

**Procedure for Conducting Breakaway Oxidation Tests with Zirconium-based Cladding Alloys**  
Argonne National Laboratory (ANL)  
March 23, 2009

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## 1. Purpose and Scope of the Tests

Performance-based tests are needed to ensure that fuel-rod cladding retains ductility following long-time oxidation in steam at temperatures in the range of 650-1050°C. Such long-time exposure to steam is especially relevant to postulated small-break loss-of-coolant accidents (LOCAs). All zirconium-based cladding alloys will experience breakaway oxidation within this temperature range if steam exposure times are long enough. Concurrent with breakaway oxidation is an increase in hydrogen pickup, which can cause cladding embrittlement. This procedure describes isothermal tests to be conducted with fresh cladding samples for determination of the minimum breakaway time. The minimum breakaway time is defined as the time required to pick up 200-wppm hydrogen through the cladding outer-surface oxide.

## 2. Background

During a LOCA, the cladding outer surface will be exposed to steam at elevated temperatures. The oxide phase (tetragonal) formed on the cladding outer surface under LOCA conditions is typically lustrous black, dense, and protective with regard to hydrogen pickup [1,2,3]. In contrast, the corrosion layer formed during normal operation is monoclinic, partially cracked, and only partially protective with respect to hydrogen pickup.

For stoichiometric zirconium oxide ( $ZrO_2$ ) formed under stress-free conditions, the tetragonal-to-monoclinic phase transformation temperature is high ( $\approx 1150^\circ C$ ). However, the tetragonal phase is stabilized at lower steam-oxidation temperatures by a combination of hypo-stoichiometry [ $ZrO_{(2-x)}$ ], compressive stress, and perhaps grain size. Stress reversals (from compressive to tensile) and/or chemical impurities (e.g., fluorine [F]) in the oxide layer and at the oxide-metal interface can induce early transformation from the tetragonal to the monoclinic phase. As this transformation results in an increase in the growth rate of the oxide-layer thickness and weight gain, it has been referred to in the literature as breakaway oxidation. Stress reversals generally develop at the oxide-metal interface after long-time (3000-6000 s) exposure to steam at  $\leq 1050^\circ C$ . The precursor to breakaway oxidation is the transition from a smooth oxide-metal interface to a scalloped interface. The amplitude of the scallops grows with increasing time until breakaway oxidation occurs. Based on surface appearance, metallographic imaging and local hydrogen content, the instability initiates locally in the cladding outer-surface oxide and grows rather quickly in the circumferential and axial directions. For Zircaloy-4 (Zry-4) oxidized at  $1000^\circ C$ , areas of gray spots or thin axial lines observed on the outer surface occur during the phase transformation. For ZIRLO oxidized at the same temperature, these areas are yellow or tan. Following the full transformation to monoclinic oxide, the metal-oxide interface is once again smooth and the outer-surface color is uniformly gray or yellow.

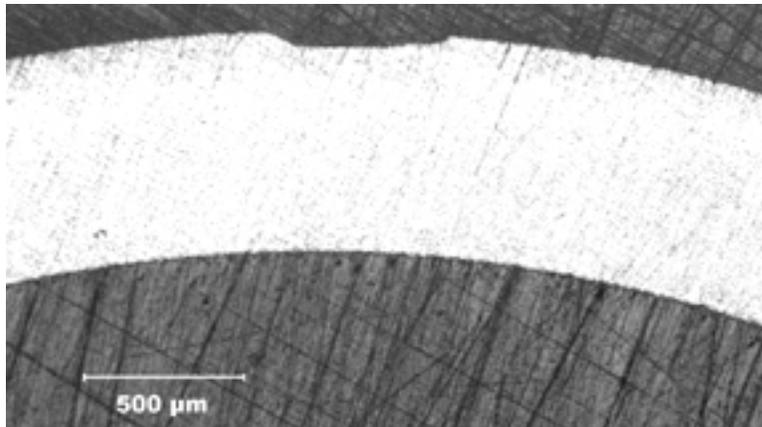
The presence of destabilizing trace impurities, especially F, and possibly the absence of stabilizing impurities (e.g., Ca), can induce early breakaway oxidation at temperatures as high as the nominal phase transition temperature for stress-free  $ZrO_2$ . The Russian Zr-1Nb alloy E110 cladding is a classic example of a material that experiences early breakaway oxidation (<600 s) due to the presence of F impurities at the metal surface and within the metal substrate [3,4].

The increase in oxide-layer-thickness growth rate associated with breakaway oxidation does not directly cause cladding embrittlement within LOCA-relevant times. The low-oxygen beta or mixed alpha-beta layer remains ductile within LOCA-relevant times due to low oxygen concentration. However, hydrogen pickup associated with breakaway does cause ductility decrease and embrittlement. As shown

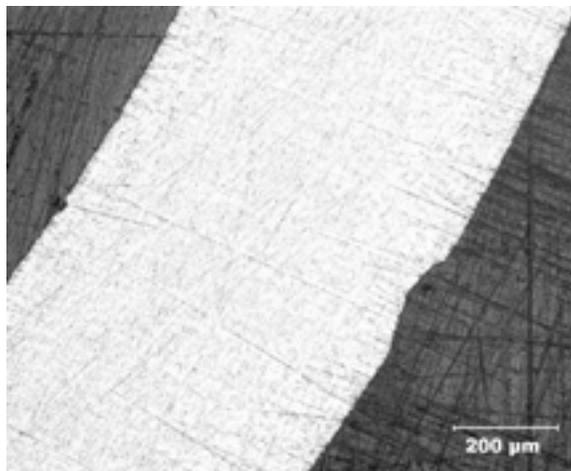
in Ref. 3, cladding oxidized for 3000-4000 s at 970-1000°C loses ductility for hydrogen pickup values > 400 wppm (see Appendix A). In order to ensure ductility as measured by ring-compression tests conducted at 135°C (275°F), the breakaway oxidation time in Ref. 3 is defined as the time corresponding to 200-wppm hydrogen pickup. At this hydrogen pickup, there is little difference between the measured post-test hydrogen content of the sample and the hydrogen pickup (i.e., weight-gain-corrected hydrogen content minus the hydrogen content in as-fabricated cladding). The hydrogen pickup rate following initiation of breakaway oxidation can be very fast such that the time to increase from 200 wppm to >400 wppm can be as short as 100 s at oxidation temperatures in the range of 970-1000°C. At lower oxidation temperatures, particularly <900°C, the oxidation rate and hydrogen generation rate are considerably lower. As the hydrogen generation rate decreases, the rate of hydrogen pickup also decreases.

The transition from tetragonal to monoclinic oxide is an instability phenomenon dependent on many manufacturing variables, particularly those affecting cladding outer-surface conditions. For susceptible alloys such as E110 [3], the presence of geometrical discontinuities due to scratches, sample ends, and a thermocouple welded to the cladding will induce earlier breakaway oxidation. Also, for E110, high-surface roughness coupled with pre-test cleaning in an hydrofluoric (HF)-containing acid induces very early breakaway oxidation in terms of both surface appearance and hydrogen pickup. For E110, the sequence of finishing operations is important. Etching with an HF-containing acid prior to polishing seems to have no significant effect on breakaway oxidation, while etching after polishing can have a very detrimental effect on breakaway oxidation time. Modern cladding alloys currently used in the U.S. are considerably more stable than E110. However, even these polished alloys with low surface roughness are sensitive to post-polishing cleaning methods. A good example of this is the breakaway oxidation times reported in the literature for Zry-4. For an older variant of Zry-4, the data generated by Leistikow and Schanz [2] give the minimum time to accumulate 200 wppm hydrogen as 1800 s, which occurs at an oxidation temperature of 1000°C. Mardon et al. [5] report a hydrogen content of 200 wppm at ≈5400 s for modern, polished AREVA Zry-4 also oxidized at 1000°C. Billone et al. [3] determined breakaway oxidation times at ≈1000°C (based on 200-wppm hydrogen pickup) of 3800 s for an older variant of Zry-4 and 5000 s for modern, polished AREVA Zry-4. Baek and Jeong [6] oxidized polished Zry-4 for 3600 s at 1000°C and measured >600 wppm hydrogen. For this case, the estimated time for 200-wppm-H pickup is in the range of 3000-3300 s. The two studies with the lower breakaway oxidation times for Zry-4 have one critical step in common. In both studies Zry-4 samples were cleaned in an HF-containing acid prior to steam oxidation: nitric-fluoric acid mixture and final cleaning in boiling water for Ref. 2 tests; and 5% HF + 45% HNO<sub>3</sub> + 50% H<sub>2</sub>O with final ultrasonic cleaning in an ethanol and acetone solution for Ref. 6 tests. In the ANL study [3], samples used to generate breakaway oxidation data were cleaned ultrasonically in ethanol followed by water. In the Mardon et al. study samples were degreased in acetone prior to testing.

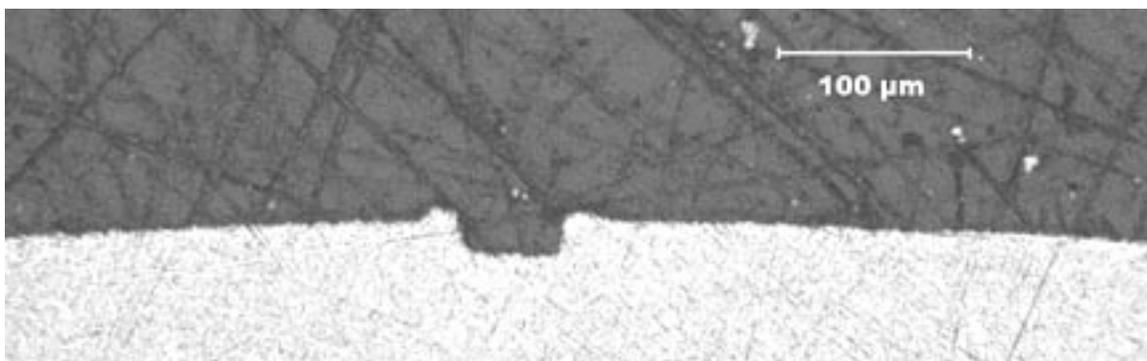
As breakaway oxidation may be sensitive to many variables related to surface finishing and cleaning, it is important to test samples that have undergone the full cleaning cycle from the polishing phase through the operations at the fuel fabrication plant to the insertion of assemblies into the reactor. Cleaning with water, chemical detergents (e.g., Alconox) or organic solvents appears to have no significant effect on breakaway oxidation time. However, post-polishing steps involving etching in an HF-containing acid, even a very light etching in a 1% HF-acid mixture for 15 s, must be simulated. In addition to simulation of post-polishing cleaning processes, scratching of the outer surface that may occur during insertion of rods into assemblies must also be simulated. Scratches can be categorized as "typical" (≈20-30 μm deep) or "design basis" (≈50-60 μm deep). Typical scratches should be quantified, and they should be simulated in the testing laboratory as they act as an initiation site for breakaway oxidation due to the effects of the geometrical discontinuity on the stress state in the oxide and at the metal-oxide interface. Examples of design-basis, typical, and ANL-machined scratches are shown in Fig. 1. The scratches shown in Figs. 1a and 1b were induced by repeated insertion of fuel rod cladding into and out of grid spacers.



(a) Example of a design-basis scratch ( $\approx 50\text{-}\mu\text{m}$  deep into wall)



(b) Example of a typical scratch ( $\approx 30\text{-}\mu\text{m}$  deep into wall)



(c) ANL-machined scratch used for breakaway oxidation studies ( $\approx 20\text{-}\mu\text{m}$  deep into wall)

Fig. 1. Examples of scratches on the outer surface of cladding: (a) low-magnification image of a design-basis scratch induced by excessive number of insertions in grid spacers; (b) medium-magnification image of a typical scratch from insertion into grid spacers; and high-magnification image of ANL-machined scratch used in breakaway oxidation studies.

Breakaway oxidation test results reported in the literature are based on isothermal test conditions. The test times listed in Ref. 3 include the time ( $\approx 80$  s) to ramp from 300°C to the target temperature and the hold time at that temperature. The added ramp time is small relative to the hold times associated with breakaway oxidation. Additional studies by Yan et al. [19] indicate that isothermal temperature tests generally give lower-bound breakaway oxidation times as compared to breakaway times determined from tests with transient temperature histories. In one of the transient tests conducted by Yan et al., the temperature was held at the critical temperature (980°C) for 2000 s, cycled five times between 930°C and 1030°C for 400 s, and then held at 980°C for 400 s. The hydrogen content and pickup were  $230 \pm 80$  wppm, which indicated that breakaway oxidation had occurred for this particular cladding alloy. Previous isothermal results for as-fabricated, pre-scratched, and pre-oxidized ( $< 1 \mu\text{m}$  film) samples gave a minimum breakaway time of  $3100 \pm 300$  s. For this particular transient, breakaway oxidation occurred at the lower bound of this range and was consistent with results for a pre-scratched sample oxidized under isothermal conditions.

The test times for the breakaway studies reported in Ref. 3 were generally  $\leq 5000$  s. Some early tests, conducted at 7200 s, resulted in excessive breakaway oxidation. Although there is no generic maximum time at elevated temperature for a LOCA, a maximum isothermal test time of 5000 s appears reasonable based on other considerations, such as the Cathcart-Pawel equivalent cladding reacted (CP-ECR) limit in the balloon ( $< 17\%$ ) when ballooning and burst are predicted to occur. The minimum breakaway oxidation time is expected to occur in the temperature range of 950-1000°C. For modern cladding alloys, the as-fabricated cladding wall thickness varies from 0.57 mm to 0.71 mm. For thin cladding that bursts, 17% CP-ECR corresponds to  $< 2400$  s at 1000°C,  $< 3300$  s at 975°C, and  $< 4600$  s at 950°C. These times decrease significantly if wall thinning is included in the calculation. For thick cladding that bursts, 17% CP-ECR corresponds to  $< 3300$  s at 1000°C,  $< 5100$  s at 975°C, and  $< 7100$  s at 950°C. With a modest 20% diametral ballooning or creep strain, these times for thicker cladding are reduced to  $< 2610$  s at 1000°C,  $< 3580$  s at 975°C, and  $< 5000$  s at 950°C. Thus, for most of these cases, breakaway oxidation times  $> 5000$  s would not be relevant because of the  $< 17\%$  CP-ECR limit. The procedure for conducting tests for  $\leq 5000$  s with emphasis on 950-1000°C oxidation temperatures is described in the following.

### **3. Sample Selection and Testing Frequency**

#### **3.1 Sample selection**

The samples selected for testing should be representative of the fueled cladding that is loaded into the reactor. In particular, samples should be exposed to the same post-polishing, outer-surface cleaning processes used prior to loading fuel assemblies into the reactor. Cleaning agents that have been found to be benign with respect to breakaway oxidation include water, chemical detergents (e.g., Alconox), and organic solvents (e.g., ethanol, acetone, etc.). However, the use of etching in an HF-containing acid mixture can initiate early breakaway oxidation in some alloys. These cleaning processes may be simulated in the laboratory.

Also, the samples should have at least one "typical" scratch observed to occur from insertion of fuel rods into assembly grid spacers. Documentation should be provided to justify the scratch depth and width. If no documentation is provided, then the scratch should extend along the length of the sample and have a depth and width of  $25 \pm 5 \mu\text{m}$  and  $\geq 25 \pm 5 \mu\text{m}$ , respectively. Cladding tube scratching may be simulated in the laboratory.

Although as-fabricated cladding may be used for scoping studies, the minimum breakaway oxidation time should be determined from scratched samples exposed to all post-polishing cleaning processes.

### 3.2 Frequency of testing

As breakaway oxidation is an instability phenomenon which is sensitive to surface roughness, surface and substrate impurities, and alloy constituents and impurities, testing should be repeated after significant changes to these variables. Some processing factors that may be significant are: revised specifications that allow  $> 0.2 \mu\text{m}$  surface roughness, a change of polishing material, introduction of post-polishing cleaning with HF-containing acid mixture, and changing cladding vendor. As it would take an extensive study to determine the breakaway-oxidation sensitivity for a particular cladding material to each of these variables, some periodic testing should be done even if minor changes are made.

## 4. Sample Preparation and Characterization

### 4.1 Hydrogen-content determination for as-fabricated samples

The hydrogen content of as-fabricated cladding is expected to be low (5-15 wppm) and to be available from the tubing vendor. It is used in the calculation to determine the hydrogen pickup during breakaway oxidation. If it is not available, it should be measured.

### 4.2 Minimum sample lengths for one- and two-sided oxidation tests

Most breakaway-oxidation testing has been performed with cladding sample lengths in the range of 25-50 mm for two-sided oxidation tests. These lengths were sufficient to minimize end effects. Therefore, the minimum sample length should be 25 mm. Although there is no maximum limit prescribed, it should be no longer than the length of the uniform temperature region of the furnace. Uniform is defined as  $\leq \pm 10^\circ\text{C}$  variation at the target temperature.

In preparing samples for one-sided oxidation tests, welded end-caps are used to prevent steam from coming into contact with the cladding inner surface. In order to minimize larger end effects due to the heat-affected zones, the minimum sample length for one-sided oxidation tests should be 75 mm.

### 4.3 End-cap mass and welding procedure for one-sided oxidation samples

Standard procedures are available for circumferential welding of end-caps to cladding samples. Because the welds and end-caps are not subjected to pressure, the end-caps should be small and the masses should be minimized as they serve as sinks for hydrogen.

### 4.4 Length, outer diameter, and wall-thickness measurements

Outer diameter and wall thickness vary somewhat along the length of fuel rod cladding. They should be measured and recorded for each sample. For cladding with a nominal diameter of 9.50 mm, the actual diameter of the sample can vary from 9.46 to 9.50 mm. The outer diameter should be determined to two decimal places (in mm) based on the average of the maximum and minimum diameters. For cladding with a nominal wall thickness of 0.57 mm, the actual wall thickness can vary from about 0.56 to 0.60 mm. Wall thickness should be determined for each sample to two decimal places (in mm) based on four readings at locations  $\approx 90^\circ$  apart. The actual sample length should be measured and recorded to one decimal place accuracy (e.g., 25.1 mm). Also, the ends of the sample should be polished to remove burrs prior to sample-length measurement. While removing burrs, it is important to avoid scratching the cladding inner-surface, especially with circumferential grooves, which would induce early hydrogen pickup. Also, the ends of the sample should be relatively flush ( $90 \pm 5^\circ$  relative to longitudinal axis). Outer diameter, wall thickness and length are used to normalize sample weight gain to exposed surface area.

#### 4.5 Pre-test cleaning with chemical detergent or organic solvent and rinsing

Appendix X1 ("Guide to Specimen Preparation") of the American Society for Testing & Materials (ASTM) Standard (G 2/G 2M – 06) for Corrosion Testing describes sample cleaning procedures in X1.2 [7]. These procedures should be followed for breakaway oxidation tests. Specifications and requirements in subsections X1.1 ("Tubes with a Second Material on Inner Diameter") and X1.3 (Etching) should be ignored. Based on Ref. 3 and subsequent work done at ANL, samples should not be etched with HF-containing acid mixture as part of the test cleaning process (see Appendix B). Following cleaning, direct contact with the sample should be avoided by using surgical gloves for handling.

#### 4.6 Pre-test sample weight measurement (after drying)

Pre-test sample weight should be measured to the nearest 0.1 mg as specified in 7.1.3 of Ref. 7. As drying after cleaning may take several hours, it is also permissible to measure pre-test sample weight after cleaning with an organic solvent such as ethanol that vaporizes rather quickly. The pre-test weight is used in the determination of sample weight gain. Although weight gain is not used as a metric for breakaway oxidation in these tests, it is used as a partial validation of the reported isothermal oxidation temperatures and a check on steam flow conditions.

### 5. Temperature Heat-up and Cool-down Rates and Heating Methods

#### 5.1 Temperature Heat-up and Cool-down Rates

For long-time isothermal tests, heating and cooling rates are not critical parameters. However, long heating and cooling times should be avoided as they may induce breakaway oxidation at earlier isothermal-temperature times (i.e., within  $\pm 20^\circ\text{C}$  of target temperature for slow ramps or for ramps with temperature overshoot). The total ramp time from  $650^\circ\text{C}$  to the target temperature (heating phase) and from the target temperature to  $650^\circ\text{C}$  should be  $<10\%$  of the isothermal test time. With regard to temperature overshoot during the heating phase, it is also not clear if this has any effect on isothermal breakaway oxidation time. However, temperature overshoot be limited to  $\leq 20^\circ\text{C}$  for  $\leq 20$  s.

Rapid cooling by means of water quench is not required for breakaway oxidation tests. However, for very slow-cooling furnaces, quench may be used to reduce the cooling time.

#### 5.2 Radiant heating

Radiant heating in a quad-elliptic furnace has been used to generate the breakaway-oxidation data [1,3,6]. This heating method, along with furnace power controlled by feedback from a thermocouple on or near the sample, allows for controlled heating rates and relatively fast cooling rates ( $<100$  s from  $1000^\circ\text{C}$  to  $650^\circ\text{C}$ ). For 25-mm-long samples with 9.50-mm outside diameter, axial temperature variations are negligible, but circumferential temperature variations are in the range of  $10\text{-}15^\circ\text{C}$ . These can be reduced by using radiant-heating furnaces with more than four lamps. However, the circumferential variation has a practical value in that a range of temperatures (e.g.,  $1000\pm 7^\circ\text{C}$ ) can be investigated with a single sample. With proper thermal benchmarking, radiant-heating furnaces are acceptable for conducting breakaway oxidation tests

#### 5.3 Resistance heating

Most breakaway oxidation tests [e.g., 2, 4, 5] have been conducted in resistance-heating furnaces. As compared to radiant-heating furnaces, these furnaces are characterized as having a larger uniform temperature zone and as having very slow heating and cooling rates. Faster heating and cooling rates are

achieved by controlled movement of the sample into and out of the furnace. Benchmark tests should be performed to determine the heating and cooling rates. It is necessary information for the determination of the time to reach the target isothermal temperature. Resistance-heating furnaces are acceptable for conducting breakaway oxidation tests.

#### 5.4 Induction Heating

Induction heating has the advantage of rapid heating and cooling rates. It has been used in the CINOG program in France (8) to generate weight-gain kinetics data for Zry-4, M5, and developmental alloys. Although the weight gain data appear reliable, it is not clear what impact this heating method would have on initiation of breakaway oxidation. It is also not clear as to whether the use of optical pyrometry to measure temperature requires etching of the cladding surface. Because of the uncertainties regarding induction heating, optical pyrometry, and required surface preparation, induction heating is not recommended for breakaway oxidation studies.

#### 5.5 Direct electrical heating

Direct electrical heating of cladding has been used in the past for LOCA-relevant studies. Because resistance and heating rate change with temperature and because of the unknown effects of such heating on breakaway oxidation, direct electrical heating of cladding is not recommended for breakaway oxidation studies. However, "indirect" electrical heating may be an acceptable method for internal heating of another material inside the cladding to generate a heat flux simulating heating of the cladding by means of decay heat from the fuel.

### **6. Temperature Control and Monitoring**

#### 6.1 Thermocouples

For the temperatures relevant to this breakaway oxidation test procedure, thermocouples (TCs) used to record temperature and/or control furnace power may be either Type K (chromel-alumel) or Type S (Pt/10%Rh-Pt). The TCs must be calibrated using instrumentation and standards that are traceable to the National Institute of Standards and Technology (NIST). Generally, this service is provided by the thermocouple vendor, who, for an extra fee, provides a Certificate of Calibration. Every TC used in the breakaway oxidation study to monitor sample temperature, either directly or indirectly, must have a Certificate of Calibration showing the results of the calibration at a minimum of two temperatures: 800°C and 1000°C. Copies of these certificates should accompany the data report. Verification should be provided demonstrating that the vendor actually did do the calibration according to standards set forth in ISO 10012-1, ISO 9001 and American National Standards Institute/National Conference of Standards Laboratories ANSI/NCSL Z540-1-1994

#### 6.2 Thermal benchmarks

Welding TCs directly onto the outer surface of the breakaway oxidation sample is not recommended. The geometric discontinuity at the TC-sample junction can induce early breakaway oxidation, which would be an artifact. Also, the presence of the TC during testing and its removal following testing will affect the accuracy of the post-test sample weight.

In most cases, the control TC will be welded onto the sample holder or as close to the sample as possible without contacting the sample. This requires thermal benchmarks to be performed to establish the relationship between the control TC that will be used during data-generating tests and the temperature of the sample outer surface. The thermal benchmarking should be performed at a minimum of two

temperatures: 1000°C and 800°C. For the work reported in Ref. 3, two-to-three TCs (120° apart) were welded directly onto the benchmark sample outer surface. These readings were compared to the readings of three TCs welded onto the sample holder at a location just above the sample. For radiant heating and large diameter ( $\approx 11$  mm) cladding, three TCs were welded directly to the cladding outer surface to better define the average and one-standard deviation cladding temperature. For smaller diameter cladding (9.50 mm), only two TCs welded directly to the cladding surface were needed. For the thermal benchmark tests, it is important that these be conducted under the same flowing steam conditions as used in the data-generating tests.

For resistance-heating furnaces, the same thermal-benchmarking method described for radiant-heating furnaces can be used. However, other methods can be used to determine the relationship between the sample temperature and the holder temperature. These furnaces come with a built-in TC that controls the power to the furnace. Thermal benchmarking can be done with a suspended and moveable TC to map out the axial variation in temperature for a sample assembled into a test train. Recorded temperatures should be compared to the TC or TCs welded to the sample holder. Circumferential temperature variations are generally small for such furnaces. The results of the thermal benchmark tests should be documented and included in the data report.

### 6.3 Weight-gain benchmarks

Following thermal benchmarking, samples should be tested without TCs welded onto the sample to determine the weight gain. These tests should be conducted at 800°C and 1000°C. The test times should be less than those that result in breakaway oxidation. For 1000°C, an isothermal test time of 2000 s is recommended. For Zry-2, Zry-4 and ZIRLO oxidized at 1000°C, the measured weight gain (normalized to the surface area exposed to steam) should be in good agreement with the Cathcart-Pawel (CP) correlation predictions. If the measured weight gain differs from the CP-predicted weight gain by  $\geq 10\%$ , then data-generating testing should not be initiated until the discrepancy is resolved. For Zr-lined Zry-2 and Zr-1Nb alloys, the measured weight gain at 1000°C is considerably less than the CP-predicted weight gain. For these materials, the results of the weight-gain benchmark should be compared to the vendor-generated database or the results given in Ref. 3 for these alloys. Below 1000°C, especially below 950°C, the CP-correlation deviates from the well-established databases for cladding alloys and ceases to be a best-estimate correlation. For the weight-gain benchmark at 800°C, the normalized measured weight-gain should be compared to a well-established vendor-generated database. The results of the weight-gain benchmark tests should be documented and included in the data report.

## 7. Water Quality, Steam Flow Rate, and Steam Pressure

### 7.1 Water quality

Purified water should be used for generating steam. Reference 7 specifies that Grade A water with  $\leq 45$  ppb oxygen should be used for corrosion tests in pressurized water and steam. Laboratory grade, Type I (distilled and/or deionized) water is also of sufficient purity for breakaway oxidation tests at  $\geq 650^\circ\text{C}$ . ASTM, the National Committee for Clinical Laboratory Standards (NCCLS, now CLSI) and ISO 3696 have similar definitions for Type I purified water.

## 7.2 Steam flow rate

The average steam flow rate used in breakaway oxidation studies should be determined (and reported) from the mass of condensed water collected during these long-time tests divided by the test time and normalized to the net cross-sectional area of the steam chamber. The average steam flow rate should be in the range of 0.5 to 30 mg/(cm<sup>2</sup> · s). Justification for this range is provided in the following.

Leistikow and Schanz (2) and Uetsuka (9) studied the effects of low steam flow rates on the oxidation kinetics of Zry-4 at 1000°C. Their results are summarized in Fig. 9 of Ref. 2. In terms of flow rate normalized to the cross-sectional area of the steam chamber, the oxidation kinetics began to decrease due to steam starvation for flow rates <0.05 mg/(cm<sup>2</sup> · s). For the Ref. 2 work, sample length was 30 mm and oxidation was two-sided. Aomi et al. (10) studied the relationship between weight gain and steam flow rate for oxidation temperatures up to 1200°C. They found that the weight gain for fixed test times and temperatures was independent of steam flow rates in the range of 0.8 to 7.8 mg/(cm<sup>2</sup> · s). Kawasaki, et al. (11) also performed high-temperature oxidation tests to determine the range of steam flow rates for which the weight gain for a given test time was independent of steam flow rate. They report this range as 3 to 28 mg/(cm<sup>2</sup> · s).

For breakaway oxidation studies conducted in steam at ≤1050°C, the results of Refs. 2, 9 and 10 are particularly relevant for the minimum steam flow rate. However, as individual sample lengths (≥25 mm for two-sided tests and ≥75 mm for one sided tests) include lengths longer than used in the Ref. 2 study and as many as five two-sided test samples may be stacked inside the steam chamber, the minimum steam flow rate is set at 0.5 mg/(cm<sup>2</sup> · s), which is ten times the minimum given in Refs. 2 and 9. For the results presented in Ref. 3, the normalized steam flow rate was 5.3±0.8 mg/(cm<sup>2</sup> · s). This rate is well above the minimum rates determined from Refs. 2, 9, 10 and 11.

Although maximum steam-flow rates of 7.8 and 28 are given in Refs. 10 and 11, it is not clear why higher steam flow rates would have an effect on weight gain and oxidation kinetics. It is desirable to have a steam-flow rate higher than 0.5 mg/(cm<sup>2</sup> · s) to reduce temperature overshoot during the heating phase for bare cladding. In Ref. 6, the authors cite a fast heating rate of 50°C/s and a temperature overshoot for about 20 s at the end of the heating ramp with a steam flow rate of 10 mg/(cm<sup>2</sup> · s). Although the maximum steam flow rate may not be as critical as the minimum steam flow rate, it should be limited to ≤30 mg/(cm<sup>2</sup> · s) for the purposes of breakaway oxidation tests.

## 7.3 Steam pressure

Breakaway oxidation tests should be conducted at a steam pressure at or slightly above atmospheric pressure. This is consistent with what was used in previous breakaway oxidation studies [2,3,6,9].

# 8. Test Procedure

The specific details of the test procedure depend on the heating furnace used. Listed below are the steps used in Ref. 3, along with some generalizations that would apply to other heating and cooling methods other than the radiant-heating furnace used in Ref. 3. Detailed steps for Ref. 3 testing are documented in Ref. 13.

## 8.1 Test train and steam chamber

The test train or sample holder and the steam chamber form a unit that should be designed to contain the steam flow and to prevent impurities, especially nitrogen, from entering the chamber. By using steam that has a pressure slightly greater than the surrounding atmosphere, the test-train/steam-chamber does not

have to be "leak-tight" to a high level to serve the functions of providing a pathway for steam flow and protecting the sample from gas-phase impurities.

In choosing the material for the test train or sample holder, it is desirable to have a non-oxidizing or limited-oxidizing material such as stainless steels or nickel alloys (e.g., Inconel 600). However, the sample must be protected from direct contact with materials such as Fe- and Ni-alloys due to the low-temperature eutectics for Zr and these elements. Hofmann and Markiewicz (12) studied the reaction rates and eutectics of Zry-4 and Inconel-718. They also present binary phase diagrams for Zr-Fe and Zr-Ni, which have eutectic temperatures as low as  $\approx 930^{\circ}\text{C}$  and  $980^{\circ}\text{C}$ , respectively. In Ref. 3, alumina inserts and zirconia washers were used between the Inconel holder and the sample to prevent such reactions from occurring.

## 8.2 Purging steam chamber and stabilizing steam flow

Prior to heating and initiating steam flow, the steam chamber is filled with gas representative of the environment of the test facility (e.g., usually air). The test chamber may be purged with a high purity inert gas (e.g., argon) prior to introducing steam flow or it may be purged with low temperature steam prior to the temperature ramp. If steam is used to purge the steam chamber, then steam flow should be maintained for 500 s prior to the temperature ramp.

Steam flow should be initiated at a test chamber temperature of  $\approx 30^{\circ}\text{C}$ . Following introduction of steam into the chamber, furnace heating should commence for a pre-test hold temperature of  $300^{\circ}\text{C}$ . Stabilization of steam flow and  $300^{\circ}\text{C}$  sample temperature will occur within 500 s.

Deviations from this procedure should be justified. Deviations that may have a significant effect on test results include heating the sample to the target temperature in an inert gas prior to introduction of steam flow. Impurities in the inert gas will result in an oxide or oxide-nitride film on the cladding that is not LOCA-relevant.

## 8.3 Ramping temperature and holding temperature at target value

The target test temperature is predetermined. It should be based on the average sample temperature. Depending on the heating method used, axial and circumferential variations could be significant. For a single sample, the axial temperature variation should be  $\leq 10^{\circ}\text{C}$  and the circumferential temperature variation should be  $\leq 20^{\circ}\text{C}$ .

For resistance furnaces, the sample heating rate is controlled by the rate of movement of the sample into the furnace heating zone. For radiant-heating furnaces, the heating rate is controlled through feedback from a thermocouple welded onto the holder to the furnace power. For the radiant heating used in Ref. 3, the temperature ramp rate was programmed to be very fast ( $>50^{\circ}\text{C/s}$ ) from  $300^{\circ}\text{C}$  to within  $50\text{--}100^{\circ}\text{C}$  of the target temperature and slow ( $2\text{--}3^{\circ}\text{C/s}$ ) from that temperature to the target temperature. This programmed ramp was designed to eliminate temperature overshoot. Typical test times from  $650^{\circ}\text{C}$  to  $1000^{\circ}\text{C}$  were  $<80$  s. It is recommended that the test time from  $650^{\circ}\text{C}$  to the target temperature be  $<100$  s for long-time isothermal tests.

## 8.4 End of heating phase and cool-down

After the target test time has been reached, furnace power should be turned off while steam flow is maintained. The rate of temperature decrease will depend on the heating method used and the method of removing the sample from the furnace. For in-situ cooling, the steam flow should be maintained until the sample temperature reaches  $800^{\circ}\text{C}$ . For the Ref. 3 work, this corresponded to a holder temperature of

700-720°C. Following this step, there should be ample moisture in the steam chamber to maintain a steam environment for cooling from 800 to 650°C.

#### 8.5 Determination of test time

The isothermal test time should be determined as the time interval between reaching within 20°C of the target temperature during the heating ramp to within 20°C of the target temperature during the cooling ramp. Depending on heating and cooling rates, this time will be about equal to the time at which the sample is at constant temperature.

### 9. Post-test Measurements and Characterization

#### 9.1 Sample drying time

In order to determine an accurate post-test sample weight, it is important that the sample be free of moisture. For drying in stagnant air, the drying time should be  $\geq 2$  hours. This time can be reduced significantly by the use of forced-air drying. Sample weight will continue to decrease during the drying process until it reaches a minimum and holds at that minimum. Whatever drying method is used, the drying time should be verified by weight measurements.

#### 9.2 Weight measurement and use of weight gain to verify oxidation temperature

The post-test sample weight should be measured to the nearest 0.1 mg as specified in 7.1.3 of Ref. 7. The weight gain (in mg) is determined by subtracting the pre-test weight from the post-test weight and normalizing this value to the steam-exposed surface area of the sample. Although this normalized weight gain is not used to determine breakaway oxidation time, it is used to validate temperature control and monitoring, as well as adequacy of steam flow and test procedures.

#### 9.3 Visual examination of sample outer surface

The sample outer surface should be examined visually and photographed. If the outer surface is smooth and lustrous black, then breakaway oxidation has not occurred and no further characterization is needed. If the outer surface is rough and dull black, then the sample may be well beyond the breakaway oxidation time as defined by the 200-wppm hydrogen pickup criterion. This condition is rarely observed at high temperature and would occur only if the discolored (gray or yellow) oxide completely delaminated and spalled off during cooling. If the sample shows any indications of discoloration (see Appendix C), then further characterization is needed.

Because of stress reversal at the ends of the sample due to the geometric discontinuity, it is possible that discoloration will appear only at the ends of the sample. Such a discontinuity is an experimental artifact. Beyond photographing such samples, no further characterization is required. However, discoloration and breakaway only at the sample ends are useful data because they indicate that the cladding material is sensitive to stress discontinuities and is close to the breakaway oxidation time. This artifact can be minimized or eliminated by machining a longitudinal scratch ( $25 \pm 5$   $\mu\text{m}$  deep and  $>25 \pm 5$   $\mu\text{m}$  wide) along the sample. Based on results presented in Ref. 3, such a scratch will induce breakaway oxidation away from the sample ends before the ends experience breakaway oxidation (see Appendix C).

#### 9.4 Hydrogen analysis for samples with outer-surface discoloration (relative to lustrous black)

Samples with outer-surface discoloration away from the sample ends and samples with rough dull-black outer-surface oxide should be further characterized by measuring the hydrogen content within the middle two-thirds of the sample. The hydrogen-analysis sample should be a ring that is sectioned to be 2-3 mm long and to include a region of discoloration. The selection of this ring is very important for scratch-free samples as hydrogen concentration is likely to have local variations ranging from 20 to 600 wppm for a corresponding average ring hydrogen content of 200 wppm. For pre-scratched samples, the hydrogen concentration along the sample is relatively uniform. As such, the precise location of the hydrogen-analysis ring is not critical. For some cladding materials, breakaway spreads very rapidly at high-oxidation temperatures (e.g., 1000°C) along the length and around the circumference of the sample such that the average hydrogen content increases from 200 wppm to 600-1000 wppm in <200 s [3]. However, for lower oxidation temperatures (e.g., 800°C), the time lag between the observation of surface discoloration and significant hydrogen pickup may be much longer [2].

For the case of multiple samples (e.g., five) tested at the same temperature and time, the reported hydrogen content for this set of samples should be reported as the average value  $\pm$  one-standard deviation. The average minus one standard deviation should be compared to 200-wppm hydrogen pickup to determine if breakaway has occurred.

There are several ways to measure hydrogen content in metals. Vacuum fusion is one method. The recommended method is documented in ASTM E1447, Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Thermal Conductivity Method [14]. This method has been used successfully to determine the hydrogen content in other metals such as Zr-alloys. The detailed procedure used to generate the results in Ref. 3 is documented in Ref. 15.

Along with the instrumentation needed (e.g., LECO RH-404 hydrogen determinator), verification of calibration coupons are available from the vendor. These titanium coupons have hydrogen contents traceable to NIST standards. Titanium coupons with 220-wppm are recommended for calibration verification. As these machines are very sensitive, it is important to verify calibration at least once in any given day prior to data generation. For hydrogen-content output that does not match visual observations (e.g., high hydrogen for lustrous black oxide or low hydrogen for gray or yellow regions of oxidized cladding), post-test calibration verification should be performed.

#### 9.5 Criterion (200-wppm H pickup) for breakaway oxidation based on retention of ductility

As shown in Appendix A, cladding rings with hydrogen pickup values  $\leq 440$  wppm oxidized at 970-1000°C are ductile at 135°C and brittle for hydrogen pickup values  $\geq 600$  wppm. The ductile-to-brittle transition is likely to occur for a hydrogen pickup of  $\approx 500$  wppm. Thus, ductility is retained for average hydrogen pickup values and post-test hydrogen values  $\leq 200$  wppm. At 970-1000°C oxidation temperatures, the transition from ductile to brittle behavior may occur within 100-200 s. The 200-wppm-H breakaway criterion is reasonable and justified at the higher oxidation temperatures at which the minimum breakaway oxidation time is most likely to occur.

#### 9.6 Characterization for one-sided and two-sided oxidation test samples

For one-sided oxidation tests, oxide is grown only on the sample outer surface. Thus, hydrogen pickup can only occur through the outer-surface oxide. However, possible hydrogen loss to the end-caps, which act as a sink for hydrogen, needs to be quantified. Hydrogen loss to the end-caps may occur by means of solid-state diffusion or gas-phase transport within the sample interior. Of these two mechanisms, gas-phase transport may be the dominant mechanism for hydrogen transport. The inner

surface is in the beta or mixed alpha-beta phase regime. Diffusion across the thin cladding wall, desorption from the cladding inner-surface and adsorption on the inner end-cap surfaces will result in a decrease in hydrogen content in the cladding metal. This effect will be more significant at the higher oxidation temperatures.

For two-sided oxidation tests, low breakaway oxidation times could be confirmed through metallographic examination to verify that breakaway occurred at the outer-surface oxide before it occurred at the inner-surface oxide. Based on one test result reported in Ref. 3, a cladding sample oxidized for  $\approx 3500$  s at  $1000^\circ\text{C}$  experienced complete tetragonal-to-monoclinic transformation at the cladding inner-surface and no such transformation at the cladding outer surface. However, the associated hydrogen pickup was only 100 wppm. Because of the curvature of the inner surface, the oxide tends to be under higher compressive stress than the outer surface. As such, cracks that form in the monoclinic oxide tend to be very tight, which limits the amount of steam absorbed into these cracks and the amount of hydrogen released and available for pickup.

## 10. Test Temperatures

Leistikow and Schanz [2] studied the oxidation kinetics and breakaway oxidation for Zry-4 over a range of temperatures ( $600$ - $1600^\circ\text{C}$  with temperature increments of  $50^\circ\text{C}$ ) for very long times ( $\leq 25$  hours). The results are extremely useful in demonstrating that breakaway oxidation time is not a monotonic function of oxidation temperature. Reinterpreting their data in terms of the 200-wppm-H criterion for breakaway, Leistikow and Schanz found minimum breakaway times of  $\approx 1800$  s at  $1000^\circ\text{C}$  and  $\approx 3600$  s at  $800^\circ\text{C}$ . These minimum times occurred at temperatures close to the phase change temperatures for Zry-4 ( $\approx 980^\circ\text{C}$  for the  $\alpha+\beta \rightarrow \beta$  transition and  $\approx 810^\circ\text{C}$  for the  $\alpha+\beta \rightarrow \alpha$  transition). Intermediate temperatures (e.g.,  $1025^\circ\text{C}$ ,  $985^\circ\text{C}$ ,  $825^\circ\text{C}$ , and  $775^\circ\text{C}$ ) were not investigated and relatively few oxidation temperatures ( $1000^\circ\text{C}$ ,  $900^\circ\text{C}$ ,  $800^\circ\text{C}$ , and  $650^\circ\text{C}$ ) were characterized in terms of increase in hydrogen content with test time. Also, although Zry-4 may be less sensitive to HF-containing acid cleaning than Nb-bearing alloys, it is not clear whether or not the cleaning process (HF-acid mixture) influenced the results.

Others have measured breakaway times for various zirconium alloys. Based on the results presented in Refs. 2, 3, 6, 16, 17, and 18, it appears highly likely that the minimum breakaway oxidation time will occur at a temperature near the upper phase-transformation temperature at which oxidation and hydrogen-generation rates are high relative to the lower phase-transformation temperature. For Zircaloy, Zr-1Nb-1Sn, and Zr-1Nb alloys the upper phase-transformation temperatures are in a rather narrow range ( $\approx 965$ - $985^\circ\text{C}$ ). The lower phase-transformation temperatures for these alloys span a larger range ( $\approx 650$ - $810^\circ\text{C}$ ).

To determine the minimum breakaway oxidation times, oxidation temperatures should include the following high temperatures:  $1050$ ,  $1030$ ,  $1015$ ,  $1000$ ,  $985$ ,  $970$ , and  $950^\circ\text{C}$ . The maximum test time should be  $5000$  s. If breakaway oxidation is observed to occur at  $< 5000$  s, the minimum time and corresponded temperature should be reported. Four additional tests should be conducted at this minimum time due to anticipated data scatter for hydrogen content or pickup. After the minimum breakaway time is determined for  $950$ - $1050^\circ\text{C}$ , a test should be conducted at  $800^\circ\text{C}$  to confirm that breakaway oxidation does not occur at this lower temperature for this particular time.

If breakaway is not observed for any of the test temperatures, then four additional tests should be conducted at  $1000^\circ\text{C}$  to determine data scatter with respect to hydrogen pickup.

Although not recommended, these tests may be conducted first with polished and cleaned cladding material prior to testing cladding with simulated fuel-fabrication plant cleaning and scratching. Such tests may be helpful in determining the breakaway sensitivity of a cladding material to oxidation temperature. However, the tests should be repeated with cladding that has been exposed to any HF-acid mixture

cleaning used at the fuel fabrication facility and that has been scratched to a wall-thickness depth of  $25\pm 5\ \mu\text{m}$  or whatever typical scratch depth that can be justified. The final results for minimum breakaway oxidation time are based on such cladding samples.

In order to minimize the number of tests, it is recommended that all tests be conducted with scratched samples that have experienced the full post-polishing cleaning process. If breakaway is not observed to occur under any of the test conditions, then the total number of tests would be reduced to 8 scoping tests, along with 4 confirmation tests at  $1000^\circ\text{C}$ . For the five tests run at  $1000^\circ\text{C}$ , hydrogen concentration should be determined for rings sectioned from all five test samples to confirm that breakaway has not occurred. If  $>200$ -wppm hydrogen is observed after 5000 s at one or more temperature, then the test time would have to be reduced until the hydrogen pickup fell below 200 wppm.

It is recommended that testing be initiated at  $1000^\circ\text{C}$  for a test time of 5000 s. If breakaway is observed based on visual examination and the hydrogen content is  $>200$  wppm, then the test time at  $1000^\circ\text{C}$  should be reduced until the hydrogen content is  $<200$  wppm or until no discoloration is observed on the cladding outer surface. Subsequent tests at higher (e.g.,  $1015^\circ\text{C}$ ) and lower (e.g.,  $985^\circ\text{C}$ ) should be conducted at the minimum time for  $1000^\circ\text{C}$  ( $\leq 5000$  s). If breakaway is observed at a lower test time for a temperature other than  $1000^\circ\text{C}$ , then that minimum time should be used as the maximum test time for subsequent temperatures. This process is documented in Ref. 3.

Test results reported in Refs. 3 and 16 indicate significant temperature sensitivity for breakaway oxidation of one cladding material. The minimum breakaway oxidation time was found to occur at  $970$ - $985^\circ\text{C}$ . Also, as breakaway oxidation is an instability phenomenon, there is considerable scatter in the data for hydrogen pickup vs. time. For an oxidation temperature of  $1000^\circ\text{C}$ , there appears to be less scatter, and the breakaway oxidation time can be determined to be  $4000\pm 200$  s for 200-wppm hydrogen pickup (see Fig. 2). However, as shown in Fig. 3, there is considerably more scatter within the critical temperature range of  $970$ - $985^\circ\text{C}$  for which the minimum breakaway time was determined to be  $3100\pm 300$  s for 200-wppm hydrogen pickup.

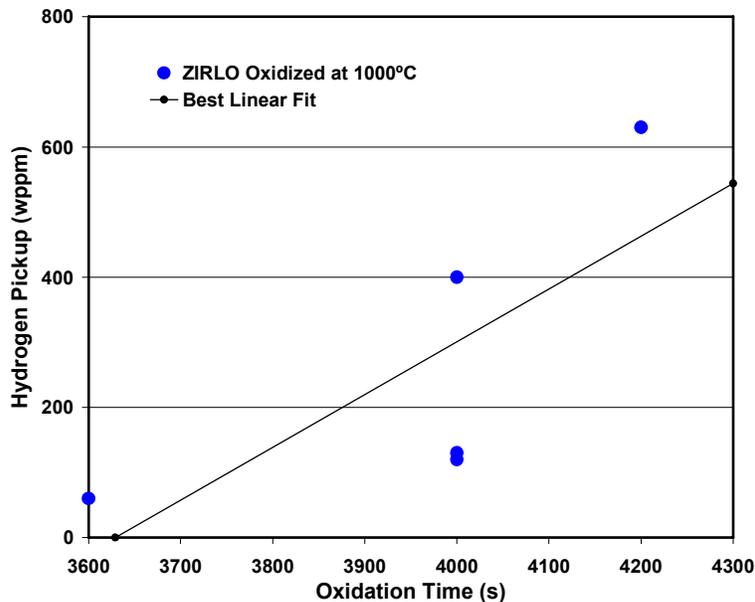


Fig. 2. Hydrogen pickup vs. test time data for as-fabricated ZIRLO oxidized at  $1000^\circ\text{C}$ .

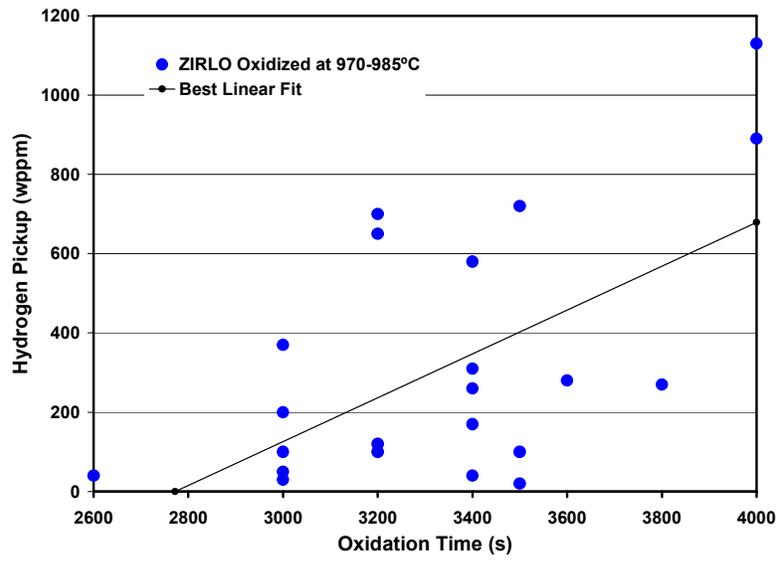


Fig. 3. Hydrogen pickup vs. test time for as-fabricated, pre-scratched and pre-oxidized ( $\approx 1\text{-}\mu\text{m}$  thick) ZIRLO oxidized at 970-985°C.

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## Appendix A

### Rationale for the 200-wppm Hydrogen Pickup Criterion for Breakaway Oxidation

Table A1 summarizes the increase in hydrogen pickup with test time for 3 of the cladding materials tested by ANL [3]. The hydrogen pickup rate was rapid for two of the cladding materials and more gradual for one of them. Given that breakaway oxidation is an instability phenomenon that can spread rapidly in the axial and circumferential directions, it is important to establish a hydrogen pickup or content limit for which cladding retains ductility. The criterion of 200-wppm hydrogen pickup was established prior to initiation of the Ref. 3 breakaway oxidation study. It was subsequently confirmed by conducting ring compression tests for samples sectioned from the breakaway oxidation samples. Table A2 and Fig. A1 summarize the results of these ring-compression tests. Ductility is maintained for  $\leq 435$  wppm average hydrogen pickup. Thus, the 200-wppm hydrogen pickup criterion is conservative by a factor of at least two. However, it is not overly conservative for high oxidation temperatures because the time needed to increase from 200-wppm to  $>400$  wppm hydrogen pickup could be as low as 100 s.

Table A1 Summary of Hydrogen Pickup vs. Test Time for Several Cladding Materials Oxidized at 970-1000°C

Cladding Material	Test T, °C	Test Time, s	Hydrogen Content, wppm	Hydrogen Pickup, wppm	Comment
15×15 Low-tin Zry-4 (Old)	985	3600	186	170	Pre-scratched Lustrous Black OD Large Gray Areas on OD
		3800	40-60	20-40	
		3900	1260	1320	
15×15 Low-tin Zry-4 (Modern)	985	5000	286	280	Gray Line on OD Large Gray Area on OD
		5400	411	410	
17×17 ZIRLO (Modern)	985	3400	174	175	Yellow Area along Pre-Scratch Lustrous Black OD Yellow Circle on OD
		3400	50	20	
		3600	267	270	

Table A2 Ductility at 135°C vs. Hydrogen Pickup for Several Cladding Materials Oxidized at 970-1000°C

Cladding Material	Test T, °C	Hydrogen Content, wppm	Hydrogen Pickup, wppm	Offset Strain at 135°C, %
15×15 Low-tin Zry-4 (Old)	985	186	170	5.2
		1260	1320	0.9
15×15 Low-tin Zry-4 (Modern)	985	286	280	6.0
		270	260	5.9
17×17 ZIRLO (Modern)	985	174	175	5.1
	985	214	215	>2
	970	416	435	4.8
	1000	555	600	0.8
	985	731	765	0.8
	985	987	1040	0.8

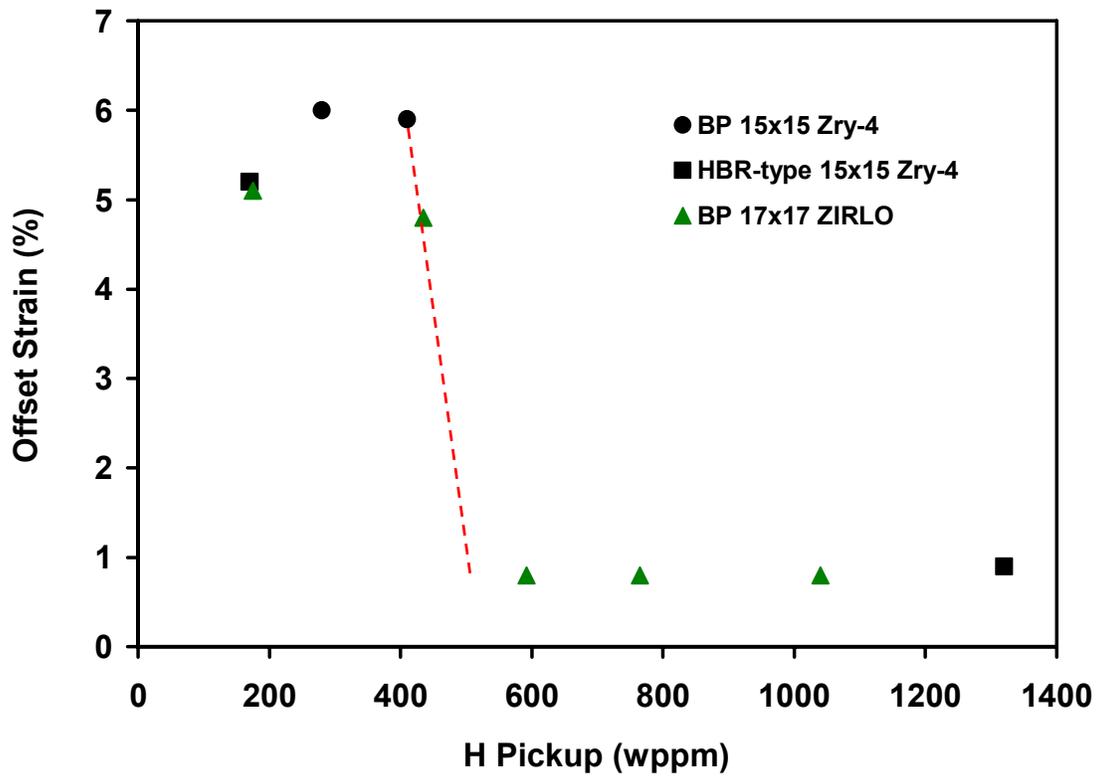


Fig. A1. Ductility (from ring compression tests at 135°C) vs. hydrogen pickup for breakaway oxidation samples oxidized at 970-1000°C. Ductile-to-brittle transition occurs at  $\approx 500$  wppm hydrogen pickup.

## Appendix B

### Negative Effects of Etching with HF-containing Acid as Part of Sample Cleaning

As part of the Ref. 3 work, 17×17 low-tin Zry-4, 17×17 ZIRLO and 17×17 M5 cladding samples were subjected to etching for 180 s in an HF-containing solution (3.5%-HF + 45%-HNO<sub>3</sub> + 51.5%-H<sub>2</sub>O) prior to ultrasonic cleaning with ethanol and water. The samples were then oxidized for 2400 s at 1000°C. The cladding materials showed different sensitivity to etching based on visual observation, with the inner surface showing more discoloration than the outer surface for each material. Hydrogen-content measurements were not performed because of the likely hydrogen pickup from inner surfaces. The outer cladding surfaces for the three oxidized materials are shown in Figs. B1a-c. Pre-etched Zry-4 and M5 exhibited lustrous black outer-surface oxides, while ZIRLO showed signs of discoloration indicative of tetragonal-to-monoclinic transformation and breakaway oxidation.

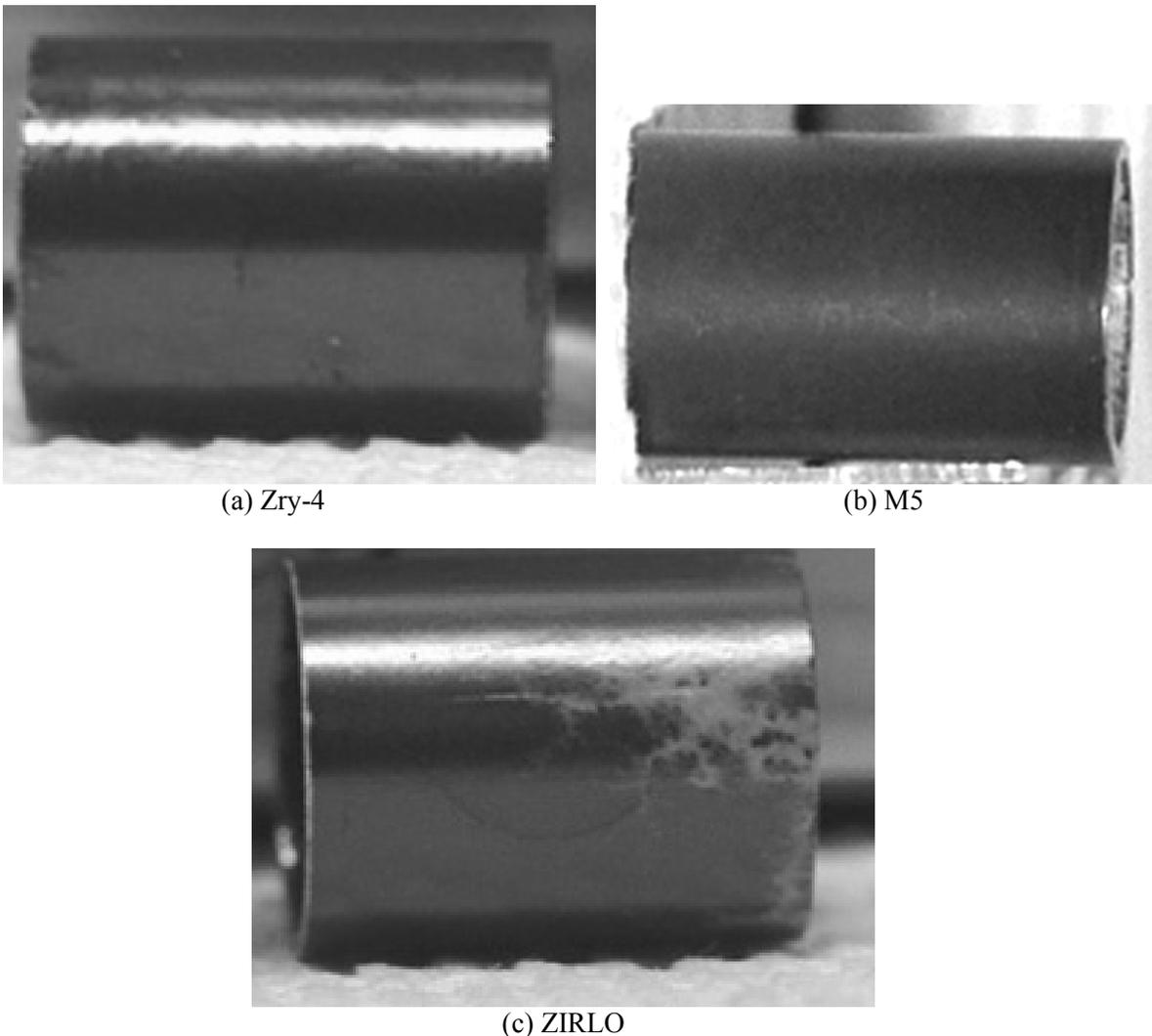
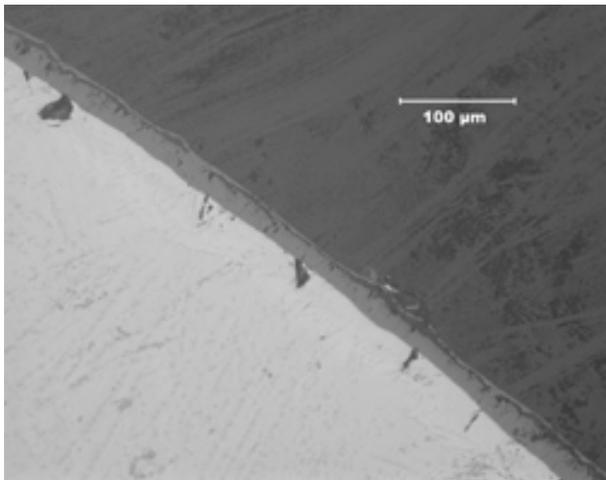


Fig. B1. Outer surfaces of samples etched for 180 s in 3.5%-HF acid mixture prior to oxidation at 1000°C for 2400-s hold time: (a) Zry-4, (b) M5 and (c) ZIRLO. (Note: surface of M5 was lustrous black, but quality of photograph is not high enough to show it.)

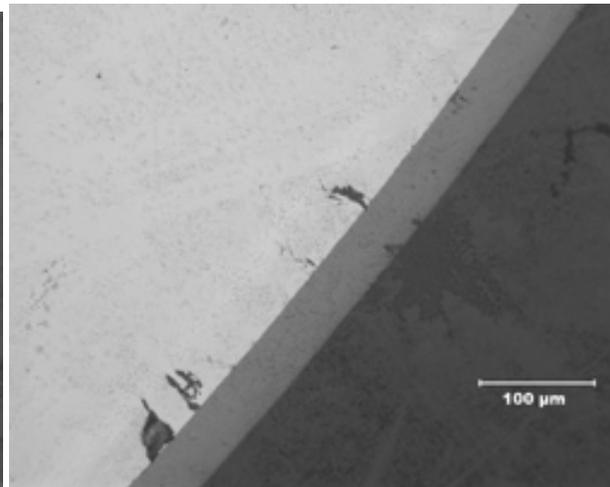
For the spent nuclear fuel (SNF) program, ZIRLO samples were etched in a 1%-HF acid solution for 180 s prior to hydriding. This worked well for the SNF application for which cladding temperatures are  $\leq 400^\circ\text{C}$  and the cladding is in a non-oxidizing environment (He-filled storage, transport, or storage-and-transport casks). However, HF-etching prior to hydriding caused breakaway oxidation for samples oxidized for only 280 s total test time with a hold time of 180 s at  $1200^\circ\text{C}$ . Figure B2a shows the appearance of the outer cladding surface after oxidation, and Figs. B2b and B2c show regions of breakaway and intact oxide layers, respectively. The surface discoloration is significant. Some of the discoloration may be due to impurities picked up during the hours of argon purging and exposure to  $\text{Ar}+30\%\text{H}_2$  at  $400^\circ\text{C}$ . Additional studies were performed with lightly etched samples exposed to the 1%-HF acid mixture for 60 s, 30 s and 15 s. These samples were not exposed to the hydriding environment, so the only source of impurity was from the acid etching. The 15-s sample was cleaned in  $80^\circ\text{C}$  distilled water prior to the standard ultrasonic cleaning in ethanol and distilled water. Figure B3 shows that surface discoloration persists even for the 15-s-etch sample following oxidation at  $\leq 1200^\circ\text{C}$  for 280 s.



(a)



(b)



(c)

Fig. B2. Appearance and morphology of outer surface oxide following etching for 180 s in 1%-HF acid bath, exposure to flowing Ar and  $\text{Ar}+30\%\text{H}_2$  for  $<10$  h at  $400^\circ\text{C}$  and oxidation for 280 s with a 180-s hold time at  $1200^\circ\text{C}$ : (a) appearance of outer surface; (b) metallographic image showing breakaway oxidation under area of discoloration; and (c) metallographic image of intact oxide layer under black surface region.



Fig. B3. Outer-surface appearance of ZIRLO sample that was etched for 15 s in a 1%-HF acid mixture, rinsed in 80°C distilled water, ultrasonically cleaned in ethanol and water baths, and heated in steam from 300°C to 1200°C in 100 s and held at 1200°C for 180 s.

## Appendix C

### Correlation between Cladding Outer-surface Appearance and Hydrogen Pickup

The breakaway oxidation tests documented in Ref. 3 were conducted with a furnace equipped with a viewing port. The window allowed viewing of about half the sample outer surface. Initial scoping tests were conducted for a fixed oxidation time. This process was refined such that tests were terminated when discoloration was observed to initiate on the cladding outer surface. As such, a considerable database was generated for outer surface appearance vs. hydrogen content and hydrogen pickup. Examples from the Ref. 3 work are presented to guide investigators on what to expect from small discoloration spots and from larger areas of surface discoloration. These examples are for test samples exposed to higher steam oxidation temperatures (970-1000°C). For these samples, small areas of discoloration correlated with hydrogen pickups in the range of 50-250 wppm, while larger areas of discoloration correlated to >400-wppm hydrogen. At lower oxidation temperatures (e.g., 800°C) with corresponding lower hydrogen generation rates, significant surface discoloration may precede 200-wppm hydrogen pickup.

For Zry-4 cladding materials, the surface discoloration (indicative of breakaway oxidation and high hydrogen pickup) progresses from lustrous black to dull black to gray. Figure C1 shows pre-breakaway H. B. Robinson (HBR) type 15×15 Zry-4 following oxidation at ≈1000°C for 3600 s. The sample is lustrous black, but the hydrogen pickup is 40 wppm, indicating that breakaway is likely to occur within a few hundred seconds beyond 3600 s. The other two samples were oxidized for long test times (5400 s and 7200 s). The outer surface of these samples is completely gray and the hydrogen pickup values are high. For Zry-4, by the time that the outer surface transforms from lustrous black to gray, the sample is well beyond breakaway initiation.

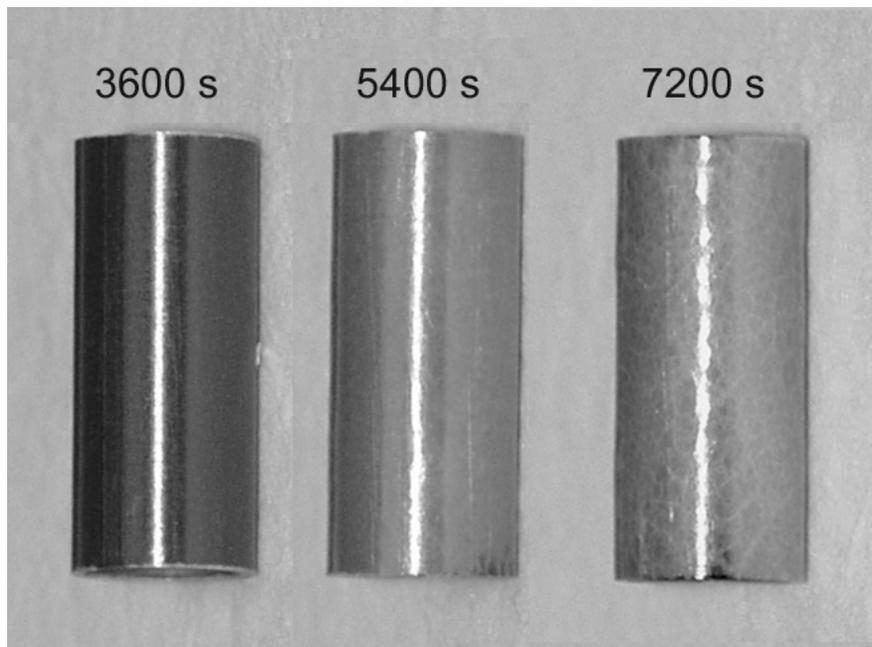
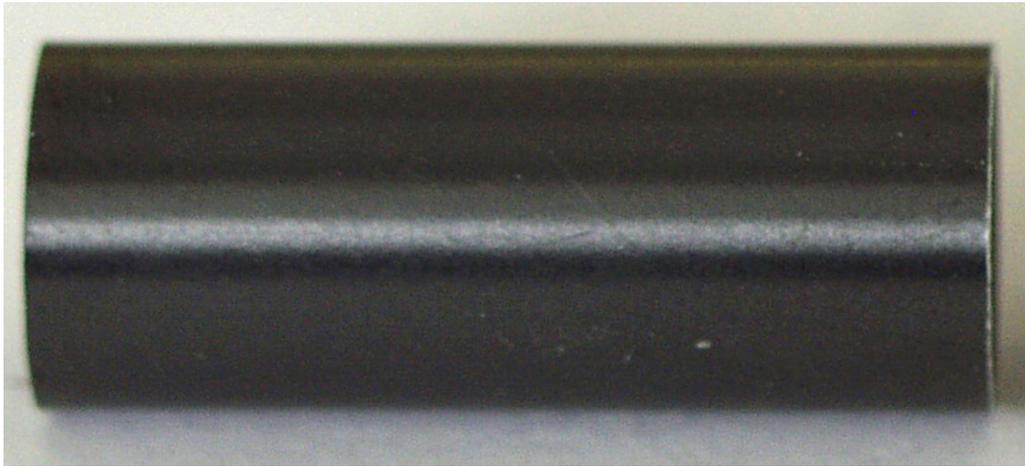


Fig. C1. Outer-surface appearance of an older vintage (HBR) of 15×15 Zry-4 following oxidation at ≈1000°C for 3600 s (lustrous black with 40-wppm hydrogen pickup), 5400 s (gray with 2300 wppm hydrogen pickup), and 7200 s (with 3100-wppm hydrogen pickup).

Similar results were obtained for 17×17 ZIRLO oxidized at 1000°C. However, for ZIRLO the color change of the outer surface was from lustrous black to yellow (or tan). Figure C2 shows the transformation of colors from lustrous black to lustrous black with yellow spots to yellow.



(a) 1500 s at 1000°C; 5-wppm hydrogen pickup



(b) 3600 s at 1000°C; 60-wppm hydrogen pickup



(c) 5000 s at 1000°C; 1350-wppm hydrogen pickup

Fig. C2. Outer surface appearance and hydrogen pickup for ZIRLO samples oxidized at 1000°C: (a) lustrous black at 1500 s, (b) lustrous black with yellow spots at 3600 s, and (c) yellow at 5000 s.

For polished 15x15 Zry-4, the minimum breakaway oxidation time is  $\approx 5000$  s and occurs at a long-time oxidation temperature of 985°C. Figure 38a in Ref. 3 shows the appearance of the outer surface of the sample oxidized at 985°C for 5000 s. It is repeated below as Fig. C3 for the convenience of the reader. The sample exhibited a gray line along the axial direction. Metallography (Figs. 38b and c in Ref. 3) confirmed that the outer-surface oxide under this gray region was in breakaway, while the inner surface oxide was still intact. Also, the circumferential variation of hydrogen was significant with a peak in hydrogen concentration under the gray layer. The sample picked up 280-wppm hydrogen, which is just beyond the 200-wppm criterion.

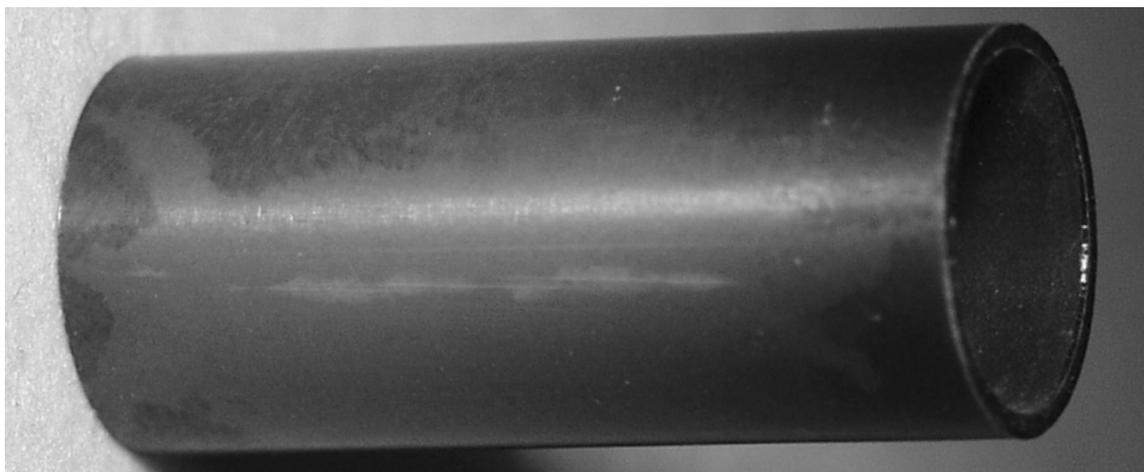


Fig. C3. Polished 15x15 Zry-4 cladding oxidized at 985°C for 5000 s. Gray line along about two-thirds of the sample length is the region under which breakaway oxidation had occurred. Circumferentially averaged hydrogen pickup was  $280 \pm 160$  wppm. Hydrogen pickup under the gray streak was  $> 460$  wppm.

Figures C4-C9 show ZIRLO samples with surface discoloration and the corresponding hydrogen pickup. It is clear from these photographs that any visual evidence of breakaway oxidation, even small spots, is indicative of initiation of local breakaway oxidation and hydrogen pickup. Figures C4-C6 correspond to Figs. 81-83 in Ref. 3. Figure C7 is taken from Ref. 16 (Fig. 2) and Figs. C8-C9 are taken from Ref. 18 (Figs. 2 and 4).

Figure C10 is from Ref. 19. The sample was oxidized at an isothermal temperature of 980°C for 2000 s. The temperature was cycled five times from 1030°C to 930°C for 400 s prior to an additional 400 s isothermal oxidation at 980°C. The surface-discoloration pattern is different from those obtained from isothermal tests and the color was a mixture of yellow and gray.

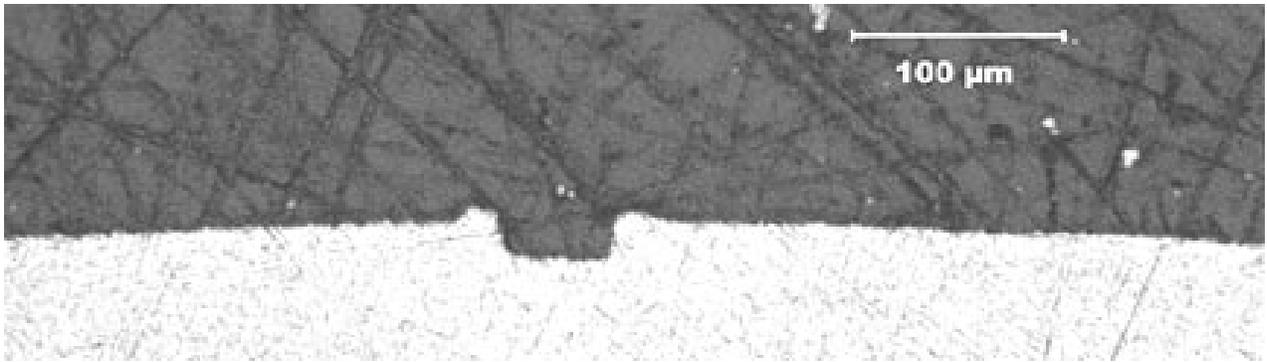


Fig. C4. Cross section of ZIRLO cladding with machined scratch  $\approx 20\text{-}\mu\text{m}$  deep into outer surface.



Fig. C5. Outer surface of scratched ZIRLO sample following oxidation at  $985^{\circ}\text{C}$  for 3400 s. Local hydrogen pickup under yellow surface was 440 wppm; average pickup was 175 wppm.

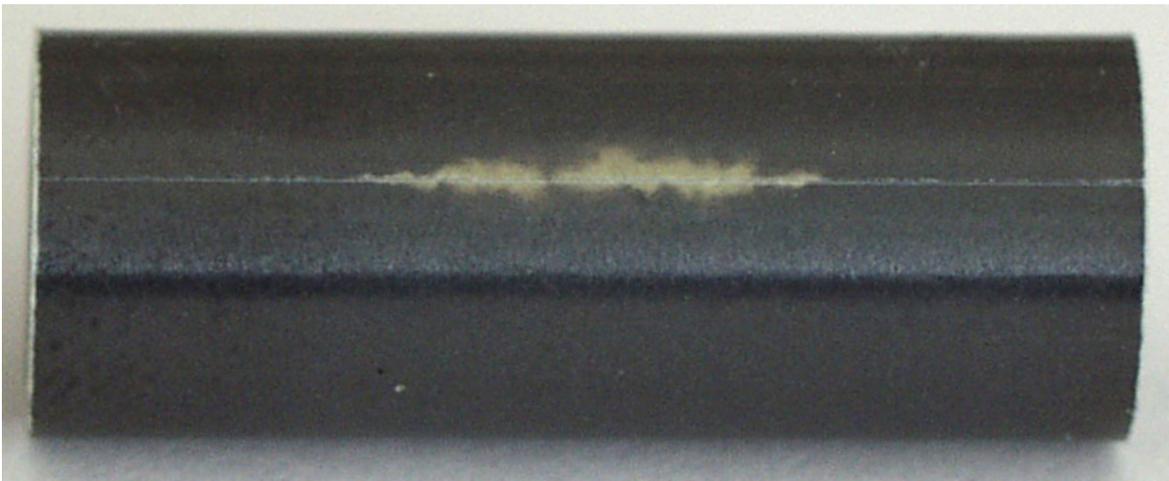


Fig. C6. Outer surface of scratched ZIRLO sample following oxidation at  $970^{\circ}\text{C}$  for 2600 s. Local hydrogen pickup under the yellow surface was 120 wppm; average pickup was 44 wppm.

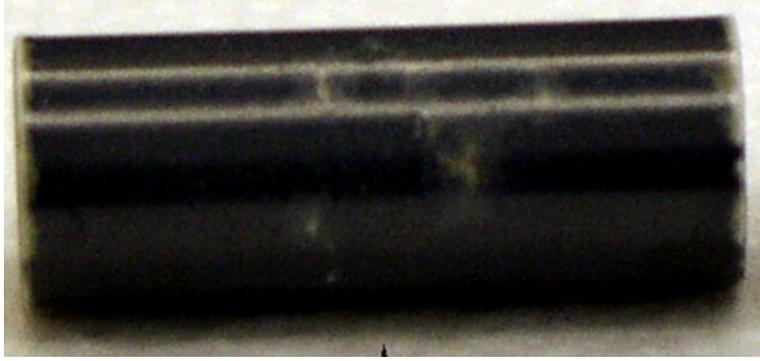


Fig. C7. Outer-surface appearance for ZIRLO sample oxidized at 1000°C for 4000 s. Hydrogen pickup was  $120 \pm 110$  wppm with  $>280$  wppm under yellow spots.

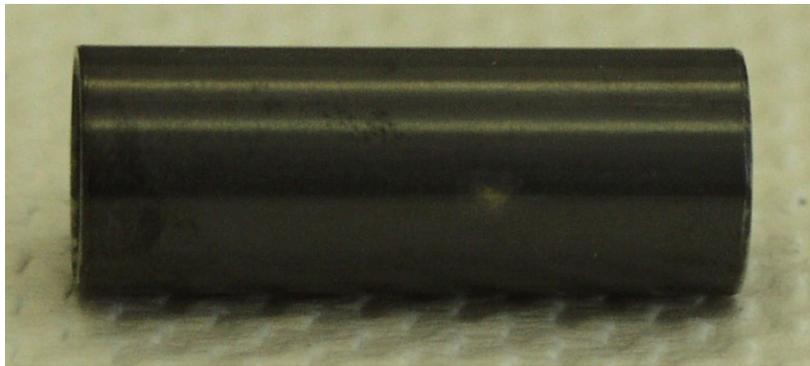


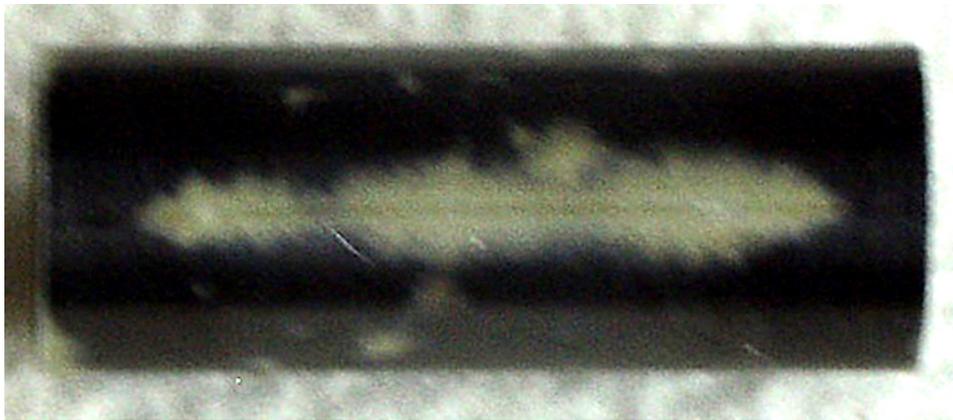
Fig. C8. Outer surface of prefilmed ZIRLO oxidized at 985°C for 3000 s. One yellow spot can be seen just to the right of the sample midplane. Hydrogen pickup in a 2-mm-long ring including the yellow spot was  $50 \pm 40$  wppm.



Fig. C9. Outer surface of prefilmed ZIRLO oxidized at 980°C 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  $120 \pm 120$  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)

Fig. C10. Outer-surface appearance of as-fabricated ZIRLO sample oxidized for a total test time of 2800 s: 2400 s at 980°C and 400 s with five temperature cycles from 930-1030°C. Hydrogen content was measured to be  $230 \pm 80$  wppm, indicating breakaway oxidation for a total test time of 2800 s.