Update on Breakaway Oxidation of Westinghouse ZIRLO Cladding

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1. Introduction

The results of previous ANL studies for the breakaway oxidation of ZIRLO cladding are published in NUREG/CR-6967 [1]. The ANL criterion for breakaway oxidation is the time corresponding to 200-wppm hydrogen pickup. Zircaloy-4 and ZIRLO materials tested retained ductility (based on ring compression tests at 135ºC) at ≤440±110 wppm hydrogen pickup and were brittle at ≥770±120 wppm hydrogen pickup. The ± value represents one standard deviation based on hydrogen measurements for four arc segments of each 8-mm-long compressed ring. Because of the rapid hydrogen pickup with time, the transition between ductile and brittle behavior was as short as 200 s. Thus, 200-wppm hydrogen pickup is a reasonably conservative criterion for breakaway oxidation based on embrittlement.

The cladding materials used for those studies included ZIRLO received from Westinghouse (W) in 2003 (ZIRLO-2003) and in 2006 (ZIRLO-2006), ZIRLO-2006 modified by ANL by machining a 20-μm deep scratch into the cladding wall along the length of the sample (ZIRLO-2006MS), and ZIRLO received from W with a thin (<1 μm) oxide layer grown at low temperature in pressurized water (ZIRLO-PF, where PF refers to pre-filmed). All results reported in Ref. 1 were generated using a long quartz-tube stream chamber (686-mm long). At the time Ref. 1 was published, ANL was not able to demonstrate the early breakaway times for ZIRLO in a short (610-mm long) steam chamber, based on a very limited number of tests conducted.

At 1000ºC, the minimum breakaway time was determined to be ≈4000 s based on tests at 3600s (60-wppm H pickup), at 4000 s (130-wppm H pickup), and at 4200 s (630-wppm H pickup). As breakaway oxidation is an instability phenomenon due to local transformation from the strong, protective, tetragonal oxide phase (lustrous black in appearance) to the weak, non-protective, monoclinic oxide phase (yellow in appearance for ZIRLO), multiple tests under the same time-temperature conditions would have generated scatter of at least ±200 s at 1000ºC. Thus, the time for ZIRLO breakaway was assessed to be 4000±200 s based on the limited data set generated. Another factor considered in establishing the ±200 s has to do with the temperature ramp rate. The test times reported by ANL include the duration from the initiation of the temperature ramp from 300ºC to the end of the 1000ºC heating phase. Typical ANL heating curves consisted of a very fast ramp from 300-950ºC in <20 s and a slower ramp from 950-1000ºC in ≈60 s to limit the short-time temperature overshoot to ≤10ºC. Thus, the breakaway times reported by ANL in Ref. 1 included a ramp time of ≈80 s.

Tests at higher (1015ºC) and lower (950-985ºC and 800ºC) temperatures were conducted to determine the temperature sensitivity of breakaway oxidation and the minimum breakaway oxidation time. Based on a more extensive data set for as-fabricated, machine-scratched, and pre-filmed ZIRLO, 3100±300 s was determined to be the minimum breakaway time within the temperature range of 970-985ºC. These studies were conducted in two campaigns with separate test trains and associated thermal benchmarks: tests with as-fabricated ZIRLO-2006 and machine-scratched ZIRLO-2006MS within a wide temperature range; and tests with ZIRLO-2006 and pre-filmed ZIRLO-PF within a narrow temperature range (970-985ºC). Results for two samples tested with a machined scratch suggested that an initial stress discontinuity had little (<200 s) effect on the breakaway time. The tests with pre-filmed ZIRLO demonstrated that a thin oxide layer grown at reactor-relevant temperature had no significant effect on breakaway oxidation time. Perhaps coincidentally, the minimum breakaway time was found to occur close to the estimated phase change ($\alpha+\beta \rightarrow \beta$) temperature for ZIRLO. The equilibrium phase change

temperature for the Zr-(1.3-1.7)Sn-0.12O-FeCr alloy Zry-4 is about 980ºC and the phase change temperature for the Zr-1Nb-0.14O alloy M5 is about 965ºC. These temperatures increase during transient heating, and they decrease as a function of increasing hydrogen content. The Zr-1Sn-1Nb-0.12O alloy ZIRLO is expected to have an $\alpha+\beta \rightarrow \beta$ equilibrium phase change temperature in the range of 965-980ºC.

Westinghouse generated an independent data set for ZIRLO, as well as for Zry-4, oxidized for 4400 s and 5400 s at temperatures in the range of 950-1020ºC [2]. Although breakaway oxidation was observed for W 15×15 Zry-4 after 4400 s, no breakaway was observed for 17×17 ZIRLO up to 5400 s. In an effort to resolve these differences, W, ANL and NRC representatives met at ANL on May 13, 2008 to compare test methodologies and results. In addition to the difference in heating method (resistance furnace for W, radiant furnace for ANL), different cleaning methods were used in accordance with ASTM standards. Westinghouse used a chemical detergent (Alconox) to clean samples prior to water rinsing, while ANL used an organic solvent (ethanol) prior to water rinsing. Although it was not anticipated that differences in sample cleaning methods would account for the differences in results, it was the easiest difference to test and possibly eliminate. It should be noted that ANL used ethanol to clean pre-oxidized (pre-filmed) ZIRLO samples. For these samples, ethanol never came into contact with the ZIRLO metal. Therefore, the early breakaway times observed for the pre-oxidized samples could not have resulted from an ethanol-metal surface reaction during cleaning.

Following the meeting, Westinghouse sent to ANL ten samples of W-cleaned ZIRLO (ZIRLO-WC), as well as a new supply of ZIRLO (ZIRLO-2008). In exchange, ANL sent to W ANL-cleaned samples. The purpose of this letter report is to describe the results of new tests performed by ANL with both W-cleaned (Alconox) and ANL-cleaned (ethanol) ZIRLO samples. To help resolve the issue of long vs. short steam chambers, these new tests were conducted using both steam chambers.

2. Materials

ANL measured the outer diameter, wall thickness, surface roughness and hydrogen content for the new test materials. Table 1 shows the comparison among materials from the ZIRLO received in 2003 though the ZIRLO received in 2008. Although it was clear from earlier testing that changes were made to the surface finish for the inner-surface of the cladding, no significant differences were found regarding the cladding outer-surface dimension and roughness, as well wall thickness and hydrogen content.

Table 1 Characterization of Westinghouse 17x17 ZIRLO Cladding

Parameter	ZIRLO 2003	ZIRLO 2006	ZIRLO 2008	W-cleaned ZIRLO-WC
Outer Diameter, mm	9.50	9.48	9.50*	9.50
Wall Thickness, mm	0.57	0.568 ± 0.003	0.578±0.006	0.584±0.003
OD Surface Roughness, μm	0.11±0.01	0.17±0.03	0.14±0.03	0.16±0.01
H Content, wppm	5±0	11±3	17±2	22±2
O Content, wppm	1185±30	1164±26	---	---

*Note: OD = 9.48±0.03 mm based on measurements at 90 locations along the 11 m of tubing.

3. Test Matrices and Results

Reference 3 describes the planned test matrix for this comparison study. Initial tests were conducted at 1000ºC in a long steam chamber. Additional tests at 970-985 ºC were conducted in a shorter steam chamber in two separate campaigns. Test conditions and results are described in the following.

3.1 Tests at 1000ºC in long steam chamber

Initial oxidation tests were conducted in a long steam chamber with the standard-length test train. W-cleaned and ANL-cleaned samples were oxidized for 4000 s at 1000ºC. The thermal benchmark for these tests is shown in Fig. 1. The benchmark was performed for a long-time hold temperature of 975±5ºC at which additional tests were to be conducted to find the minimum breakaway time. The circumferential temperature variation of 10ºC is based on the readings of the two TCs welded onto the sample. It should be noted that the TCs welded onto the sample reached 975ºC in ≈80 s, experienced a 10ºC overshoot from 80 s to 160 s, and then decreased to a hold temperature of 975ºC for the time period of 1400 to 2800 s. The slow decrease from 980 to 975ºC occurred during a period in which the control thermocouple had a constant reading and the furnace power was constant. The drift in the sample-welded TC may have been the result of an oxide layer growing between the TCs welded to the sample and the metal surface. As such, in addition to ±5ºC circumferential temperature variation, there may be a 5ºC uncertainty in long-time sample TC readings. In order to achieve a long-time hold temperature of 1000ºC, the furnace power was increased based on the relationship established in the benchmark between the furnace power, the holder control TC, and the sample TC.

Figure 2 shows the visual appearance of the two test samples. It is clear that the ANL-cleaned sample experienced more extensive breakaway oxidation than the W-cleaned sample. However, although barely visible in Fig. 2, the W-cleaned sample had small yellow spots on the outer surface indicating that it was very close to breakaway oxidation. Table 2 summarizes the results of these two tests in the context of results for previous tests conducted at an oxidation temperature of 1000ºC. The ANL-cleaned sample, with the extensive yellow regions, picked up 400±240 wppm hydrogen, while the W-cleaned sample picked up 120±110 wppm hydrogen. The hydrogen results for the W-cleaned sample indicate that local breakaway oxidation had occurred. Based on ANL experience, the W-cleaned sample was < 200 s away from >200 wppm hydrogen pickup after 4000 s at 1000ºC. As shown in Table 2 and Fig. 3, this result is consistent with results previously obtained for ANL-cleaned samples. Thus, for an oxidation temperature of 1000ºC, no significant effects of Alconox vs. ethanol cleaning were observed.

Metallography was performed for the W-cleaned sample to verify that local breakaway of the outer surface oxide was responsible for the hydrogen pickup. Images were taken at the standard eight locations corresponding to angular orientations separated by ≈45º. One location indicated breakaway of the outer-surface oxide (see Fig. 4a) which includes both cracked monoclinic outer-surface oxide and tetragonal oxide. For the other seven locations, no tetragonal-to-monoclinic phase change was observed at the outer surface. For all eight images, the inner-surface oxide showed no signs of the transformation or breakaway oxidation. The metallographic results are consistent with the local hydrogen readings: high hydrogen content under yellow spots and low hydrogen content in regions under lustrous black oxide.

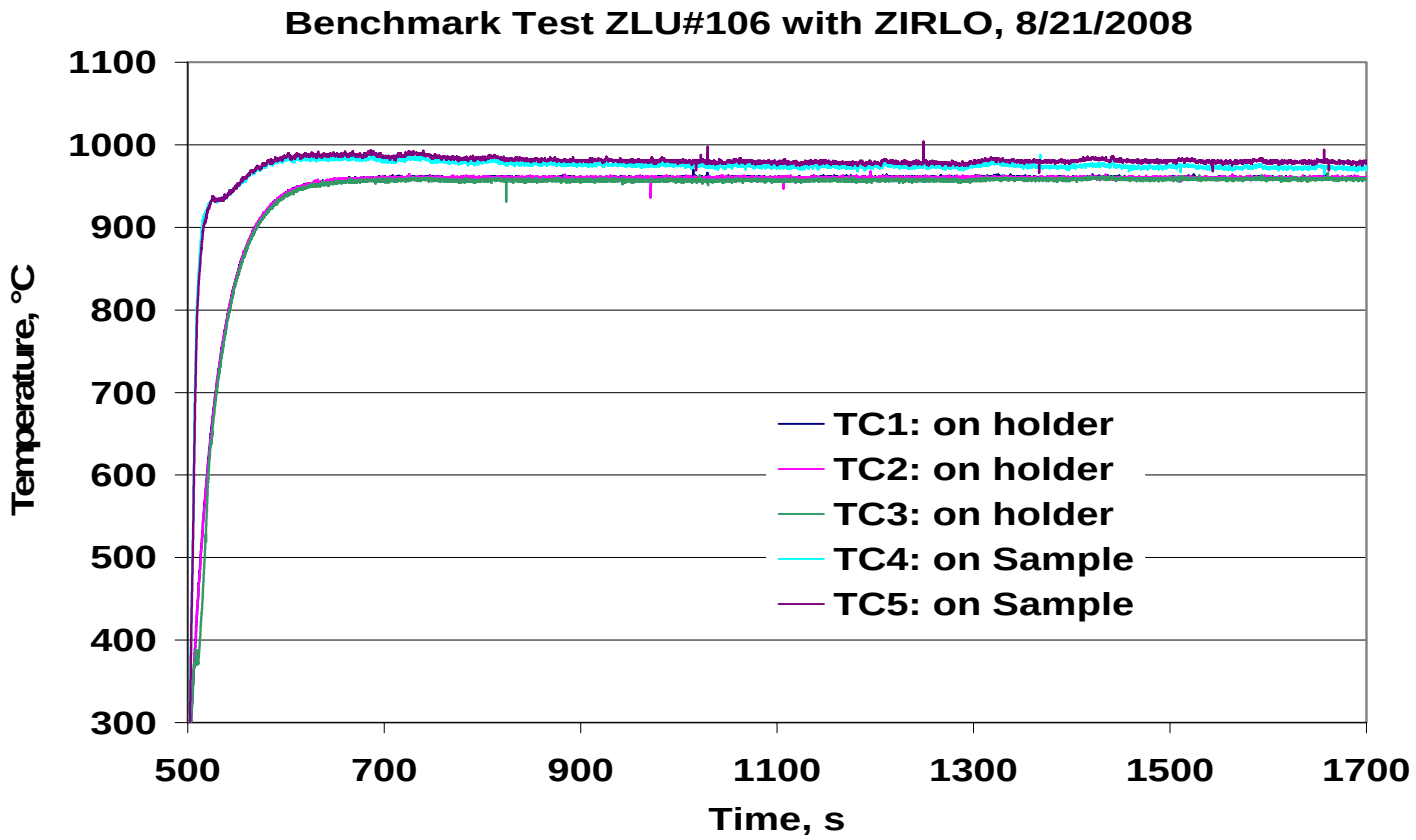


Fig. 1. Thermal benchmark results with two TCs welded onto as-fabricated, 17×17 ZIRLO-2008 cladding. The long-time sample hold temperature was 975±5ºC, where 975ºC is the average of the two sample TC readings.

Table 2 Results of ZIRLO Oxidation Tests at 1000ºC (see Table 1 for description of ZIRLO materials)

Material	Test Time[a], s	Measured Weight Gain, mg/cm^2	LECO H-content L_H, wppm	H-pickup[b] ΔC_H, wppm	Comment
ZIRLO-2006	1500	8.7	15	5	---
ZIRLO-2003	2440	10.8	36	30	---
ZIRLO-2003	3480	11.7	102	100	ID Oxide Breakaway
ZIRLO-2006	3600	11.4	68	60	---
ZIRLO-2006	4000	12.6	131±12	130±10	---
ZIRLO-2008	**4000**	**13.3**	**390±220**	**400±240**	**See Fig. 2**
ZIRLO-WC	**4000**	**12.6**	**130±100**	**120±110**	**See Fig. 2**
ZIRLO-2006	4200	14.3	610±370	630±400	

[a]Time from ramp initiation at 300ºC to end of hold temperature; ramp time is ≈80 s.

[b]Hydrogen pickup (ΔC_H) referenced to as-fabricated sample weight: $\Delta C_H = (1 + 5.4\times10^{-3}\ Wg)\ L_H - C_{Hi}$, where C_{Hi} is as-fabricated hydrogen content and Wg is measured weight gain.

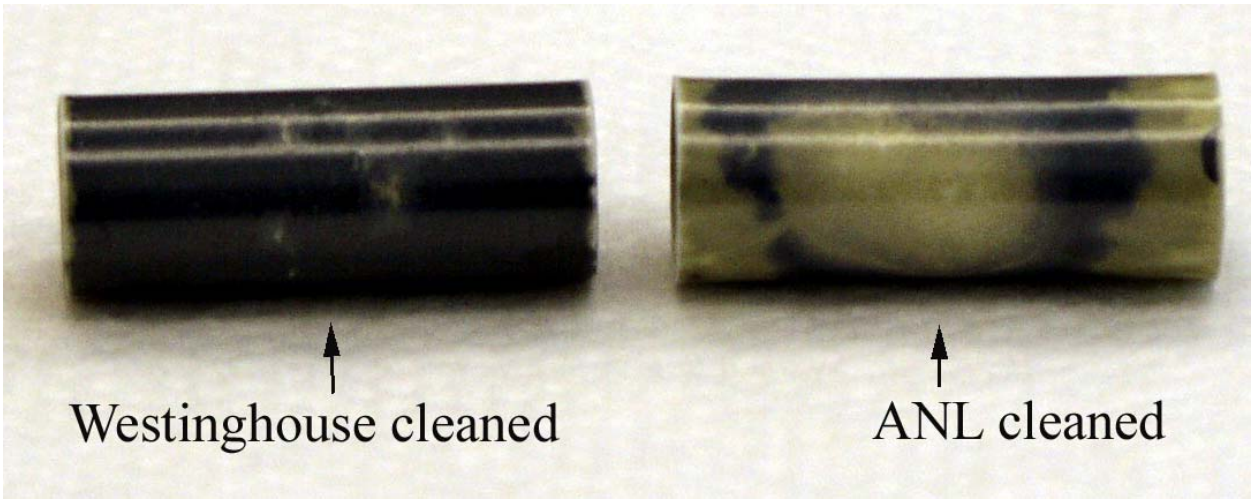


Fig. 2. Surface appearances of W-cleaned and ANL-cleaned ZIRLO samples after 4000 s at 1000ºC oxidation temperature. The W-cleaned sample has small yellow spots on the outer surface indicating very local breakaway oxidation.

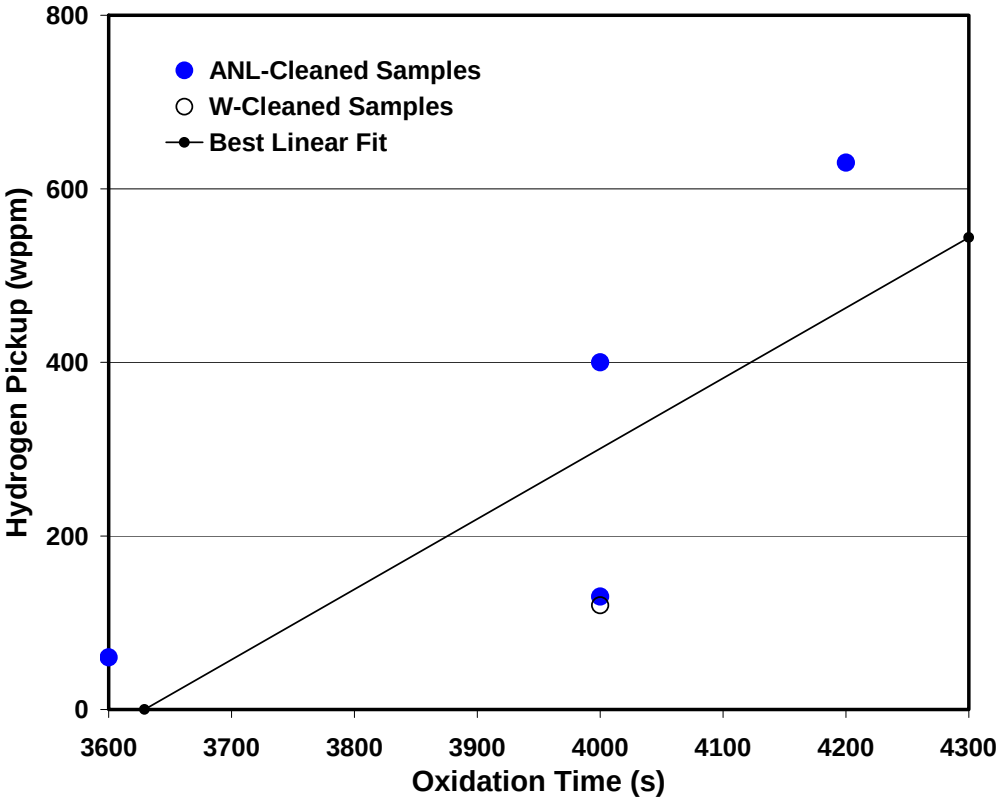
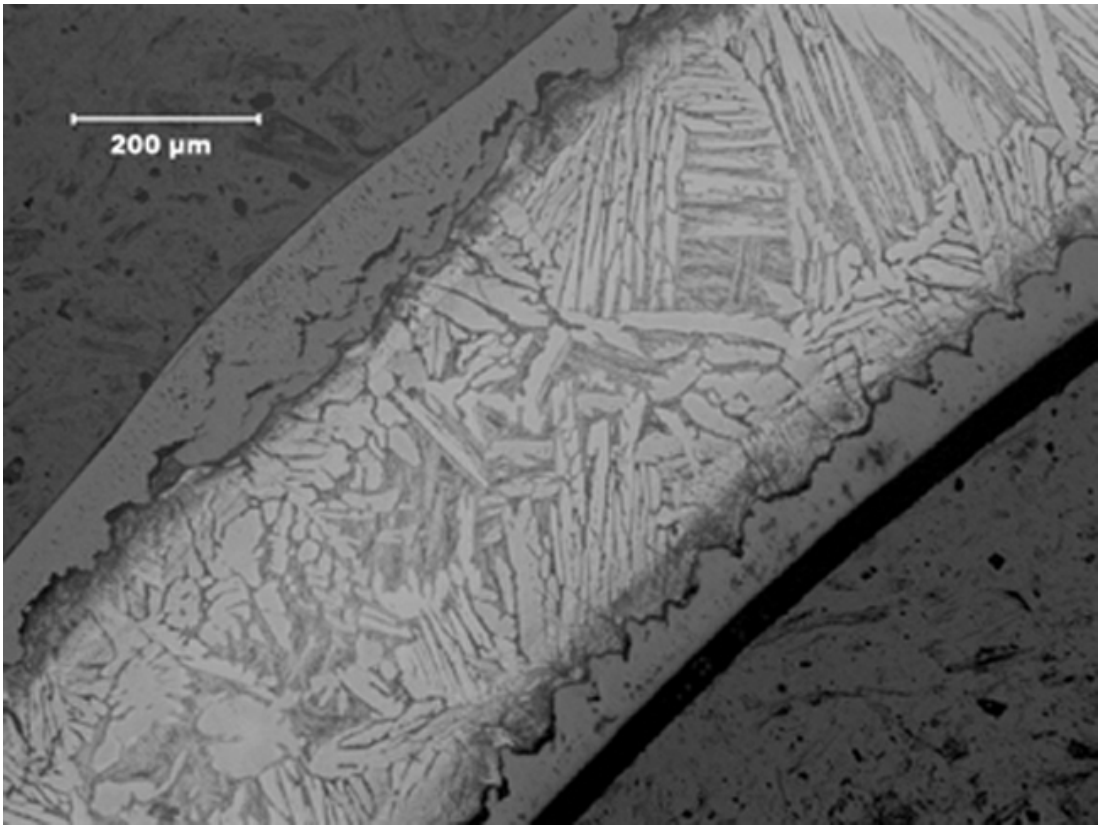


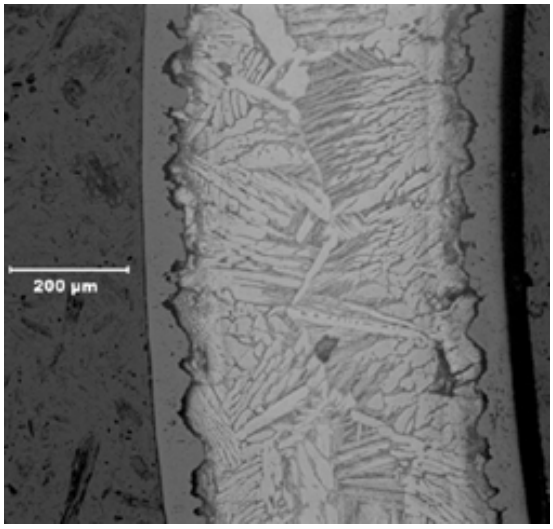
Fig. 3. Hydrogen pickup for ANL-cleaned and W-cleaned ZIRLO samples oxidized at 1000ºC in steam. ANL breakaway oxidation criterion is time to pick up 200-wppm hydrogen.

The hydrogen content shown in Fig. 3 for the new ANL-cleaned sample was measured for a 2-mm-long ring sectioned from near the center of the sample. An 8-mm-long ring was sectioned from the adjacent area and subjected to a ring-compression test at 135ºC. The sample proved to be extremely brittle and failed at a much lower load than other samples tested. The hydrogen content measured for the 8-mm long, compressed ring (555±133 wppm) was even higher than for the central 2-mm-long ring (390±220 wppm). The corresponding hydrogen pickup for the 8-mm-long ring is 600±150 wppm. This ring-compression data point is plotted in Fig. 5, along with the data in NUREG/CR-6967 Fig. 63, to better define the hydrogen range for ductile-to-brittle transition for breakaway oxidation samples. Based on Fig. 5, the ductile-to-brittle transition hydrogen level for breakaway-oxidation samples oxidized at ≤1000ºC is between 440 and 600 wppm. Based on interpolation, the ductile-to-brittle transition hydrogen pickup is estimated to be ≈500±50 wppm. It should also be noted that the circumferential variation in hydrogen content (> ±100 wppm) is very large for average hydrogen contents in this range (see Fig. 6).

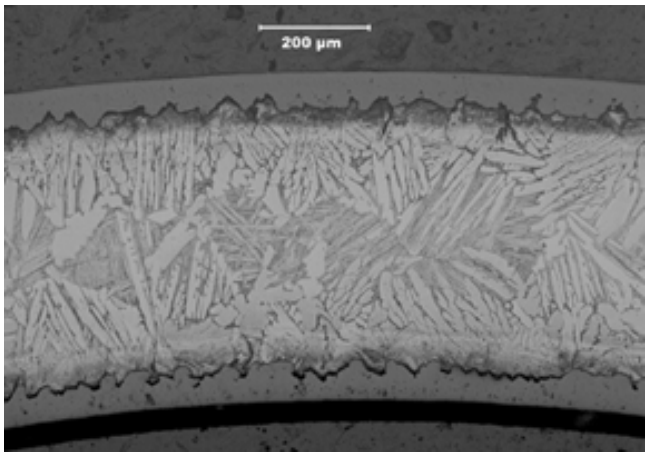
In accordance with Ref. 3, three tests were conducted with machine-scratched ZIRLO-2008 samples oxidized for 3600 s at target temperatures of 1000ºC, 985ºC, and 970ºC. However, prior to running these tests, the LOCA apparatus was moved for display purposes and returned to its approximate location in the lab. As the apparatus was not "leveled" after this movement, the actual oxidation temperatures are uncertain. None of these samples experienced significant hydrogen pickup or showed signs of yellow oxide on the surface. For completeness, these results are presented in Appendix A. However, due to temperature uncertainty, the results are not used in the determination of breakaway oxidation time.



(a) Area 8: local hydrogen content > 280 wppm under yellow outer-surface spot



(b) Area 7



(c) Area 1

Fig. 4. Metallographic images at the same cross section for the W-cleaned sample oxidized for 4000 s at 1000ºC: (a) Area 8, which exhibits an outer-surface arc length of ≈0.4 mm with monoclinic oxide; (b) Area 7 with tetragonal oxide; and (c) Area 1 with tetragonal oxide.

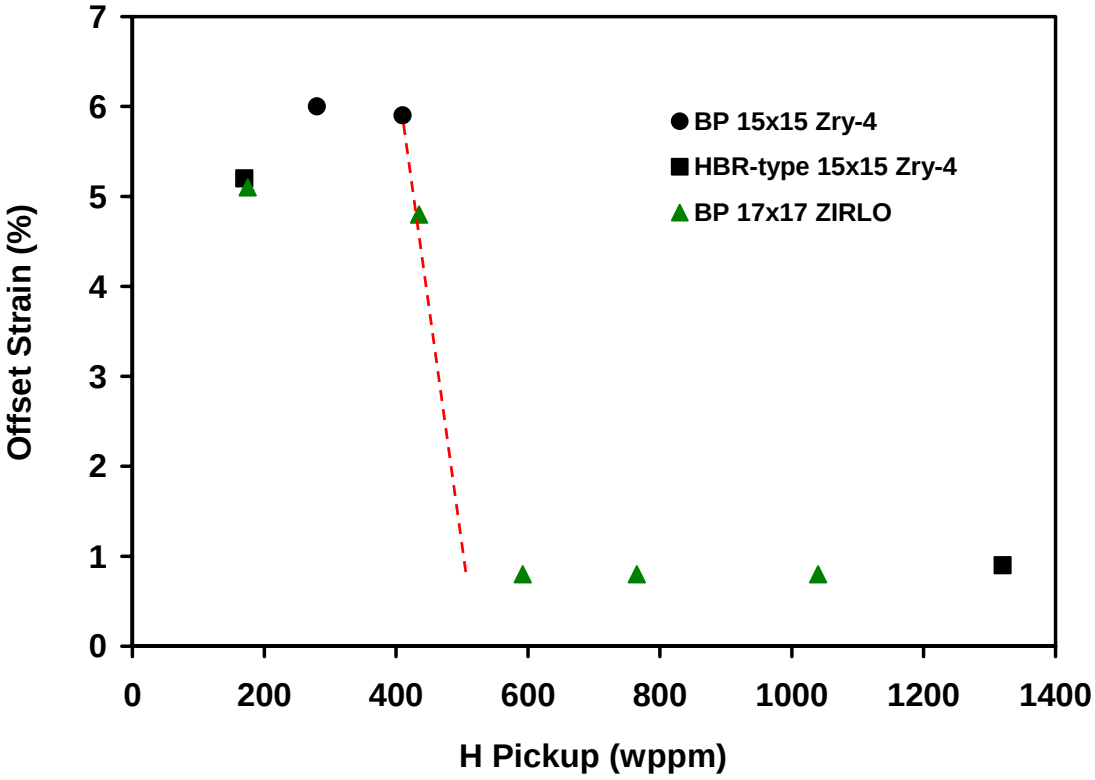


Fig. 5. Offset strains at 135ºC for Zry-4 and ZIRLO rings following oxidation at 970-1000ºC, local-to-global breakaway oxidation, and cooling without quench.

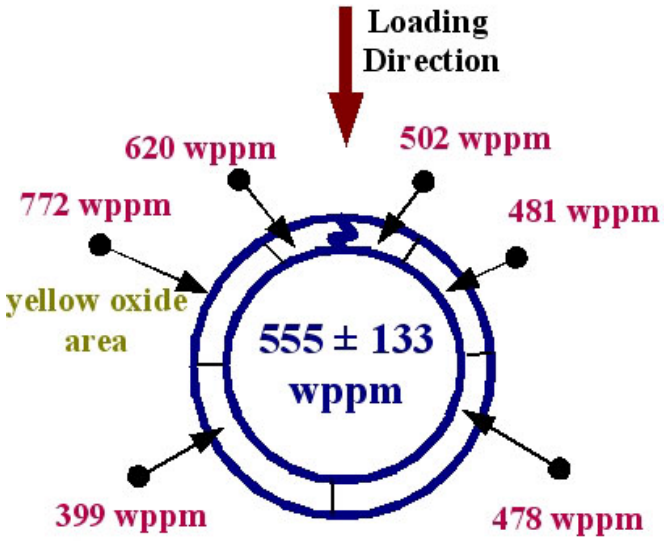


Fig. 6. Circumferential variation in hydrogen content measured after ring-compression testing for an 8-mm-long ring sectioned from an ANL-cleaned sample oxidized at 1000ºC for 4000 s.

3.2 Tests at ≈980ºC in short steam chamber with temperature overshoot

Concurrent with breakaway oxidation studies, a test train for a shorter steam chamber was thermally benchmarked for a hold temperature of 1200ºC to conduct high-temperature embrittlement tests. It was time-consuming to switch back and forth between test trains and chambers for breakaway and high-temperature embrittlement studies. Therefore, a short test chamber was used for the next sequence of breakaway tests, and the furnace power was scaled to give a long-time hold temperature of ≈985ºC. Two tests were run with W-cleaned samples oxidized for 3200 s, and one test was run with an ANL-cleaned sample oxidized for 3400 s. All three samples exhibited significant yellow areas on the outer surfaces indicating extensive breakaway. Following these tests, TCs were welded onto a fresh ZIRLO sample to determine more precisely the temperature history. As shown in Fig. 7, the scaling of furnace power resulted in a long-time hold temperature of 981±4ºC (≈980±5ºC). However, unlike other histories, this one had considerable overshoot early in the transient. The cladding temperature rose rapidly (18 s) to ≈1065ºC and was above 985ºC for ≈20 s. Other than a faster rise to high temperature, it is not clear what effect an early temperature excursion would have on breakaway oxidation occurring ≈3000 s later. As the purpose of the tests was to compare the performance of ANL- and W-cleaned ZIRLO samples exposed to the same steam flow and temperature conditions, the results from this series of tests are considered valid for that purpose. The hydrogen pickup was high (≈700 wppm) for the samples and well beyond the 200-wppm hydrogen-pickup criterion for breakaway. The results (see Table 3 and Fig. 8) are significant because there was no apparent difference between the W- and ANL-cleaned samples. Also, for the first time at ANL, breakaway oxidation was observed using a short steam chamber.

3.3 Tests at 985ºC in short steam chamber with no temperature overshoot

The third set of tests was conducted with the same short test train and steam chamber as was used to generate the results reported in 3.2. However, the control parameters were reset to eliminate temperature overshoot. The temperature history determined from the new thermal benchmark is shown in Fig. 9. The long-time hold temperature was 975±3ºC. Also shown in Fig. 9 are the histories of the control TC and one other TC, both welded to the sample holder. The control TC readings are only a few degrees lower than the sample readings. As it was determined that these tests would be conducted at 985ºC, the control TC was reset to give an increase of 10ºC and a corresponding sample temperature of 985ºC (985±5ºC). One ANL-cleaned sample was oxidized for 3500 s with a corresponding hydrogen pickup of 720 wppm. The companion test with the W-cleaned sample picked up only 20 wppm after 3500 s. An additional test was run for 3800 s with a W-cleaned sample. The hydrogen pickup at 3800 s was beyond 200 wppm (270 wppm) indicating a breakaway time of ≈3700 s. Although breakaway oxidation was delayed for the W-cleaned samples, the results may be within data scatter for this oxidation temperature.

Table 3 summarizes the new results generated in the temperature range of 980-985ºC, as well as previous results generated for as-fabricated, machine-scratched, and pre-filmed ZIRLO in the temperature range of 970-985ºC. Hydrogen pickup values are plotted in Fig. 10 as a function of test time for all data in Table 3. Based on these results, as well as expected data scatter for an instability phenomenon such as breakaway oxidation, it is clear that effects of Alconox (W) vs. ethanol (ANL) pre-test cleaning are not large enough to explain the differences in W (>5400 s) and ANL (≈3100 s) minimum oxidation times.

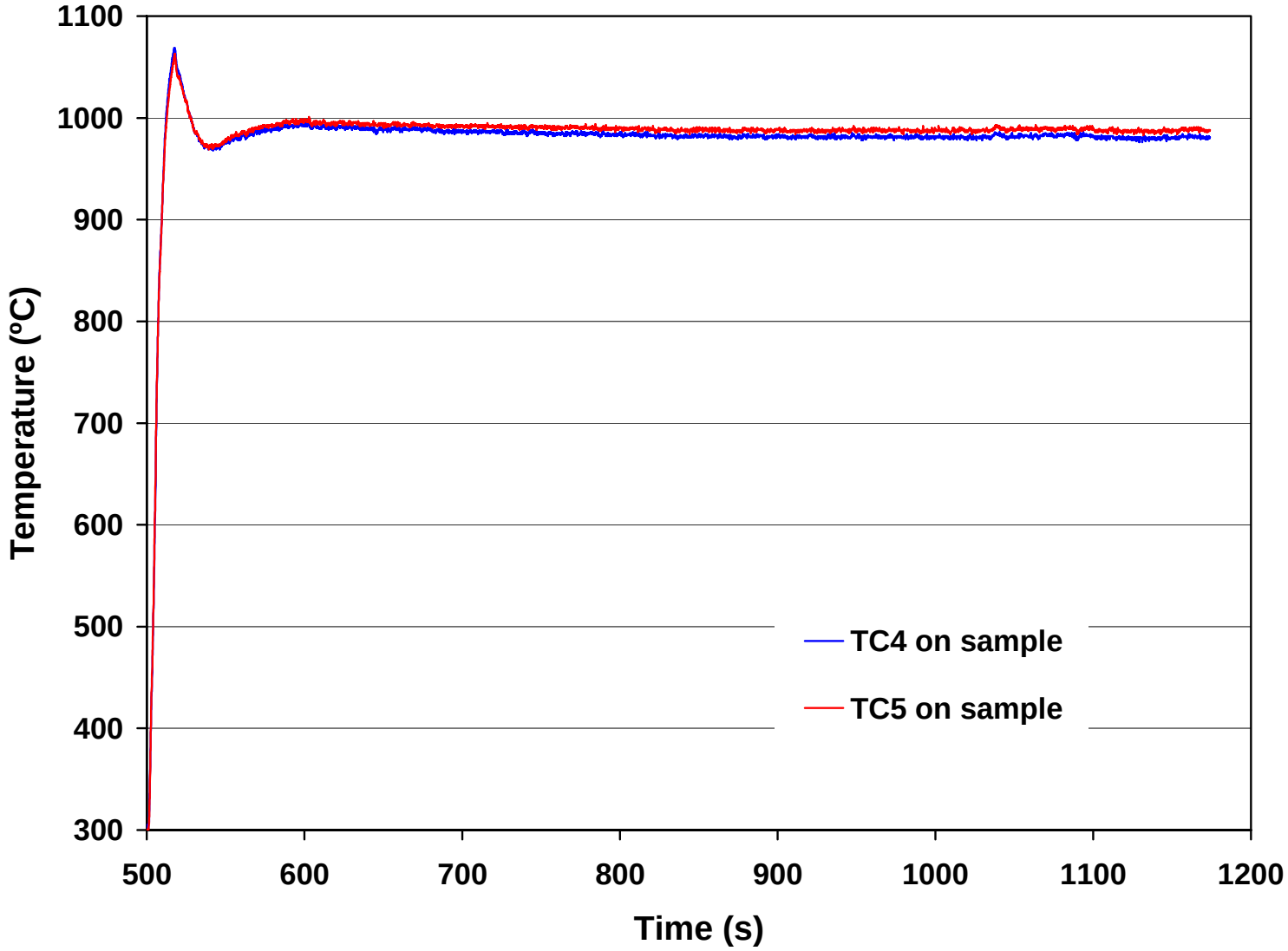
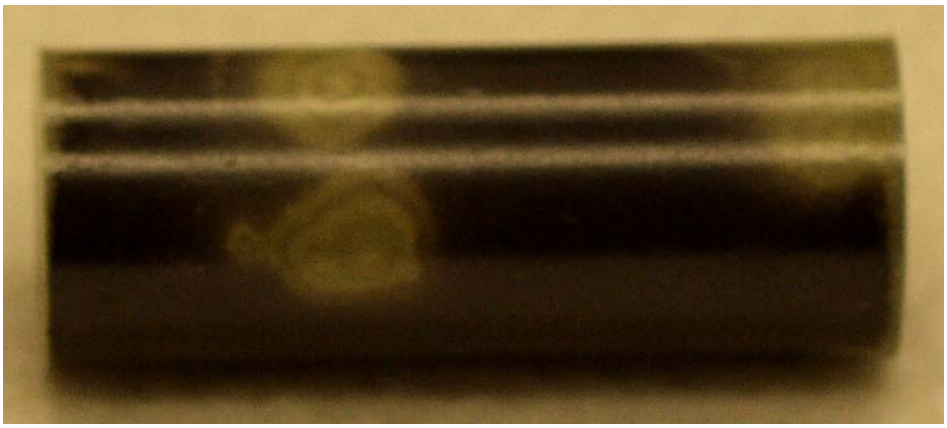
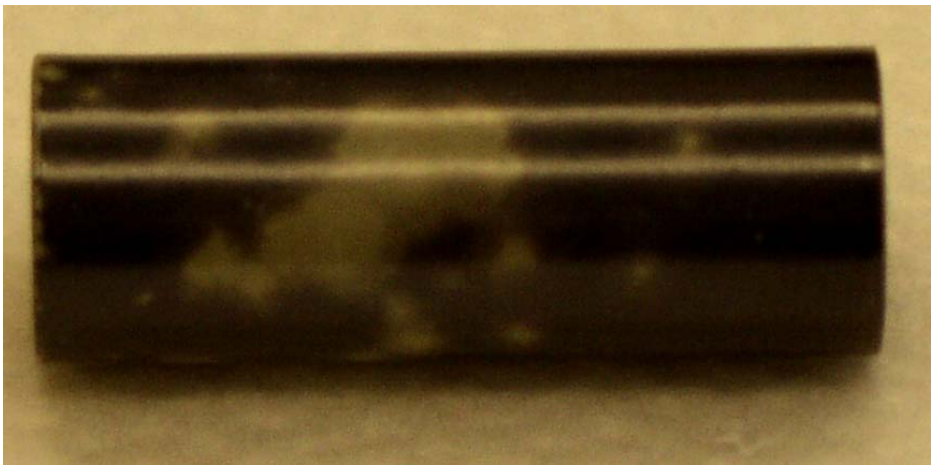


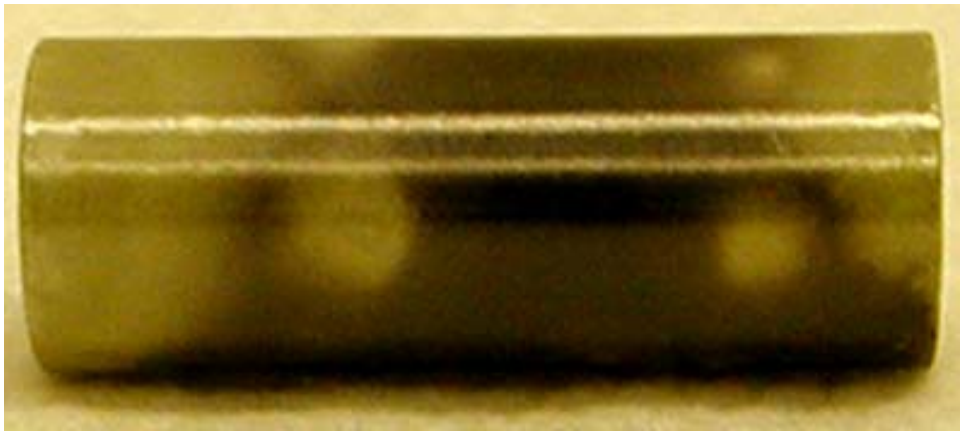
Fig. 7. Thermal benchmark results for test ZLU#129. Overshoot was ≈1065ºC and long time hold temperature was about 980±5ºC.



(a) ANL-cleaned sample after 3400 s at 980ºC



(b) W-cleaned sample #1 after 3200 s at 980ºC



(c) W-cleaned sample #2 after 3200 s at 980ºC

Fig. 8. Surface appearances of ANL-cleaned and W-cleaned samples after oxidation at 980ºC: (a) ANL-cleaned sample after 3400 s; (b) first W-cleaned sample after 3200 s; and (c) second W-cleaned sample after 3200 s.

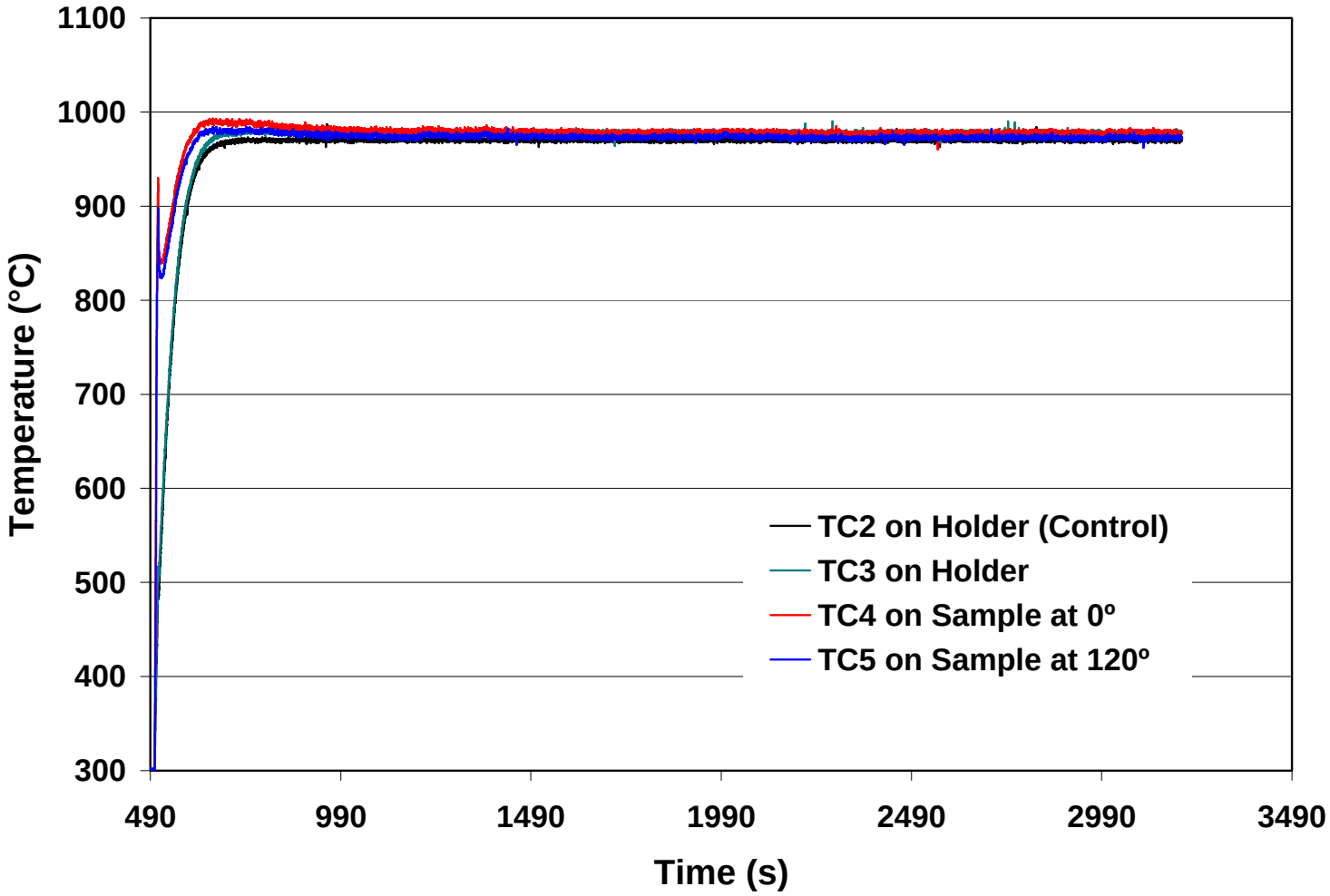


Fig. 9. Thermal benchmark results for test ZLU#132. Long-time hold temperature is 975±3ºC. The holder control temperature was increased by 10ºC for data generating tests. The long-time sample temperature for the data-generating tests was increased to 985±5ºC.

Table 3 Results of ZIRLO Oxidation Tests at 970-985ºC (see Table 1 for description of ZIRLO materials); results for new tests are listed in bold font

Material	Test T ºC	Test Time[a], s	Measured Weight Gain, mg/cm^2	LECO H-content L_H, wppm	H-pickup[b] ΔC_H, wppm	Comment
ZIRLO-2006MS	970	2600	7.8	50	40	Scratched
ZIRLO-2006	970	3000	8.1	200±150	200±160	---
ZIRLO-2006	970	3400	8.6	570±90	580±90	
ZIRLO-2006	975	3000	9.0	40	30	---
ZIRLO-2006	975	3500	8.7	110±50	100±50	---
ZIRLO-2006	980	3000	11.8	350±120	370±130	
ZIRLO-PF	980	3200	8.7	130±120	120±120	
ZIRLO-PF	980	3200	8.8	100±100	100±100	
ZIRLO-WC	**980**	**3200**	**8.4**	**690±90**	**700±100**	**W-cleaned T-overshoot**
ZIRLO-WC	**980**	**3200**	**8.4**	**630±120**	**650±120**	**W-cleaned T-overshoot**
ZIRLO-2008	**980**	**3400**	**11.4**	**---**	**---**	**Breakaway T-overshoot**
ZIRLO-2006	985	3000	9.1	100±40	100±40	---
ZIRLO-PF	985	3000	9.0	60	50	Pre-filmed
ZIRLO-2006	985	3400	9.6	50	40	---
ZIRLO-2006MS	985	3400	9.9	180±140	170±150	Scratched
ZIRLO-2006	985	3400	9.4	300±160	310±170	
ZIRLO-PF	985	3400	9.3	260±140	260±150	Pre-filmed
ZIRLO-2008	**985**	**3500**	**9.5**	**700±120**	**720±120**	**---**
ZIRLO-WC	**985**	**3500**	**9.2**	**40**	**20**	**W-cleaned**
ZIRLO-2006	985	3600	10.0	280±160	280±170	---
ZIRLO-WC	**985**	**3800**	**8.9**	**280±60**	**270±60**	**W-cleaned**
ZIRLO-PF	985	4000	11.9	1070±90	1130±100	Pre-filmed
ZIRLO-2006	985	4000	11.8	850±140	890±150	---

[a]Time from ramp initiation at 300ºC to end of hold temperature.

[b]Hydrogen pickup (ΔC_H) referenced to as-fabricated sample weight: $\Delta C_H = (1 + 5.4\times10^{-3}\ Wg)\ L_H - C_{Hi}$, where C_{Hi} is as-fabricated hydrogen content and Wg is measured weight gain.

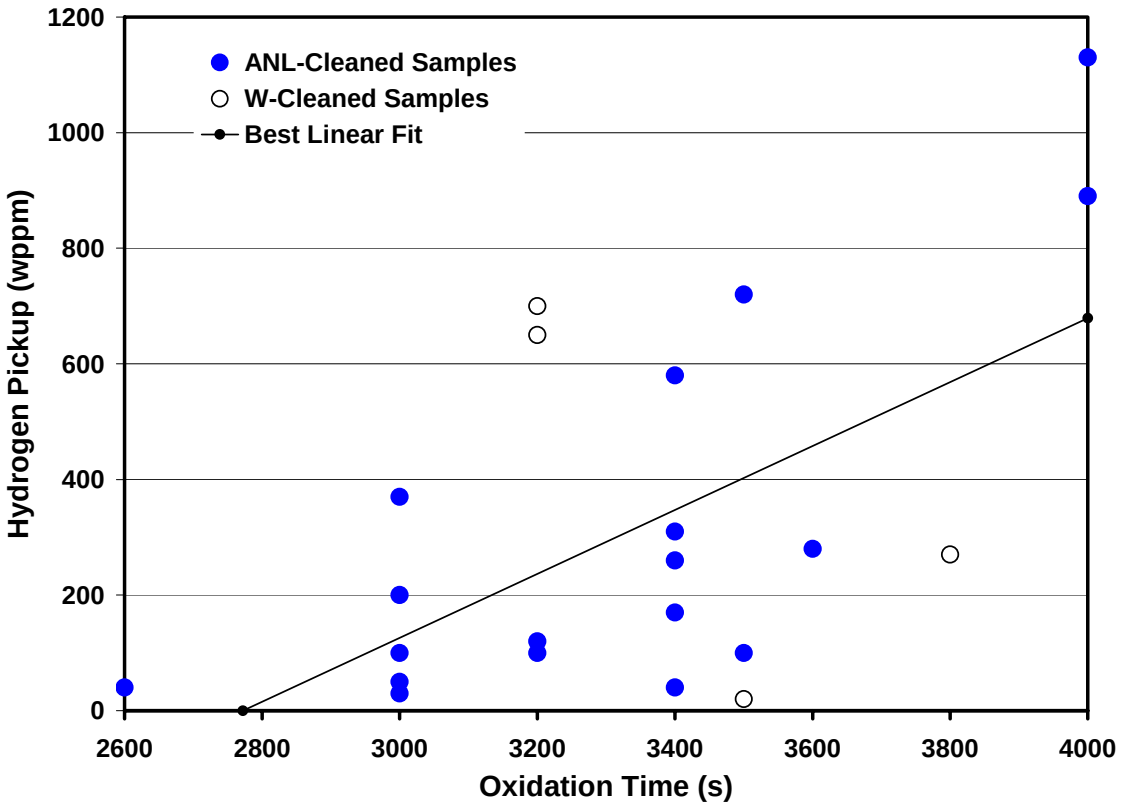


Fig. 10. Hydrogen pickup for ANL-cleaned and W-cleaned samples oxidized at 970-985ºC in steam. ANL-cleaned samples include as-fabricated, machine-scratched (20-µm depth), and pre-filmed (<1-µm oxide) ZIRLO. Breakaway oxidation criterion is time to pick up 200-wppm hydrogen.

4. Discussion

Based on results of tests conducted at 1000ºC for 3600-4200 s – four with ANL-cleaned samples and one with a W-cleaned sample, no effect of Alconox (W) cleaning vs. ethanol (ANL) cleaning could be observed. The breakaway oxidation time for ZIRLO cladding oxidized at 1000ºC remains at 4000±200 s. It is anticipated that additional tests conducted by ANL at 1000ºC would also give breakaway times within this range. However, it remains unclear as to why Westinghouse does not observe breakaway at 1000ºC for test times of 4400 s and 5400 s [2]. It should be noted that the appearance of the outer-surface oxide may be deceiving. Based on the photograph of the W-cleaned sample (Fig. 2), it does not appear that the sample has experienced any significant breakaway. The yellow spots observed on the surface are very small. However, hydrogen measurements indicated a significant hydrogen pickup (>280 wppm) in a quarter section of the ring containing small yellow spots. Although the average hydrogen pickup (120±110 wppm) is <200-wppm (breakaway criterion), it is clear that 200-wppm hydrogen pickup would be exceeded in <200 s of additional oxidation time. Metallographic images for the W-cleaned sample were very revealing because the test was terminated early in the breakaway process. One of the eight cross-sectional areas indicated cracked monoclinic oxide at the outer surface spanning an arc length of ≈0.4 mm (≈1% of the circumference), while the other images at ≥45º from this location indicated the wavy, scalloped oxide-metal interface reported by Leistikow and Schanz [4,5] as a precursor to monoclinic oxide formation, but no monoclinic oxide formation.

Because of the relative "predictability" of breakaway oxidation time for ZIRLO at 1000ºC, it is recommended that a detailed comparison be made for W-tested and ANL-tested samples oxidized at this temperature. The new tests Westinghouse will perform in their improved apparatus should be used for the comparison, which should include weight gain for pre-breakaway samples and high-resolution metallographic images of the oxide-metal interface showing the amplitude and wave length of the scalloping. Westinghouse will oxidize ZIRLO samples at 1000ºC, as well as at 960-1010ºC, for 4400 s. If breakaway is observed by Westinghouse at 4400 s with either W- or ANL-cleaned samples, it is recommended that the oxidation time be lowered to ≈4000 s to generate pre-breakaway oxidation samples. It would add considerable insight into the breakaway process, as well as possible remaining differences between W and ANL results, to compare maximum amplitude of the scalloped oxide-metal interface.

As shown in Fig. 10, breakaway oxidation times as low as 3000 s have been observed by ANL following oxidation at 970-985ºC. Unlike the results at 1000ºC, there is considerable scatter within this highly sensitive temperature range. Previous results indicated a minimum breakaway time of 3100±300 s for as-fabricated, pre-scratched, and pre-filmed ZIRLO samples oxidized at 970-985ºC. These results were generated in two test campaigns with two independently calibrated test trains. Given that circumferential temperature variations within ANL's radiant heating furnace are ≈10ºC and long-time hold temperature readings from TCs welded onto the oxidizing sample drift downward by ≈5ºC, a smooth data trend is not expected for breakaway time vs. average temperature for 970-985ºC oxidation temperatures. Multiple tests (e.g., 10) conducted at 970, 980 and 985ºC for the same test time might generate as much scatter as shown in Fig. 10 for 3000-3800 s test times at different average temperatures.

The new results generated for several ANL-cleaned samples and four W-cleaned samples do exhibit scatter, but that scatter appears consistent with previous results. For two of the W-cleaned samples oxidized at 980ºC, there was excessive hydrogen pickup indicating < 3200-s breakaway oxidation time. For two other W-cleaned samples, the breakaway oxidation time was ≈3700 s, based on interpolation. The differences in behavior for these last two W-cleaned samples is not large enough to explain the >2000 s difference in W vs. ANL minimum breakaway oxidation times at 970-985ºC.

Both Alconox-cleaning and ethanol cleaning result in shinier ZIRLO outer surfaces relative to the as-fabricated ZIRLO that has been received from Westinghouse. Based on breakaway oxidation results for pre-oxidized (pre-filmed) ZIRLO cleaned with ethanol, it is clear that no detrimental ethanol-metal surface reaction occurs during ANL sample cleaning. The pre-oxidized samples, whose metal surfaces never came into contact with ethanol, exhibited the same breakaway oxidation behavior as bare ZIRLO samples, which had been cleaned in ethanol prior to testing..

5. Conclusions and Recommendations

No significant effects of Alconox (W) vs. ethanol (ANL) pretest cleaning were found on breakaway oxidation time for ZIRLO cladding samples oxidized at 1000ºC. After 4000 s at 1000ºC, the hydrogen pickup for both the ANL-cleaned sample (400 wppm) and the W-cleaned sample (120 wppm) were within expected data scatter. Combining the two new data points with three data points previously generated for 1000ºC oxidation temperature and test times of 3600-4200 s, the linear best fit to the data gives a minimum breakaway time of about 3900 s for 1000ºC. If additional tests were to be conducted by ANL at 1000ºC, it is anticipated that breakaway oxidation times would remain within the range of 4000±200 s.

Four new tests with W-cleaned samples and two new tests with ANL-cleaned samples were conducted within the narrow temperature range of 980-985ºC. Two W-cleaned samples had significant hydrogen pickup after 3200 s. Two other W-cleaned samples had delayed hydrogen pickup such that the breakaway time was interpolated to be ≈3700 s. The ANL-cleaned samples had high hydrogen pickup for oxidation times in the range of 3400-3500 s. Based on three testing campaigns, ANL has accumulated 23 hydrogen-pickup data points for oxidation temperatures within the range of 970-985ºC and test times in the range of 2600-4000 s. A best-fit line for the data indicates a minimum breakaway time of 3100 s. However, there is considerable data scatter for this oxidation temperature range. Most of the data are included in the minimum breakaway oxidation time of 3100±300 s for 970-985ºC. This breakaway time at 970-985ºC could be increased (e.g., to 3300±400 s) to encompass the new data generated for two of the W-cleaned samples. However, inclusion of these two data points does not change the best-estimate minimum breakaway oxidation time (3100 s). From that perspective, the previously recommended 3100±300 s is preferred for the minimum breakaway oxidation time for the ZIRLO tested at ANL.

At this point, it remains unclear as to why Westinghouse data indicate a minimum breakaway time for ZIRLO >5400 s for oxidation temperatures in the range of 950-1020ºC. Although the W-reported temperatures are not as precise as the ANL-reported temperatures, Westinghouse performed tests in 10ºC increments. Westinghouse is in the process of testing ANL-cleaned and W-cleaned samples in an improved test apparatus. Clearly, further comparisons of test procedures and results should occur after Westinghouse generates its new data set. If significant data discrepancy remains after Westinghouse's new study, particularly at 1000ºC oxidation temperature, then it is recommended that the next meeting among ANL, NRC, and W be conducted at Westinghouse Science and Technology Department (STD). This would allow ANL the opportunity to observe Westinghouse test procedures and tested samples. In addition, it would be very useful if Westinghouse were to generate some high-magnification images of the oxide layer for 1000ºC-oxidized samples with emphasis on the pre-breakaway scalloped metal-oxide interface. ANL would like to compare its results to W results for the amplitude of the scallops. The amplitude of the scallops, especially the maximum amplitude, grows with oxidation time and is a precursor to local tetragonal-to-monoclinic oxide transformation, as well as hydrogen pickup and breakaway.

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Appendix A

Results of Additional Tests with Machine-scratched, ANL-cleaned samples

Three tests were conducted in the LOCA apparatus after it was re-positioned without leveling the apparatus. These three tests used pre-scratched samples, "target" oxidation temperatures of 1000ºC, 985ºC, and 970ºC and a fixed test time (3600 s). It was anticipated that breakaway oxidation would occur along the machine scratches for the 985ºC and 970ºC samples. Figure 1 shows the thermal benchmark at 975ºC for the test train used. However, movement of the apparatus and repositioning it without leveling the base resulted in uncertainties in the actual sample temperatures. For completeness, the results are presented in Table A.1. However, due to the temperature uncertainty, these results were not used for data analysis. A comparison of measured weight gains for previous samples and the three samples listed in Table A.1 indicates that the actual temperatures are lower than the target temperatures.

Table A.1 Additional Tests Conducted with Machine-scratched ZIRLO-2008; target temperatures are listed, but actual sample temperatures are unknown

Material	Target Test T, ºC	Actual Test T, ºC	Test Time[a], s	Measured Weight Gain, mg/cm^2	LECO H-content L_H, wppm	H-pickup[b] ΔC_H, wppm
ZIRLO-2008MS	1000	<1000	3600	10.3	56±13	40±15
ZIRLO-2008MS	985	<985	3600	8.6	40±10	30±10
ZIRLO-2008MS	970	<970	3600	7.4	33±5	20±5

[a]Time from ramp initiation at 300ºC to end of hold temperature; ramp time is ≈80 s.

[b]Hydrogen pickup (ΔC_H) referenced to as-fabricated sample weight: $\Delta C_H = (1 + 5.4\times10^{-3}\ Wg)\ L_H - C_{Hi}$, where C_{Hi} is as-fabricated hydrogen content and Wg is measured weight gain.