Progress Report on Breakaway Oxidation of Bare and Prefilmed ZIRLO

Y. Yan, T. Burtseva and M. C. Billone
May 30, 2007

Summary

Breakaway oxidation results for as-fabricated (bare) ZIRLO are presented in the draft LOCA NUREG report. These results were generated in 2006 with the LOCA Oxidation Apparatus located in Lab G-117. Prior to conducting data-generating tests, furnace-control parameters were chosen to give a long-time hold-temperature of 1000ºC based on two thermocouples (TCs) welded 120º apart onto a ZIRLO sample and three TCs welded 120º apart on the holder just above the sample. For the data-generating tests, as-fabricated ZIRLO samples were oxidized with no thermocouples welded onto the sample surface. Temperature control was achieved through feedback from the holder control TC to the furnace power. Most of the tests were conducted in range of 950-1015ºC. A linear relationship was assumed between the holder temperature and the sample surface temperature. The results indicated that the breakaway oxidation time – time for a 2-mm-long ring sectioned from near the middle of the sample to pick up ≥200 wppm hydrogen – decreased as the oxidation temperature decreased from 1015ºC (>4000 s) to 1000ºC (4000 s) to 985ºC (3500 s) to 970ºC (3000 s). At 950ºC, the breakaway oxidation time was >3000 s, indicating a minimum breakaway time around 970ºC. However, given the temperature distribution around the cladding (±5-10ºC depending on the test train used) and the scaling method used for extrapolation to lower temperatures, the minimum breakaway oxidation time may occur within the temperature range of 970±15ºC.

As part of the study of the effects of surface finish and surface chemistry on breakaway oxidation, pre-oxidized (prefilmed) ZIRLO samples, supplied by Westinghouse, were subjected to breakaway oxidation tests. The ZIRLO samples (25-mm-long) were exposed to high-pressure water at 360ºC for 36 hours, which resulted in outer- and inner-surface oxide layers <1-µm thick. These conditions should be more representative of the cladding surface during a beginning-of-life LOCA. The prefilmed samples were oxidized at 975-985ºC to determine if the tight pre-oxide layer would increase the breakaway oxidation time.

Recently, the LOCA Oxidation Apparatus was moved to Lab EL-208, the quartz tube was replaced and a new test train was constructed. The movement resulted in a slight shift in the radial location of the uniform heating zone. Numerous thermal benchmark tests were conducted to determine the optimum position of the quartz-tube/test-train to minimize circumferential temperature gradients. Bare ZIRLO was used for the thermal benchmark, which gave a long-time hold temperature of 975±8ºC (see Fig. 1). Test results are listed in Table 1. Bare ZIRLO oxidized at 980ºC for 3000 s picked up 370±125 wppm H (post-breakaway), while oxidation at 985ºC for 3400 s resulted in 310±170 wppm H pickup (post-breakaway). A prefilmed sample oxidized at 985ºC for 3400 s picked up 260±145-wppm H (just beyond breakaway). Two prefilmed samples oxidized at 980ºC for 3200 s had 100±100 and 120±120 wppm H pickup. These results suggest a minimum breakaway oxidation time of 3300±100 s for prefilmed ZIRLO. The 2006 and 2007 results can be combined to conclude that the minimum breakaway-oxidation time for bare and prefilmed ZIRLO is 3200±200 s and occurs at 980±10ºC.

Discussion

Because breakaway oxidation is an instability phenomenon, data scatter could be significant from multiple tests conducted under the same oxidation conditions. Although the results in Table 1 suggest that the minimum breakaway time is highly sensitive to 5ºC changes in oxidation temperature, it is unlikely that this is the case. If multiple tests had been conducted at 975ºC, 980ºC, and 985ºC, it is more likely that there would be overlap in the data sets for hydrogen pickup vs. test time. This is especially true for the ANL test samples, which had a circumferential temperature variation of 16ºC.

For Zry-4 samples undergoing breakaway oxidation, generally gray areas (within circles or along axial bands) were observed on the cladding outer surface. For ZIRLO, these areas were yellow, instead of gray. It is not clear if the color is significant or indicative of a particular chemical impurity at the surface or within the substrate. However, the local hydrogen content is measured to be significantly higher under both gray (Zry-4) and yellow (ZIRLO) surface areas, as compared to under black areas, during the transition from stable oxide growth to breakaway oxidation. The large standard deviation in Table 1 for the pre- and post-breakaway samples is due to circumferential variation in hydrogen content. The ratio of this deviation to the average hydrogen content decreases with time-beyond breakaway due to more and more of the surface oxide transforming to the monoclinic phase, to hydrogen pickup through the larger monoclinic-oxide surface area, and to hydrogen diffusion in the cladding.

One of the samples in Table 1 was selected for metallographic examination: prefilmed ZIRLO oxidized at 985ºC for 3400 s with 260±145 wppm H pickup. The purpose of the metallographic imaging was to determine if breakaway oxidation of the outer surface was responsible for the hydrogen pickup. Metallographic images are shown in Figs. 6a-c. Figure 6a shows the cracks in the outer-surface oxide layer below the yellow surface area and the non-cracked inner-surface oxide layer, indicating that hydrogen pickup was through the outer-surface oxide layer. Figure 6b shows another circumferential location with the inner-surface oxide layer in a pre-breakaway oxide condition, most of the outer-surface oxide in pre-breakaway, and a small fraction of the outer-surface oxide with cracks, indicating transition to breakaway. Figure 6c shows a cross-sectional region under the black outer-surface oxide. No breakaway oxidation is observed for the outer- and inner-surface oxide layers. These results confirm that hydrogen pickup resulted from breakaway oxidation of the prefilmed outer surface of the ZIRLO sample.

No mechanism could be identified to suggest that the breakaway oxidation time for ZIRLO should be less than the breakaway time for Zry-4. However, it is difficult to compare the ANL results for Zry-4 and ZIRLO because the cladding alloys were fabricated by different vendors and possible differences in later-stage processes (e.g., etching with HF-containing acid mixture during intermediate fabrication steps; use of SiC vs. Al_2O_3 for belt polishing and/or sand-blasting; etc.) may result in differences in surface/substrate chemistry and microstructure.

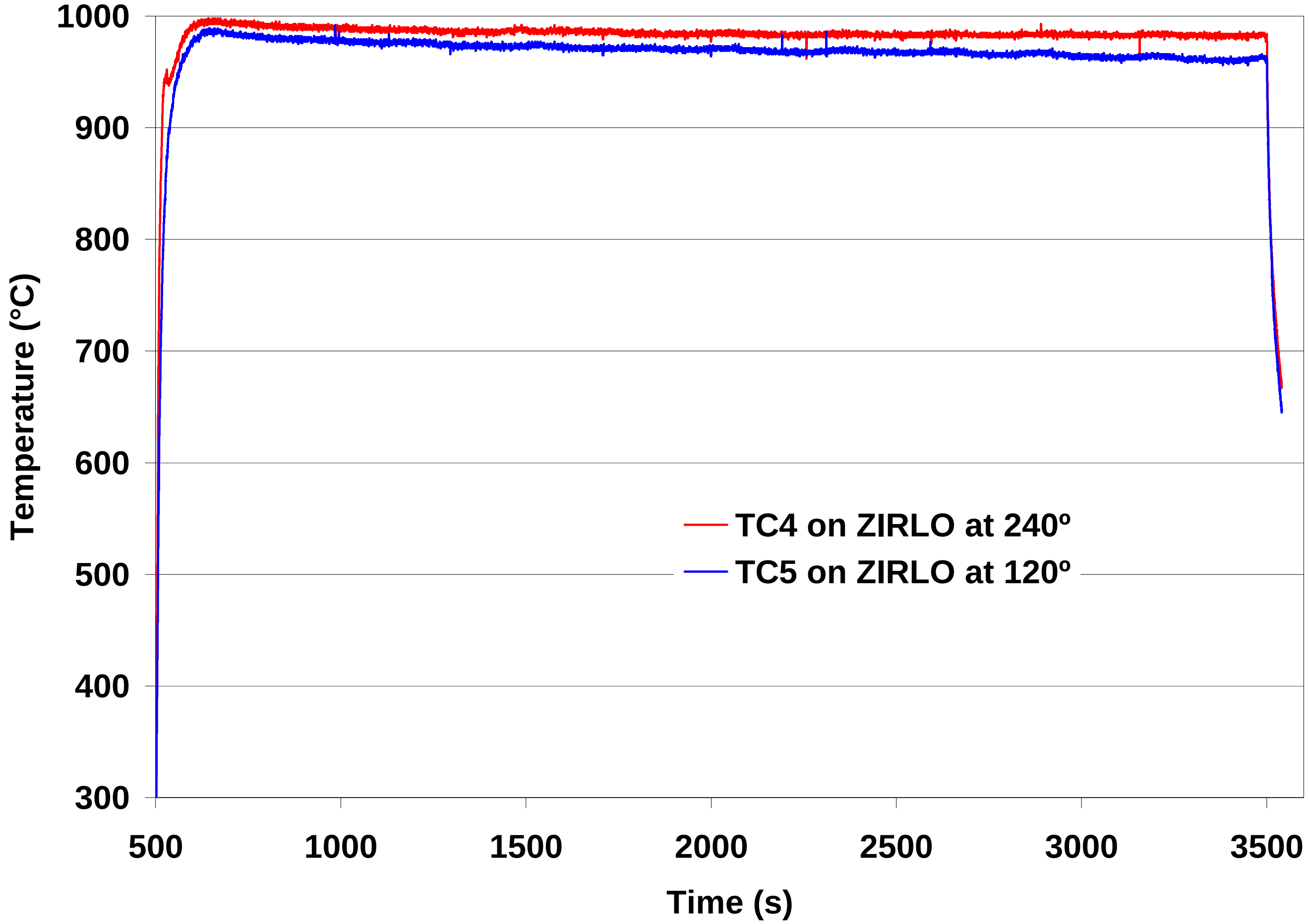


Fig. 1. Thermal benchmark for 2007 breakaway oxidation tests with bare and prefilmed (<1-µm-thick oxide layer) ZIRLO. The long-time hold temperature is 975±8ºC.

Table 1 Data Summary for ZIRLO Breakaway Oxidation Tests at 975-985°C; "bare" samples are as-fabricated ZIRLO; "prefilmed" ZIRLO samples, provided by Westinghouse, were exposed to 360ºC pressurized water for 36 hours; samples were cooled from the hold temperature to RT without quench

ZIRLO Samples	T °C	Test Time[a] s	Measured Wg, mg/cm^2	Hydrogen Content (L_H) wppm	Hydrogen Pickup (ΔC_H)[b] wppm	Comment
Bare	975	3000	9.01	39±2	30±2	Small yellow spot on OD
Bare	975	3500	8.65	108±46	100±50	Small yellow area on OD
Bare	980	3000	9.10	352±118	370±125	Post-breakaway
Bare	985	3000	9.43	104±40	100±40	Small yellow area on OD
Bare	985	3400	9.65	303±164	310±170	Post-breakaway
Prefilmed	985	3000	9.00	59±35	50±40	Small yellow spot on OD (see Fig. 2)
Prefilmed	985	3400	9.28	259±138	260±145	Post-breakaway (see Fig. 3)
Prefilmed	985	4000	11.99	1070±89	1130±100	Post-breakaway (see Fig. 4)
Prefilmed	980	3200	8.67	125±116	120±120	2 yellow spots on OD surface (see Fig. 5)
Prefilmed	980	3200	8.84	101±98	100±100	Yellow spots on OD surface

[a]Includes time from beginning of ramp at 300ºC to end of hold time at oxidation temperature.
[b]Hydrogen pickup (ΔC_H) is referenced to the 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 (11 wppm).

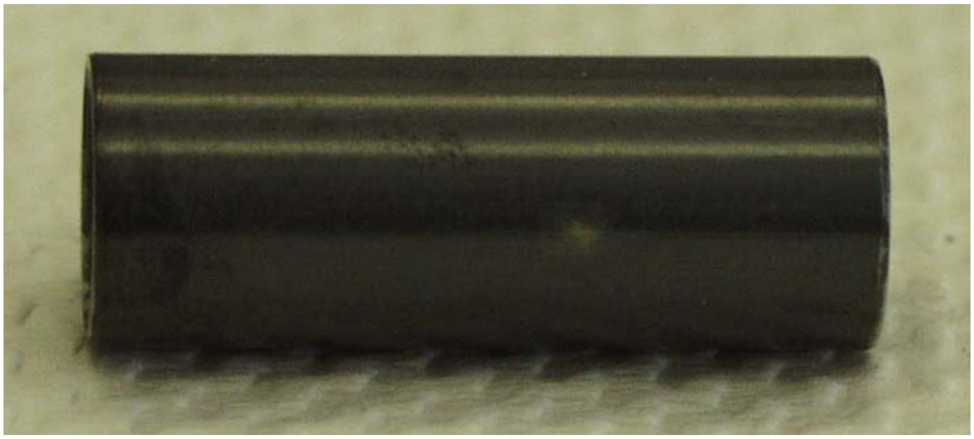
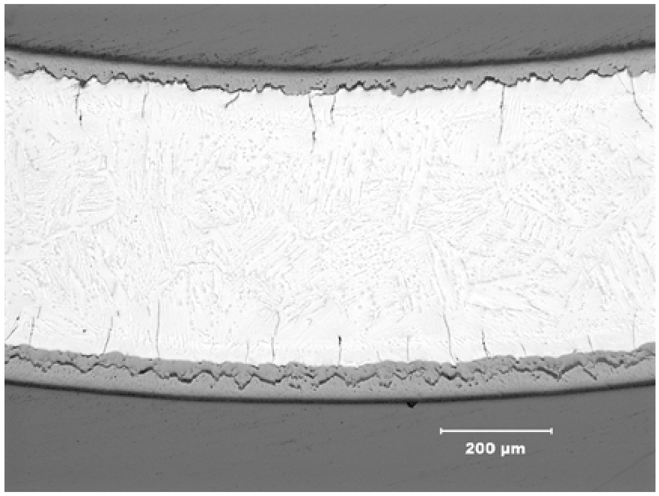


Fig. 2. Outer surface of prefilmed ZIRLO oxidized at 985ºC for 3000 s. One yellow spot can be seen just to the right of the sample midplane. Hydrogen pickup in a 2-mm-long ring including the yellow spot was 50±40 wppm (pre-breakaway).

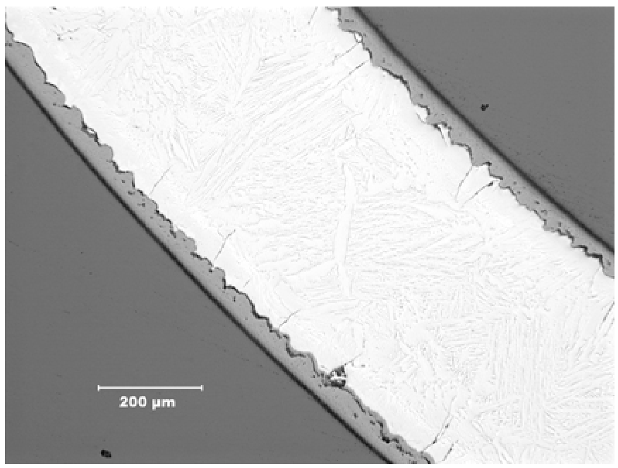
Fig. 3. Outer surface of prefilmed ZIRLO oxidized at 985ºC for 3400 s. Large yellow area can be seen to the right of the sample midplane. Hydrogen pickup in a 2-mm-long ring including the yellow area was 260±145 wppm (post-breakaway). Metallographic imaging was performed for a cross section that included the outer-surface oxide layer under the yellow area.

Fig. 4. Outer surface of prefilmed ZIRLO oxidized at 985ºC for 4000 s. Most of the outer surface is yellow, which is indicative of the tetragonal-to-monoclinic transformation of the oxide layer. Hydrogen pickup in a 2-mm-long ring sectioned from the sample midplane was 1130±100 wppm, which indicates that significant breakaway oxidation has occurred.

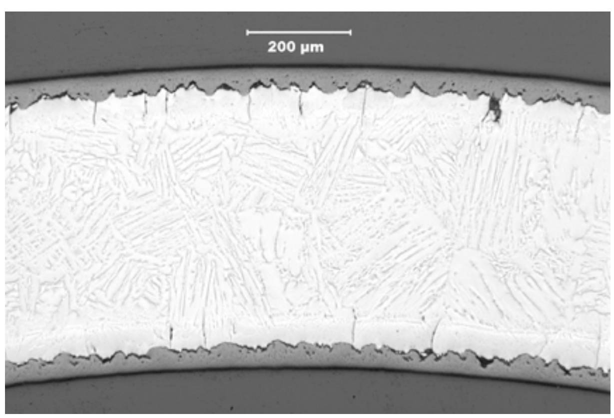
Fig. 5. Outer surface of prefilmed ZIRLO oxidized at 980ºC for 3200 s. Two small yellow spots can be observed. Hydrogen pickup in a 2-mm-long ring sectioned to include a yellow spot was 120±120 wppm, with 300-wppm hydrogen under the spot. For a sibling sample tested under the same conditions, the local hydrogen content under the yellow spot was 470 wppm.



(a)



(b)



(c)

Fig. 6. Metallographic images of prefilmed ZIRLO sample oxidized at 985ºC for 3400 s: (a) segment under yellow area in Fig. 3 showing breakaway oxidation in outer-surface oxide layer; (b) segment adjacent to yellow area showing breakaway in lower-right corner of outer-surface oxide layer; and (c) segment under black area showing no breakaway oxidation.