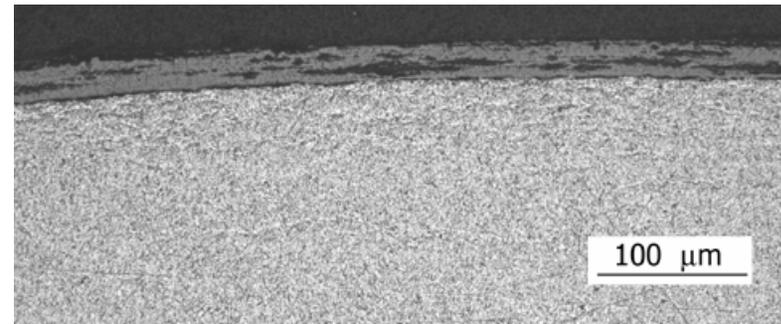


Micrographs Taken from a Sample Sectioned near the Middle of High-Burnup ZIRLO Segment (648A)



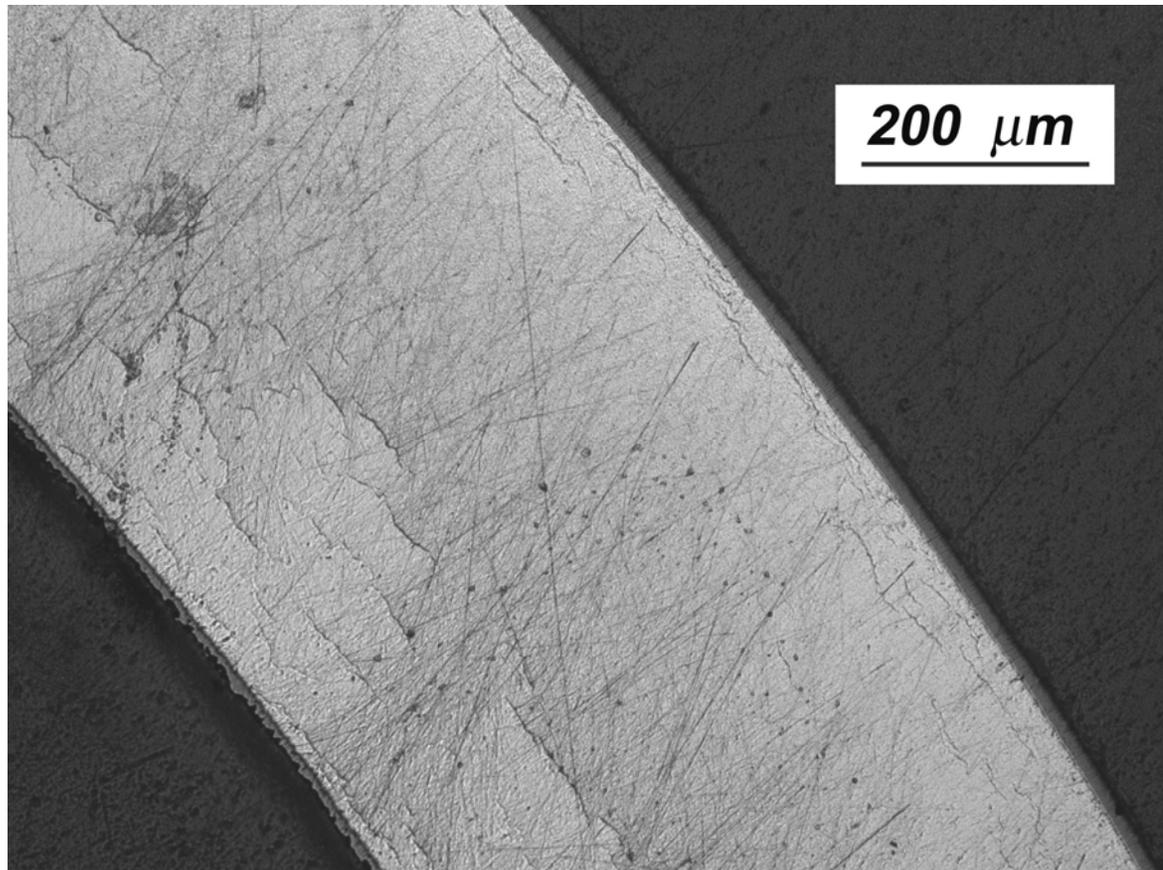
cladding cross section

corrosion layer

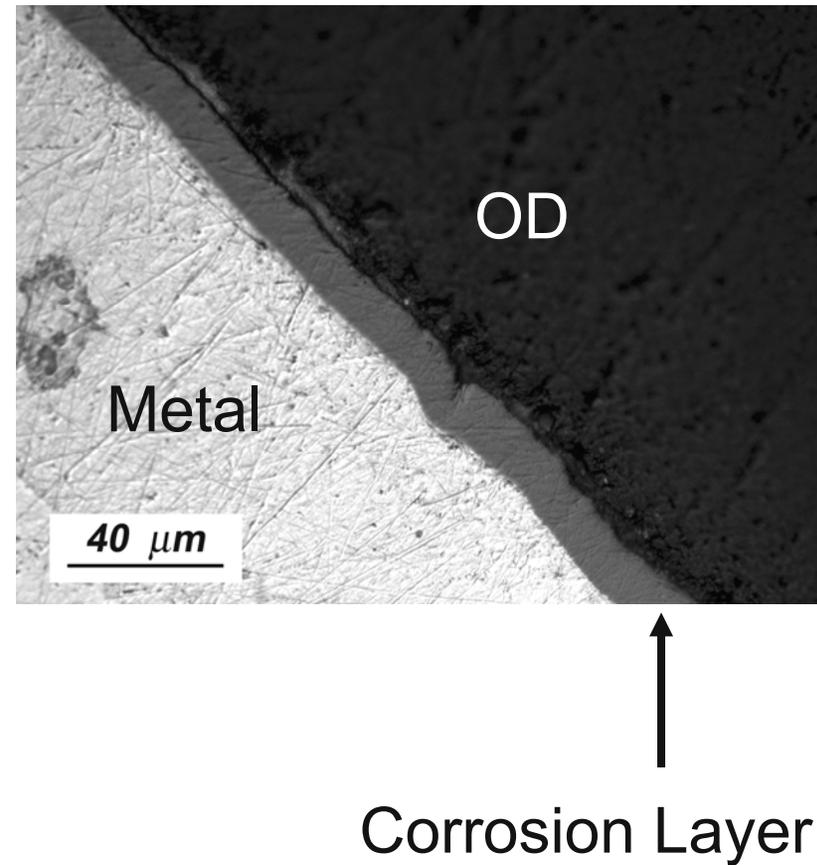
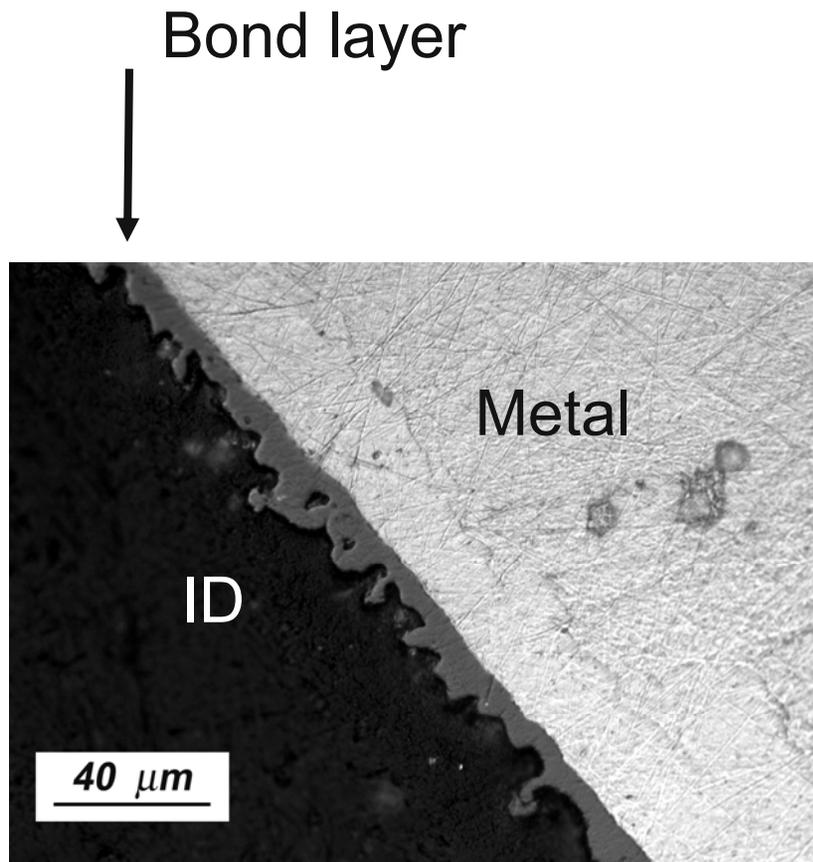


fuel-cladding bond

Enlarged View of M5 Sample 645B Cross Section



Micrographs of M5 Sample 645B OD and ID



Determination of Metal Hydrogen Content for Corroded Cladding

■ Standard Hot-Cell Approach

- Measure total hydrogen in cladding sample ($H_C + H_M + H_B$)
 - Where C = corrosion layer, M = metal; B = fuel-cladding bond
- Measure total mass of cladding sample ($M_C + M_M + M_B$)
- Report $L_H = [(H_C + H_M + H_B) / (M_C + M_M + M_B)] \times 10^6$ in wppm
- Metal hydrogen content ($H_M/M_M \times 10^6$) may be greater (usual case) or less than L_H

■ ANL-Recommended Methodology to Determine Hydrogen in Metal

- Measure mass/length of ≥ 25 -mm-long cladding sample
- Measure OD (profilometry)
- Section metallography sample
- Determine metal OD and wall thickness from profilometry/metallography
- Calculate metal mass/length and determine mass correction factor
- Pre-heat cladding sample to about 600°C (??) to drive off hydrogen in corrosion and bond layers; then do hydrogen measurement.

ANL Determination of Metal Hydrogen Content for Corroded Cladding Subjected to Oxidation Tests

Pre-test hydrogen content in the metal:

$$C_{HM} = F_{Wg} \times F_{MM} \times (L_H)_{POX}$$

Weight-gain correction factor: $F_{Wg} = M_{Post-OX} / M_{Pre-OX}$

Metal-mass correction factor $F_{MM} = (M_s/L) / (M_m/L)$

$(L_H)_{POX}$: post-oxidation LECO hydrogen measurement

Assumption #1: all post-test hydrogen is in cladding metal

Assumption #2: no hydrogen pickup by metal during LOCA transient

$M_{Post-OX}$: post-test sample mass

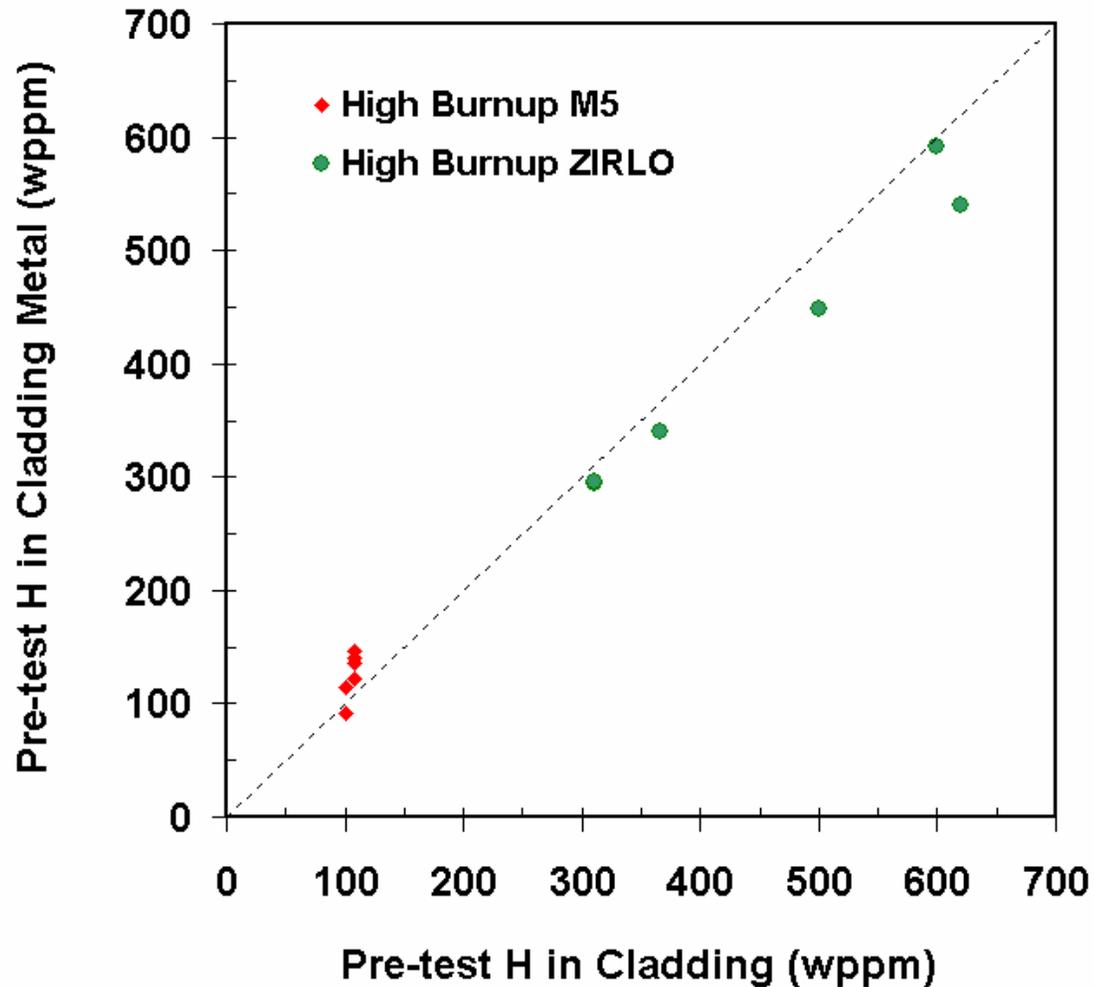
M_{Pre-OX} : pre-test sample mass

M_s : pre-test sample mass (including corrosion and bond layers)

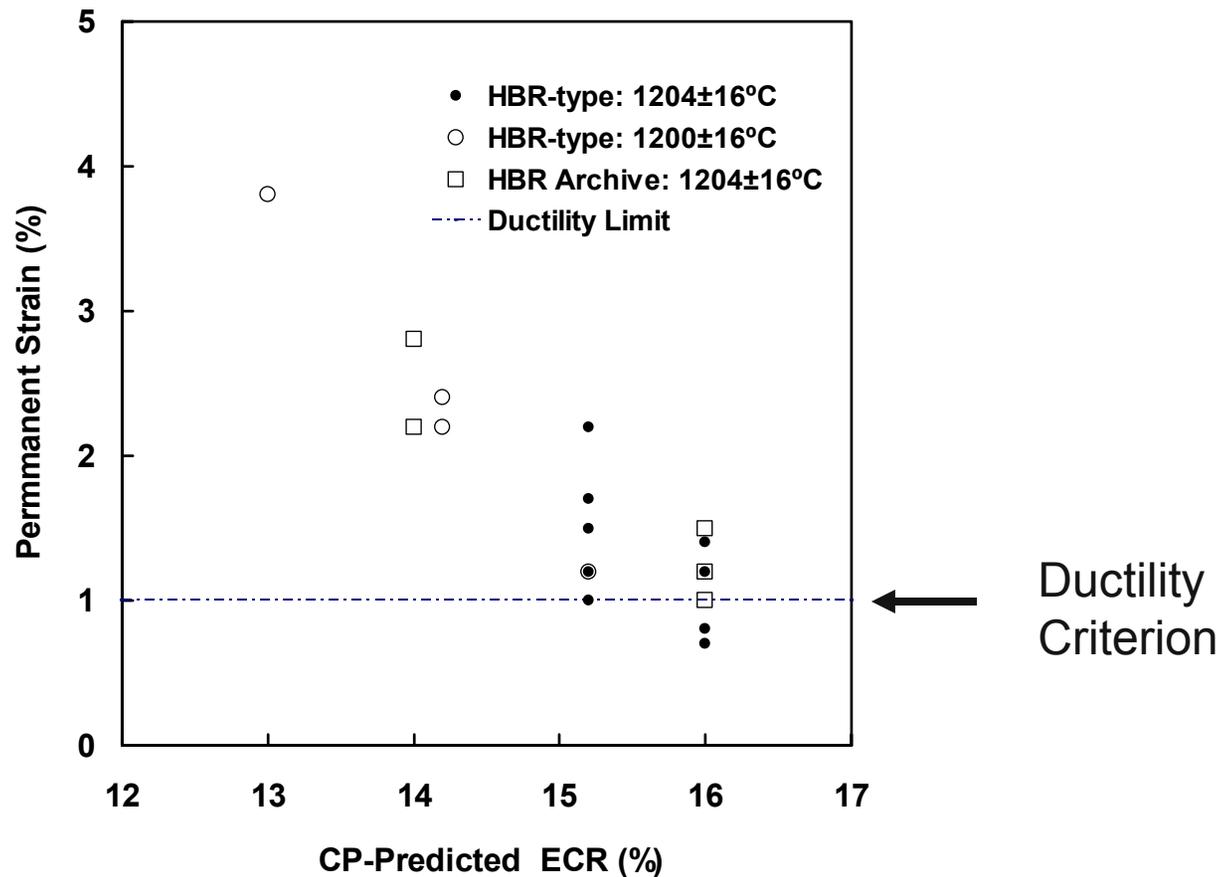
M_m : pre-test metal mass (determined from profilometry & metallography)

L: pre-test sample length

Hydrogen Content in Metal vs. in Corroded Cladding for Pre-test Samples



Embrittlement Threshold for HBR-Type Zry-4 oxidized at 1200°C and Quenched at 800°C: Results of Multiple Tests



Permanent strain: $1.5 \pm 0.4\%$ at 15.2% CP-ECR, $1.1 \pm 0.3\%$ at 16% CP-ECR and $< 1\%$ at 17% CP-ECR; **ductile-to-brittle transition is 16% CP-ECR**

Relationship between Offset Strain and Permanent Strain near the Embrittlement Threshold (Permanent Strains: 0.8-2.3%)

Determination of the ductile-to-brittle transition oxidation level (CP-ECP) based on offset strain (δ_p/D_o in %)

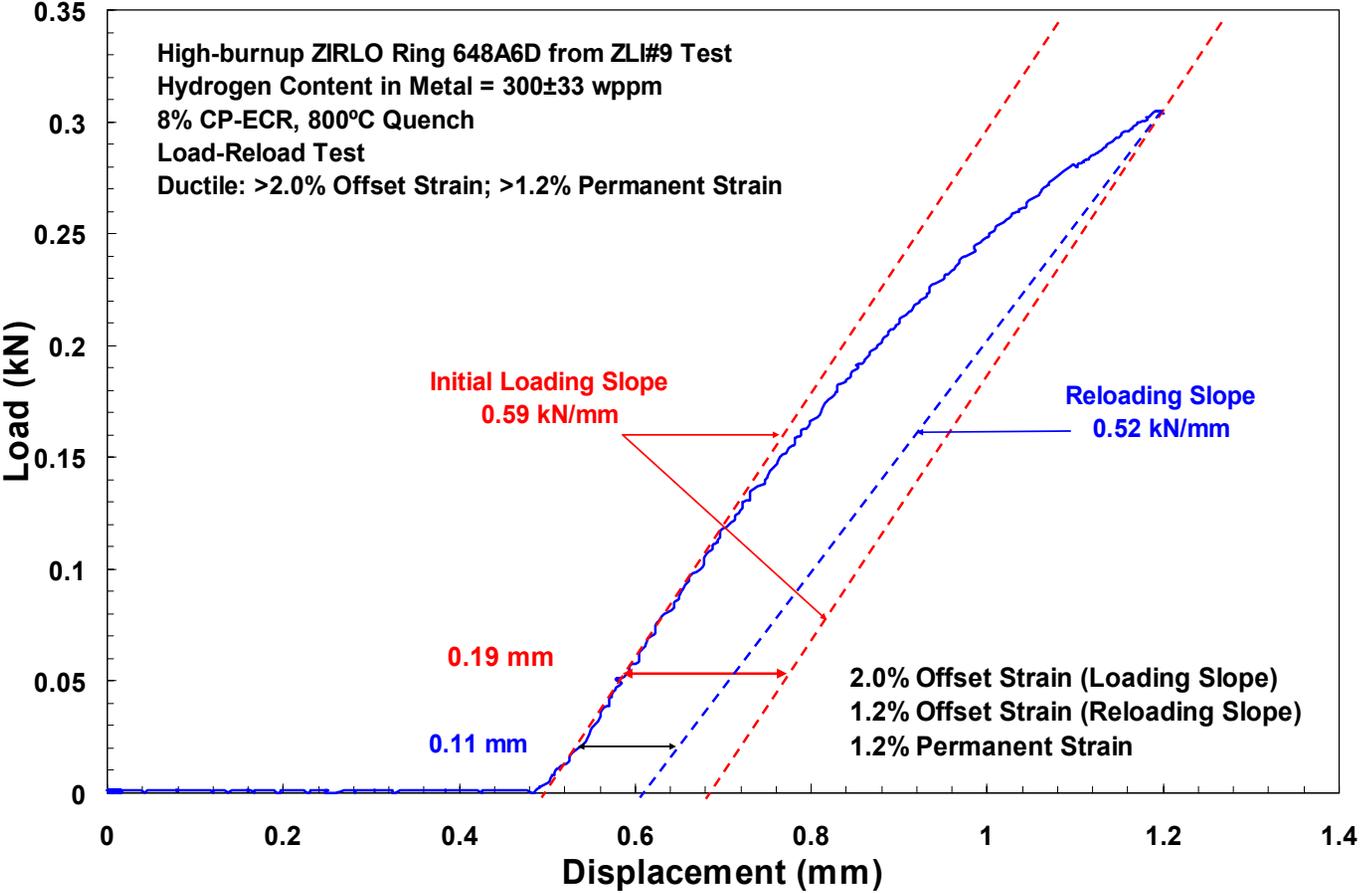
Inherent error in offset strain because the unloading slope is less than the loading slope used to determine offset displacement. Difference between offset strain and permanent strain (d_p/D_o in %) has been characterized as a function of oxidation level (CP-ECR) for low values of permanent strain (0.8-2.3%)

$$\delta_p/D_o - d_p/D_o = 0.60\% + 0.0534 \text{ CP-ECR}$$

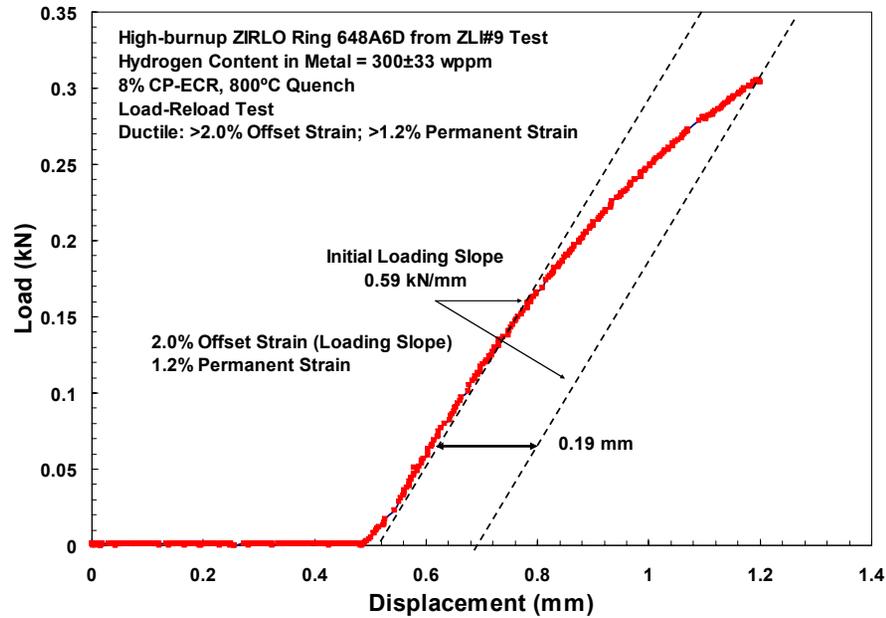
Set permanent strain (d_p/D_o) to 1% to get offset strain criterion:

$$\delta_p/D_o \geq 1.60\% + 0.0534 \text{ CP-ECR}$$

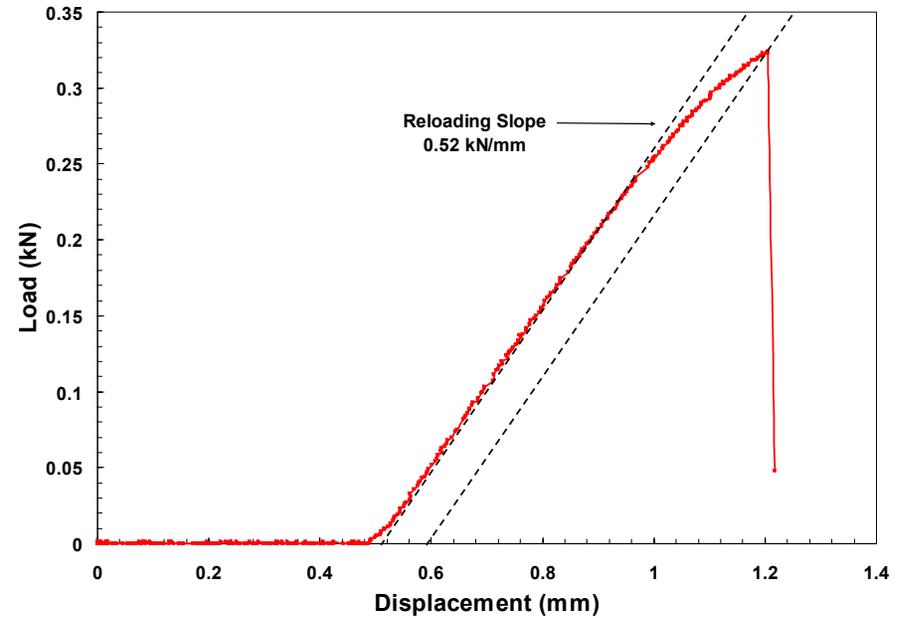
Inherent Error in Offset Strain Methodology for High-Burnup ZIRLO Ring Unloaded/Reloaded before Failure



Inherent Error in Offset Strain Methodology for High-Burnup ZIRLO Ring Unloaded/Reloaded before Failure

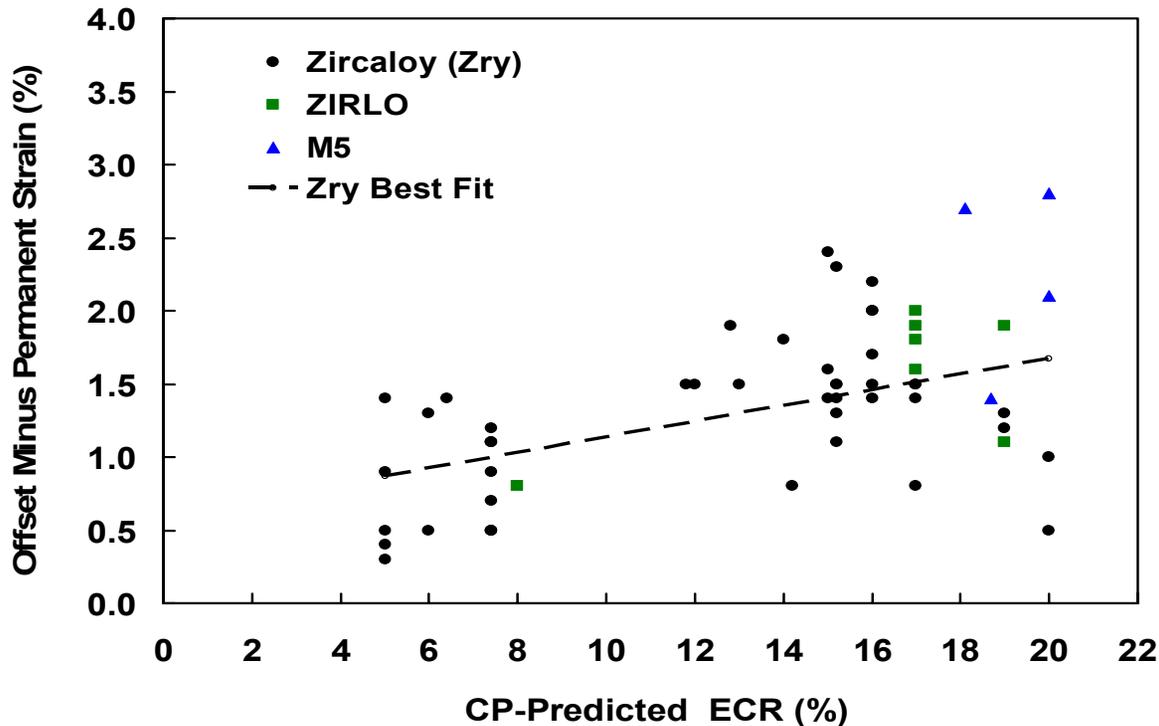


Initial Loading



Reloading

Difference in Offset and Permanent Strains as a Function of Oxidation Level (CP-ECR) near the Embrittlement Threshold



- Low values of permanent strain at oxidation levels (CP-ECR)
 - Low CP-ECR levels (5-10%): pre-H Zry-4 and high-burnup Zry-4 and ZIRLO samples
 - Intermediate CP-ECR levels (10-18%): high-burnup ZIRLO and M5 samples
 - High CP-ECR levels (15-20%): as-fabricated cladding materials.
- Samples oxidized at 1200°C and ring-compressed at 135°C and 0.033 mm/s