U.S. NUCLEAR REGULATORY COMMISSION
OFFICE OF NUCLEAR REGULATORY RESEARCH

Month Year
Division 1

DRAFT REGULATORY GUIDE

Contact: M. Flanagan
(301) 251-7547

DRAFT REGULATORY GUIDE DG-1261

(Proposed New Regulatory Guide)

CONDUCTING PERIODIC TESTING FOR BREAKAWAY OXIDATION BEHAVIOR

A. INTRODUCTION

This guide describes a method that the U.S. Nuclear Regulatory Commission (NRC) considers acceptable to implement the requirements in Title 10, Section 50.46c, of the *Code of Federal Regulations* (10 CFR 50.46c) (Ref. 1), for an embrittlement mechanism, referred to as a "breakaway oxidation," that may occur during prolonged exposure to elevated cladding temperature during a loss-of-coolant accident (LOCA).

In 10 CFR 50.46c, the NRC calls for measurement of the onset of breakaway oxidation for a zirconium cladding alloy based on an acceptable experimental technique. The regulations also call for the evaluation of the measurement relative to emergency core cooling system performance, and periodic testing and reporting of the values measured. This regulatory guide describes an experimental technique acceptable to the NRC staff to measure the onset of breakaway oxidation in order to support a specified and acceptable limit on the total accumulated time that a cladding may remain at high temperature, as required by 10 CFR 50.46c. This regulatory guide also describes a method acceptable to the NRC to implement the periodic testing and reporting requirements in 10 CFR 50.46c.

The NRC issues regulatory guides to describe to the public methods that the staff considers acceptable for use in implementing specific parts of the agency's regulations, to explain techniques that the staff uses in evaluating specific problems or postulated accidents, and to provide guidance to applicants. Regulatory guides are not substitutes for regulations and compliance with them is not required.

This regulatory guide contains information collection requirements covered by 10 CFR Part 50 that the Office of Management and Budget (OMB) approved under OMB control number 3150-0011. The NRC may neither conduct nor sponsor, and a person is not required to respond to, an information collection request or requirement unless the requesting document displays a currently valid OMB control

Pre-Decisional

This regulatory guide is being issued in draft form to involve the public in the early stages of the development of a regulatory position in this area. It has not received final staff review or approval and does not represent an official NRC final staff position. Public comments are being solicited on this draft guide (including any implementation schedule) and its associated regulatory analysis or value/impact statement. Comments should be accompanied by appropriate supporting data. Written comments may be submitted to the Rules, Announcements, and Directives Branch, Office of Administration, U.S. Nuclear Regulatory Commission, Washington, DC 20555-0001; submitted through the NRC's interactive rulemaking Web page at http://www.nrc.gov; or faxed to (301) 492-3446. Copies of comments received may be examined at the NRC's Public Document Room, 11555 Rockville Pike, Rockville, MD. Comments will be most helpful if received by [insert date - 75 days from issuance].

Electronic copies of this draft regulatory guide are available through the NRC's interactive rulemaking Web page (see above); the NRC's public Web site under Draft Regulatory Guides in the Regulatory Guides document collection of the NRC Library at http://www.nrc.gov/reading-rm/doc-collections/; and the NRC's Agencywide Documents Access and Management System (ADAMS) at http://www.nrc.gov/reading-rm/adams.html, under Accession No. ML110840089. The regulatory analysis may be found in ADAMS under Accession No. ML112520277.

number. This regulatory guide is a rule as designated in the Congressional Review Act (5 U.S.C. 801–808). However, OMB has not found it to be a major rule as designated in the Congressional Review Act.

Pre-Decisional

Page

A. INTRODUCTION 1
B. DISCUSSION 4
Background 4
Description of Breakaway Oxidation Phenomenon 4
Breakaway Oxidation Testing 5
Establishing the Onset of Breakaway Oxidation 6
Periodic Testing 6
Reporting Results of Periodic Testing 6
C. REGULATORY POSITION 7
D. IMPLEMENTATION 8
GLOSSARY 10
REFERENCES 11
APPENDIX A: Procedure for Conducting Breakaway Oxidation Tests with Zirconium-Based Cladding Alloys A-1
APPENDIX B: Rationale for the 200-wppm Hydrogen Pickup Criterion for Breakaway Oxidation B-1
APPENDIX C: Negative Effects of Etching with Hydrofluoric-Containing Acid as Part of Sample Cleaning C-1
APPENDIX D: Correlation between Cladding Outer-Surface Appearance and Hydrogen Pickup D-1
APPENDIX E: Overview and Logic Diagram to Illustrate Sample Test Matrices E-1

Pre-Decisional

B. DISCUSSION

Background

In 1996, the NRC initiated a fuel-cladding research program intended to investigate the behavior of high-exposure fuel cladding under accident conditions. This research program included an extensive LOCA research and testing program at Argonne National Laboratory (ANL), as well as jointly funded programs at the Kurchatov Institute (Ref. 2) and the Halden Reactor Project (Ref. 3), to develop the body of technical information needed to evaluate LOCA regulations for high-exposure fuel. The agency has summarized the research findings in Research Information Letter 0801, "Technical Basis for Revision of Embrittlement Criteria in 10 CFR 50.46," dated May 30, 2008 (Ref. 4). The detailed experimental results from the program at ANL appear in NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," issued July 2008 (Ref. 5).

The research program identified new cladding embrittlement mechanisms and expanded the NRC's knowledge of previously identified mechanisms. One of the embrittlement mechanisms investigated in NRC's LOCA research program is called "breakaway oxidation," which is described below.

Description of Breakaway Oxidation Phenomenon

Zirconium dioxide can exist in several crystallographic forms (allotropes). The normal tetragonal oxide that develops under LOCA conditions is dense, adherent, and protective with respect to hydrogen pickup. However, conditions might occur during a small-break LOCA (such as extended time-at-temperature around 1,000 degrees Celsius (°C) (1,832 degrees Fahrenheit (°F))) that promote a transformation to the monoclinic phase. The monoclinic phase is the oxide phase that is grown during normal operation and is neither fully dense nor protective. The tetragonal-to-monoclinic transformation is an instability that initiates at local regions of the metal-oxide interface and grows rapidly throughout the oxide layer. Because this transformation results in an increase in oxidation rate, it is referred to as breakaway oxidation.

Along with this increase in oxidation rate caused by cracks in the monoclinic oxide, there is significant hydrogen pickup. Hydrogen that enters in this manner during a postulated LOCA promotes rapid embrittlement of the cladding. If breakaway oxidation occurs, the embrittlement process is accelerated and the oxidation limits or time-at-temperature criteria are no longer effective to preclude embrittlement.

Figure 1 illustrates the damaging effects of breakaway oxidation. This sample of the Russian alloy E110 (an older version no longer representative of commercial cladding) was exposed to high-temperature steam oxidation for a hold time of 1,350 seconds at 1,000 °C (1,832 °F). Breakaway oxidation, delamination, and spallation are evident. Hydrogen pickup was approximately 4,200 weight parts per million (wppm).

Pre-Decisional

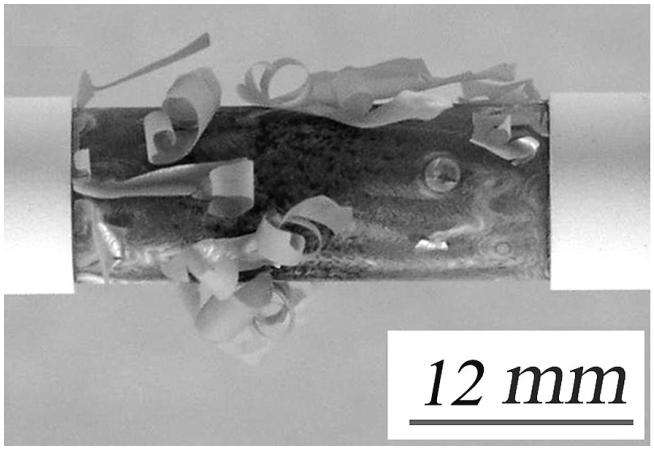


Figure 1. E110 cladding test specimen
Source: NUREG/CR-6967

Although all zirconium alloys will eventually experience breakaway oxide phase transformation when exposed to long durations of high-temperature steam oxidation, alloying composition and manufacturing process parameters (e.g., surface roughness) influence the timing of this phenomenon. As shown in Table 1, several domestic cladding alloys tested as part of the NRC's LOCA research program proved to be less susceptible to early breakaway oxidation.

Table 1. Breakaway Test Results

Alloy	Measured Minimum Breakaway Time	Temperature at which Minimum Breakaway Time Was Measured
Zircaloy-2	>5,000 seconds	1,000 °C
Zircaloy-4	5,000 seconds	986 °C
ZIRLO™	3,000 seconds	970 °C
M5	>5,000 seconds	1,000 °C

Breakaway Oxidation Testing

The purpose of the requirements in 10 CFR 50.46c is to ensure core coolability during and following a LOCA. If breakaway oxidation occurs, the embrittlement process is accelerated. Therefore, the postquench ductility analytical limits established in accordance with 10 CFR 50.46c are no longer effective to preclude embrittlement, and core coolability may not be maintained even if the analytical limits on peak cladding temperature and local oxidation (surrogate for time-at-elevated-temperature) are not exceeded. Specifically, 10 CFR 50.46c calls for (1) measurement of the onset of breakaway oxidation for a zirconium cladding alloy based on an acceptable experimental technique and (2) evaluation of the measurement relative to emergency core cooling system performance.

The NRC's LOCA research program revealed that different zirconium-based alloys have varying susceptibility to breakaway oxidation that is dependent on factors such as alloy content, manufacturing process, and surface preparation, among others (Refs. 2, 5–6). Therefore, 10 CFR 50.46c includes a periodic testing and reporting requirement to confirm that slight composition changes or manufacturing changes have not inadvertently altered the cladding's susceptibility to breakaway oxidation.

Pre-Decisional

Establishing the Onset of Breakaway Oxidation

The experimental procedure provided in Appendix A to this regulatory guide defines a procedure acceptable to the NRC staff to measure the onset of breakaway oxidation (Appendices B through E are provided to expand on critical aspects of the testing procedure in Appendix A). This experimental procedure may be used to characterize the onset of breakaway oxidation as a function of temperature for a zirconium cladding alloy. For zirconium cladding alloys, the experimental results of breakaway testing would be provided as part of the documentation supporting the staff's review and approval of the new fuel design (i.e., a license amendment request or vendor topical report). The applicant would provide details of the experimental technique (unless the experiments were conducted in accordance with Appendix A to this regulatory guide) and the results of experiments conducted as a function of temperature.[1]

Periodic Testing

To confirm that slight composition changes or manufacturing changes have not inadvertently altered the cladding's susceptibility to breakaway oxidation, 10 CFR 50.46c calls for periodic measurement of the onset of breakaway oxidation. To meet this requirement, it is acceptable to use the experimental procedure provided in Appendix A to this regulatory guide to measure the onset of breakaway oxidation and to reduce the test matrix that is described in Section A-10.

Specifically, it is acceptable to measure the onset of breakaway oxidation for each reload batch for only the temperature at which the minimum time to breakaway oxidation was measured and to demonstrate that breakaway oxidation is not experienced within the time of the established analytical limit. An observation of a lustrous black oxide or a measurement of less than 200-wppm hydrogen pickup (see Appendix B for further discussion) after this test would be sufficient to demonstrate that breakaway oxidation had not occurred during the test. In this case, a total of five repeat tests at the temperature at which the minimum time to breakaway oxidation was measured and the time of the cladding alloy's established analytical limit is acceptable to address variability and demonstrate continued acceptable performance.

For test times below the established time for breakaway oxidation, all five samples must exhibit lustrous black oxides on the cladding outer surface or hydrogen contents less than 200 wppm to conclude that changes in processing parameters or time-dependent variables (e.g., new versus used polishing belt or wheel) did not cause a change in breakaway oxidation time.

Reporting Results of Periodic Testing

In 10 CFR 50.46c, the NRC requires, in part, that the values measured in periodic breakaway testing be reported to the NRC. The objective of periodic testing is to confirm that a cladding's susceptibility to breakaway oxidation has not been altered. Therefore, it is acceptable to report only changes in the time to the onset of breakaway oxidation.

Pre-Decisional

[1] Section A-10, "Test Temperatures," in the procedure detailed in Appendix A specifies that the test matrix should include measurements at 1,050, 1,030, 1,015, 1,000, 985, 970, 950, and 800 ºC and defines the extent of replicate testing for the purpose of characterizing variability.

C. REGULATORY POSITION

1. Establish the susceptibility to breakaway oxidation for a zirconium cladding alloy.

a. Define the minimum time to the onset of breakaway oxidation following the experimental procedure provided in Appendix A to this regulatory guide, or an alternative acceptable experimental procedure.
b. Provide the results of breakaway testing as part of the documentation supporting the staff's review and approval of a fuel design (i.e., a license amendment request or vendor topical report).

2. Conduct periodic testing to confirm that slight composition changes or manufacturing changes have not inadvertently altered the cladding's susceptibility to breakaway oxidation.

a. Follow the experimental procedure provided in Appendix A to this regulatory guide, or an alternative acceptable experimental procedure, to retest cladding performance on an established periodic basis.
b. It is acceptable to measure the onset of breakaway oxidation for only the temperature at which the minimum time to breakaway oxidation was measured. Also, as-manufactured cladding may be used if the initial testing (see Regulatory Position 1) showed that surface scratches and postmanufacture cleaning processes have insignificant effects (i.e., results are within data scatter) on breakaway oxidation time.
c. Address variability by conducting five repeat tests at the temperature at which the minimum time to breakaway oxidation was determined during the initial testing (see Regulatory Position 1).

3. Report the results.

a. As specified by 10 CFR 50.46c, the results of periodic testing shall be provided within the annual ECCS report.
b. It is acceptable to report only changes in the time to the onset of breakaway oxidation.

Pre-Decisional

D. IMPLEMENTATION

The purpose of this section is to provide information on how applicants and licensees[2] may use this guide and information regarding the NRC's plans for using this regulatory guide. In addition, it describes how the NRC staff complies with the Backfit Rule (10 CFR 50.109) and any applicable finality provisions in 10 CFR Part 52.

Use by Licensees

Licensees may voluntarily[3] use the guidance in this document to demonstrate compliance with the underlying NRC regulations. Methods or solutions that differ from those described in this regulatory guide may be deemed acceptable if they provide sufficient basis and information for the NRC staff to verify that the proposed alternative demonstrates compliance with the appropriate NRC regulations.

Licensees may use the information in this regulatory guide for actions which do not require NRC review and approval such as changes to a facility design under 10 CFR 50.59 that do not require prior NRC review and approval. Licensees may use the information in this regulatory guide or applicable parts to resolve regulatory or inspection issues.

Use by NRC Staff

During regulatory discussions on plant specific operational issues, the staff may discuss with licensees various actions consistent with staff positions in this regulatory guide, as one acceptable means of meeting the underlying NRC regulatory requirement. Such discussions would not ordinarily be considered backfitting even if prior versions of this regulatory guide are part of the licensing basis of the facility. However, unless this regulatory guide is part of the licensing basis for a facility, the staff may not represent to the licensee that the licensee's failure to comply with the positions in this regulatory guide constitutes a violation.

If an existing licensee voluntarily seeks a license amendment or change and (1) the NRC staff's consideration of the request involves a regulatory issue directly relevant to this new or revised regulatory guide and (2) the specific subject matter of this regulatory guide is an essential consideration in the staff's determination of the acceptability of the licensee's request, then the staff may request that the licensee either follow the guidance in this regulatory guide or provide an equivalent alternative process that demonstrates compliance with the underlying NRC regulatory requirements. This is not considered backfitting as defined in 10 CFR 50.109(a)(1) or a violation of any of the issue finality provisions in 10 CFR Part 52.

The NRC staff does not intend or approve any imposition or backfitting of the guidance in this regulatory guide. The NRC staff does not expect any existing licensee to use or commit to using the guidance in this regulatory guide, unless the licensee makes a change to its licensing basis. The NRC staff does not expect or plan to request licensees to voluntarily adopt this regulatory guide to resolve a generic regulatory issue. The NRC staff does not expect or plan to initiate NRC regulatory action which would require the use of this regulatory guide. Examples of such unplanned NRC regulatory actions include issuance of an order requiring the use of the regulatory guide, requests for information under

[2] In this section, "licensees" refers to licensees of nuclear power plants under 10 CFR Parts 50 and 52; and the term "applicants," refers to applicants for licenses and permits for (or relating to) nuclear power plants under 10 CFR Parts 50 and 52, and applicants for standard design approvals and standard design certifications under 10 CFR Part 52.

[3] In this section, "voluntary" and "voluntarily" means that the licensee is seeking the action of its own accord, without the force of a legally binding requirement or an NRC representation of further licensing or enforcement action.

Pre-Decisional

10 CFR 50.54(f) as to whether a licensee intends to commit to use of this regulatory guide, generic communication, or promulgation of a rule requiring the use of this regulatory guide without further backfit consideration.

If a licensee believes that the NRC is either using this regulatory guide or requesting or requiring the licensee to implement the methods or processes in this regulatory guide in a manner inconsistent with the discussion in this Implementation section, then the licensee may file a backfit appeal with the NRC in accordance with the guidance in NUREG-1409 and NRC Management Directive 8.4.

Pre-Decisional

GLOSSARY

alpha layer—For the purposes of this regulatory guide, refers to the zirconium phase that is characterized by a hexagonally close-packed crystal structure and is stable at room temperature. At high temperatures, the beta phase is stable; however, dissolved oxygen can stabilize the alpha phase at high temperature.

beta layer—For the purposes of this regulatory guide, refers to the zirconium phase that is characterized by a cubic crystal structure and is stable at elevated temperatures of approximately 1,000 °C.

breakaway oxidation—For the purposes of this regulatory guide, the fuel-cladding oxidation phenomenon in which the weight gain rate deviates from normal kinetics. This change occurs with a rapid increase of hydrogen pickup during prolonged exposure to a high-temperature steam environment, which promotes loss of cladding ductility.

corrosion—For the purposes of this regulatory guide, the formation of a zirconium oxide layer resulting from the reaction of zirconium with coolant water during normal operation.

loss-of-coolant accident (LOCA)—A hypothetical accident that would result from the loss of reactor coolant, at a rate in excess of the capability of the reactor coolant makeup system, from breaks in pipes in the reactor coolant pressure boundary up to and including a break equivalent in size to the double-ended rupture of the largest pipe in the reactor coolant system.

oxidation—For the purpose of this regulatory guide, the formation of a zirconium oxide layer resulting from the reaction of zirconium with high-temperature steam during LOCA conditions.

monoclinic oxide—For the purposes of this regulatory guide, the oxide phase that develops during normal operation and is neither fully dense nor protective. Although the oxide phase that typically develops under LOCA conditions is the tetragonal oxide phase, conditions might occur during a small-break LOCA (such as extended time-at-temperature around 1,000 °C (1,832 °F)) that promote a transformation to the monoclinic phase.

tetragonal oxide—For the purposes of this regulatory guide, the oxide phase that develops under LOCA conditions that is dense and adherent and that is observed to be protective with respect to hydrogen pickup.

Pre-Decisional

REFERENCES[1]

1. 7X FR XXXXX, "Proposed Rule FRN," *Federal Register*, Volume 7X, Number XXX, p. XXXX, Washington, DC, June 31, 2011. (*insert FRN of proposed rule reference when available*)

2. NUREG/IA-0211, "Experimental Study of Embrittlement of Zr-1%Nb VVER Cladding under LOCA-Relevant Conditions," U.S. Nuclear Regulatory Commission, Washington, DC, March 2005. (ADAMS Accession No. ML051100343)

3. IFE/KR/E-2008/004, "LOCA Testing of High Burnup PWR Fuel in the HBWR. Additional PIE on the Cladding of the Segment 650-5," Institute for Energy Technology, Kjeller, Norway, April 2008. (ADAMS Accession No. ML081750715)

4. Research Information Letter 0801, "Technical Basis for Revision of Embrittlement Criteria in 10 CFR 50.46," U.S. Nuclear Regulatory Commission, Washington, DC, May 30, 2008. (ADAMS Accession No. ML081350225)

5. NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," U.S. Nuclear Regulatory Commission, Washington, DC, July 2008. (ADAMS Accession No. ML082130389)

6. Yan, Y., T.A. Burtseva, and M.C. Billone, "High-Temperature Steam-Oxidation Behavior of Zr-1Nb Cladding Alloy E110," *Journal of Nuclear Materials*, 393(3): 433–448.

Pre-Decisional

[1] Publicly available NRC published documents are available electronically through the NRC Library at: http://www.nrc.gov/reading-rm/doc-collections/. The documents can also be viewed on-line or printed for a fee in the NRC's Public Document Room (PDR) at 11555 Rockville Pike, Rockville, MD; the mailing address is USNRC PDR, Washington, DC 20555; telephone 301-415-4737 or (800) 397-4209; fax (301) 415-3548; and e-mail pdr.resource@nrc.gov.

APPENDIX A

PROCEDURE FOR CONDUCTING BREAKAWAY OXIDATION TESTS WITH ZIRCONIUM-BASED CLADDING ALLOYS

Contents

A-1. PURPOSE AND SCOPE OF THE TESTS A-3

A-2. BACKGROUND A-3

A-3. SAMPLE SELECTION AND TESTING FREQUENCY A-7
A-3.1. Sample Selection A-7
A-3.2. Frequency of Testing A-8

A-4. SAMPLE PREPARATION AND CHARACTERIZATION A-8
A-4.1. Hydrogen-Content Determination for As-Fabricated Samples A-8
A-4.2. Minimum Sample Lengths for One- and Two-Sided Oxidation Tests A-8
A-4.3. End-Cap Mass and Welding Procedure for One-Sided Oxidation Test Samples A-8
A-4.4. Length, Outer-Diameter, and Wall-Thickness Measurements A-9
A-4.5. Pretest Cleaning with Chemical Detergent or Organic Solvent and Rinsing A-9
A-4.6. Pretest Sample Weight Measurement (after Drying) A-9

A-5. TEMPERATURE HEATUP AND COOLDOWN RATES AND HEATING METHODS A-9
A-5.1. Temperature Heatup and Cooldown Rates A-9
A-5.2. Radiant Heating A-10
A-5.3. Resistance Heating A-10
A-5.4. Induction Heating A-10
A-5.5. Direct Electrical Heating A-10

A-6. TEMPERATURE CONTROL AND MONITORING A-10
A-6.1. Thermocouples A-10
A-6.2. Thermal Benchmarks A-11
A-6.3. Weight-gain Benchmarks A-11

A-7. WATER QUALITY, STEAMFLOW RATE, AND STEAM PRESSURE A-12
A-7.1. Water Quality A-12
A-7.2. Steamflow Rate A-12
A-7.3. Steam Pressure A-13

A-8. TEST PROCEDURE A-13
A-8.1. Test Train and Steam Chamber A-13
A-8.2. Purging Steam Chamber and Stabilizing Steam Flow A-13
A-8.3. Ramping Temperature and Holding Temperature at Target Value A-14
A-8.4. End of Heating Phase and Cooldown A-14
A-8.5. Determination of Test Time A-14

Pre-Decisional

A-9. POSTTEST MEASUREMENTS AND CHARACTERIZATION A-14
A-9.1. Sample Drying Time A-14
A-9.2. Weight Measurement and Use of Weight Gain to Verify Oxidation Temperature A-15
A-9.3. Visual Examination of Sample Outer Surface A-15
A-9.4. Hydrogen Analysis for Samples with Outer-Surface Discoloration (Relative to Lustrous Black) A-15
A-9.5. Criterion (200-wppm Hydrogen Pickup) for Breakaway Oxidation Based on Retention of Ductility A-16
A-9.6. Characterization for One-Sided and Two-Sided Oxidation Test Samples A-16

A-10. TEST TEMPERATURES A-17

A-11. REFERENCES A-20

Pre-Decisional

A-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 650–1,050 degrees Celsius (ºC). Such long-time exposure to steam is especially relevant to postulated small-break loss-of-coolant accidents (LOCAs). All zirconium (Zr)-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 to determine the minimum breakaway time. The minimum breakaway time is defined as the time required to pick up 200-weight parts per million (wppm) hydrogen through the cladding outer-surface oxide.

A-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 respect to hydrogen pickup (Refs. 1, 2, and 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 (≈1,150 ºC). 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 chemical impurities (e.g., fluorine) 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 (3,000–6,000 seconds (s)) exposure to steam at ≤1,050 ºC. 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 1,000 ºC, 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 fluorine, and possibly the absence of stabilizing impurities (e.g., calcium), can induce early breakaway oxidation at temperatures as high as the nominal phase transition temperature for stress-free ZrO_2. The Russian Zr-1% niobium (Nb) alloy E110 cladding is a classic example of a material that experiences early breakaway oxidation (<600 s), possibly because of the presence of fluorine impurities at the metal surface and within the metal substrate (Refs. 3 and 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 NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents,"

Pre-Decisional

issued July 2008 (Ref. 3), cladding oxidized for 3,000–4,000 s at 970–1,000 ºC loses ductility for hydrogen pickup values >400 wppm (see Appendix B). In order to ensure ductility as measured by ring-compression tests conducted at 135 ºC (275 degrees Fahrenheit (ºF)), the breakaway oxidation time in NUREG/CR-6967 (Ref. 3) is defined as the time corresponding to 200-wppm hydrogen pickup. The term "hydrogen pickup" refers to the measured hydrogen level for a sample normalized to the preoxidation mass of the sample from which the as-fabricated hydrogen content is subtracted. The term "hydrogen content" refers to the total hydrogen content in the postoxidized sample normalized to the mass of the oxidized sample. At 200-wppm hydrogen pickup, there is little difference between the measured posttest hydrogen content of the sample and the hydrogen pickup. 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 970–1,000 ºC. At lower oxidation temperatures, particularly <900 ºC, the oxidation rate and hydrogen generation rate are considerably lower. As the hydrogen generation rate decreases, the rate of hydrogen pickup also decreases.

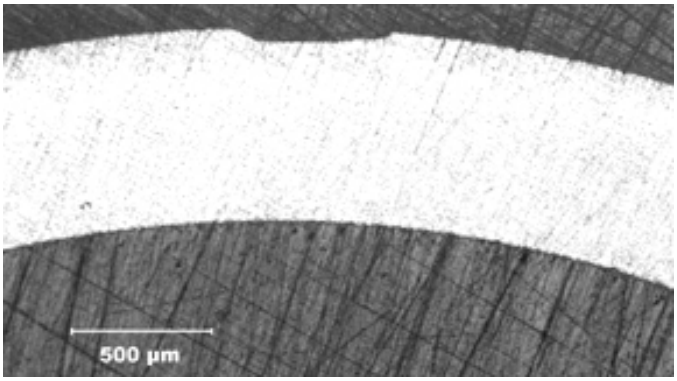
The transition from tetragonal to monoclinic oxide is an instability phenomenon dependent on many manufacturing variables, particularly those affecting cladding outer-surface conditions. For susceptible alloys such as E110 (Ref. 3), the presence of geometrical discontinuities due to scratches, sample ends, and a thermocouple (TC) welded to the cladding will induce earlier breakaway oxidation. Also, for E110, high-surface roughness coupled with pretest cleaning in a 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 before 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 United States are considerably more stable than E110. However, even these polished alloys with low surface roughness are sensitive to postpolishing 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 (Ref. 2) give the minimum time to accumulate 200 wppm of hydrogen as 1,800 s, which occurs at an oxidation temperature of 1,000 ºC. Mardon, et al. (Ref. 5) report a hydrogen content of 200 wppm at ≈5,400 s for modern, polished AREVA Zry-4 also oxidized at 1,000 ºC. NUREG/CR-6967 (Ref. 3) determined breakaway oxidation times at ≈1,000 ºC (based on 200-wppm hydrogen pickup) of 3,800 s for an older variant of Zry-4 and 5,000 s for modern, polished AREVA Zry-4. Baek and Jeong (Ref. 6) oxidized polished Zry-4 for 3,600 s at 1,000 ºC and measured >600 wppm of hydrogen. For this case, the estimated time for 200-wppm hydrogen pickup is in the range of 3,000–3,300 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 before steam oxidation: nitric-fluoric acid mixture and final cleaning in boiling water for the Leistikow and Schanz (Ref. 2) tests; and 5% HF + 45% HNO_3 + 50% H_2O with final ultrasonic cleaning in an ethanol and acetone solution for the Baek and Jeong (Ref. 6) tests. In the Argonne National Laboratory (ANL) study described in NUREG/CR-6967 (Ref. 3), samples used to generate breakaway oxidation data were cleaned ultrasonically in ethanol followed by water. In the Mardon study (Ref. 5), samples were degreased in acetone before 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, postpolishing 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 the postpolishing cleaning processes, scratching of the outer surface that may occur during insertion of rods into assemblies must also be simulated. Cladding surface imperfections and scratches should be quantified and simulated in the testing laboratory because they act as initiation

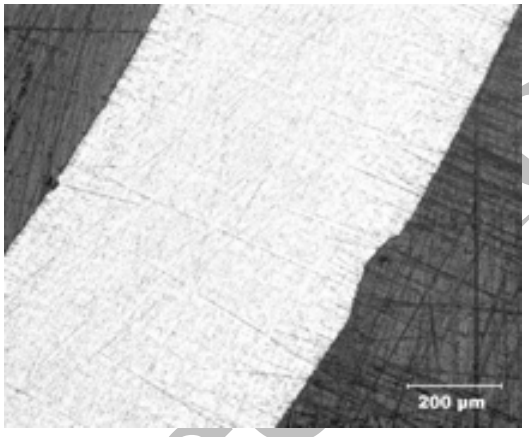
Pre-Decisional

sites for breakaway oxidation due to the effects of the geometrical discontinuity on the stress state in the oxide and at the metal–oxide interface. A "design-basis" scratch should be established based on manufacturing experience and may be assembly-design specific or cladding-material specific. 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 of 50±5 micrometers (μm) and a width of ≥50±5 μm, defined as bounding based on metallographic observations made of scratches induced by repeated insertion of fuel rod cladding into and out of grid spacers. Examples of bounding, design-basis, and ANL-machined scratches are shown in Figure A-1. The scratches shown in Figure A-1(a) and (b) were induced by repeated insertion of fuel rod cladding into and out of grid spacers.

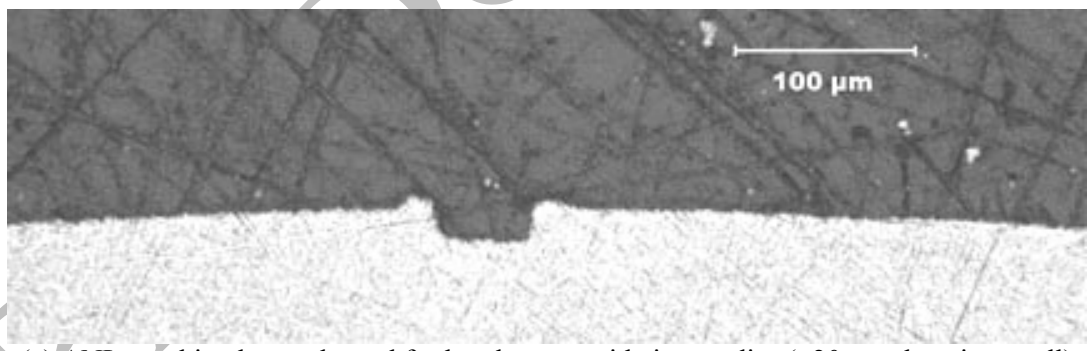
Pre-Decisional



(a) Example of a bounding scratch (≈50-µm deep into wall)



(b) Example of a design-basis scratch (≈30-µm deep into wall)



(c) ANL-machined scratch used for breakaway oxidation studies (≈20-µm deep into wall)

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

Draft Decisional

Breakaway oxidation test results reported in the literature are based on isothermal test conditions. The test times listed in NUREG/CR-6967 (Ref. 3) include the time (≈80 s) to ramp from 300 ºC 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. (Ref. 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 ºC) for 2,000 s, cycled five times between 930 ºC and 1,030 ºC for 400 s, and then held at 980 ºC for 400 s. The hydrogen content and pickup were 230±80 wppm, which indicated that breakaway oxidation had occurred for this particular cladding alloy. Previous isothermal results for as-fabricated, prescratched, and preoxidized (<1 μm film) samples gave a minimum breakaway time of 3,100±300 s. For this particular transient, breakaway oxidation occurred at the lower bound of this range and was consistent with results for a prescratched sample oxidized under isothermal conditions.

The test times for the breakaway studies reported in NUREG/CR-6967 (Ref. 3) were generally ≤5,000 s. Some early tests, conducted at 7,200 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 5,000 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 rupture are predicted to occur. The minimum breakaway oxidation time is expected to occur in the temperature range of 950–1,000 ºC. For modern cladding alloys, the as-fabricated cladding wall thickness varies from 0.57 millimeter (mm) to 0.71 mm. For thin cladding that ruptures, 17% CP-ECR corresponds to <2,400 s at 1,000 ºC, <3,300 s at 975 ºC, and <4,600 s at 950 ºC. These times decrease significantly if wall thinning is included in the calculation. For thick cladding that ruptures, 17% CP-ECR corresponds to <3,300 s at 1,000 ºC, <5,100 s at 975 ºC, and <7,100 s at 950 ºC. With a modest 20% diametral ballooning or creep strain, these times for thicker cladding are reduced to <2,610 s at 1,000 ºC, <3,580 s at 975 ºC, and <5,000 s at 950 ºC. Thus, for most of these cases, breakaway oxidation times >5,000 s would not be relevant because of the ≤17% CP-ECR limit. The procedure for conducting tests for ≤5,000 s with emphasis on 950–1,000 ºC oxidation temperatures is described in the following sections.

A-3. Sample Selection and Testing Frequency

A-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 postpolishing, outer-surface cleaning processes used before 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). 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 design-basis or bounding 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 of 50±5 μm and a width of ≥50±5 μm, defined as bounding based on metallographic observations made of scratches induced by repeated insertion of fuel rod cladding into and out of grid spacers. Cladding tube scratching may be simulated in the laboratory.

Pre-Decisional

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

A-3.2 Frequency of Testing

Because breakaway oxidation is an instability phenomenon that 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-µm surface roughness, a change of polishing material, introduction of postpolishing cleaning with an HF-containing acid mixture, and changing the 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. Specifically, it is acceptable to measure the onset of breakaway oxidation annually for each reload batch for only the temperature at which the minimum time to breakaway oxidation was measured and to demonstrate that breakaway oxidation is not experienced within the time of the established analytical limit.

If it has been shown that scratches and postpolishing cleaning have an insignificant effect (i.e., results within data scatter) on the minimum breakaway oxidation time, then as-manufactured cladding may be used for periodic testing.

A-4. Sample Preparation and Characterization

A-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.

A-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 ≤ ±10 ºC 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 presence of welding heat-affected zones, the minimum sample length for one-sided oxidation tests should be 75 mm.

A-4.3 End-Cap Mass and Welding Procedure for One-Sided Oxidation Test 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.

Pre-Decisional

The room-temperature pressure inside the welded cladding sample should be low enough to give an internal pressure at the target oxidation temperature that is less than the external steam pressure. Also, it is recommended that the gas remaining inside the cladding sample be free of impurities (e.g., nitrogen).

A-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 ≈90º 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 before 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±5º relative to the longitudinal axis). Outer diameter, wall thickness, and length are used to normalize sample weight gain to exposed surface area.

A-4.5 Pretest Cleaning with Chemical Detergent or Organic Solvent and Rinsing

Appendix X1, "Guide to Specimen Preparation," to American Society for Testing and Materials (ASTM) G2/G2M-06, "Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680ºF [360ºC] or in Steam at 750ºF [400ºC]," describes sample cleaning procedures in Section X1.2 (Ref. 7). These procedures should be followed for breakaway oxidation tests. Specifications and requirements in Sections X1.1 (on tubes with a second material on the inner diameter) and X1.3 (on etching) should be ignored. Based on NUREG/CR-6967 (Ref. 3) and subsequent work by ANL, samples should not be etched with an HF-containing acid mixture as part of the test cleaning process (see Appendix B). After cleaning, direct contact with the sample should be avoided by using surgical gloves for handling.

A-4.6 Pretest Sample Weight Measurement (after Drying)

Pretest sample weight should be measured to the nearest 0.1 milligram (mg) as specified in Section 7.1.3 of ASTM G2/G2M-06 (Ref. 7). Because drying after cleaning may take several hours, it is also permissible to measure pretest sample weight after cleaning with an organic solvent, such as ethanol, that vaporizes quickly. The pretest 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 steamflow conditions.

A-5. Temperature Heatup and Cooldown Rates and Heating Methods

A-5.1 Temperature Heatup and Cooldown Rates

For long-time isothermal tests, heating and cooling rates are not expected to be critical parameters. However, long heating and cooling times should be avoided because they may induce breakaway oxidation at earlier isothermal-temperature times. The total ramp time from 650 ºC to the

Pre-Decisional

target temperature (heating phase) and from the target temperature to 650 ºC should be <10% of the isothermal test time. It is also not clear if temperature overshoot during the heating phase has any effect on isothermal breakaway oxidation time. However, temperature overshoot should be limited to ≤20 ºC for ≤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.

A-5.2 Radiant Heating

Radiant heating in a quad-elliptic furnace has been used to generate breakaway-oxidation data (Refs. 1, 3, and 6). This heating method, along with furnace power controlled by feedback from a TC on or near the sample, allows for controlled heating rates and relatively fast cooling times (<100 s from 1,000 ºC to 650 ºC). For 25-mm-long samples with a 9.50-mm outside diameter, axial temperature variations are negligible, but circumferential temperature variations are in the range of 10–15 ºC. These can be reduced by using radiant-heating furnaces with more than four lamps. However, the circumferential variation has a practical value because a range of temperatures (e.g., 1,000±10 ºC) can be investigated with a single sample. With proper thermal benchmarking, radiant-heating furnaces are acceptable for conducting breakaway oxidation tests.

A-5.3 Resistance Heating

Most breakaway oxidation tests (e.g., Refs. 2, 4, and 5) have been conducted in resistance-heating furnaces. Compared to radiant-heating furnaces, these furnaces have a larger uniform temperature zone and have 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—necessary information for the determination of the time to reach the target isothermal temperature. Resistance-heating furnaces are acceptable for conducting breakaway oxidation tests.

A-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 (Ref. 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 whether the use of optical pyrometry to measure temperature requires etching of the cladding surface. Because of the uncertainties about induction heating, optical pyrometry, and required surface preparation, induction heating is not recommended for breakaway oxidation studies.

A-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.

Pre-Decisional

A-6. Temperature Control and Monitoring

A-6.1 Thermocouples

For the temperatures relevant to this breakaway oxidation test procedure, the TCs used to record temperature and control furnace power may be either Type K (chromel-alumel) or Type S (platinum (Pt)/10% rhodium-Pt). The TCs must be calibrated using instrumentation and standards that are traceable to the National Institute of Standards and Technology (NIST). Typically, this service is provided by the TC 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 ºC and 1,000 ºC. Copies of these certificates should accompany the data report. Verification should be provided demonstrating that the vendor actually did the calibration according to the standards in internationally recognized standards organizations, such as the International Organization for Standardization (ISO), and American National Standards Institute/National Conference of Standards Laboratories (ANSI/NCSL).

A-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 after testing will affect the accuracy of the posttest 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: 1,000 ºC and 800 ºC. For the work reported in NUREG/CR-6967 (Ref. 3), two or three TCs (120º 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 (≈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 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.

A-6.3 Weight-Gain Benchmarks

After thermal benchmarking, samples should be tested without TCs welded onto the sample to determine the weight gain. These tests should be conducted at 800 ºC and 1,000 ºC. The test times should be less than those that result in breakaway oxidation. For 1,000 ºC, an isothermal test time of

Pre-Decisional

2,000 s is recommended. For Zircaloy-2 (Zry-2), Zry-4, and ZIRLO™ alloys oxidized at 1,000 ºC for ≤2,000 s, the measured weight gain (normalized to the surface area exposed to steam) was in good agreement with the Cathcart-Pawel (CP) correlation predictions (Ref. 3). If the measured weight gain differs from the CP-predicted weight gain by ≥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 1,000 ºC was considerably less than the CP-predicted weight gain (Ref. 3). For these materials, the results of the weight-gain benchmark should be compared to the vendor-generated database or the results given in NUREG/CR-6967 (Ref. 3) for these alloys. Below 1,000 ºC, especially below 950 ºC, 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 ºC, 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.

A-7. Water Quality, Steamflow Rate, and Steam Pressure

A-7.1 Water Quality

The NRC staff strongly recommends that purified water be used for generating steam. NUREG/CR-6967 (Ref. 3) testing indicated that water quality can influence the measured time to the onset of breakaway oxidation. The recommendations on water quality are intended to prevent initiating early breakaway oxidation due to experimental artifacts.

ASTM G2/G2M–06 (Ref. 7) specifies that Grade A water with ≤45 parts per billion of oxygen should be used for corrosion tests in pressurized water and steam. Laboratory-grade Type I (distilled or deionized) water is also of sufficient purity for breakaway oxidation tests at ≥650 ºC. ASTM, the National Committee for Clinical Laboratory Standards (now the Clinical and Laboratory Standards Institute), and ISO 3696 have similar definitions for Type I purified water.

A-7.2 Steamflow Rate

The average steamflow rate used in breakaway oxidation studies should be determined (and reported) from the mass of condensed water collected during these long-time tests or by the mass of water that is input to the steam chamber divided by the test time and normalized to the net cross-sectional area of the steam chamber. The average steamflow rate should be in the range of 0.5 to 30 mg/square centimeter per second ($cm^2 \cdot s$). Justification for this range is provided in the following paragraphs.

Leistikow and Schanz (Ref. 2) and Uetsuka (Ref. 9) studied the effects of low steamflow rates on the oxidation kinetics of Zry-4 at 1,000 ºC. Their results are summarized in Leistikow and Schanz, Figure 9 (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 $mg/(cm^2 \cdot s)$. For the Leistikow and Schanz work, the sample length was 30 mm and oxidation was two-sided. Aomi, et al. (Ref. 10) studied the relationship between weight gain and steamflow rate for oxidation temperatures up to 1,200 ºC. They found that the weight gain for fixed test times and temperatures was independent of steamflow rates in the range of 0.8 to 7.8 $mg/(cm^2 \cdot s)$. Kawasaki, et al. (Ref. 11) also performed high-temperature oxidation tests to determine the range of steamflow rates for which the weight gain for a given test time was independent of steamflow rate. They report this range as 3 to 28 $mg/(cm^2 \cdot s)$.

For breakaway oxidation studies conducted in steam at ≤1,050 ºC, the results of Leistikow and Schanz, Uetsuka, and Aomi, et al. (Refs. 2, 9, and 10) are particularly relevant for the minimum steamflow rate. However, because individual sample lengths (≥25 mm for two-sided tests and ≥75 mm

Pre-Decisional

for one-sided tests) include lengths longer than used in the Leistikow and Schanz study and as many as five two-sided test samples may be stacked inside the steam chamber, the minimum steamflow rate is set at 0.5 mg/(cm^2 · s), which is 10 times the minimum given in Leistikow and Schanz and Uetsuka (Refs. 2 and 9). For the results presented in NUREG/CR-6967 (Ref. 3), the normalized steamflow rate was 5.3±0.8 mg/(cm^2 · s). This rate is well above the minimum rates determined from Leistikow and Schanz (Ref. 2), Uetsuka (Ref. 9), Aomi, et al. (Ref. 10), and Kawasaki, et al. (Ref. 11).

Although Aomi, et al. (Ref. 10) and Kawasaki, et al. (Ref. 11) give maximum steamflow rates of 7.8 and 28 mg/(cm^2 · s) respectively, it is not clear why higher steamflow rates would have an effect on weight gain and oxidation kinetics. It is desirable to have a steamflow rate higher than 0.5 mg/(cm^2 · s) to reduce temperature overshoot during the heating phase for bare cladding. Baek and Jeong (Ref. 6) cite a fast heating rate of 50 ºC/s and a temperature overshoot for about 20 s at the end of the heating ramp with a steamflow rate of 10 mg/(cm^2 · s). Although the maximum steamflow rate may not be as critical as the minimum steamflow rate, it should be limited to ≤30 mg/(cm^2 · s) for the purposes of breakaway oxidation tests.

A-7.3 Steam Pressure

Breakaway oxidation tests should be conducted at a steam pressure at or slightly above atmospheric pressure. This is consistent with the pressures that were used in previous breakaway oxidation studies (Refs. 2, 3, 6, and 9).

A-8. Test Procedure

The specific details of the test procedure depend on the heating furnace used. Described below are the steps used in NUREG/CR-6967 (Ref. 3), along with some generalizations that would apply to other heating and cooling methods than the radiant-heating furnace used in that study. Detailed steps for NUREG/CR-6967 testing are documented in Reference 13.

A-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 and steam chamber do 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 nonoxidizing or limited-oxidizing material such as stainless steels or nickel (Ni) alloys (e.g., Inconel 600). However, the sample must be protected from direct contact with materials such as iron (Fe) and Ni alloys because of the low-temperature eutectics for Zr and these elements. Hofmann and Markiewicz (Ref. 12) studied the reaction rates and eutectics of Zry-4 and Inconel 718. They also presented binary phase diagrams for Zr-Fe and Zr-Ni, which have eutectic temperatures as low as ≈930 ºC and 980 ºC, respectively. In NUREG/CR-6967 (Ref. 3), alumina inserts and zirconia washers were used between the Inconel holder and the sample to prevent such reactions from occurring. Testing laboratories may institute controls other than those used in NUREG/CR-6967 to prevent eutectic reactions between Zr-based alloys and the test train materials.

A-8.2 Purging Steam Chamber and Stabilizing Steam Flow

Pre-Decisional

Before heating and initiating steam flow, the steam chamber is filled with gas representative of the environment of the test facility (e.g., usually air). It is strongly recommended that the test chamber be purged with a high-purity inert gas (e.g., argon) before introducing steam flow or that it be purged with low-temperature steam before the temperature ramp. Deviations that may have a significant effect on test results include heating the sample to the target temperature in an inert gas before 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. If steam is used to purge the steam chamber, then steam flow should be maintained for 500 s before the temperature ramp.

Steam flow should be initiated at a test chamber temperature of ≈30 ºC. After introduction of steam into the chamber, furnace heating should commence for a pretest hold temperature of 300 ºC. Stabilization of steam flow and 300 ºC sample temperature will occur within 500 s.

A-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 ≤10 ºC and the circumferential temperature variation should be ≤20 ºC. These variations are the differences between the maximum and minimum temperatures.

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 TC welded onto the holder to the furnace power. For the radiant heating used in NUREG/CR-6967 (Ref. 3), the temperature ramp rate was programmed to be very fast (>50 ºC/s) from 300 ºC to within 50–100 ºC of the target temperature and slow (2–3 ºC/s) from that temperature to the target temperature. This programmed ramp was designed to eliminate temperature overshoot. Typical test times from 650 ºC to 1,000 ºC were <80 s. It is recommended that the test time from 650 ºC to the target temperature be <100 s for long-time isothermal tests.

A-8.4 End of Heating Phase and Cooldown

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 ºC. For the NUREG/CR-6967 (Ref. 3) work, this corresponded to a holder temperature of 700–720 ºC. Following this step, there should be ample moisture in the steam chamber to maintain a steam environment for cooling from 800 to 650 ºC.

A-8.5 Determination of Test Time

The isothermal test time should be the time interval between reaching within 20 ºC of the target temperature during the heating ramp to cooling within 20 ºC 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. If recommended heating and cooling times are used, the test time can be determined as the time above 650 °C or the time between initiation of the heating ramp and the initiation of the cooling ramp (as was done in the ANL study).

Pre-Decisional

A-9. Posttest Measurements and Characterization

A-9.1 Sample Drying Time

In order to determine an accurate posttest sample weight, it is important that the sample be free of moisture. For drying in stagnant air, the drying time should be ≥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.

A-9.2 Weight Measurement and Use of Weight Gain to Verify Oxidation Temperature

The posttest sample weight should be measured to the nearest 0.1 mg as specified in Section 7.1.3 of ASTM G2/G2M-06 (Ref. 7). The weight gain (in mg) is determined by subtracting the pretest weight from the posttest 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 the adequacy of steam flow and test procedures.

A-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 indication of discoloration (see Appendix C), 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±5 μm deep and >25±5 μm wide) along the sample. Based on results presented in NUREG/CR-6967 (Ref. 3), such a scratch will induce breakaway oxidation away from the sample ends before the ends experience breakaway oxidation (see Appendix C).

A-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 prescratched 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., 1,000 ºC) 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 (Ref. 3).

Pre-Decisional

However, for lower oxidation temperatures (e.g., 800 ºC), the time lag between the observation of surface discoloration and significant hydrogen pickup may be much longer (Ref. 2).

For the case of multiple samples (e.g., five) tested at the same temperature and time, the hydrogen content for this set of samples should be reported as the average value plus or minus one standard deviation. The average minus-one standard deviation should be compared to the 200-wppm hydrogen pickup to determine if breakaway has occurred. It is also acceptable to use the 200-wppm hydrogen content of the postoxidized sample (i.e., total sample hydrogen mass normalized to mass of oxidized sample) as the breakaway oxidation criterion.

There are several ways to measure hydrogen content in metals. Vacuum fusion is one method. The recommended method is documented in ASTM E1447-09, "Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Thermal Conductivity/Infrared Detection Method" (Ref. 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 NUREG/CR-6967 (Ref. 3) are documented in Reference 15.

Along with the necessary instrumentation (e.g., LECO RH-404 hydrogen determinator), calibration standards, which are NIST-traceable and provided by the vendor, are needed. These calibration standards are titanium coupons with hydrogen contents traceable to NIST standards. Titanium coupons with 218 wppm are recommended for calibration and verification of calibration. As these machines are very sensitive, it is important to perform calibration at least once in any given day before 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), posttest calibration verification should be performed by testing a 218-wppm standard as an unknown (i.e., with the same calibration constant determined before testing).

A-9.5 Criterion (200-wppm Hydrogen Pickup) for Breakaway Oxidation Based on Retention of Ductility

As shown in Appendix B, cladding rings with hydrogen pickup values ≤440 wppm oxidized at 970–1,000 ºC are ductile at 135 ºC and brittle for hydrogen pickup values ≥600 wppm. The ductile-to-brittle transition is likely to occur for a hydrogen pickup of ≈500 wppm. Thus, ductility is retained with an appropriate amount of conservatism for average hydrogen pickup values and posttest hydrogen values ≤200 wppm. At 970–1,000 ºC oxidation temperatures, the transition from ductile to brittle behavior may occur within 100–200 s. The 200-wppm -hydrogen breakaway criterion is reasonable and justified at the higher oxidation temperatures at which the minimum breakaway oxidation time is most likely to occur.

A-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.

Pre-Decisional

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 NUREG/CR-6967 (Ref. 3), a cladding sample oxidized for ≈3,500 s at 1,000 ºC 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 on 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.

A-10. Test Temperatures

Leistikow and Schanz (Ref. 2) studied the oxidation kinetics and breakaway oxidation for Zry-4 over a range of temperatures (600–1,600 ºC, with temperature increments of 50 ºC) for very long times (≤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-hydrogen criterion for breakaway, Leistikow and Schanz found minimum breakaway times of ≈1,800 s at 1,000 ºC and ≈3,600 s at 800 ºC. These minimum times occurred at temperatures close to the phase change temperatures for Zry-4 (≈980 ºC for the α+β→β transition and ≈810 ºC for the α+β→α transition). Intermediate temperatures (e.g., 1,025 ºC, 985 ºC, 825 ºC, and 775 ºC) were not investigated, and relatively few oxidation temperatures (1,000 ºC, 900 ºC, 800 ºC, and 650 ºC) 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 Zr alloys. Based on the results presented in References 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 Zircaloys, Zr-1Nb-1Sn, and Zr-1Nb alloys, the upper phase-transformation temperatures are in a rather narrow range (≈965–985 ºC). The lower phase-transformation temperatures for these alloys span a larger range (≈650–810 ºC).

To determine the minimum breakaway oxidation times, oxidation temperatures should include the following high temperatures: 1,050 ºC, 1,030 ºC, 1,015 ºC, 1,000 ºC, 985 ºC, 970 ºC, and 950 ºC—resulting in seven separate tests. The maximum test time should be 5,000 s. 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 smooth and lustrous black, indicating breakaway oxidation has not occurred for any of the test temperatures, then four additional tests should be conducted at 1,000 ºC to confirm repeatability. Finally, two additional tests should be conducted: a test at 800 ºC and a second test at 1,000 ºC on a sample with a bounding or design-basis scratch. If the outer surface is smooth and lustrous black following all of the nine test conditions, no further testing is necessary to characterize the breakaway behavior.

If the outer surface is rough and dull black following any test in the initial oxidation temperature set (950 ºC–1,050 ºC), then the sample may be well beyond the breakaway oxidation time as defined by the 200-wppm hydrogen pickup criterion, and the hydrogen content should be measured. If breakaway oxidation is observed to occur at <5,000 s, the minimum time and corresponding temperature should be reported. Four additional tests should be conducted at this minimum time because of anticipated data scatter for hydrogen content or pickup. After the minimum breakaway time is determined for 950–1,050 ºC, a test should be conducted at 800 ºC to confirm that breakaway oxidation does not occur at this

Pre-Decisional

lower temperature for this particular time. Finally, five repeat tests at the minimum breakaway time should be conducted on a sample with a bounding or design-basis scratch to determine the influence of a surface defect on the measured time to breakaway behavior.

Appendix E provides an overview and logic diagram to illustrate the testing matrix described above.

Although not recommended, these tests may be conducted first with polished and cleaned cladding material before 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 50±5 μm or whatever design-basis 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, the NRC staff recommends that all tests be conducted with scratched samples that have experienced the full postpolishing 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 eight scoping tests, along with four confirmation tests at 1,000 ºC. For the five tests run at 1,000 ºC, all five samples must exhibit lustrous black oxides or <200-wppm hydrogen to conclude that the minimum breakaway oxidation time is >5,000 s. If >200-wppm hydrogen pickup is observed after 5,000 s at one or more temperatures, then the test time would have to be reduced until the hydrogen pickup fell below 200 wppm.

The NRC staff recommends that testing be initiated at 1,000 ºC for a test time of 5,000 s. If breakaway is observed based on visual examination and the hydrogen content is >200 wppm, then the test time at 1,000 ºC 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., 1,015 ºC) and lower (e.g., 985 ºC) temperatures should be conducted at the minimum time for 1,000 ºC (≤5,000 s). If breakaway is observed at a lower test time for a temperature other than 1,000 ºC, then that minimum time should be used as the maximum test time for subsequent temperatures. This process is documented in NUREG/CR-6967 (Ref. 3).

Test results reported in NUREG/CR-6967 (Ref. 3) and Yan, et al. (Ref. 16) indicate significant temperature sensitivity for the breakaway oxidation of one cladding material. The minimum breakaway oxidation time was found to occur at 970–985 ºC. Also, as breakaway oxidation is an instability phenomenon, considerable scatter was observed in the data for hydrogen pickup versus time. For an oxidation temperature of 1,000 ºC, there appeared to be less scatter, and the breakaway oxidation time was determined to be 4,000±200 s for 200-wppm hydrogen pickup (see Figure A-2). However, as shown in Figure A-3, considerably more data scatter was observed within the critical temperature range of 970–985 ºC, for which the minimum breakaway time was determined to be 3,100±300 s for 200-wppm hydrogen pickup.

Pre-Decisional

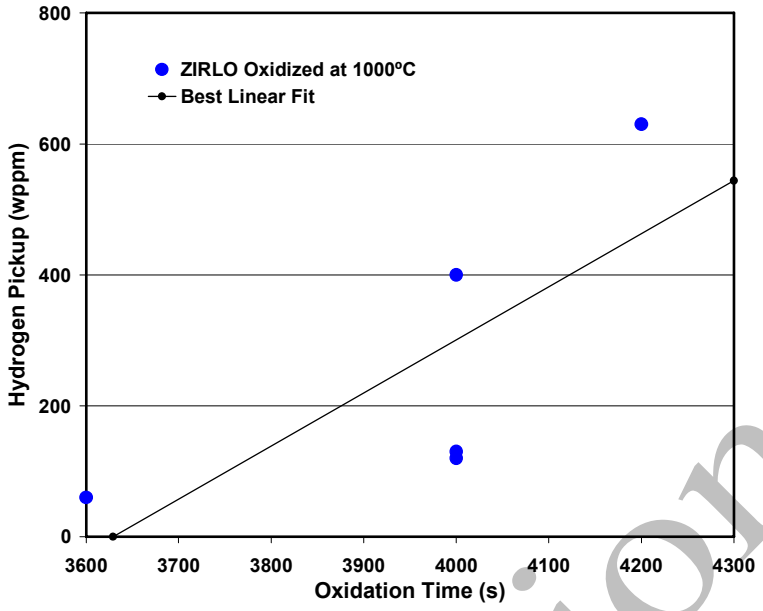


Figure A-2. Hydrogen pickup vs. test time data for as-fabricated ZIRLO™ oxidized at 1,000 ºC

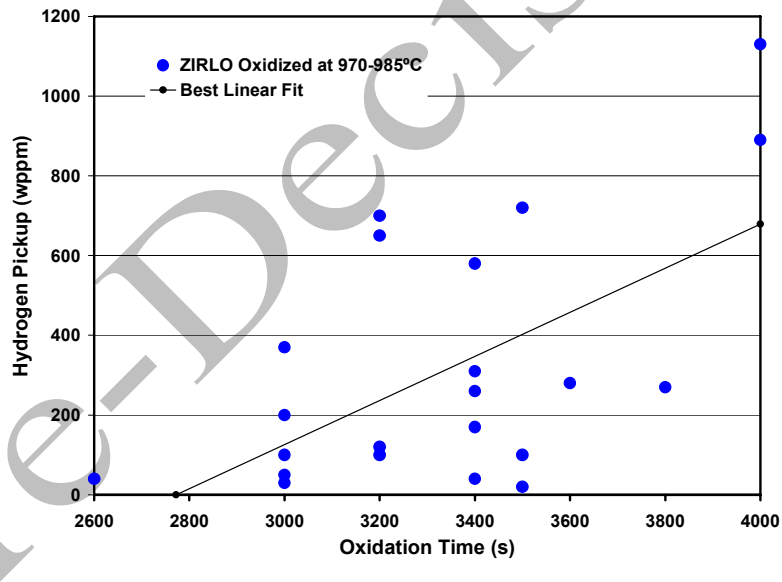


Figure A-3. Hydrogen pickup vs. test time for as-fabricated, prescratched, and preoxidized (≈1-µm thick) ZIRLO™ oxidized at 970–985 ºC

Pre-Decisional

A-11. References[1]

1. ORNL/NUREG-17, "Zirconium Metal-Water Oxidation Kinetics IV. Reaction Rate Studies," U.S. Nuclear Regulatory Commission, Washington, DC, August 1977.

2. Leistikow, S., and G. Schanz, "Oxidation Kinetics and Related Phenomena of Zircaloy-4 Fuel Cladding Exposed to High Temperature Steam and Hydrogen-Steam Mixtures under PWR Accident Conditions," *Nuclear Engineering and Design*, 103: 65–84.

3. NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," U.S. Nuclear Regulatory Commission, Washington, DC, July 2008. (Agencywide Documents Access and Management System. (ADAMS) Accession No. ML082130389)

4. NUREG/IA-0211, "Experimental Study of Embrittlement of Zr-1%Nb VVER Cladding under LOCA-Relevant Conditions," U.S. Nuclear Regulatory Commission, Washington, DC, March 2005. (ADAMS Accession No. ML051100343)

5. Mardon, J.P., J.C. Brachet, L. Portier, V. Maillot, T. Forgeron, A. Lesbros, et al., "Influence of Hydrogen Simulating Burn-Up Effects on the Metallurgical and Thermal-Mechanical Behavior of M5™ and Zircaloy-4 Alloys under LOCA Conditions," ICONE13-50457, *13th International Conference on Nuclear Engineering*, Beijing, China, May 16-20, 2005.

6. Baek, J.H., and Y.H. Jeong, "Breakaway Phenomenon of Zr-based Alloys during a High-Temperature Oxidation," *Journal of Nuclear Materials*, 372: 152–159. (Available at www.sciencedirect.com.)

7. ASTM G2/G2M-06, "Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680ºF [360ºC] or in Steam at 750ºF [400ºC]," ASTM International, West Conshohocken, PA, 2006.[2]

8. Claude Grandjean and Georges Hache, "A State of the Art Review of Past Programmes Devoted to Fuel Behaviour under Loss-of-Coolant Conditions. Part 3. Cladding Oxidation. Resistance to Quench and Post-Quench Loads," IRSN Technical Report DPAM/SEMCA 2008-093, Institut de Radioprotection et de Sûreté Nucléaire, Fontenay-aux-Roses, France, 2008.

9. H. Uetsuka, "Oxidation of Zircaloy-4 under Limited Steam Supply at 1000 and 1300ºC," Kernforschungszentrum Karlsruhe (KfK) 3848, Kernforschungszentrum Karlsruhe GmbH, Postfach 360, 76021 Karlsruhe, 1984.

10. M. Aomi, M. Nakatuka, et al., "Behavior of BWR Fuel Cladding Tubes under Simulated LOCA Conditions," ICONE-7435, 7th International Conference on Nuclear Engineering, 1999.

---

[1] Publicly available NRC published documents are available electronically through the NRC Library at: http://www.nrc.gov/reading-rm/doc-collections/. The documents can also be viewed on-line or printed for a fee in the NRC's Public Document Room (PDR) at 11555 Rockville Pike, Rockville, MD; the mailing address is USNRC PDR, Washington, DC 20555; telephone 301-415-4737 or (800) 397-4209; fax (301) 415-3548; and e-mail pdr.resource@nrc.gov.

[2] Copies of American Society for Testing and Materials (ASTM) standards may be purchased from ASTM, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, Pennsylvania 19428-2959; telephone (610) 832-9585. Purchase information is available through the ASTM Web site at http://www.astm.org.

Pre-Decisional

11. Kawasaki, S., T. Furuta, and M. Suzuki, "Oxidation of Zircaloy-4 under High Temperature Steam Atmosphere and Its Effect on Ductility of Cladding," *Journal of Nuclear Science and Technology*, 15(8): 589–596.

12. P. Hofmann and M. Markiewicz, "Chemical Interactions between As-Received and Pre-Oxidized Zircaloy-4 and Inconel-718 at High Temperatures, Kernforschungszentrum Karlsruhe (KfK) 4729, Kernforschungszentrum Karlsruhe GmbH, Postfach 360, 76021 Karlsruhe, June 1994.

13. Y. Yan, "Work Plan for the Breakaway Oxidation of ZIRLO™ Cladding at 800-1015ºC," ANL Intra-Laboratory Memo, IPS-490-00-01, Feb. 9, 2007.

14. ASTM E1447-05, "Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Thermal Conductivity/Infrared Detection Method," ASTM International, West Conshohocken, PA, 2005.

15. T. Burtseva, "Procedure for Hydrogen Analysis of Refractory Metals," ANL Intra-Laboratory Memo, IPS-467-00-00, Nov. 25, 2005.

16. Y. Yan, T. Burtseva, and M. Billone, "Update on Breakaway Oxidation of Westinghouse ZIRLO™ Cladding," ANL letter report to NRC, Jan. 8, 2009. (ADAMS Accession No. ML091330334)

17. Y. Yan, T. A. Burtseva and M.C. Billone, "Breakaway Oxidation Tests for M5 Cladding," ANL letter report to NRC, July 31 2009. (ADAMS Accession No. ML092710536)

18. Y. Yan, T. Burtseva and M.C. Billone, "Progress Report on Breakaway Oxidation of Bare and Prefilmed ZIRLO™," ANL letter report to NRC, May 30, 2007. (ADAMS Accession No. ML080800314)

19. Y. Yan, T.A. Burtseva, and M.C. Billone, "Breakaway Oxidation of ZIRLO™ Exposed to Transient Temperature Histories," ANL letter report to NRC, July 31, 2009. (ADAMS Accession No. ML092710523)

Pre-Decisional

APPENDIX B

RATIONALE FOR THE 200-WPPM HYDROGEN PICKUP CRITERION FOR BREAKAWAY OXIDATION

Table B-1 summarizes the increase in hydrogen pickup, with test times for three of the cladding materials tested by Argonne National Laboratory (see NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," issued July 2008, Agencywide Documents Access and Management System Accession No. ML082130389). 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-weight parts per million (wppm) hydrogen pickup was established before initiation of the NUREG/CR-69673 breakaway oxidation study. It was subsequently confirmed by conducting ring compression tests for samples sectioned from the breakaway oxidation samples. Table B-2 and Figure B-1 summarize the results of these ring-compression tests. Ductility is maintained for a ≤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 seconds (s).

Table B-1. Summary of Hydrogen Pickup vs. Test Time for Several Cladding Materials Oxidized at 970–1,000 ºC

Cladding Material	Test T, ºC	Test Time, s	Hydrogen Content, wppm	Hydrogen Pickup, wppm	Comment
15×15 Low-Tin Zry-4 (Old)	985	3,600 3,800 3,900	186 40–60 1,260	170 20–40 1,320	Prescratched Lustrous Black outer surface Large Gray Areas on outer surface
15×15 Low-Tin Zry-4 (Modern)	985	5,000 5,400	286 411	280 410	Gray Line on outer surface Large Gray Area on outer surface
17×17 ZIRLO™ (Modern)	985	3,400 3,400 3,600	174 50 267	175 20 270	Yellow Area along Prescratch Lustrous Black outer surface Yellow Circle on outer surface

Table B-2. Ductility at 135 ºC vs. Hydrogen Pickup for Several Cladding Materials Oxidized at 970–1,000 ºC

Cladding Material	Test T, ºC	Hydrogen Content, wppm	Hydrogen Pickup, wppm	Offset Strain at 135 ºC, %
15×15 Low-Tin Zry-4 (Old)	985	186	170	5.2
		1,260	1,320	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
	1,000	555	600	0.8
	985	731	765	0.8
	985	987	1040	0.8

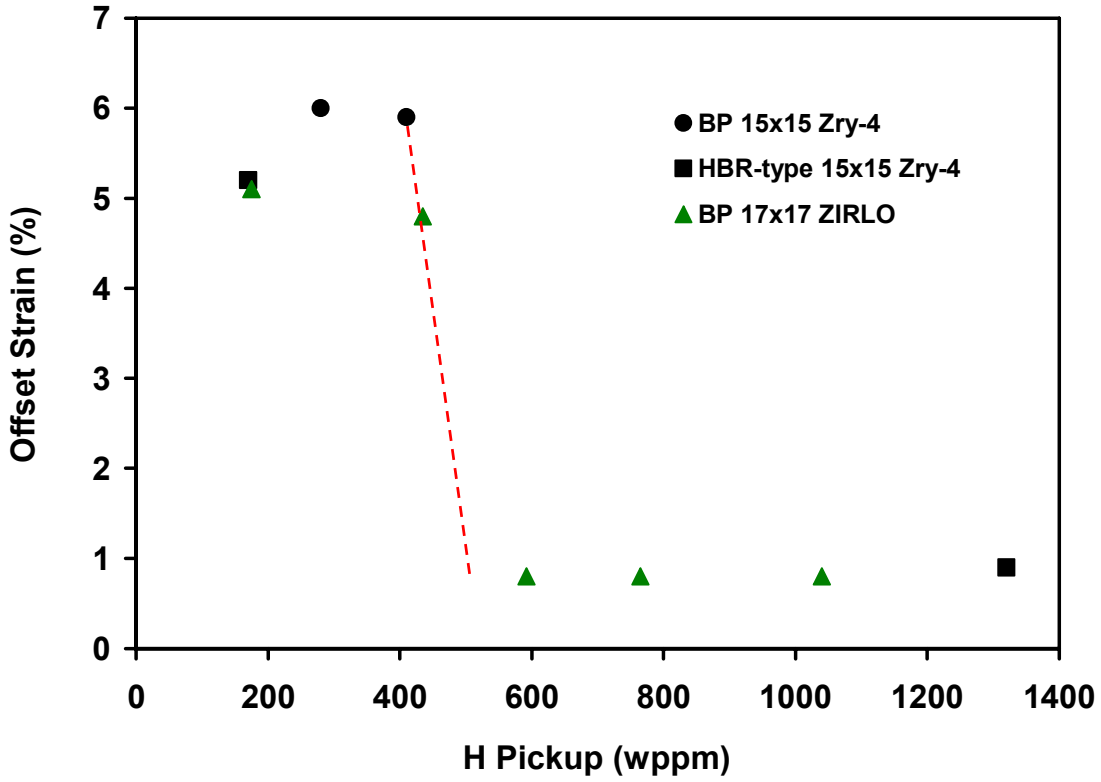
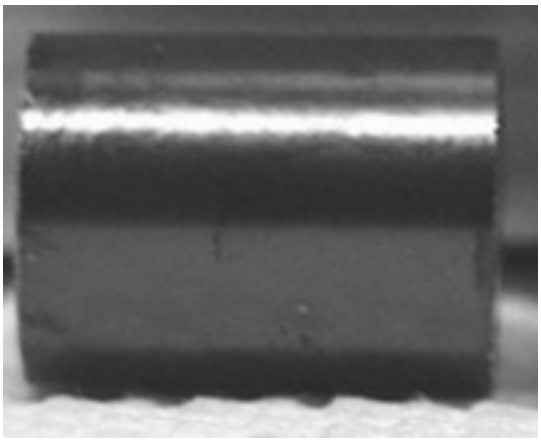


Figure B-1. Ductility (from ring compression tests at 135 ºC) vs. hydrogen pickup for breakaway oxidation samples oxidized at 970–1,000 ºC. Ductile-to-brittle transition occurs at ≈500 wppm hydrogen pickup. "BP" refers to "belt polished" cladding and HBR-type refers to cladding comparable to H.B. Robinson vintage cladding.

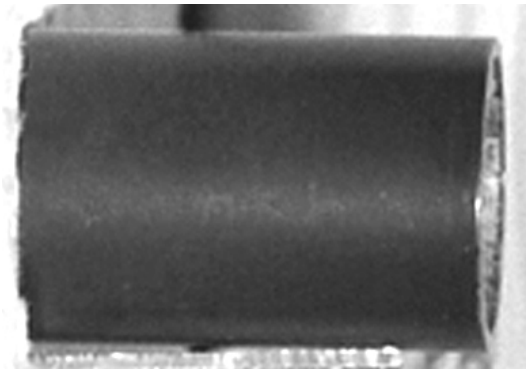
APPENDIX C

NEGATIVE EFFECTS OF ETCHING WITH HYDROFLOURIC-CONTAINING ACID AS PART OF SAMPLE CLEANING

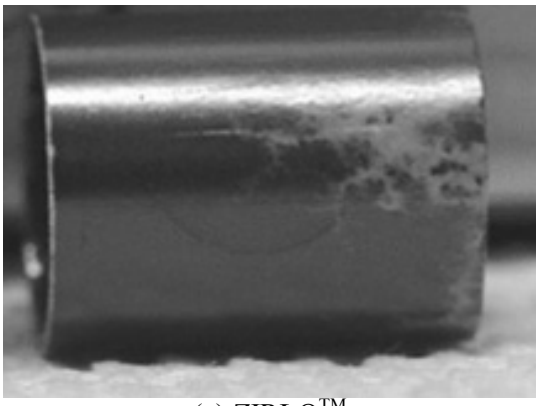
As part of the work in NUREG/CR-6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," issued July 2008 (Agencywide Documents Access and Management System Accession No. ML082130389), 17×17 low-tin Zircaloy-4 (Zry-4), 17×17 ZIRLO™, and 17×17 M5 alloy cladding samples were subjected to etching for 180 seconds (s) in a hydrofluoric (HF)-containing solution (3.5%-HF + 45%-HNO_3 + 51.5%-H_2O) before ultrasonic cleaning with ethanol and water. The samples were then oxidized for 2,400 s at 1,000 degrees Celsius (ºC). 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 Figure C-1. 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.



(a) Zry-4



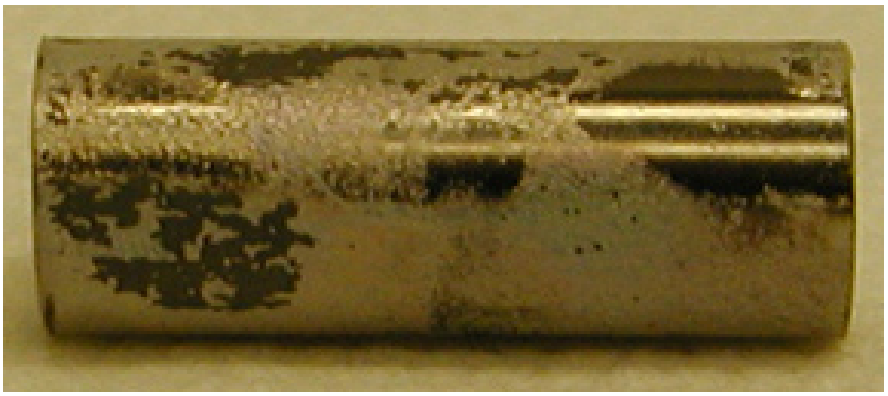
(b) M5



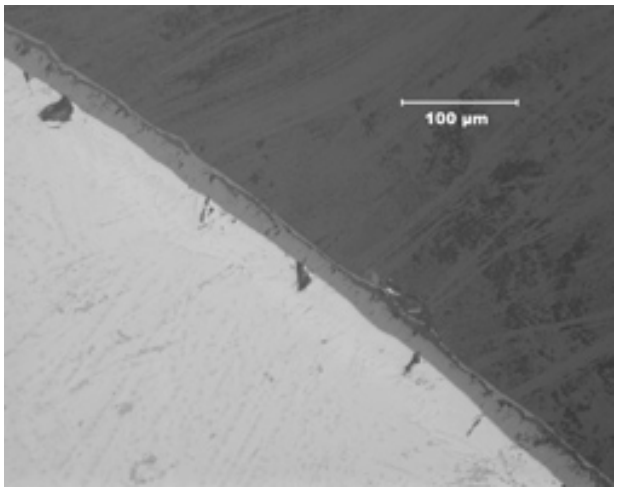
(c) ZIRLO™

Figure C-1. Outer surfaces of samples etched for 180 s in a 3.5%-HF acid mixture before oxidation at 1,000 ºC for 2,400-s hold time: (a) Zry-4, (b) M5, and (c) ZIRLO™. (Note: The surface of M5 was lustrous black, but the quality of the photograph is not high enough to show it.)

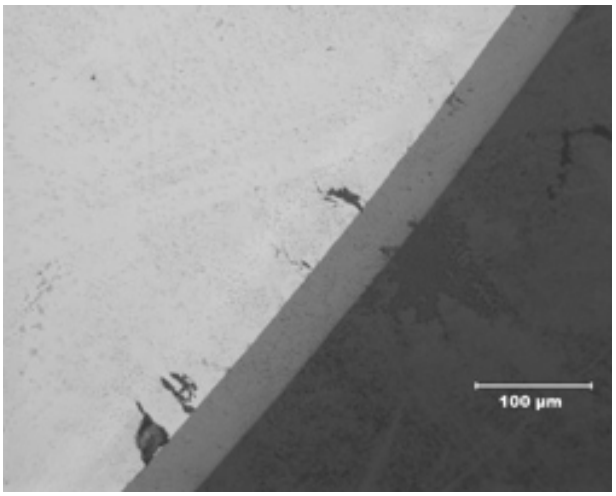
For the spent nuclear fuel program, ZIRLO™ samples were etched in a 1%-HF acid solution for 180 s before hydriding. This worked well for the spent nuclear fuel application, for which cladding temperatures are ≤400 ºC and the cladding is in a nonoxidizing environment (helium-filled storage, transport, or storage-and-transport casks). However, HF-etching before hydriding caused breakaway oxidation for samples oxidized for only 280 s total test time with a hold time of 180 s at 1,200 ºC. Figure C-2a shows the appearance of the outer cladding surface after oxidation, and Figures C-2b and C-2c 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 Ar+30%H_2 at 400 ºC. 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 ºC distilled water before the standard ultrasonic cleaning in ethanol and distilled water. Figure C-3 shows that surface discoloration persists even for the 15-s-etch sample following oxidation at ≤1,200 ºC for 280 s.



(a)



(b)



(c)

Figure C-2. Appearance and morphology of outer-surface oxide following etching for 180 s in 1%-HF acid bath, exposure to flowing argon (Ar) and Ar+30%H_2 for <10 hours at 400 ºC and oxidation for 280 s with a 180-s hold time at 1,200 ºC: (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.

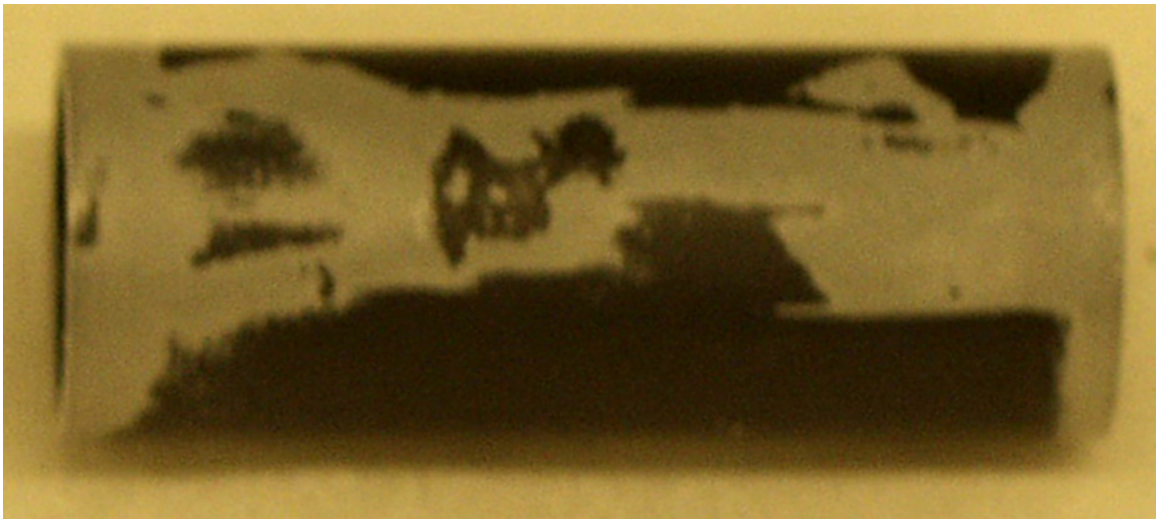


Figure C-3. Outer-surface appearance of ZIRLO™ sample that was etched for 15 s in a 1%-HF acid mixture, rinsed in 80 ºC distilled water, ultrasonically cleaned in ethanol and water baths, and heated in steam from 300 ºC to 1,200 ºC in 100 s and held at 1,200 ºC for 180 s. The hydrogen pickup was 510±30 wppm.

APPENDIX D

CORRELATION BETWEEN CLADDING OUTER-SURFACE APPEARANCE AND HYDROGEN PICKUP

The breakaway oxidation tests documented in Ref. 1 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 a result, a considerable database was generated for outer-surface appearance versus hydrogen content and hydrogen pickup. Examples from the Ref. 3 work are presented here to guide investigators on what to expect from small discoloration spots and from larger areas of surface discoloration. These examples are from test samples exposed to higher steam oxidation temperatures (970–1,000 degrees Celsius (ºC)). For these samples, small areas of discoloration correlated with hydrogen pickups in the range of 50–250 weight parts per million (wppm), while larger areas of discoloration correlated to >400 wppm of hydrogen. At lower oxidation temperatures (e.g., 800 ºC) with corresponding lower hydrogen generation rates, significant surface discoloration may precede 200-wppm hydrogen pickup.

For Zircaloy-4 (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 D-1 shows prebreakaway H.B. Robinson (HBR)-type 15×15 Zry-4 following oxidation at ≈1,000 ºC for 3,600 seconds (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 3,600 s. The other two samples were oxidized for long test times (5,400 s and 7,200 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.

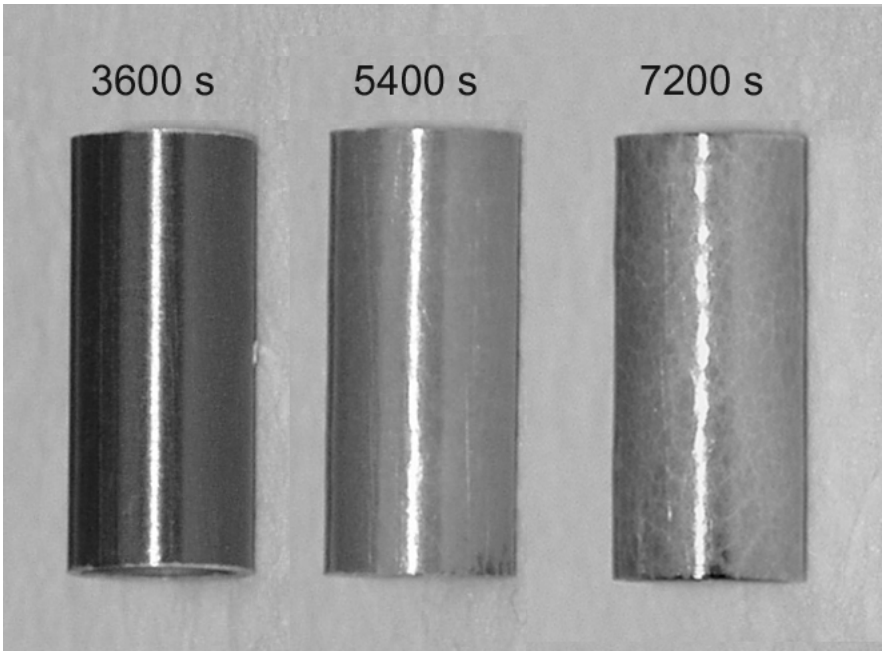
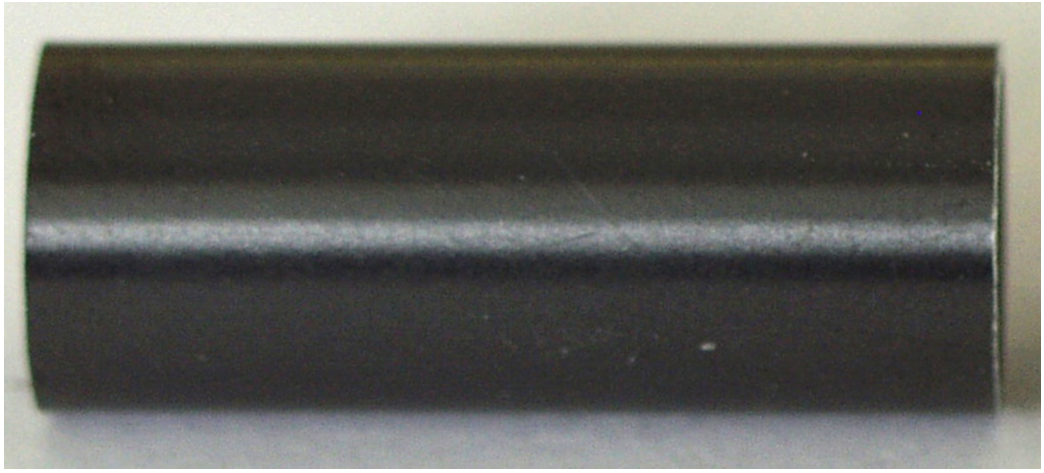


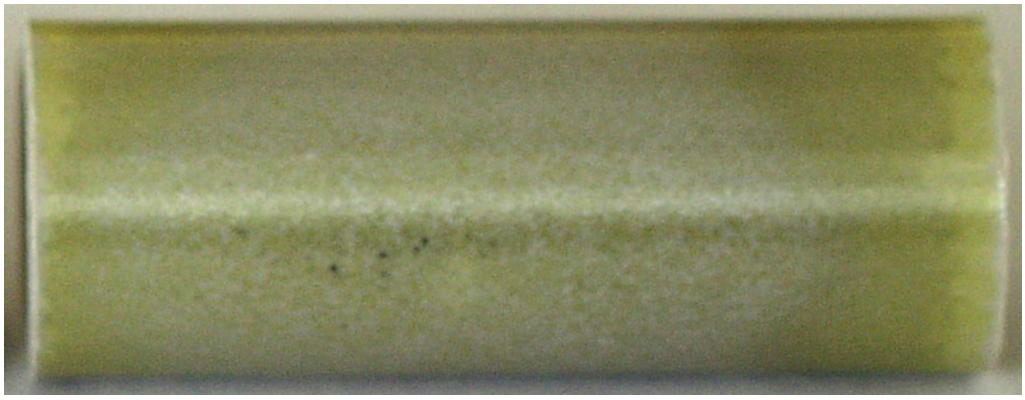
Figure D-1. Outer-surface appearance of an older vintage (HBR) of 15×15 Zry-4 following oxidation at ≈1,000 ºC for 3,600 s (lustrous black with 40-wppm hydrogen pickup), 5,400 s (gray with 2,300-wppm hydrogen pickup), and 7,200 s (with 3,100-wppm hydrogen pickup).

Similar results were obtained for 17×17 ZIRLO™ oxidized at 1,000 ºC. However, for ZIRLO™, the color change of the outer surface was from lustrous black to yellow (or tan). Figure D-2 shows the transformation of colors from lustrous black to lustrous black with yellow spots to yellow.



(a) 1,500 s at 1,000 ºC; 5-wppm hydrogen pickup

(b) 3,600 s at 1,000 ºC; 60-wppm hydrogen pickup



(c) 5,000 s at 1,000 ºC; 1,350-wppm hydrogen pickup

Figure D-2. Outer-surface appearance and hydrogen pickup for ZIRLO™ samples oxidized at 1,000 ºC: (a) lustrous black at 1,500 s, (b) lustrous black with yellow spots at 3,600 s, and (c) yellow at 5,000 s.

For polished 15×15 Zry-4, the minimum breakaway oxidation time is ≈5,000 s and occurs at a long-time oxidation temperature of 985 ºC. Figure 38a in Ref. 1 shows the appearance of the outer surface of the sample oxidized at 985 ºC for 5,000 s (it is included below as Figure D-3 for the convenience of the reader). The sample exhibited a gray line along the axial direction. Metallography (Figures 38b and c in Ref. 1) 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.

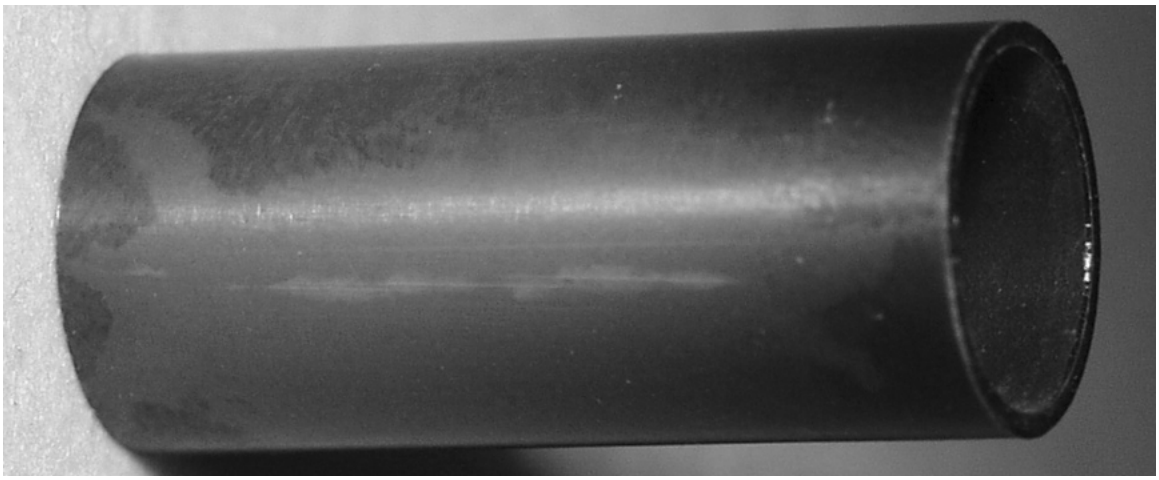


Figure D-3. Polished 15x15 Zry-4 cladding oxidized at 985 ºC for 5,000 s. The gray line along about two-thirds of the sample length is the region under which breakaway oxidation had occurred. Circumferentially averaged hydrogen pickup was 280±160 wppm. Hydrogen pickup under the gray streak was >460 wppm.

Figures D-4 to D-9 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 D-4 to D-6 correspond to Figures 81 to 83 in Ref. 1. Figure D-7 is taken from Ref. 2, Figure 2, and Figures D-8 and D-9 are taken from Ref. 3, Figures 2 and 4.

Figure D-10 is from Ref. 4. The sample was oxidized at an isothermal temperature of 980 ºC for 2,000 s. The temperature was cycled five times from 1,030 ºC to 930 ºC for 400 s before an additional 400-s isothermal oxidation at 980 ºC. The surface-discoloration pattern is different from those obtained from isothermal tests, and the color is a mixture of yellow and gray.

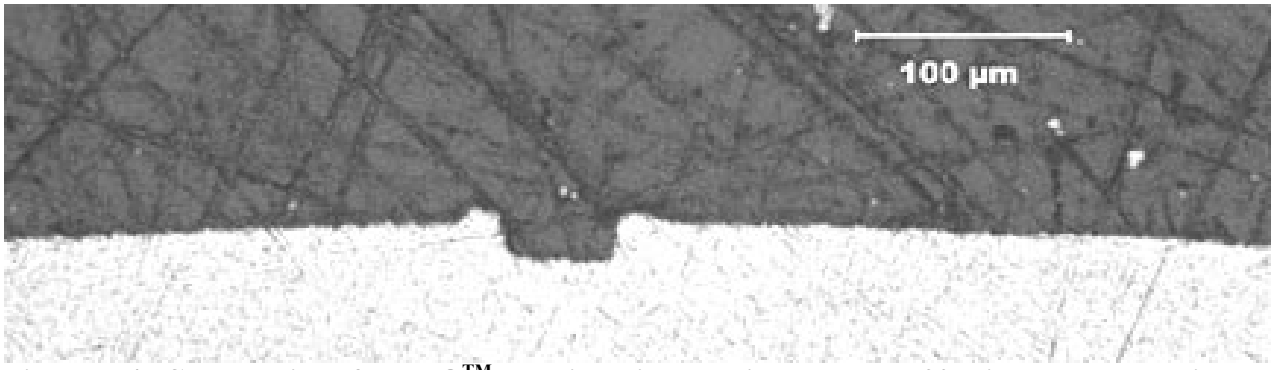


Figure D-4. Cross section of ZIRLO™ cladding with machined scratch ≈20-micrometers deep into outer surface

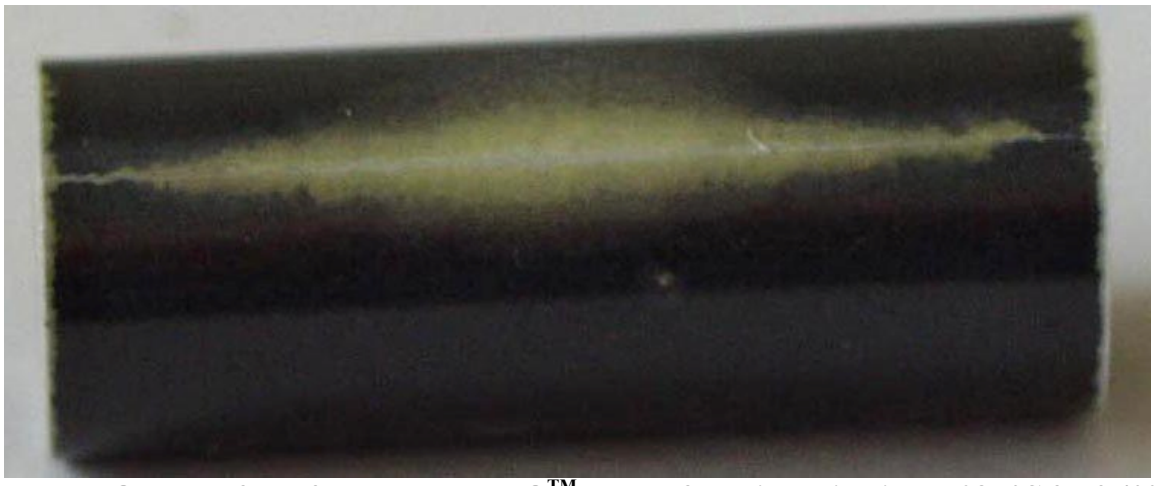


Figure D-5. Outer surface of scratched ZIRLO™ sample following oxidation at 985 ºC for 3,400 s. Local hydrogen pickup under the yellow surface was 440 wppm; average pickup was 175 wppm.

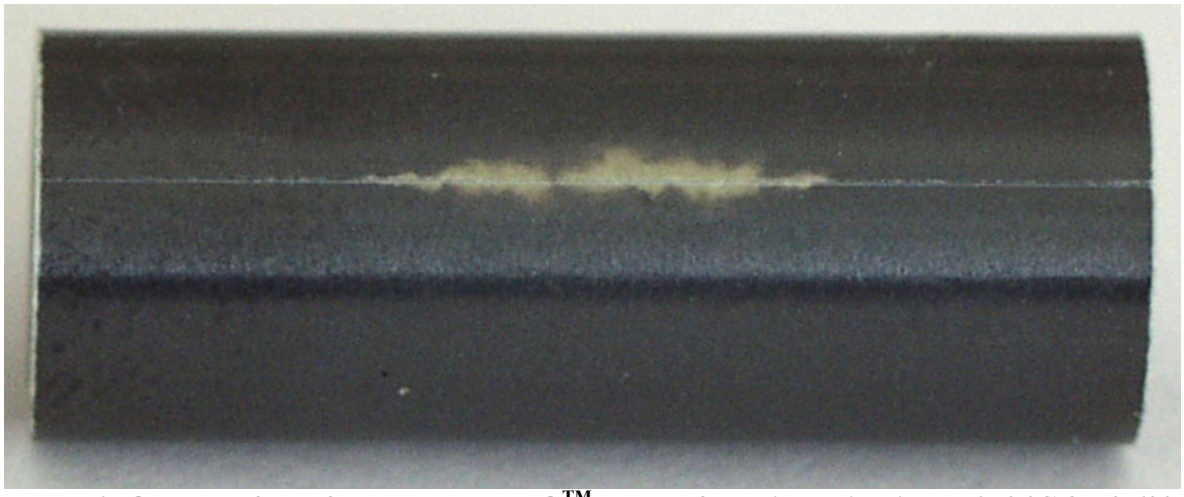


Figure D-6. Outer surface of scratched ZIRLO™ sample following oxidation at 970 ºC for 2,600 s. Local hydrogen pickup under the yellow surface was 120 wppm; average pickup was 44 wppm.

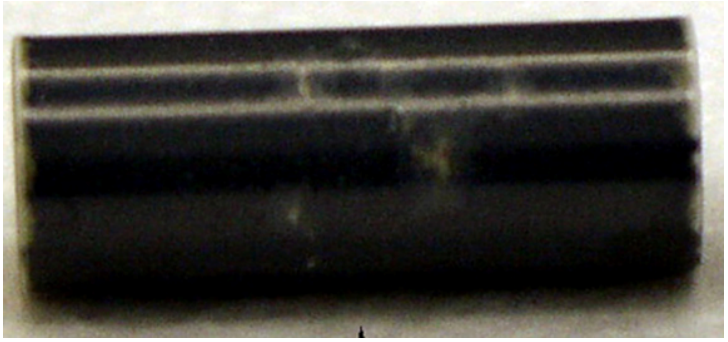


Figure D-7. Outer-surface appearance for ZIRLO™ sample oxidized at 1,000 ºC for 4,000 s. Hydrogen pickup was 120±110 wppm with >280 wppm under the yellow spots.

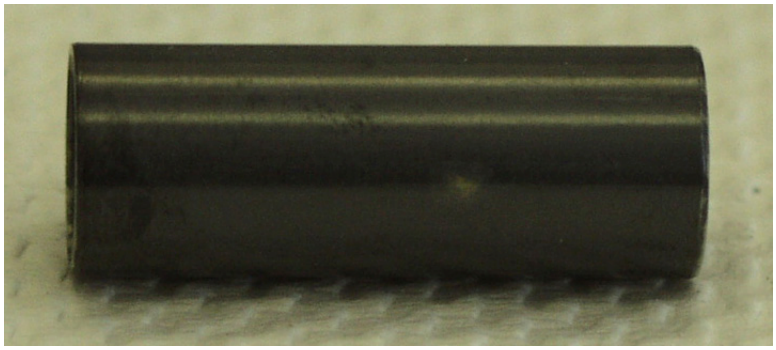


Figure D-8. Outer surface of prefilmed ZIRLO™ oxidized at 985 ºC for 3,000 s. One yellow spot can be seen just to the right of the sample midplane. Hydrogen pickup in a 2-mm-long ring including the yellow spot was 50±40 wppm.

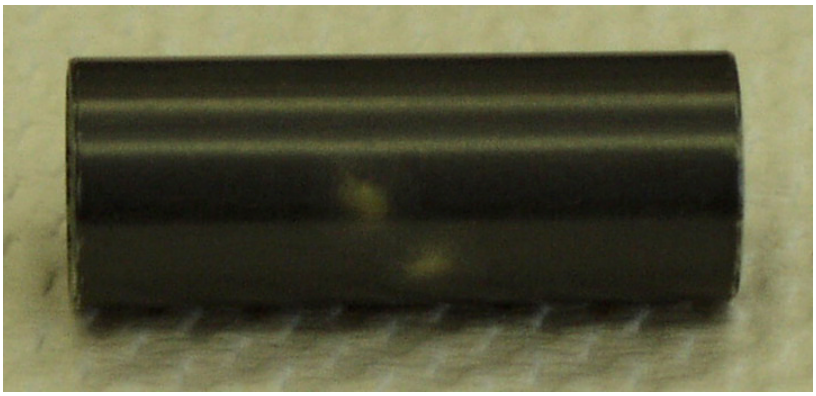
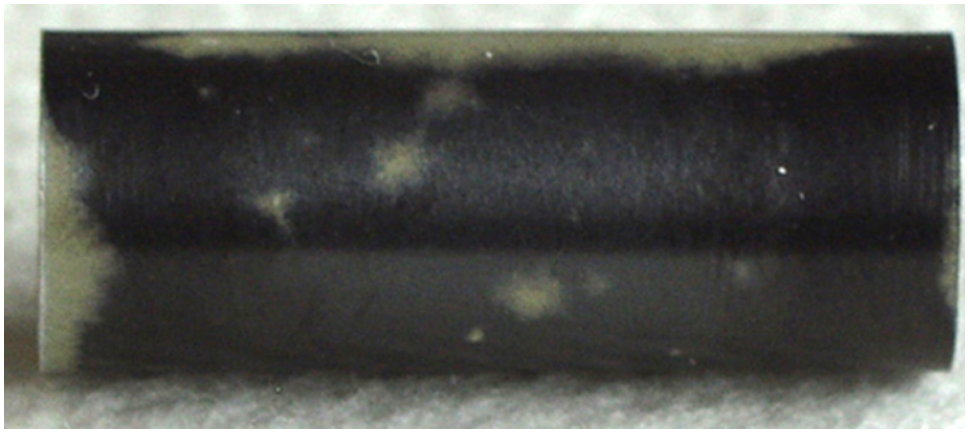
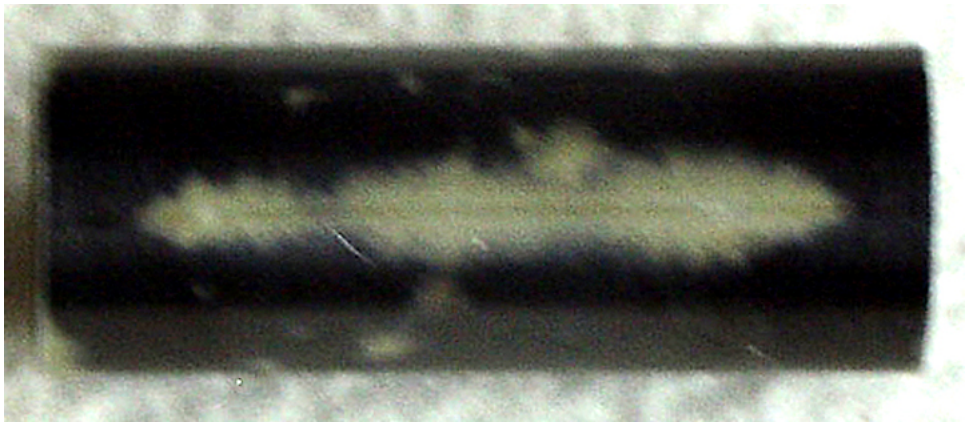


Figure D-9. Outer surface of prefilmed ZIRLO™ oxidized at 980 ºC for 3,200 s. Two small yellow spots can be observed. Hydrogen pickup in a 2-mm-long ring sectioned to include a yellow spot was 120±120 wppm, with 300-wppm hydrogen under the spot. For a sibling sample tested under the same conditions, the local hydrogen content under the yellow spot was 470 wppm.



(a)



(b)

Figure D-10. Outer-surface appearance of as-fabricated ZIRLO™ sample oxidized for a total test time of 2,800 s: 2,400 s at 980 ºC and 400 s with five temperature cycles from 930 to 1,030 ºC. Hydrogen content was measured to be 230±80 wppm, indicating breakaway oxidation for a total test time of 2,800 s.

References[1]

1. NUREG/CR 6967, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," U.S. Nuclear Regulatory Commission, Washington, DC, July 2008. (Agencywide Documents Access and Management System. (ADAMS) Accession No. ML082130389)

2. Y. Yan, T. Burtseva, and M. Billone, "Update on Breakaway Oxidation of Westinghouse ZIRLOTM Cladding," ANL letter report to NRC, Jan. 8, 2009. (ADAMS Accession No. ML091330334)

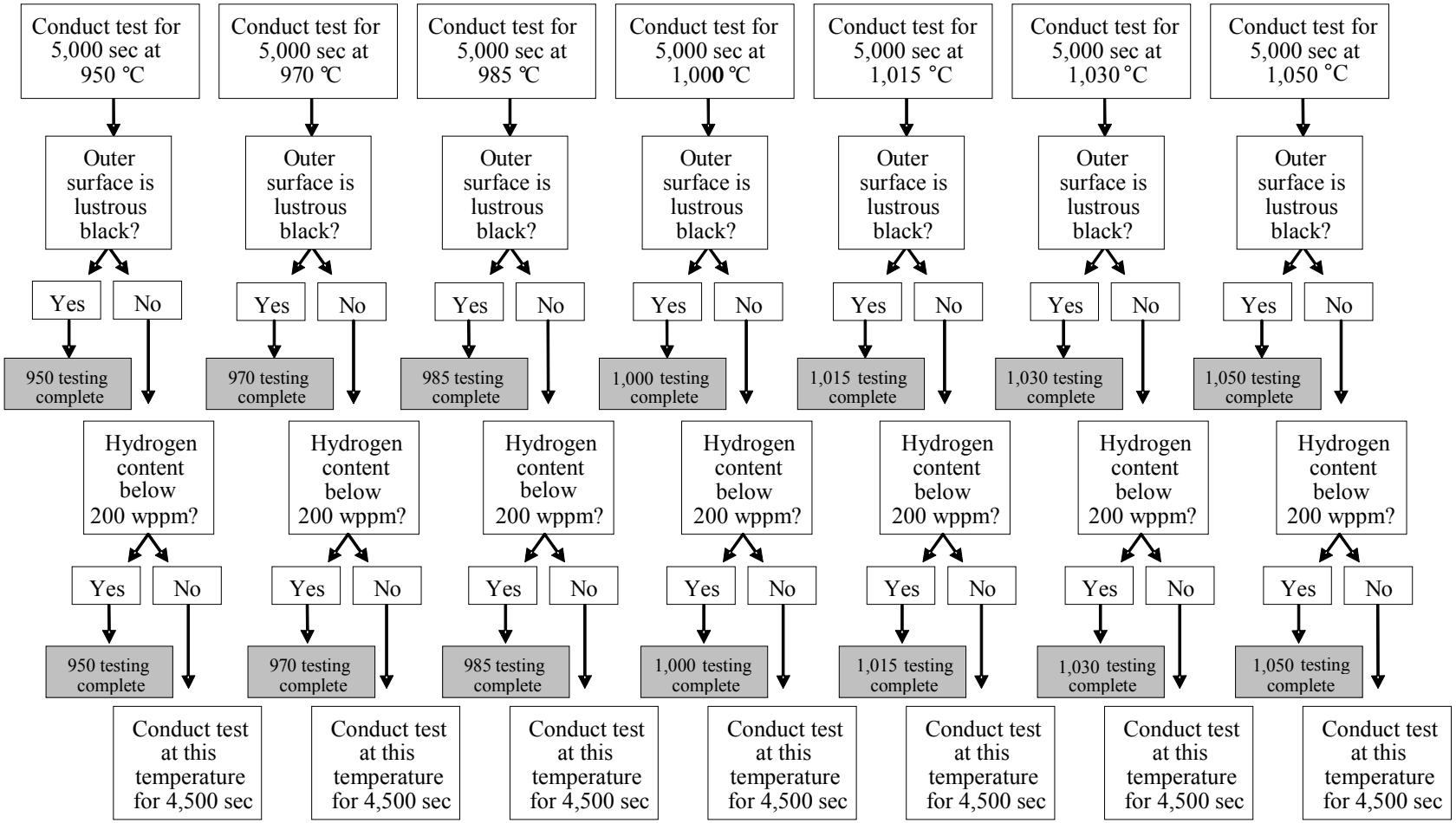
3. Y. Yan, T. Burtseva and M.C. Billone, "Progress Report on Breakaway Oxidation of Bare and Prefilmed ZIRLOTM," ANL letter report to NRC, May 29, 2007. (ADAMS Accession No. ML080800314)

4. Y. Yan, T.A. Burtseva, and M.C. Billone, "Breakaway Oxidation of ZIRLOTM Exposed to Transient Temperature Histories," ANL letter report to NRC, April, 2009. (ADAMS Accession No. ML092710523)

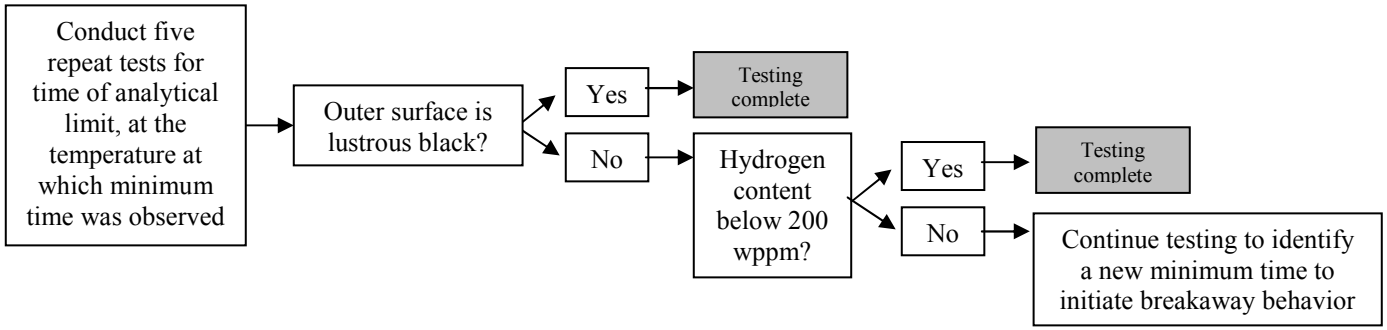
[1] Publicly available NRC published documents are available electronically through the NRC Library at: http://www.nrc.gov/reading-rm/doc-collections/. The documents can also be viewed on-line or printed for a fee in the NRC's Public Document Room (PDR) at 11555 Rockville Pike, Rockville, MD; the mailing address is USNRC PDR, Washington, DC 20555; telephone 301-415-4737 or (800) 397-4209; fax (301) 415-3548; and e-mail pdr.resource@nrc.gov.

APPENDIX E
OVERVIEW AND LOGIC DIAGRAM TO ILLUSTRATE SAMPLE TEST MATRICES

The test matrix below illustrates the sample test matrix described in Section A-10, "Test Temperatures," of Appendix A to this regulatory guide for initial characterization of a cladding alloy's breakaway oxidation behavior. The test matrix begins with seven tests, conducted incrementally within the range of temperature at which breakaway may occur.



The logic diagram can be repeated for each reduction in time increment. Time reduction increments of 500 seconds are recommended as a practical increment to search for a reduced time scale at which breakaway oxidation does not occur. Once each temperature has been tested with a logic diagram conclusion of "xxx °C testing complete," 10 additional tests may be conducted to demonstrate repeatability and to characterize the influence of a surface scratch. To confirm reliable measurement of the minimum test time, four of the additional tests could be conducted at the temperature at which the minimum test time was recorded (if none of the initial test series resulted in observation of breakaway behavior, four tests at 1,000 °C should be conducted). To characterize the influence of a surface scratch, five repeat tests, at the conditions (time and temperature) of the minimum observed breakaway behavior, could be conducted on samples with a bounding or design-basis scratch. Finally, a test conducted at 800 ºC could be used to confirm that breakaway oxidation does not occur at this lower temperature for the time identified as the minimum time within the range of 950–1,050 °C.

To elaborate on the two possible breakaway criteria within the logic diagram, it is useful to refer to Figure D-2b in Appendix D to this regulatory guide. In this image, yellow spots are observed on the surface of the cladding. This observation would lead to the "No" tree of the logic diagram above, which asks if the outer surface is lustrous black. The logic tree then calls for a hydrogen content measurement. In this case, 60-wppm hydrogen was measured. This observation would lead to the "Yes" tree of the logic diagram above and therefore complete testing for a particular temperature with the conclusion that breakaway oxidation had not occurred for the test temperature and time combination.

In the case of periodic testing, the U.S. Nuclear Regulatory Commission staff considers it acceptable to measure the onset of breakaway oxidation annually for only the temperature at which the minimum time to breakaway oxidation was measured and to demonstrate that breakaway oxidation is not experienced within the time of the established analytical limit. The test matrix below illustrates the reduced test matrix described in the body of this regulatory guide.