Breakaway Oxidation of ZIRLO under Transient Temperature Conditions

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July 31, 2009

1. Introduction

Breakaway oxidation results in increases in oxidation rate and hydrogen pickup, which are associated with the tetragonal-to-monoclinic phase transformation that initiates near the metal-oxide interface during steam oxidation of zirconium-based alloys. The ANL criterion for breakaway oxidation is the time corresponding to 200-wppm hydrogen pickup. Technical background and data for breakaway oxidation are documented in NUREG/CR-6967 [1] and in a subsequent letter report to NRC [2]. The breakaway oxidation data reported in Refs. 1-2 were generated under essentially isothermal test conditions. Additional breakaway tests with ZIRLO cladding have been conducted under transient temperature conditions to determine if such conditions would accelerate the breakaway oxidation process and lead to shorter breakaway times.

2. Materials

Test samples (25.4-mm long) used in this study are from 17×17 ZIRLO cladding received from Westinghouse in 2008. ANL measured the outer diameter, wall thickness, surface roughness, and hydrogen content for this cladding. Table 1 shows the comparison among the ZIRLO received in 2003, in 2006, and in 2008. Although it was clear from earlier testing that changes were made to the inner-surface finish of ZIRLO cladding subsequent to ZIRLO-2003 production, no significant differences were found regarding the cladding outer-surface dimension and roughness, as well the wall thickness and hydrogen content.

3. Results

Transient breakaway oxidation tests were conducted with three temperature profiles, as show in Fig. 1. Test conditions and results are described in the following.

3.1 Test ZLU#139 for Transient #1

Test ZLU#139 was conducted with a temperature profile corresponding to Transient #1 (Fig. 1). This is a single step change: hold the sample at 1045°C for 1000 s, and then decrease the temperature to 980°C for a 3000-s hold time. The thermal benchmark for this test is shown in Fig. 2. The long-time hold temperature in Step 1 was 1040±3ºC. The circumferential temperature variation of 3ºC is based on the readings of the two thermocouples (TCs) welded to the sample. The 5ºC drift in the long-time sample TC readings may be due to some oxide growth between the TCs and the cladding metal surface. As such, there may have been a 5ºC uncertainty in long-time metal temperature, in addition to ±3ºC circumferential variation. Also shown in Fig. 2 is the history of the control TC, which was welded to the sample holder.

Table 1 Characterization of Westinghouse 17×17 ZIRLO Cladding

Parameter	ZIRLO-2003	ZIRLO-2006	ZIRLO-2008
Outer Diameter, mm	9.50	9.48	9.50
Wall Thickness, mm	0.57	0.568 ± 0.003	0.578±0.006
OD Surface Roughness, μm	0.11±0.01	0.17±0.03	0.14±0.03
H Content, wppm	5±0	11±3	17±2
O Content, wppm	1185±30	1164±26	---
Outer-surface Appearance	No scratches	No scratches	No scratches

The control TC readings are only a few degrees lower than the sample readings. In order to achieve long-time hold temperatures of 1045ºC and 980ºC for Transient #1, the furnace power was adjusted based on the benchmark relationship established between the furnace power, the holder control TC, and the sample TCs. The control TC temperature history for Test ZLU#139 is shown in Fig. 3.

The ZLU#139 sample had a lustrous black outer surface (see Fig. 4a). Also, its measured weight gain (see Table 2) was lower than the CP-predicted weight gain calculated for the Transient #1 temperature history. There were no indications of breakaway behavior after 4000-s total oxidation time for this sample.

3.2 Test ZLU#140 for Transient #2

Test ZLU#140 was conducted with a temperature profile corresponding to the Transient #2 temperature history. This was also a single step-change test: hold at 975°C for 1500 s and then increase temperature to 1000°C for a 2500-s hold time. As shown in Fig. 2, the long-time hold temperature is relatively stable. Therefore, no benchmark test was conducted after Test ZLU#139. In order to achieve long-time hold temperatures of 975ºC and 1000ºC for Transient #2, the furnace power was adjusted based on the benchmark relationship established between the furnace power, the holder control TC, and the sample TC. The control TC temperature history for Test ZLU#140 is shown in Fig. 5.

The ZLU#140 sample had a lustrous black outer surface (see Fig. 4b). Also, its measured weight gain (see Table 2) was lower than the CP-predicted weight gain calculated for the Transient #2 temperature profile. There were no indications of breakaway behavior after 4000-s total oxidation time for this test sample.

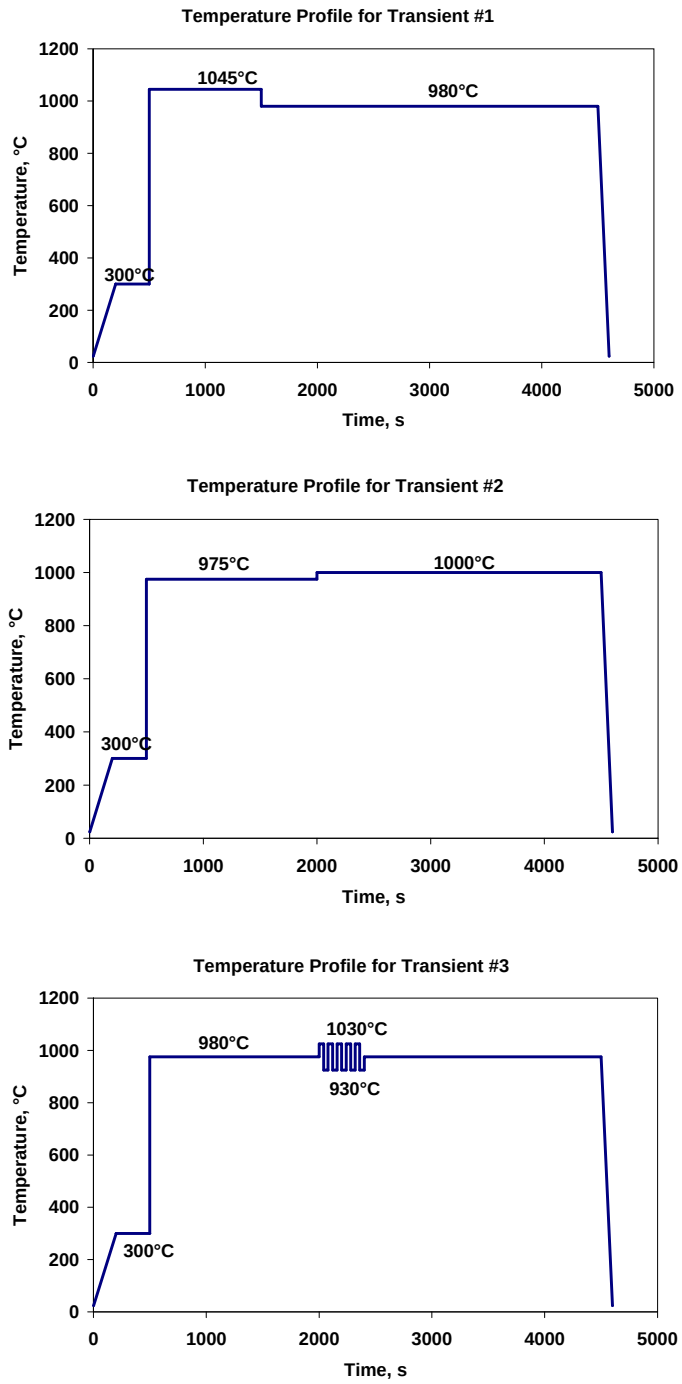


Fig. 1. Schematic of transient temperature histories for breakaway oxidation tests with ZIRLO cladding samples.

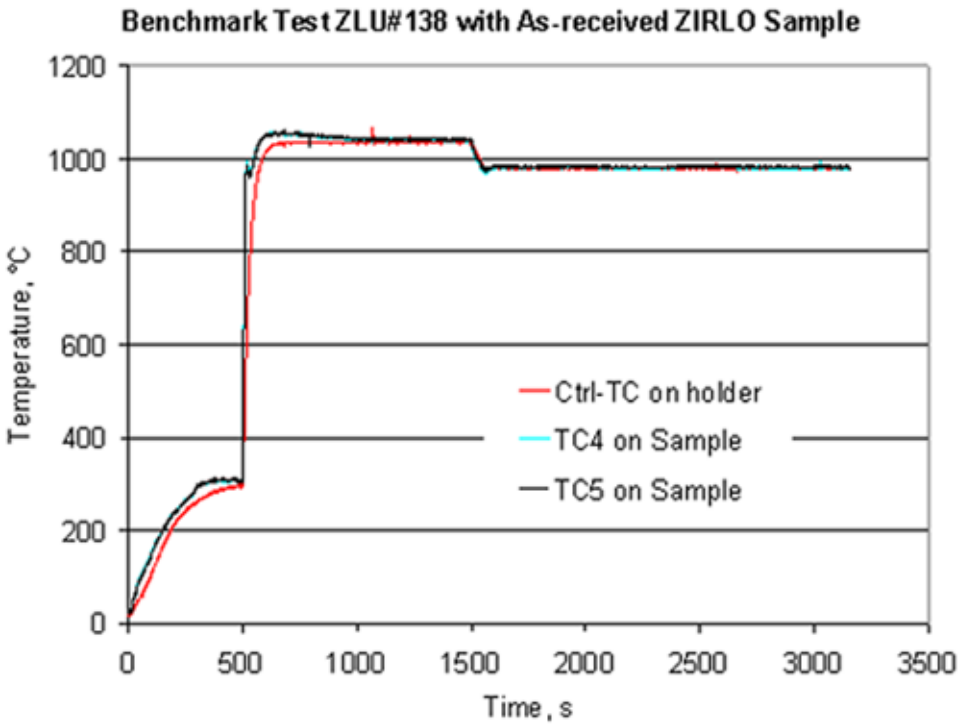


Fig. 2. Thermal benchmark results with two TCs welded onto as-fabricated, 17×17 ZIRLO-2008 cladding. The long-time sample hold temperature was 1040±3ºC.

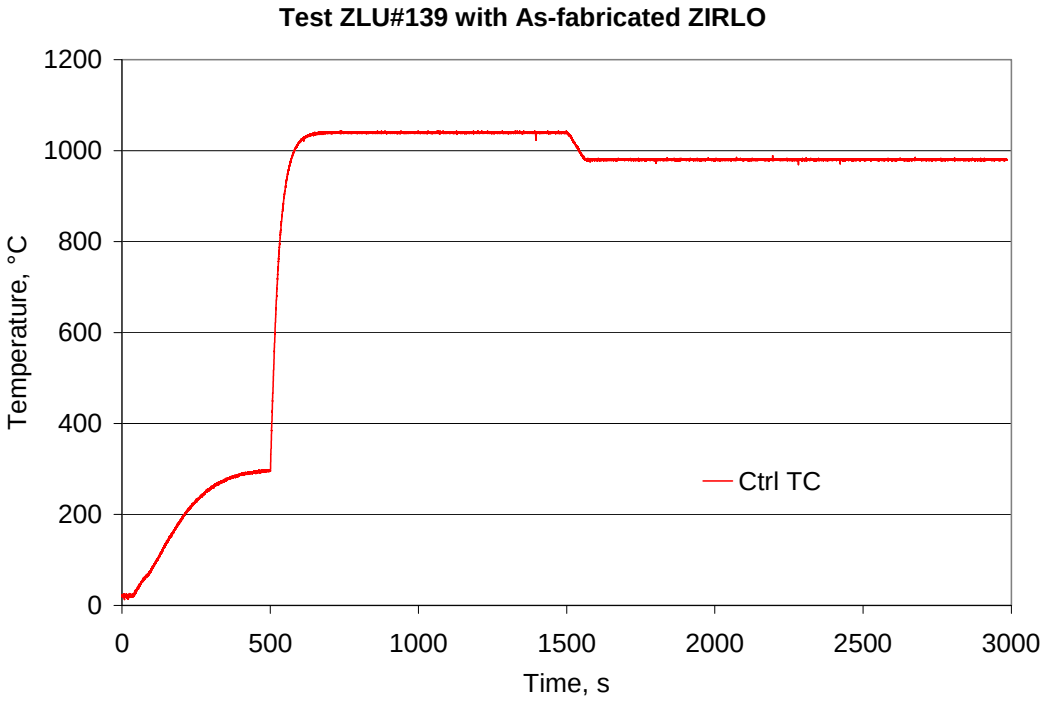


Fig. 3. Temperature history of the control TC for Test ZLU#139.

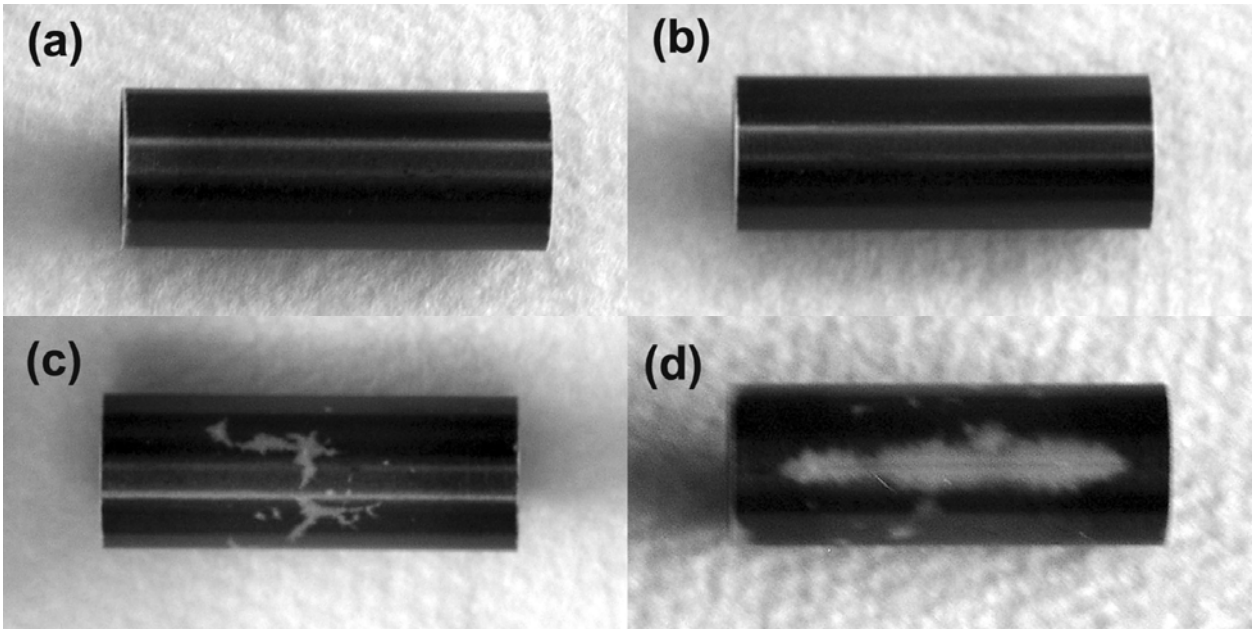


Fig 4. Appearance of as-received ZIRLO cladding outer-surface after steam oxidation tests (a) ZLU#139 for Transient #1, (b) ZLU#140 for Transient #2, (c) ZLU#142 for Transient #3, and (d) ZLU#143 for a modified Transient #3. Photos are in gray scale.

3.3 Tests ZLU#142 – 143 for Transient #3

Two thermal-cycling tests were performed for Transient #3. Test ZLU#142 was run with ZIRLO cladding at 980°C for 1500 s, then 5 cycles from 930°C to 1030°C for about 400 s, followed by 980°C for 1400 s. For ZLU#143, the temperature profile was modified slightly: the initial hold time at 980°C was increased from 1500 s to 2000 s, the temperature was cycled during the 2000-2400 s time interval, and the sample was held at 980°C during the 2400-2800 s time interval.

The control-thermocouple temperature histories for Tests ZLU#142 and ZLU#143 are shown in Figs. 6 and 7, respectively. Although the measured sample weight gains (see Table 2) were lower than the CP-predicted weight gains, surface discoloration was observed for both samples (see Figs. 4c and 4d). The ZLU#142 sample had small, but significant, yellow-gray areas on the outer surface and extensive (middle 75%) yellow-gray areas on the inner-surface after 3300-s total test time. The region just to the right of the ZLU#142 sample mid-plane had more discoloration than the mid-plane due to yellow-gray areas around the back of the sample, which are not visible in Fig. 4c. The reverse was true for the ZLU#143 sample after 2800-s total test time: extensive yellow-gray area on the outer surface and yellow-gray spots on the inner surface. Breakaway oxidation for both samples was confirmed by outer-surface discoloration (Figs. 4c and 4d) and hydrogen content (see Table 2). However, some of the hydrogen in the ZLU#142 sample may have come from inner-surface breakaway oxidation. Based on previous results obtained from testing ZIRLO-2003 [1], the hydrogen pickup from inner-surface breakaway is expected to be <100 wppm (see Table 29 and Fig. 55 in Ref. 1).

Table 2 Results of ZIRLO-2008 Transient Oxidation Tests (see Table 1 for ZIRLO-2008 characteristics)

Test ID	Transient Type	Total Test Time[a], s	CP-predicted Weight Gain[b], mg/cm^2	Measured Weight Gain, mg/cm^2	LECO H-content, wppm	H-pickup[c], wppm	Comment
ZLU#139	1	4000	14.3	9.5	---	---	Lustrous black OD
ZLU#140	2	4000	13.5	8.1	---	---	Lustrous black OD
ZLU#142	3	3300	11.6	8.5	425±35	427±36	Small OD yellow areas; extensive ID yellow area
ZLU#143	3	2800	10.8	8.2	232±76	225±79	Extensive OD yellow area: small ID yellow areas

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

[b]The Cathcart Pawel (CP)-predicted weight gain is calculated with temperature profiles shown in Figure 1.

[c]Hydrogen pickup is referenced to the as-fabricated sample weight.

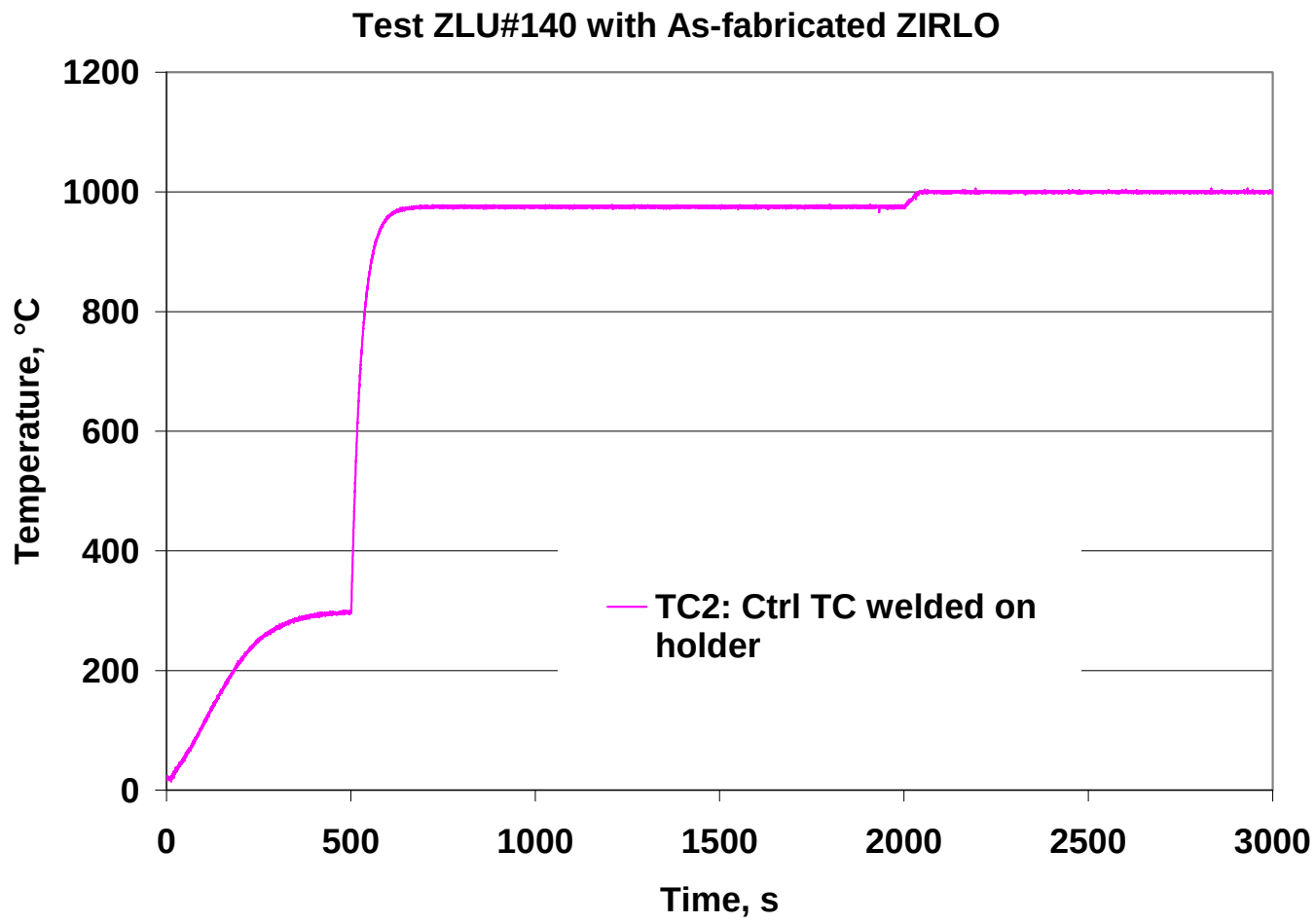


Fig. 5. Temperature history of the control TC for Test ZLU#140.

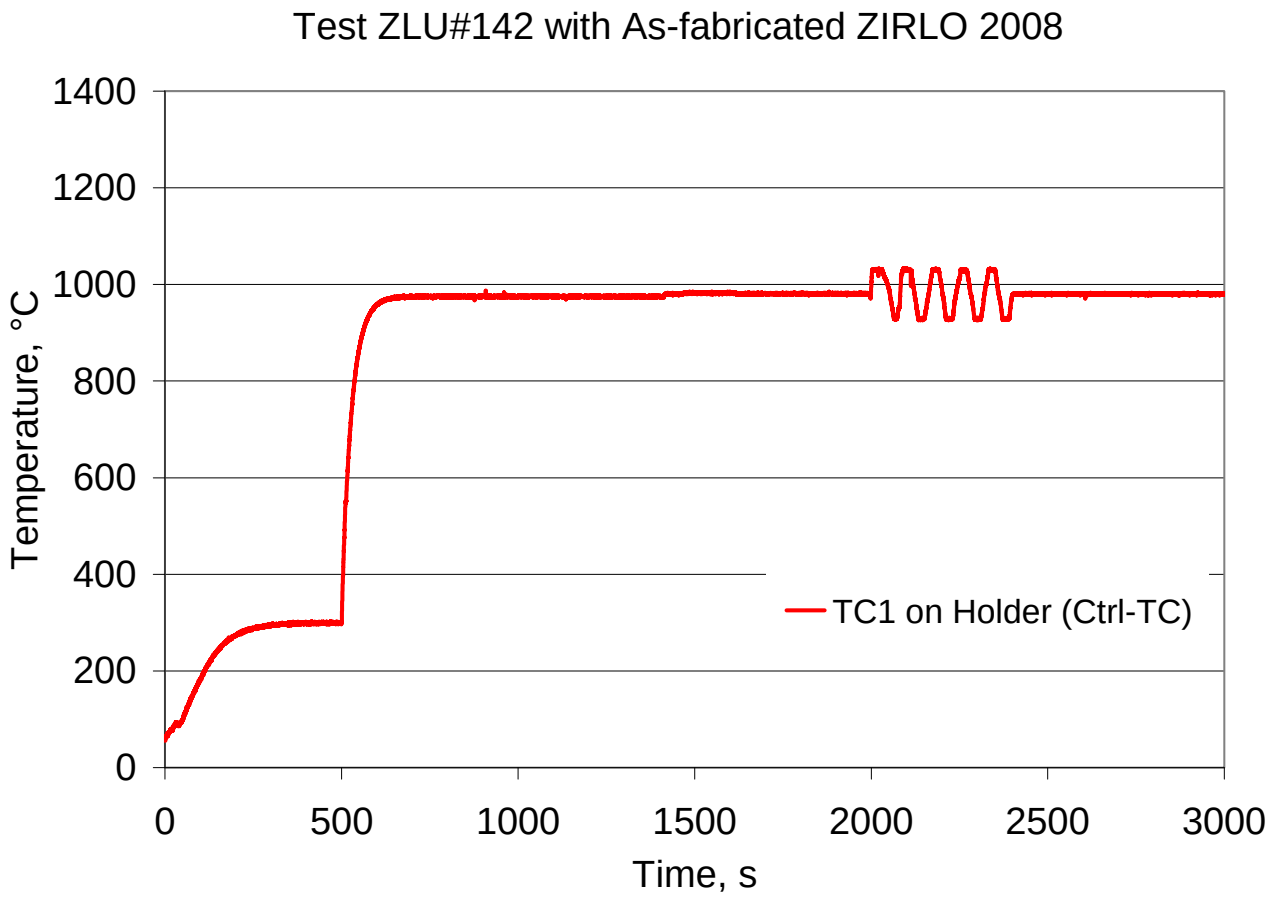


Fig. 6. Temperature history of the control TC for Test ZLU#142. Hold time following cycling was 1400 s.

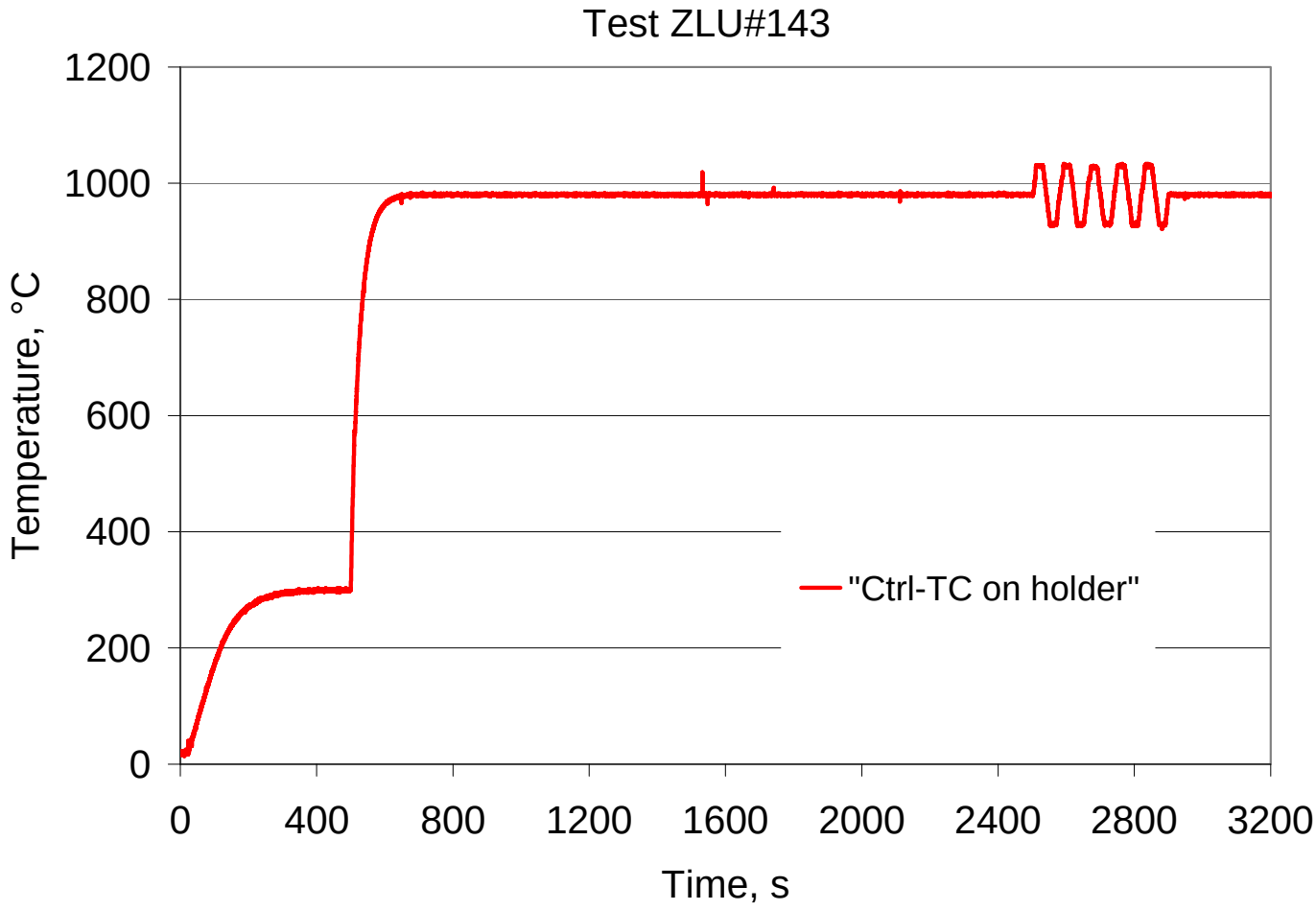


Fig. 7. Temperature history of the control TC for Test ZLU#143. Hold time following cycling was 400 s.

4. Discussion

In general, breakaway oxidation of zirconium-based alloys is associated with local formation of monoclinic oxide at the metal-oxide interface during oxidation in steam. It has been reported that the monoclinic-to-tetragonal and tetragonal-to-monoclinic transformations do not occur at a fixed temperature [4]. The ranges of the transformation vary for both the forward and the reverse transformations, depending on impurities (type and concentration), grain size, stoichiometry, and thermal history. In addition, the transformation temperature can be reduced as the compressive stress increases.

Although it is not clear at which temperature the oxide phase transformation takes place for the ZIRLO alloy, previous ANL breakaway oxidation results for ZIRLO cladding [1, 2] indicate minimum breakaway oxidation times occur within the range of 3100±300 s for isothermal oxidation temperatures of 970-985ºC. At a slightly higher oxidation temperature (1000ºC), the minimum breakaway oxidation time for ZIRLO is extended to 4000±200 s. We also found that a rapid temperature rise with ≈60ºC overshoot for a very short time appeared to have some effect on long-time breakaway [2]. However, no conclusions could be drawn because the hydrogen-pickup results were within data scatter for long-time temperatures of 970-985ºC. Therefore, it was of interest to determine if this type of transient, i.e. Transient #1, could lead to shorter breakaway times.

The results of Test ZLU#139 with a long-time overshoot to 1045ºC followed by long time at 980ºC showed no signs of breakaway oxidation for 4000-s total test time. Both the outer surface appearance (lustrous black) and the weight gain (low) indicated that breakaway oxidation had not occurred. In accordance with standardized test procedures for breakaway oxidation [3], no hydrogen analysis was performed for this sample. For Test ZLU#140, the temperature was held at 975ºC for 1500 s and then raised to 1000ºC for 2500 s. Based on visual appearance of the outer surface (lustrous black) and the measured weight gain (low), there were no indications of breakaway behavior after 4000-s total test time. For both step-increase and step-decrease transients, the results indicated that breakaway oxidation times for these transient tests were longer than those for isothermal tests conducted at about 980ºC.

The monoclinic-to-tetragonal transformation is accompanied by a sudden volume change and by anisotropic thermal expansion behavior of the lattice parameter, which disrupt the oxide. The purpose of the cycling tests under Transient #3 conditions was to determine whether localized stresses induced by the phase transformation and differential thermal expansion could disrupt the tetragonal layer near the metal-oxide interface, which in turn might reduce the breakaway time near the critical breakaway temperature. To investigate this, two thermal cycling tests were run during which the average cladding temperature was held at the 980 ºC throughout the transient and five cycles were introduced during a 400-s interval with temperatures in the range of 930-1030ºC: after 1500 s for ZLU#142 and after 2000 s for ZLU#143. Following the cycling, the samples were held at 980ºC for 1400 s (ZLU#142) and 400 s (ZLU#143). Both samples exhibited significant yellow areas on the outer surfaces indicating breakaway for total test times (including 80-s ramp from 300 ºC) of 3300 s (ZLU#142) and 2800 s (ZLU#143). The

average hydrogen pickup near the mid-plane for the ZLU#143 sample was 225 wppm after 2800 s. The large circumferential variation in hydrogen content (≈170 wppm based on four arc segments) indicates that the test was terminated early enough in the breakaway process such that concentration-driven hydrogen diffusion was not extensive. The local hydrogen pickup from under the yellow area was >300 wppm. Thus, with temperature cycling around an average temperature of 980ºC, the breakaway oxidation time was about 2800 s.

Figure 8 shows the yellow breakaway regions on the ZLU#143 sample outer surface. Some grayish/white areas were also observed, and some of these were in the center of the yellow areas. Since the oxide color is strongly influenced by stoichiometry, as well as impurities, this change might indicate an increase in the O-to-Zr ratio. A high-magnification image of a small yellow area (Fig. 8b) shows the morphology of the monoclinic phase on the ZLU#143 sample outer surface. The center area appears grayish/white surrounded by yellow areas. Figure 9 shows the transition area from black to yellow in the region marked "T" in Fig. 8a. The cladding longitudinal axis is delineated by an arrow in Figs. 8a and 9a. It is interesting to observe that the yellow areas have a rougher outer surface than the black areas. This feature was also observed within the small area of yellow, monoclinic oxide shown in Fig. 8b.

The longer test time for ZLU#142 made the results more difficult to analyze. There was extensive discoloration within the middle 75% of the sample inner surface, and the additional 500 s allowed for more axial and circumferential diffusion of hydrogen. As shown in Fig. 10, rings were sectioned from an axial region that was ≈3 to 11 mm from the center of the sample. The hydrogen pickup values were determined to be 427±36 wppm, 312±31 wppm, 221±41 wppm, and 153±38 wppm, with the highest value for a ring closest to the center of the sample. The highest value is for a ring with yellow-gray oxide over the whole inner surface and with yellow-gray oxide over about 40% of the outer surface. The lowest value is from a ring near the end with lustrous black oxide on both inner- and outer-surfaces. Given the relatively small circumferential variation and the relatively large hydrogen content in the ring with black inner- and outer-surface oxides, it is clear that significant hydrogen diffusion occurred during the additional 500 s test time (3300 s for ZLU#142 and 2800 s for ZLU#143). During this additional 500 s, hydrogen pickup through inner- and outer-surface oxides would tend to increase the local hydrogen content and diffusion would tend to decrease the local hydrogen content. Although it is reasonable to assume that outer-surface breakaway and >200-wppm hydrogen pickup through the outer surface occurred based on appearance of the outer surface, there is no way to determine how much of the measured hydrogen entered through the outer surface.

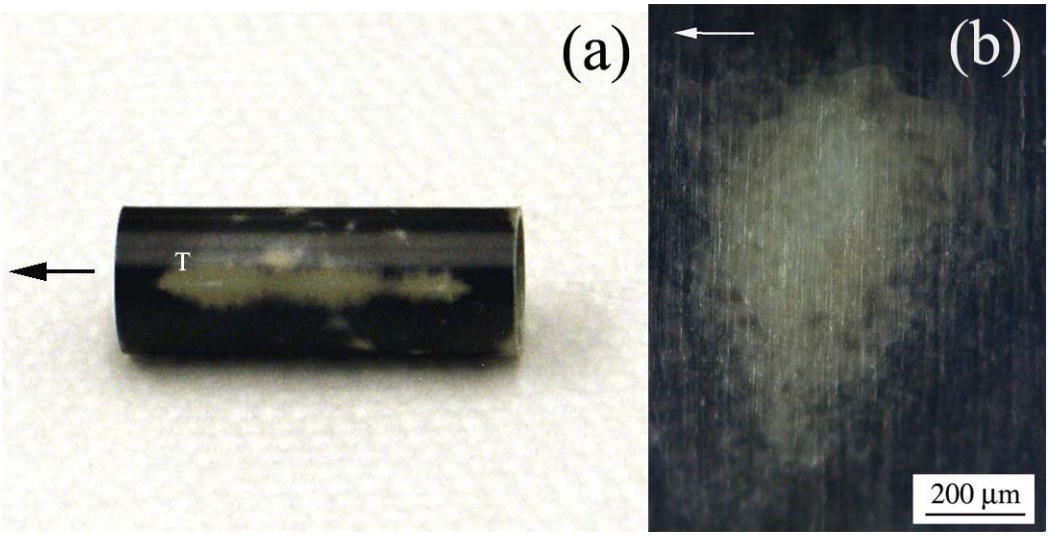


Fig. 8. (a) ZIRLO sample after steam-oxidation at Transient #3 condition for 2800 s total test time with cycling from 930°C to 1030°C (Test ZLU#143), and (b) high-magnification image showing transition area for monoclinic oxide growth.

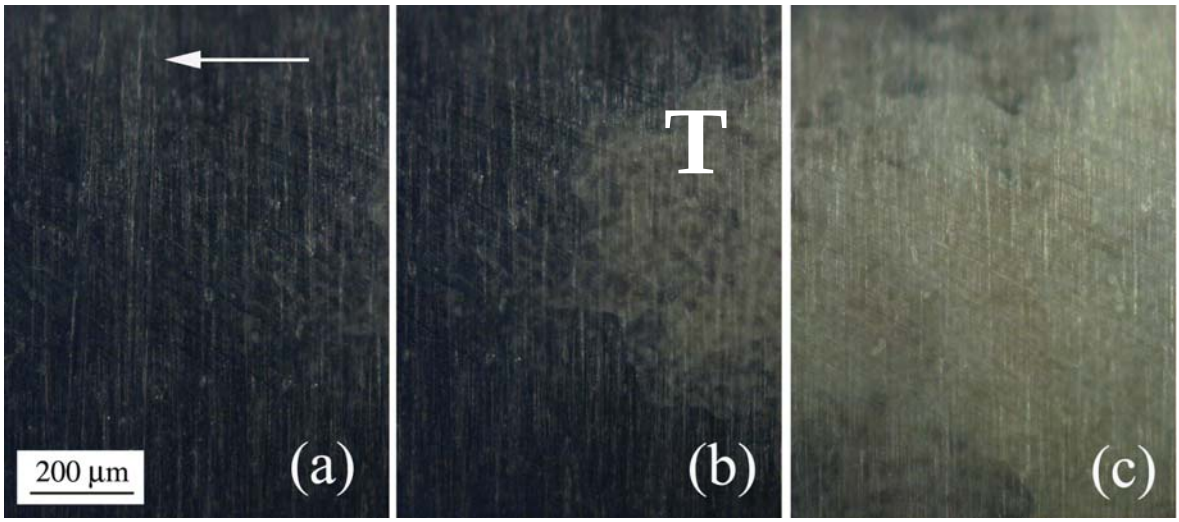
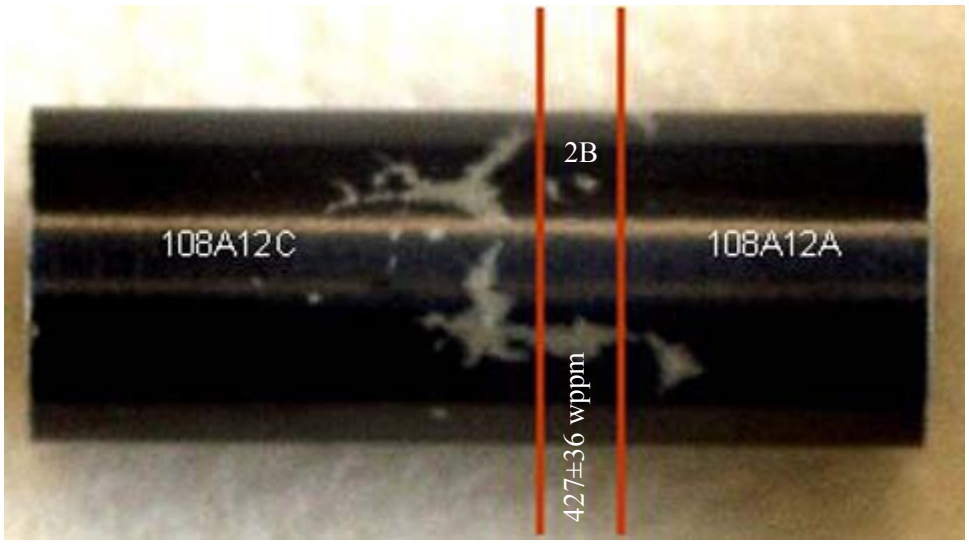
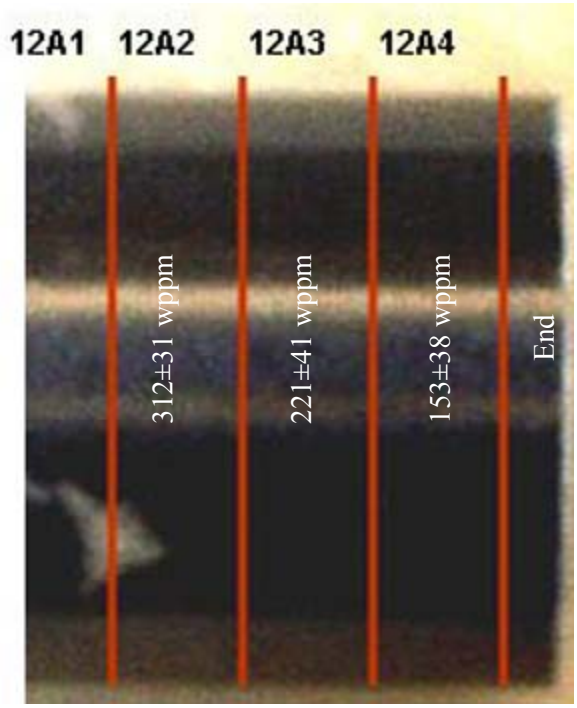


Fig. 9. High-magnification images of Area T in Fig. 8a showing different areas of ZLU#143 sample outer surface: (a) lustrous black area, (b) transition area from black-to-yellow, and (c) yellow area.



(a)



(b)

Fig. 10. Axial distribution of hydrogen pickup for the ZLU#142 sample.

The monoclinic-to-tetragonal phase transformation in ZrO_2 can be characterized as an athermal process, for which the transformation does not occur at a fixed temperature, but takes place over a range of temperatures. The proportion of the tetragonal phase within that range does not change with time as long as the temperature remains constant. A plot of tetragonal-phase percentage vs. temperature gives the characteristic S-curves [4] with a hysteresis gap of 208°C (width of hysteresis loop at midpoint). For example, a conversion of 50% of tetragonal phase occurs at 1086°C in the forward reaction (monoclinic-to-tetragonal with increasing temperature), and this proportion remains until 878°C in reverse reaction (tetragonal-to-monoclinic with decreasing temperature). For a conversion of 10% tetragonal phase in reverse reaction, the transformation temperature may be as low as 804°C. However, the transition temperature in our breakaway oxidation tests can be quite different from the results in Ref. 4 because the tetragonal phase can exist at even lower temperatures due to other factors, such as stress, grain size, hypostoichiometry, and impurities.

The 2800-s breakaway time for temperature-cycled sample ZLU#143 is comparable to the breakaway time for a pre-scratched ZIRLO sample oxidized under isothermal conditions at 970°C [1]. Prior to that earlier testing, a 20-μm-deep, rectangular-shaped scratch was machined along the length of the outer surface (see Fig. 1c in Ref. 3). After oxidation, a yellow region was observed along the middle third of the scratch, and the hydrogen pickup was 44 wppm. Based on the large hydrogen-pickup data set for smooth cladding, it was estimated that the sample would have picked up >200-wppm hydrogen by ≈2800 s. Thus, the effects of temperature cycling on breakaway oxidation time appear to be comparable to the effects of surface-scratched samples oxidized under isothermal conditions. With regard to the combined effects of surface scratches and transient histories with temperature cycling, this would require a very large number of tests to determine. Such combined effects were beyond the scope of the present investigation.

5. Conclusions

5.1 Effects of step change in temperature

Previous results for long-time tests conducted under isothermal conditions indicated longer breakaway oxidation times for ZIRLO oxidized at 1000°C (4000±200 s) than at 970-985°C (3100±300 s). Recent tests were conducted with step changes from 1045°C to 980°C and from 975°C to 1000°C. The samples from these tests exhibited no signs of breakaway oxidation for 4000-s total test time. These results indicate that isothermal-temperature-history tests give a lower-bound on the minimum breakaway oxidation time for transient tests with step temperature changes.

5.2 Effects of temperature cycling

Two tests were conducted with five temperature cycles from 930°C to 1030°C and an average long-time temperature of 980°C. Based on outer-surface appearance, it is clear that both samples had regions of breakaway oxidation. The sample with the shorter total test time (2800 s) exhibited extensive outer-surface discoloration, and the hydrogen pickup (225 wppm) indicated that the breakaway oxidation time was the test time (2800-s). This time falls within the scatter band (3100±300 s) measured under isothermal temperature conditions for ZIRLO. It is also comparable to the results for a pre-scratched sample oxidized under isothermal conditions at 970°C. Figure 11 shows the data for the temperature-cycling test samples, for pre-scratched samples oxidized at isothermal temperatures (970-985°C), and for smooth samples oxidized at isothermal temperatures (970-985°C). From Fig. 11, it appears that transient temperature cycling has about as much effect on ZIRLO breakaway oxidation time as pre-scratching samples prior to isothermal oxidation. Based on the tests performed, it appears that isothermal tests, particularly those conducted with pre-scratched samples, give a reasonable lower bound for the breakaway oxidation time for samples exposed to transient histories with temperature cycling.

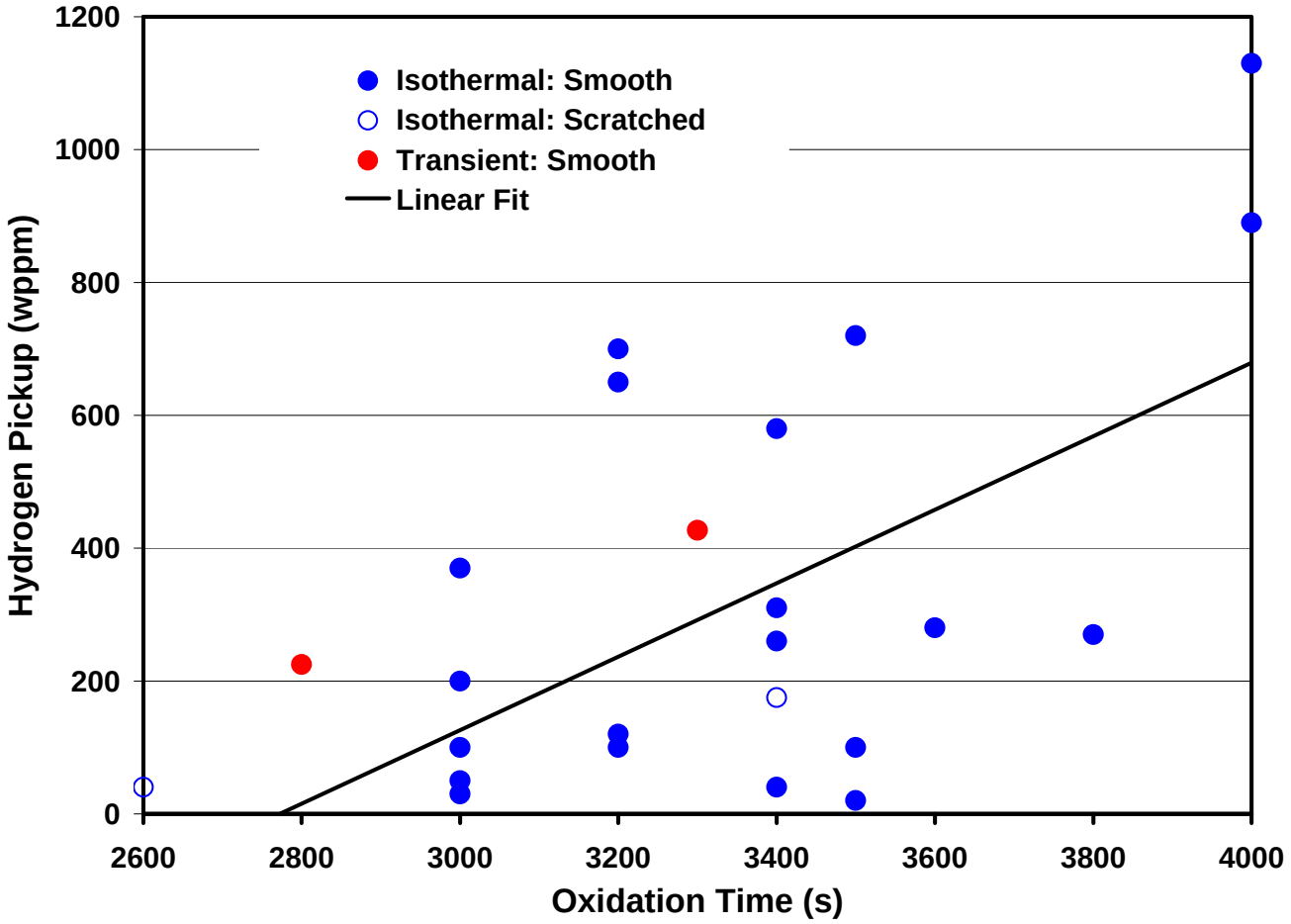


Fig. 11. Hydrogen-pickup vs. time data for ZIRLO oxidized in steam at 970-985°C: smooth samples oxidized under isothermal conditions; pre-scratched (≈20-μm depth) samples oxidized under isothermal conditions at 970°C and 985°C; and smooth samples oxidized with five thermal cycles from 930-1030°C for 400 s and 980°C isothermal temperature. The ANL metric for minimum breakaway oxidation time is the time corresponding to 200-wppm hydrogen pickup.

References

1. M. Billone, Y. Yan, T. Burtseva, and R. Daum, "Cladding Embrittlement During Postulated Loss-of-Coolant Accidents," NUREG/CR-6967, July 2008; available online in NRC ADAMS as ML082130389 at http://www.nrc.gov/NRC/reading-rm/adams.html

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4. G.M. Wolten, J. Amer. Ceram. Soc. 46, 418 (1963).

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