

**Procedure for Conducting Oxidation and Post-Quench Ductility Tests with
Zirconium-based Cladding Alloys**

Argonne National Laboratory (ANL)

March 31, 2009

Contents	1
1. Purpose and Scope of Tests	3
2. Background	3
3. Sample Selection and Testing Frequency	4
3.1 Sample selection	4
3.2 Frequency of Testing	4
4. Sample Preparation and Characterization	4
4.1 Hydrogen-content determination for as-fabricated and prehydrided samples	4
4.2 Minimum sample lengths for one- and two-sided oxidation tests	5
4.3 End-cap mass and welding procedure for one-sided oxidation test samples	5
4.4 Length, outer diameter, and wall thickness measurements	5
4.5 Pre-test cleaning with chemical detergent or organic solvent and rinsing	5
4.6 Pre-test sample weight measurement (after drying)	6
5. Temperature Heat-up and Cool-down Rates and Heating Methods	6
5.1 Temperature heat-up and cool-down rates	6
5.2 Radiant heating	7
5.3 Resistance heating	7
5.4 Induction heating	7
5.5 Direct electrical heating	7
6. Temperature Control and Monitoring	7
6.1 Thermocouples	7
6.2 Thermal benchmarks	8
6.3 Weight-gain benchmarks	8
7. Water Quality, Steam Flow Rate, and Steam Pressure	9
7.1 Water quality	9
7.2 Steam flow rate	9
7.3 Steam pressure	9
8. Procedure for Oxidation and Quench Tests	10
8.1 Test train and steam chamber	10
8.2 Purging steam chamber and stabilizing steam flow	10
8.3 Ramping temperature and holding temperature at target value	10
8.4 End of heating phase and cool-down	11

8.5 Determination of equivalent cladding reacted (ECR)	11
9. Post-oxidation-quench Measurements and Characterization	11
9.1 Sample drying time	11
9.2 Weight measurement and use of weight gain to verify oxidation temperature	11
9.3 Hydrogen content measurement	11
10. Matrix for Oxidation and Quench Tests	12
10.1 As-fabricated cladding	12
10.2 Prehydrided cladding	12
11. Procedure for Conducting Ring Compression Post-quench Ductility (PQD) Tests	13
11.1 Pre-test activities	13
11.2 Test temperature and crosshead displacement rate	14
11.3 Test conduct	14
11.4 Test termination	14
11.5 Post-test measurements	15
12. Data Reporting and Assessment	15
12.1 Hydrogen level, test temperature, test time, CP-ECR, offset strain, and permanent strain	15
12.2 Determination of ductile-to-brittle transition CP-ECR	16
References	18
Appendix A. Ring-compression Results for RT and 135°C Tests with As-fabricated Cladding Samples	20
Appendix B. Examples of Load-displacement Curves, Offset Strains and Permanent Strains for Oxidized and Quenched Cladding Samples	29
Appendix C. Relationship between Offset Strain and Permanent Strain	38

Procedure for Conducting Oxidation and Post-Quench Ductility Tests with Zirconium-based Cladding Alloys

Argonne National Laboratory (ANL)

March 31, 2009

1. Purpose and Scope of the Tests

Performance-based tests are needed to ensure that fuel-rod cladding retains ductility following oxidation in steam at $\leq 1200^{\circ}\text{C}$ and quench at $\leq 800^{\circ}\text{C}$. This procedure describes the tests to be conducted with fresh and prehydrided cladding samples for determination of the ductile-to-brittle transition oxidation level as a function of hydrogen-content and either the hold temperature or the maximum oxidation temperature for samples that embrittle during the heating ramp. The oxidation level is defined as the equivalent cladding reacted (ECR) calculated using the Cathcart-Pawel (CP) weight gain correlation. Retention of post-quench ductility (PQD) is defined as the accumulation of $\geq 1\%$ permanent strain prior to failure during ring-compression loading at a temperature of 135°C and a displacement rate of 0.033 mm/s . The ductile-to-brittle transition oxidation level is defined as the maximum CP-ECR (rounded to the nearest percent) for which ductility is retained.

2. Background

During a loss-of-coolant accident (LOCA), the cladding outer surface will be exposed to steam at elevated temperatures. This results in the growth of an outer-surface oxide layer, an oxygen-stabilized metal alpha layer and a low oxygen-content metal beta layer. The oxide and alpha layers are brittle, but the beta layer will retain ductility as long as its oxygen content is low (e.g., $< 0.6\text{ wppm}$). This is close to the oxygen solubility limit at 1200°C for the beta layer of as-fabricated cladding. As such, modern cladding alloys used in U.S. reactors oxidized at 1200°C will retain ductility up to a calculated oxidation level of 17-20% CP-ECR [1], where CP refers to the use of the Cathcart-Pawel [2] weight-gain correlation for the ECR calculation. However, hydrogen pickup during reactor operation can cause a significant decrease in the ductile-to-brittle transition oxidation level (e.g., from 19% to 5% for 550 wppm (weight parts per million) hydrogen [1]). Hydrogen increases the oxygen solubility limit in the beta layer, as well as the rate of diffusion of oxygen into that layer. In addition, for oxidized cladding that undergoes very rapid cooling during quench, hydrogen is intrinsically embrittling.

In addition to oxygen pickup from the cladding outer surface, the cladding inner surface can pick up oxygen from the fuel-cladding bond and from fuel that may be adherent to this bond. This burnup-dependent phenomenon results in an oxygen stabilized alpha layer on the inner surface and additional oxygen pickup by the beta layer.

For cladding that balloons and bursts during the LOCA heating ramp, a third source of oxygen is available from the steam that enters through the burst opening. Thus, within the localized balloon region ($\approx 75\text{-}100\text{ mm}$), an oxide layer will form on the cladding inner-surface and hydrogen pickup (secondary hydriding) will occur through this surface, especially near the neck regions of the balloon which experience delayed inner-surface oxide formation.

In order to characterize PQD of cladding outside the balloon region, it is sufficient to perform tests using non-pressurized and non-deformed cladding samples. Such tests have been conducted using two-sided oxidation [1] and outer-surface-only oxidation [3] with cladding samples sectioned from as-fabricated Zircaloy (Zry-2, Zry-4), ZIRLO, and M5, prehydrided Zry-4 [1,3] and M5 [3], and high-burnup Zry-4, ZIRLO and M5 [1]. The procedures used by ANL for conducting oxidation-quench testing and

PQD testing are documented in Ref. 1. The purposes of the procedures that follow are both to generalize the ANL methods to include a range of acceptable methods and to describe the methods in finer detail.

3. Sample Selection and Testing Frequency

3.1 Sample selection

Although it is desirable to use samples representative of the fueled cladding that is loaded into the reactor, generally it is sufficient to select samples from finished cladding after polishing and cleaning processes. The one exception would be if post-polishing cleaning at the fuel fabrication facility includes etching with an hydrofluoric (HF)-containing acid mixture. If this is the case, then this step should also be used on cladding prior to sample selection as such treatment can result in early embrittlement even at temperatures as high as 1200°C.

3.2 Frequency of testing

Unlike breakaway-oxidation embrittlement, high-temperature embrittlement is relatively insensitive to minor variations in alloy composition and surface finishing. For cladding materials fabricated within specifications, PQD testing should be performed once for a particular cladding material and does not have to be repeated at a specified frequency. The effects of hydrogen on PQD are far more detrimental to cladding ductility than are minor changes to fabrication processes.

4. Sample Preparation and Characterization

4.1 Hydrogen-content determination for as-fabricated and prehydrided samples

The hydrogen content of as-fabricated cladding is expected to be low (5-15 wppm) and to be available from the tubing vendor. If it is not available, it should be measured. For prehydrided cladding used to simulate high-burnup effects, measurement of hydrogen content from locations close to sample locations is essential. Most techniques for prehydriding cladding are company-proprietary. However, based on reported results, the methods used result in samples with relatively uniform (<10%) hydrogen concentration along the axis and circumference of the sample. As shown in Ref. 4, the pre-test radial distribution of hydrogen is relatively unimportant as hydrogen homogenizes across the cladding wall very quickly for $T \geq 900^\circ\text{C}$.

There are several ways to measure hydrogen content in metals. Vacuum fusion is one method. The recommended method is documented in American Society for Testing & Materials ASTM E1447, Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Fusion Thermal Conductivity Method [5]. This method has been used successfully to determine the hydrogen content in other metals such as Zr-alloys. The detailed procedure used to generate the results in Ref. 1 is documented in Ref. 6.

Along with the instrumentation needed (e.g., LECO RH-404 hydrogen determinator), verification of calibration coupons are available from the vendor. These titanium coupons have hydrogen contents traceable to National Institute of Standards and Technology (NIST) standards. Titanium coupons with 220 wppm are recommended for calibration verification. As these machines are very sensitive, it is important to verify calibration at least once in any given day prior to data generation. For hydrogen-content measurements that appear to be inconsistent, post-measurement calibration verification should be performed.

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

The minimum sample length for two-sided oxidation samples should be 25 mm. This length was used for the oxidation-quench phase of the testing reported in Ref. 1. Part of the motivation for this relatively short sample length was the limited supply of high-burnup cladding available for use in the ANL program. A length of 30 mm would have been more convenient, as it would have allowed three 8-mm-long ring compression samples and a few post-oxidation hydrogen samples to be sectioned from a single oxidation-quench sample. Although there is no maximum limit prescribed, the two-sided oxidation sample should be no longer than the length of the uniform temperature region of the furnace. Uniform is defined as $\leq \pm 10^\circ\text{C}$ variation at the target temperature.

In preparing samples for one-sided oxidation tests, welded end-caps are used to prevent steam from coming into contact with the cladding inner surface. In order to minimize larger end effects due to the heat-affected zones and possible hydrogen diffusion from the sample to the end-caps, the minimum sample length for one-sided oxidation tests should be 75 mm. For prehydrided samples, axial distribution of hydrogen before end-cap welding and after oxidation testing should be measured to determine how much of the 75 mm is available for PQD testing.

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

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

4.4 Length, outer diameter, and wall-thickness measurements

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

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

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

4.6 Pre-test sample weight measurement (after drying)

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

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

5.1 Temperature heat-up and cool-down rates

For a given oxidation level and hydrogen content, the heating rate to 1200°C is a critical parameter for samples that embrittle after short test times: weight gain accumulated at lower temperatures results in lower beta-layer oxygen content at the end of the heating phase and higher ductility. For samples with as-fabricated levels of hydrogen, test times at 1200°C leading to embrittlement are in the range of 300-500 s for 0.57-0.67 mm thick cladding exposed to two-sided oxidation. Embrittlement times at 1200°C for one-sided oxidation tests with as-fabricated cladding samples are considerably longer than 500 s. As such, the embrittlement oxidation level is less sensitive to heating rate for as-fabricated cladding than it is for prehydrided cladding. The heating rate from 300°C to 1000°C should be relatively fast ($>20^{\circ}\text{C/s}$ or <35 s to reach 1000°C) and the heating rate from 1000°C to 1200°C should be $>2^{\circ}\text{C/s}$ (<100 -s duration). Use of slower heating rates that lead to higher embrittlement oxidation levels should be justified. The cooling rate from 1200°C to the quench temperature (i.e., the wetting temperature at which very rapid cooling occurs) may be important, but it is less critical than the heating rate. The cooling rate to the quench temperature should be $>2^{\circ}\text{C/s}$ (e.g., <200 s from 1200°C to 800°C). Use of slower cooling rates should be justified. The recommended quench temperature is 800°C. Use of lower quench temperatures should be justified. Based on results presented in Ref. 1, no difference in ductile-to-brittle transition was observed for as-fabricated cladding materials cooled with or without quench. For prehydrided Zry-4, no significant difference was found in ductility for samples quenched at 800°C, 700°C, and 600°C, as all samples were brittle. However, prehydrided samples at the same hydrogen content and CP-ECR were ductile following cooling without quench. With regard to temperature overshoot during the heating phase, it can have a significant effect on embrittlement oxidation level for prehydrided samples. As such, temperature overshoot should be limited to $\leq 20^{\circ}\text{C}$ for ≤ 20 s.

As the target oxidation temperature is decreased from 1200°C to 1100°C to 1000°C, the embrittlement oxidation level becomes less sensitive to heating rate. However, to standardize heating rates for these lower temperatures, the heating rate to within 100°C of the target hold temperature should be $>20^{\circ}\text{C/s}$ and the heating rate from that temperature (e.g., 1000°C or 900°C) to the hold temperature should be $>2^{\circ}\text{C/s}$. Similarly, the cooling rate to the quench temperature (800°C) should be $>2^{\circ}\text{C/s}$. The use of lower heating rates, cooling rates, and quench temperatures should be justified.

For "uncontrolled" cooling rates (e.g., those due to furnace and sample cooling), the cooling rate will decrease with cooling time. The rates listed above refer to average values determined from $\Delta T/\Delta t$. For controlled cooling rates (e.g., by means of a thermocouple (TC) welded to the sample with feedback to furnace power), constant cooling rates may be achieved. For a postulated LOCA transient temperature history, the cooling rate increases from the maximum temperature to the wetting temperature. Although this cooling history is difficult to simulate experimentally, a constant cooling rate comes closer than one that decreases with time.

5.2 Radiant heating

Radiant heating in a quad-elliptic furnace has been used to generate the PQD data reported in Ref. 1. This heating method, along with furnace power controlled by feedback from a thermocouple on or near the sample, allows for controlled heating rates and relatively fast cooling rates ($>10^{\circ}\text{C/s}$ or <40 s from 1200°C to 800°C). For 25-mm-long samples with 9.50-mm OD, axial temperature variations are negligible, but circumferential temperature variations are in the range of $10\text{-}15^{\circ}\text{C}$ for cladding outer diameters ranging from 9.50 to 11.0 mm. These can be reduced by using radiant-heating furnaces with more than four lamps. With proper thermal benchmarking, radiant-heating furnaces are acceptable for generating PQD specimens for ductility determination.

5.3 Resistance heating

Resistance heating has been used to generate the results reported in Ref. 3. As compared to radiant-heating furnaces, these furnaces are characterized as having a larger uniform temperature zone and as having very slow heating and cooling rates. Faster heating and cooling rates are achieved by controlled movement of the sample into and out of the furnace. Benchmark tests should be performed to determine the heating and cooling rates. With proper thermal benchmarking, radiant-heating furnaces are acceptable for generating PQD specimens for ductility determination.

5.4 Induction Heating

Induction heating has the advantage of rapid sample heating and cooling rates. It has been used in the CINOG program in France (8) to generate weight-gain kinetics data for Zry-4, M5, and developmental alloys. Although the data from these tests appear reliable, reported weight gains for Zry-4 are about 10-12% lower than those predicted using the CP correlation and are in better agreement with the weight gain correlation (LS) derived by Leistikow and Schanz [9] using data from resistance heating. However, this should not be an important factor in determining the embrittlement oxidation level as calculated with the CP weight-gain correlation as long as the oxidation temperatures are accurate. These temperatures are determined using optical pyrometry. With proper thermal benchmarking, induction-heating furnaces might be acceptable for generating PQD samples. However, as it is not clear how to do the benchmarking, the use of induction heating is not recommended for preparing PQD samples.

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, direct electrical heating of cladding is not recommended for preparing PQD samples. However, "indirect" electrical heating may be an acceptable method for internal heating of another material inside the cladding to generate a heat flux simulating heating of the cladding by means of decay heat from the fuel.

6. Temperature Control and Monitoring

6.1 Thermocouples

For oxidation temperatures $\leq 1200^{\circ}\text{C}$, Type S (Pt/10%Rh-Pt) thermocouples (TCs) should be used to record temperature and control furnace power. The TCs should be calibrated using instrumentation and standards that are traceable to the National Institute of Standards and Technology (NIST). Generally, this service is provided by the thermocouple vendor, who, for an extra fee, provides a Certificate of Calibration. Every TC used to measure sample temperature either directly or indirectly should have a Certificate of Calibration showing the results of the calibration at three temperatures: 1200°C , 1100°C ,

and 1000°C. Copies of these certificates should accompany the data report. Verification should be provided demonstrating that the vendor actually did do the calibration according to standards set forth in ISO 10012-1, ISO 9001 and ANSI/NCSL Z540-1-1994.

6.2 Thermal benchmarks

For short (e.g., 25-30 mm) two-sided oxidation samples, direct welding of TCs onto the sample outer surface is not recommended for data-generating tests. The interaction between the TC and the cladding metal causes a local flaw. Also, it is difficult to get an accurate post-test weight measurement after removing the welded TCs. Although measured weight gain is not used to determine the oxidation level (CP-ECR), it is used to check that the target temperature was achieved.

For longer two-sided and one-sided oxidation samples, TCs may be welded near the sample ends for data generating tests. For one-sided samples, in particular, the TC may be welded to the cladding outer-surface in the heat-affected zone.

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. Generally, the control TC will experience slower heating and cooling rates than the sample. The thermal benchmarking should be performed at three sample temperatures: 1200°C, 1100°C and 1000°C. An important phase of the benchmarking is to determine the control TC temperature at which quench water should be introduced to get rapid cooling of the sample at the prescribed temperature. For the work reported in Ref. 1, two-to-three TCs (120° apart) were welded directly onto the benchmark sample outer surface. These readings were compared to the readings of three TCs welded onto the sample holder at a location just above the sample. For radiant heating and large-diameter (≈11 mm) cladding, three TCs were welded directly to the cladding outer surface to better define the average and one-standard deviation cladding temperature. For smaller diameter cladding (9.50 mm), only two TCs welded directly to the cladding surface were needed. For the thermal benchmark tests, it is important that these be conducted under the same flowing steam conditions as used in the data-generating tests.

For resistance-heating furnaces, thermal-benchmarking methods similar to the ones described for radiant-heating furnaces could be used. However, other methods commonly used (e.g., suspended and movable TC) may not be adequate for characterizing the heating rate of the sample. Samples with low thermal mass and high initial heats of oxidation, exposed to low steam slow rates, may heat up much faster than more massive sample holders. The results of the thermal benchmark tests should be documented and included in the data report.

6.3 Weight-gain benchmarks

Following thermal benchmarking, samples should be tested without TCs welded onto the sample to determine the weight gain. These tests should be conducted at 1200°C, 1100°C, and 1000°C for a test time corresponding to 10% CP-ECR. For all cladding materials tested in the ANL program [1], weight gains were comparable to each other and to the CP-correlation predictions at oxidation temperatures of 1200°C and 1100°C. If the measured weight gain for these oxidation temperatures differed from the CP-predicted weight gain by ≥10%, then data-generating tests were not initiated until the root cause of the problem was found and corrected [1]. Generally, this occurred only when the TCs used for the thermal benchmarking read 15-20°C higher or lower than the actual sample temperature, even though the TCs were certified by the vendor. As weight gain appears to be dependent on heating method, the weight gain for a particular cladding material should deviate by <10% from the established database for that material prior to initiating data-generating tests. For Zr-lined Zry-2 and Zr-1Nb alloys, the measured weight gain

at 1000°C is considerably lower than the CP-predicted weight gain. For these materials, the results of the weight-gain benchmark should be compared to the published or vendor-proprietary material-specific databases. The weight-gain benchmarks are designed as a supplement to the thermal benchmarks to ensure adequate TC readings and adequate steam flow. The results of the weight-gain benchmark tests should be documented and included in the data report.

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

7.1 Water quality

Purified water should be used for generating steam. Reference 7 specifies that Grade A water with ≤ 45 ppb oxygen should be used for corrosion tests in pressurized water and steam. Laboratory grade, Type I (distilled and/or deionized) water is also of sufficient purity for oxidation tests at $\geq 1000^\circ\text{C}$. ASTM, the National Committee for Clinical Laboratory Standards (NCCLS, now CLSI) and ISO 3696 have similar definitions for Type I purified water.

7.2 Steam flow rate

The average steam flow rate used to oxidize PQD samples should be determined (and reported) from the mass of condensed water collected during the test divided by the test time and normalized to the net cross-sectional area of the steam chamber. The average steam flow rate should be in the range of 0.8 to 30 $\text{mg}/(\text{cm}^2 \cdot \text{s})$. Justification for this range is provided in the following.

Leistikow and Schanz (9) and Uetsuka (10) studied the effects of low steam flow rates on the oxidation kinetics of Zry-4 at 1000°C. Their results are summarized in Fig. 9 of Ref. 9. 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 $< 0.05 \text{ mg}/(\text{cm}^2 \cdot \text{s})$. For the Ref. 9 work, sample length was 30 mm and oxidation was two-sided. Aomi et al. (11) studied the relationship between weight gain and steam flow rate for oxidation temperatures up to 1200°C. They found that the weight gain for fixed test times and temperatures was independent of steam flow rates in the range of 0.8 to 7.8 $\text{mg}/(\text{cm}^2 \cdot \text{s})$. Kawasaki, et al. (12) also performed high-temperature oxidation tests to determine the range of steam flow rates for which the weight gain for a given test time was independent of steam flow rate. They report this range as 3 to 28 $\text{mg}/(\text{cm}^2 \cdot \text{s})$.

Although maximum steam-flow rates of 7.8 and 28 are given in Refs. 11 and 12, it is not clear why higher steam flow rates would have an effect on weight gain and oxidation kinetics. It is desirable to have a steam-flow rate higher than 0.8 $\text{mg}/(\text{cm}^2 \cdot \text{s})$ to reduce temperature overshoot during the heating phase for bare cladding. Although the maximum steam flow rate may not be as critical as the minimum steam flow rate, it should be limited to $\leq 30 \text{ mg}/(\text{cm}^2 \cdot \text{s})$. The use of steam flow rates $> 30 \text{ mg}/(\text{cm}^2 \cdot \text{s})$ should be justified.

7.3 Steam pressure

Oxidation tests for preparation of PQD samples should be conducted at a steam pressure at or slightly above atmospheric pressure. This is consistent with steam pressures used in previous studies (e.g., Refs. 1-3).

8. Procedure for Oxidation and Quench Tests

The specific details of the test procedure depend on the heating furnace used. Listed below are the steps used in Ref. 1, along with some generalizations that would apply to other heating and cooling methods, e.g., those used in Ref. 3.

8.1 Test train and steam chamber

The test train or sample holder and the steam chamber form a unit that should be designed to contain the steam flow and to prevent impurities, especially nitrogen, from entering the chamber. By using steam that has a pressure slightly greater than the surrounding atmosphere, the test-train/steam-chamber does not have to be "leak-tight" to a high level to serve the functions of providing a pathway for steam flow and protecting the sample from gas-phase impurities.

In choosing the material for the test train or sample holder, it is desirable to have a non-oxidizing or limited-oxidizing material such as stainless steels or nickel alloys (e.g., Inconel 600). However, the sample must be protected from direct contact with materials such as Fe- and Ni-alloys due to the low-temperature eutectics for Zr and these elements. Hofmann and Markiewicz (13) studied the reaction rates and eutectics of Zry-4 and Inconel-718. They also present binary phase diagrams for Zr-Fe and Zr-Ni, which have eutectic temperatures as low as $\approx 930^{\circ}\text{C}$ and 980°C , respectively. In Ref. 1, alumina inserts and zirconia washers were used between the Inconel holder and the sample to prevent such reactions from occurring.

8.2 Purging steam chamber and stabilizing steam flow

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

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

Deviations from this procedure should be justified. Deviations that may have a significant effect on test results include heating the sample to the target temperature in an inert gas prior to introduction of steam flow. Impurities in the inert gas will result in an oxide or oxide-nitride film on the cladding that is not LOCA-relevant. Also, the heat of oxidation would be very high for such a scenario, leading to significant temperature overshoot.

8.3 Ramping temperature and holding temperature at target value

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

For resistance furnaces, the sample heating rate is controlled by the rate of movement of the sample into the furnace heating zone. For radiant-heating furnaces, the heating rate is controlled through feedback from a TC welded onto the holder to the furnace power. For the radiant heating used in Ref. 1,

the temperature ramp rate for as-fabricated cladding materials was programmed to be very fast ($>50^{\circ}\text{C/s}$) from 300°C to within $50\text{-}100^{\circ}\text{C}$ of the target temperature and slow ($2\text{-}3^{\circ}\text{C/s}$) from that temperature to the target temperature. This programmed ramp was designed to eliminate temperature overshoot. In later studies with prehydrided cladding and high-burnup cladding, the 1200°C tests were conducted with rapid heating to 1000°C followed by slower heating ($2\text{-}3^{\circ}\text{C/s}$) to 1200°C .

8.4 End of heating phase and cool-down

After the target test time has been reached, furnace power should be turned off or decreased in a controlled manner 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°C . For the Ref. 1 work, this corresponded to a holder temperature of $700\text{-}720^{\circ}\text{C}$. Following this step, there was ample moisture in the steam chamber during the very brief period between steam flow and quench-water flow.

8.5 Determination of Equivalent Cladding Reacted (CP-ECR)

The CP-ECR is calculated to determine test time. It should be calculated by integration of the CP weight-gain rate correlation with respect to test time. Equations 5 and 6 from Ref. 1 are repeated below for conversion of CP weight gain (Wg in g/cm^2) to oxidation level (ECR in %):

$$\text{One-sided oxidation} \quad \text{ECR} = 43.9 [(Wg/h)/(1 - h/Do)], \quad (1)$$

$$\text{Two-sided oxidation} \quad \text{ECR} = 87.8 Wg/h, \quad (2)$$

where h is cladding thickness in cm, and Do is cladding OD in cm.

9. Post-oxidation-quench Measurements and Characterization

9.1 Sample drying time

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

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

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

9.3 Hydrogen content measurement

If it has been demonstrated and documented that prehydrided samples have very little axial variation in hydrogen content, then post-test hydrogen analysis would not be needed. Significant axial variation is

defined as >30 wppm along the test sample length. For such samples, post-test hydrogen analyses could be performed using 2-3 mm long rings sectioned from both sides of the 8-mm-long ring compression sample. Alternatively, post-test hydrogen analysis could be performed using the 8-mm-long rings after ring-compression testing. In either case, post-test hydrogen values should be corrected for weight gain so that the reference weight for hydrogen content is the pre-test weight. Hydrogen pickup during the oxidation-quench phase is expected to be small (<20 wppm) based on the results presented in Ref. 1 as long as breakaway oxidation does not occur.

10. Matrix for Oxidation and Quench Tests

10.1 As-fabricated cladding

Based on the results presented in Ref. 1, embrittlement of as-fabricated cladding is not expected to occur at oxidation temperatures of 1100°C and 1000°C for oxidation levels up to 20% CP-ECR. The reason for this is the relatively low oxygen solubility limit in Zr-based cladding alloys. Even after the beta layer is saturated with oxygen, it retains ductility. Further oxidation simply increases the oxide and oxygen-stabilized alpha layer thickness values and reduces the beta layer thickness. Strength (i.e., maximum load at failure) continues to decrease, but ductility remains essentially constant. It is not recommended that PQD tests be conducted at <1200°C with as-fabricated cladding.

At an oxidation temperature of 1200°C, the oxygen solubility limit (e.g., 0.6 wt. % for Zry-4) in Zr-based cladding alloys is close to the embrittlement limit at a ring-compression test temperature of 135°C. Cladding materials experience a significant decrease in ductility (from >40% to <10%) in the oxidation range of 10% to 17% CP-ECR following oxidation at 1200°C. As such, it is recommended that scoping tests be performed at oxidation levels of 10%, 13%, 17% and 20% CP-ECR. For each oxidation sample \geq 30-mm-long, at least three ring-compression samples can be sectioned. Based on these results, additional tests can be performed in a narrow CP-ECR range. If the cladding is ductile at 17% and brittle at 20%, then multiple tests can be performed at 18% and 19% CP-ECR to determine the ductile-to-brittle transition CP-ECR. Three oxidation-quench tests are recommended at these intermediate CP-ECR values to give nine PQD data points at each oxidation level. This would be sufficient to determine the ductile-to-brittle transition to the nearest percent CP-ECR.

10.2 Prehydrided cladding

For tests with prehydrided cladding, the hydrogen contents selected should be in a range relevant to the cladding material. It has been a common practice to rely on corrosion-layer-thickness data, for which there is a lot of data as a function of axial position and burnup, and a hydrogen pickup fraction to determine hydrogen content in the cladding. However, the hydrogen pickup fraction is not very reliable because it varies with corrosion-layer thickness, axial location, and burnup. Also, the hydrogen measured in hot cells for defueled cladding samples includes the hydrogen in the corrosion layer and the hydrogen in the cladding metal. In expressing it in units of wppm, the total weight of the sample (corrosion layer, metal, fuel-cladding bond, and both fission products and actinides within and adherent to the bond) is used. This practice may be relatively accurate for low-burnup cladding with thin corrosion layers and no fuel-cladding bond. However, the hydrogen in the cladding metal may be lower or higher than what is reported for intermediate and high-burnup cladding. Only the hydrogen in the metal contributes to embrittlement. Hydrogen levels used in PQD testing with prehydrided cladding materials should cover the range of hydrogen in the metal of irradiated cladding.

For samples to be oxidized at \leq 1200°C (i.e., >2°C/s heating rate from 1000°C to the 1200°C hold temperature), the ductile-to-brittle transition oxidation level is highly dependent on the hydrogen content. For this oxidation temperature, the Ref. 1 embrittlement thresholds for prehydrided and high-burnup

Zry-4, as well as high-burnup M5 and ZIRLO, as a function of hydrogen content may be used as a guide in selecting the range of oxidation levels to be included in the test matrix. For low hydrogen contents (<150 wppm) typical of what has been measured for high-burnup M5, the results presented in Ref. 3 may be used as a guide. PQD data are also presented in Ref. 3 for prehydrided M5 and Zry-4 oxidized at lower test temperatures. For a specific hydrogen content (e.g., 300 wppm), the first test should be conducted at the CP-ECR determined from Ref. 1 embrittlement data (e.g., 10% CP-ECR for 300 wppm hydrogen). Depending on the results, the second test should be conducted at a CP-ECR 2% higher (if ductile at 10%) or lower (if brittle at 10%). Assuming that ductile and brittle oxidation levels have been found, then three tests should be conducted at the intermediate CP-ECR to confirm the embrittlement threshold. For high-burnup ZIRLO with 300 wppm hydrogen, the material was brittle at 10% and ductile at 8% CP-ECR. The embrittlement threshold was determined to be 9% CP-ECR. However, additional high-burnup ZIRLO was not available to conduct a confirmation test at 9% CP-ECR.

11. Procedure for Conducting Ring Compression Post-quench Ductility (PQD) Tests

11.1 Pre-test activities

The materials test system (MTS) used to conduct ring compression tests should be subjected to an annual verification of calibration with regard to measurement of compressive loads by the load cell, the determination of crosshead displacement, and the determination of crosshead speed. The calibration should be performed to NIST-traceable standards. This service is offered by the vendor (e.g., Instron), who provides documentation of calibration verification.

The thermocouple (TC) or thermocouples (TCs) used to control furnace or oven power corresponding to a ring test temperature of 135°C should be calibrated to a NIST-traceable standard. The TC vendor provides this service for a fee and supplies a certificate of calibration along with the TC. The calibration should be performed at 135°C. A variety of TCs could be used at this low temperature. Type K (chromel-alumel) thermocouples are recommended. The standard deviation between the TC reading and the NIST-traceable standard is quite low (e.g., $\pm 0.3^\circ\text{C}$ for room temperature (RT) to 200°C).

In addition to the annual verification of calibration, six ring compression tests should be performed using as-fabricated cladding to determine the relationship between offset and permanent displacements: three tests at RT and three tests at 135°C. Appendix A gives the results of six tests conducted with as-fabricated ZIRLO. This specific verification of calibration is also used to determine if the measured loads are reasonable.

Rings sectioned from LOCA oxidation-quench samples should be 8.0 ± 0.5 mm long and should not include oxidized ends (two-sided samples) or weld heat-affected zones (one-sided samples). For two-sided oxidation samples, it is sufficient to cut off 1-2 mm from the ends of the oxidation samples. The ends of the sectioned rings should be deburred, and the samples should be cleaned in a chemical detergent or organic solvent following deburring.

Following sectioning, the length of the rings should be measured to one decimal place (e.g., 7.9 mm) and the minimum and maximum diameter of the oxidized rings should be measured to two decimal places (e.g., 9.51 mm). As the ring should be positioned such that the minimum diameter aligns with the loading direction, only the minimum diameter is used in the calculation of permanent displacement and strain. Micrometers used to measure length and diameter should be calibrated to a NIST-traceable standard.

11.2 Test temperature and crosshead displacement rate

It is recommended that an oven, rather than a furnace, be used to heat the test ring to 135°C. For such uniform heating, it is sufficient to use a single TC in contact with the inner-surface of the sample at the bottom support position. The spring-loading of the TC also serves to fix the location of the ring relative to the top loading rod. Tests in such a heating device should be conducted at a test temperature of 135±1°C. The PQD tests results in Ref. 1 for as-fabricated and prehydrided LOCA samples used oven heating for the table-top Instron Model 5566 materials test system, along with a single TC strapped to the bottom inner surface of the ring.

It is more common that the materials test system would be equipped with a clam-shell radiant heating furnace provided by the vendor. Such furnaces are known to result in circumferential temperature gradients for rings due to the relationship between the ring location and the focal point of the furnace.. For such furnaces, the bottom TC, which is in intimate contact with the sample, should be used to control furnace power to achieve a steady temperature of 135°C. Additional TCs at the 3 and 9 o'clock position, which initially contact the sample through spring loading, should be used to determine the circumferential variation in temperature. These TCs, which contact the sample outer surface with mild spring loading, are less accurate than the bottom TC. Tests should be initiated at a time when the average deviation of the side TC readings is ≤5°C relative to the 135°C control TC reading.

This heating and temperature monitoring method, along with an Instron Model 8511 servohydraulic materials test system, has been used to generate the Ref. 1 results for high-burnup cladding LOCA samples. The results presented in Appendix A were generated with the Instron 8511.

The crosshead displacement rate for ring compression samples should be 0.033 mm/s (2 mm/minute). This rate is consistent with what has been used in past research efforts [1,3], and it is slow enough to allow test termination after the first significant load drop.

11.3 Test conduct

The test should be conducted in the "displacement-controlled mode" rather than the "force-controlled mode." Software inputs include the constant displacement rate and the maximum displacement. The maximum displacement (i.e., crosshead travel) is important to protect the control thermocouple and the MTS itself. Due to the "bow-tie" shape of a highly deformed ring, the maximum displacement should be less than the inner diameter of the cladding minus the TC diameter. For standard 17×17 cladding with an inner diameter of about 8.3 mm, the maximum displacement should be < 6 mm.

Test conduct is standard with regard to set up and operation. Details are given in Ref. 14 for ring compression tests conducted with the screw-type Instron Model 5566 used to generate data reported in Ref. 1 for as-fabricated and prehydrided cladding.

11.4 Test termination

The preferred method for ending the test is to release the compressive load as soon as there is a sharp load drop >30%. This is achieved by simply pushing the reset button. Given the slow displacement rate, there is ample time to terminate the test very shortly after the load-drop is observed. Based on the experience reported in Ref. 1, load drops in the range of 30-50% indicate a single through-wall crack, which may be very tight or loose due to recoil following test termination. For tight cracks, an accurate post-test diameter can be measured in the loading direction. For a single loose crack, the post-test diameter reading is not very accurate. For load drops of about 70-80%, the sample should have two cracks. For load drops of 80-100%, it is likely that the sample cracked into three or four pieces.

The more common method used in ring-compression testing (e.g., Ref. 3) is to run the test for a fixed displacement. As multiple cracks are likely to occur, no useful post-test diameter can be measured. Although this method is acceptable, it is not recommended as the only data that can be obtained are the offset displacement and strain.

11.5 Post-test measurements

After removing the compressed ring from the oven or furnace, cooling to RT occurs rather quickly. The sample should be examined visually to determine if cracking has occurred, the number of cracks, and the location of the cracks. For samples that are likely to have a single tight crack, the visual examination should include one at about 4X magnification to verify that the crack is through-wall (from examination of ring ends) and extends along the whole length of the sample (from examination of outer and inner surfaces).

If the test was terminated following a steep 30-40% load drop and visual examination indicates a single tight crack, then the outer diameter in the loading direction should be measured.

The offset displacement should be determined from the load-displacement curve using methods illustrated in Appendices B and C. In general, this means mathematically unloading the sample at the load just prior to the steep load drop. The linearized slope (i.e., ring stiffness in kN/mm) of the initial loading curve is used to do the mathematical unloading. For ductile rings that exhibit a gradual load drop with increasing displacement, the offset strain determination is dependent of the visual examination. If the post-test sample does have a through-wall crack, then the offset strain should be determined based on the location on the curve for which the load has decreased by 50%. For samples that have no post-test cracks, the full load-displacement curve is used to determine the offset displacement. These cases are not very important in the determination of the ductile-to-brittle transition oxidation level, as they represent samples with very high ductility.

To convert offset and permanent displacement to strain, it is recommended that the outer-diameter of the as-fabricated cladding be used to normalize these displacements. Prehydrogenating samples will result in a small increase in the outer diameter and the wall thickness. Oxidation will result in additional increases in diameter and wall thickness. However, these increases have only a small effect on the calculated normalized displacements. It is recommended that strain be reported in percent as displacement divided by the diameter of the as-fabricated cladding used for oxidation or for prehydrogenating and oxidation. If the post-oxidation diameter in the loading direction is used to calculate strain, it should be reported along with the displacements and the converted strains.

After determination of the offset and permanent strains, the compressed ring should be used to measure the post-oxidation hydrogen content in the ring. This hydrogen content should be corrected for weight gain. The measurement should be performed if oxidation samples are expected to have >10% axial and circumferential variation in hydrogen content relative to the average hydrogen content.

12. Data Reporting and Assessment

12.1 Hydrogen level, test temperature, test time, CP-ECR, offset strain, and permanent strain

Tabular results should include hydrogen level, test temperature, test time (from 300°C to the quench time), CP-ECR, offset strain and permanent strain. In a footnote, it should be clarified as to which diameter was used to determine strain from displacement.

Graphical results should include the load-displacement curves (including determination of offset strain) and summary graphs of offset strain vs. CP-ECR and permanent strain vs. CP-ECR.

12.2 Determination of ductile-to-brittle transition CP-ECR

Rings that exhibit $\geq 1\%$ permanent strain are classified as ductile. The 1% is based on uncertainties in diameter readings, in recoil (or spring-back) of cracked rings vs. intact rings, and in diameter reduction due to flaking off of oxide. It is also based on trend curves of permanent strain vs. CP-ECR. For samples that are clearly brittle, measured permanent strains are generally in the range of 0.2-0.8%, which for cladding with an outer diameter of 9.50 mm corresponds to 0.2-0.8 mm permanent displacement. These displacements and strains are considered to be in the "noise" of uncertainty. The ductile-to-brittle transition CP-ECR is defined as the CP-ECR corresponding to 1% permanent strain (i.e., the maximum CP-ECR for which ductility is retained). For multiple data points at the same sample and test conditions, the average permanent strain should be calculated. The ductile-to-brittle CP-ECR should be based on average permanent strain $\geq 1\%$. As it is unlikely to measure exactly 1% permanent strain, the CP-ECR may be determined from interpolation between an oxidation level for which the permanent strain is $>1\%$ (ductile) and an oxidation level for which the permanent strain is $<1\%$. These CP-ECR values should differ by no more than 2%. The ductile-to-brittle transition oxidation level should be reported to the nearest percent. For example, if the sample is ductile at 8% CP-ECR and brittle at 10% CP-ECR, the transition CP-ECR would be reported as 9%. However, it is recommended that three confirmation tests be conducted at 9% CP-ECR. Figure 1 shows an example from the work reported in Ref. 1 for as-fabricated HBR-type 15×15 Zry-4. Based on multiple oxidation tests in a narrow range and multiple ring-compression samples, the permanent strains were $1.5 \pm 0.4\%$ at 15.2% CP-ECR and $1.1 \pm 0.3\%$ at 16% CP-ECR. Based on linear extrapolation, the transition CP-ECR is calculated to be 16%.

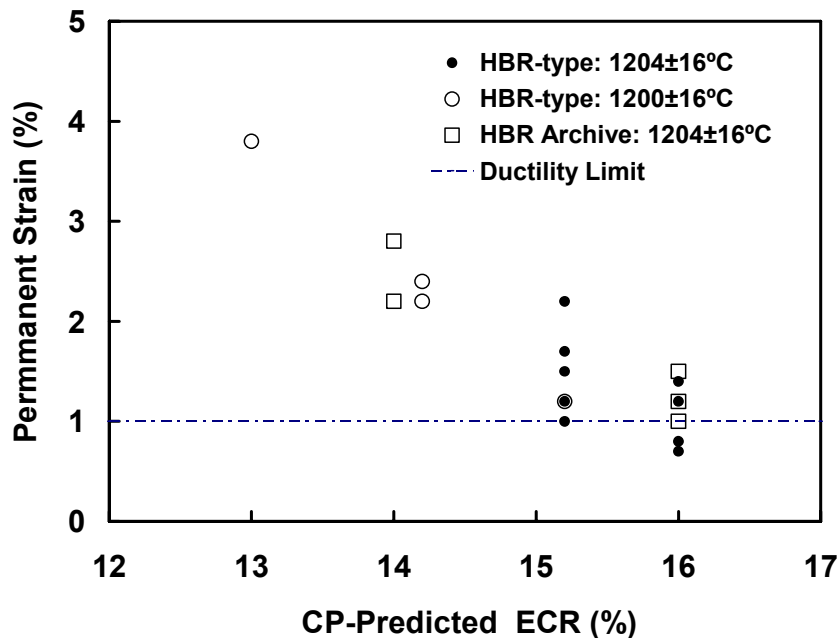


Fig. 1. Determination of ductile-to-brittle transition CP-ECR based on the permanent strain criterion ($\geq 1\%$ implies ductility) for as-fabricated HBR-type 15×15 Zry-4 oxidized at $\approx 1200^\circ\text{C}$ and quenched at 800°C . The recommended transition oxidation level is 16% CP-ECR based on average permanent strain $\geq 1\%$.

If ring-compression tests are not interrupted at the first significant load drop, then the ring will crack into pieces, which renders measurement of post-test diameter impractical and unreliable. One must rely on offset displacement and strain to assess whether or not a ring is ductile or brittle. The method for determining the offset displacement has an inherent error because the unknown unloading slope will always be less than the loading slope. Appendix C summarizes the data reported in Ref. 1, along with the HBR data presented in Fig. 1, for rings sectioned from cladding alloys oxidized at 1200°C. The trend curve shown in Fig. C1 indicates that the error associated with offset strain displacement increases with calculated oxidation level (CP-ECR). This leads to the following ductility criterion based on offset strain:

$$\text{Offset Strain} \geq 1.60 + 0.0534 \text{ CP-ECR} \quad (3)$$

Equation 3 gives $\geq 1.9\%$ at 5% CP-ECR and $\geq 2.7\%$ at 20% CP-ECR. However, because of the large data scatter in Fig. C1, the one-sigma lower bound should be used for the offset strain. This method is illustrated in the following example.

The offset strains corresponding to the permanent strain data shown in Fig. 1 are plotted in Fig. 2.

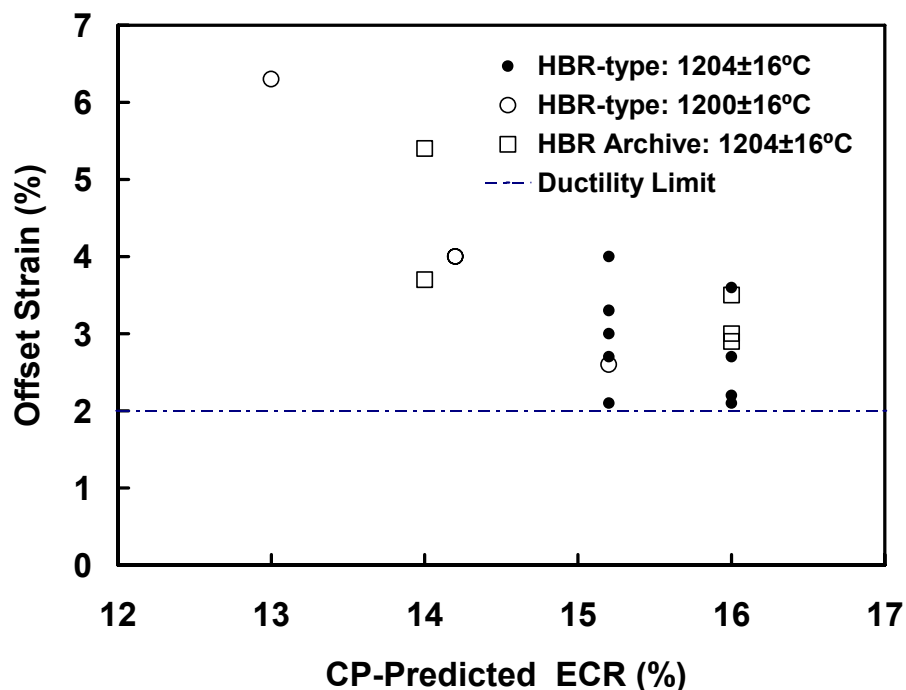


Fig. 2. Offset strains determined for as-fabricated HBR-type 15×15 Zry-4 oxidized at $\approx 1200^\circ\text{C}$ and quenched at 800°C (see Fig. 1 for corresponding permanent strains).

Unlike permanent strains, offset strains level off to about 3% at 15.2 and 16.0 CP-ECR: $3.0 \pm 0.7\%$ at 15.2% CP-ECR and $2.9 \pm 0.5\%$ at 16.0% CP-ECR. Based on Eq. 3, offset strains $\geq 2.5\%$ imply ductility at 16% CP-ECR. The average offset strain minus one sigma is 2.3% at 15.2% CP-ECR and 2.4% at 16% CP-ECR. These values are very close to the ductility limit. By interpolation between the data at 14.2% and 15.2% CP-ECR, the ductile-brittle-transition CP-ECR would be 15%. Thus there is a penalty of 1% CP-ECR in using the less-precise offset-strain criteria as compared to the permanent strain criteria.

References

1. Michael Billone, Yong Yan, Tatiana Burtseva, and Robert Daum, "Cladding Embrittlement during Postulated Loss-of-Coolant Accidents," NUREG/CR-6967, July, 2008; available online in NRC ADAMS as ML082130389 at <http://www.nrc.gov/NRC/reading-rm/adams.html>.
2. J. V. Cathcart, R. E. Pawel, R. A. McKee, R. E. Druschel, G. J. Yurek, J. J. Campbell, and S. H. Jury, "Zirconium Metal-Water Oxidation Kinetics IV. Reaction Rate Studies," ORNL/NUREG-17, Aug. 1977.
3. J. P. Mardon, J. C. Brachet, L. Portier, V. Maillot, T. Forgeron, A. Lesbros, and N. Waeckel, "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 Intl. Conf. on Nucl. Eng., Beijing, China, May 16-20, 2005, pp. 1-9.
4. Fumihisa Nagase and Hiroshi Uetsuka, "Hydrogen Morphology and Hydrogen Embrittlement of Zircaloy Fuel Cladding used in NSRR/HBO Experiment," Procs. Intl. Topical Meeting on Light Water Reactor Fuel Performance, Portland, OR, March 2-6, 1997, American Nuclear Society, La Grange Park, IL (1997), 677-684.
5. ASTM E1447 – 05, "Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by the Inert Gas Thermal Conductivity Method," Book of Standards, Vol. 03.05, ASTM International, West Conshohocken, PA (2005); also available online at <http://www.astm.org/standards/E1447.html>.
6. T. Burtseva, "Procedure for Hydrogen Analysis of Refractory Metals," ANL Intra-Laboratory Memo, IPS-467-00-00, Nov. 25, 2005.
7. ASTM Designation G 2/G 2M – 06, "Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium and Their Alloys In Water at 680°F [360°C] or in steam at 750°F [400°C], ASTM International, 100 Barr harbor Drive, West Conshohocken, PA (2006) 1186-1193.
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 (2008).
9. S. Leistikow 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," Nucl. Eng. and Des. 103 (1987) 65-84.
10. H. Uetsuka, "Oxidation of Zircaloy-4 under limited steam supply at 1000 and 1300°C," KfK 3848 (1984).
11. M. Aomi, M. Nakatuka, et al., "Behavior of BWR fuel cladding tubes under simulated LOCA conditions," 7th International Conference on Nuclear Engineering, ICONE-7435 (1999)
12. S. Kawasaki, T. Furuta, and M. Suzuki, "Oxidation of Zircaloy-4 under High Temperature Steam Atmosphere and Its Effect on Ductility of Cladding," J. Nucl. Sci. Tech. (JNST), Vol. 15, No. 8 (1978) 589-596.

13. P. Hofmann and M. Markiewicz, "Chemical Interaction between as-received and pre-oxidized Zircaloy-4 and Inconel-718 at High Temperatures, KFK 4729, June 1994.
14. T. A. Burtseva, "Procedure for Conducting Ring-Compression Tests in Laboratory DL-102A," ANL-IPS Memo, IPS-495-00-00, Nov. 26, 2007.

Appendix A

Ring-compression Results for RT and 135°C Tests with As-fabricated Cladding Samples

Document IPS-495-00-00 [14] describes the procedure for verification of calibration, for test conduct and for data interpretation for ring compression tests (RCTs) conducted with the Instron Model 5566 Material Test System (MTS) located in DL-102A. For ring-compression tests, Phase 3 describes pre-data-generation tests to assure that the Instron, as well as associated control and data acquisition systems, is performing within the expected range. Such tests should be conducted with any materials test system (MTS) prior to the generation of post-quench ductility (PQD) data, particularly if the MTS has been used to conduct other tests (e.g., axial tensile tests) requiring modification to the load train, if the machine has been idle for more than a couple of months, or if the yearly calibration-verification is overdue. Three tests at RT and three tests at 135°C are to be conducted with as-fabricated cladding rings at 2 mm/minute (0.033 mm/s) to a maximum crosshead displacement of 2 mm. The data output (load-displacement curves) are to be analyzed in terms of the measured loading stiffness K_m (linearized slope of the load vs. displacement curve in kN/mm) and the measured offset displacement (δ_o , in mm). The measured loading stiffness K_m is compared to the calculated ring stiffness K_c according to the text book formula:

$$K_c = (1/1.8) E L (h/R)^3, \quad (A1)$$

where E is Young's modulus in kN/mm^2 , L is the actual length of the ring in mm, h is the wall thickness in mm, and R is the ring mid-wall radius in mm. Equation A1 is applicable to the elastic behavior of a thin-wall ring of uniform length, outer diameter, and wall thickness.

The reference length for the test rings is 8 mm. However, as offset displacement should be independent of ring length and stiffness varies linearly with ring length, actual values of sectioned rings may be within the range 8.0 ± 1.0 mm. The wall thickness (h) and the outer diameter (D_o) will vary somewhat along the length of cladding tubes. The pre-test wall thickness for each sample should be measured at four circumferential orientations (0° , 90° , 180° and 270°). The value of h used in Eq. A1 is the average of the four readings. The pre-test minimum [$(D_{oi})_{\min}$] and maximum [$(D_{oi})_{\max}$] outer diameters should be determined for each sample and averaged to give D_{oi} , where the "i" refers to initial or pre-test value. The value of R used in Eq. A1 is calculated from the relationship $R = (D_{oi} - h)/2$. Young's modulus, E , for cladding alloys is assumed to be the same as the modulus reported for Zry-4: $E = 93 \text{ kN/mm}^2$ (93,000 MPa) at RT and $E = 88 \text{ kN/mm}^2$ (88,000 MPa) at 135°C. For rings of uniform length, thickness, and outer diameter, the measured stiffness should be within about 10% of the calculated stiffness for machines with relatively high load-train stiffness. Because machine compliance tends to reduce the measured stiffness, the expectation is that the measured stiffness will be less than or equal to the calculated stiffness. Measured stiffness values $\geq 10\%$ higher than the values predicted by Eq. A1 indicate that the load cell and/or crosshead displacement indicator may be out of calibration.

The offset displacement (δ_p) is to be compared to the permanent displacement (d_p), which is determined from the difference in the pre-test and post-test diameters in the loading direction. The ring is to be positioned in the Instron such that the loading direction is along the minimum pre-test diameter. Based on the error introduced by assuming that the unloading stiffness is equal to the loading stiffness, the expectation is that $\delta_p < d_p$ and that the difference is $\delta_p - d_p \leq 0.2$ mm, which is based on an extensive data set for as-fabricated cladding displaced to 1.5-2.0 mm at RT and 2 mm/minute in the Instron 5566.

Two assessments are made using the measured stiffness and offset displacement values: one is precision (repeatability) and the other is adequacy of load and displacement measurements. The most important determination of the adequacy of the Instron materials test system (MTS) is the repeatability of

offset and permanent displacements, as well as the difference of these two numbers. In making this assessment, the measured stiffness should be normalized to 8 mm by multiplying the measured stiffness by (8-mm/L): $K_{mn} = (8\text{-mm/L}) K_m$. The calculated stiffness should also be normalized to 8-mm to give K_{cn} . Also, as the stiffness is highly dependent on the wall thickness, this factor should be taken into account in the data assessment.

The procedure described in IPS-495-00-00 Phase 3 is should be used for any MTS, including the ANL Instron 8511, which is used to perform ring compression tests with oxidized high-burnup cladding samples. The motivation for conducting the ring-compression verification tests for the Instron 8511, as well as the results, is presented in this appendix as an example of the procedure to follow and the methodology for interpreting the results.

The Instron 8511 had not been used since the end of August 2008 (5 months) and was overdue for the detailed yearly calibration-verification. As the high-burnup cladding samples are very valuable, it is important to check out all features of the test system prior to conducting data-generating ring compression tests with high-burnup samples. The room-temperature tests serve to check out the physical components, the data control software and the data acquisition software. The elevated temperature tests serve to check out the physical and software components of the furnace system, as well as the performance of the Instron at 135°C. Prior to conducting the elevated temperature tests with control and monitoring thermocouples, it must be demonstrated that the thermocouples have been calibrated to a NIST-traceable standard. The option is available to have the vendor do this calibration and supply a certificate for each thermocouple in a batch of thermocouples or one thermocouple in the batch. If only one thermocouple in a batch has a calibration certificate, then the thermocouples to be used to control and monitor ring temperature must be calibrated by comparison to the certified thermocouple. Generally, Type K thermocouples are used to monitor low temperatures such as 135°C. The expected error for this type of thermocouple is $\pm 0.3^\circ\text{C}$ relative to a NIST-traceable standard.

As Instron 8511 is a servo-hydraulic machine, some checkout was conducted to ensure that all moving parts, all auxiliary equipment and all data recorders functioned properly. Three ring compression tests were then conducted. Based on the RT results (see Table A1 and Figures A1-A3), the average difference between the offset and permanent displacement was 0.19 mm, which is consistent with previous experience. Therefore, the Instron 8511 crosshead displacement indicator was determined to be accurate enough for ring compression testing. The measured loading stiffness values were about 16% lower than the predicted values. The loading stiffness is expected to be \leq the calculated stiffness due to the influence of machine compliance. Based on past experience with the Instron Model 5566, the measured stiffness has been within 10% of the calculated stiffness. The Instron Model 8511 has a much longer load train, higher machine compliance, and lower machine stiffness. This accounts for the difference between measured and calculated stiffness values. Although load is not an important parameter in ring-compression ductility tests, the stiffness results indicate that the load-cell output values are adequate for ring compression tests.

The results at 135°C (see Table A1 and Figs. A4-A6) proved to be more consistent than the RT results. For ductility determination, the most important parameter is the difference between offset displacement and permanent displacement, which was 0.20 mm on average. The measured stiffness values were about 8% lower than the calculated values, which suggested adequate load-cell performance at 135°C.

The results of the six tests support the continued use of the Instron Model 8511 for performing RCT ductility tests using oxidized high-burnup cladding samples.

Table A1 Results of Instron 8511 Checkout Tests to Verify Calibration for Conducting Ring Compression Tests at a Displacement Rate of 0.0333 mm/s; K_c is calculated ring stiffness (i.e., spring constant), K_m is stiffness determined from linearized slope of load displacement curve, subscript "n" refers to stiffness normalized to 8 mm, δ_p is the offset displacement determined from the load-displacement curve, and d_p is the permanent displacement in the loading direction determined from pre-test diameter minus post-test diameter.

Sample ID	Test T, °C	D_{oi} , mm	L, mm	h, mm	K_{cn} , kN/mm	K_m , kN/mm	K_{mn} , kN/mm	δ_p , mm	d_p , mm	$\delta_p - d_p$, mm
109B1	RT	9.49	7.67±0.06	0.587±0.003	0.95	0.77	0.80	1.24	1.07	0.17
109B2	RT	9.49±0.01	7.75±0.06	0.589±0.003	0.96	0.77	0.79	1.18	1.00	0.18
109B3	RT	9.49±0.01	8.03±0.02	0.589±0.003	0.96	0.85	0.85	1.31	1.08	0.23
RT Summary	RT	9.49	7.82	0.59	0.96		0.81	1.24	1.05	0.19
109B4	132±5	9.495±0.005	7.81±0.02	0.589±0.003	0.90	0.81	0.83	1.40	1.21	0.19
109B5	135±5	9.495±0.005	8.01±0.07	0.590±0.003	0.91	0.83	0.83	1.40	1.21	0.19
109B9	135±5	9.475±0.005	8.21±0.06	0.588±0.003	0.91	0.85	0.83	1.40	1.17	0.23
135°C Summary		9.49	8.00	0.59	0.91		0.83	1.40	1.20	0.20

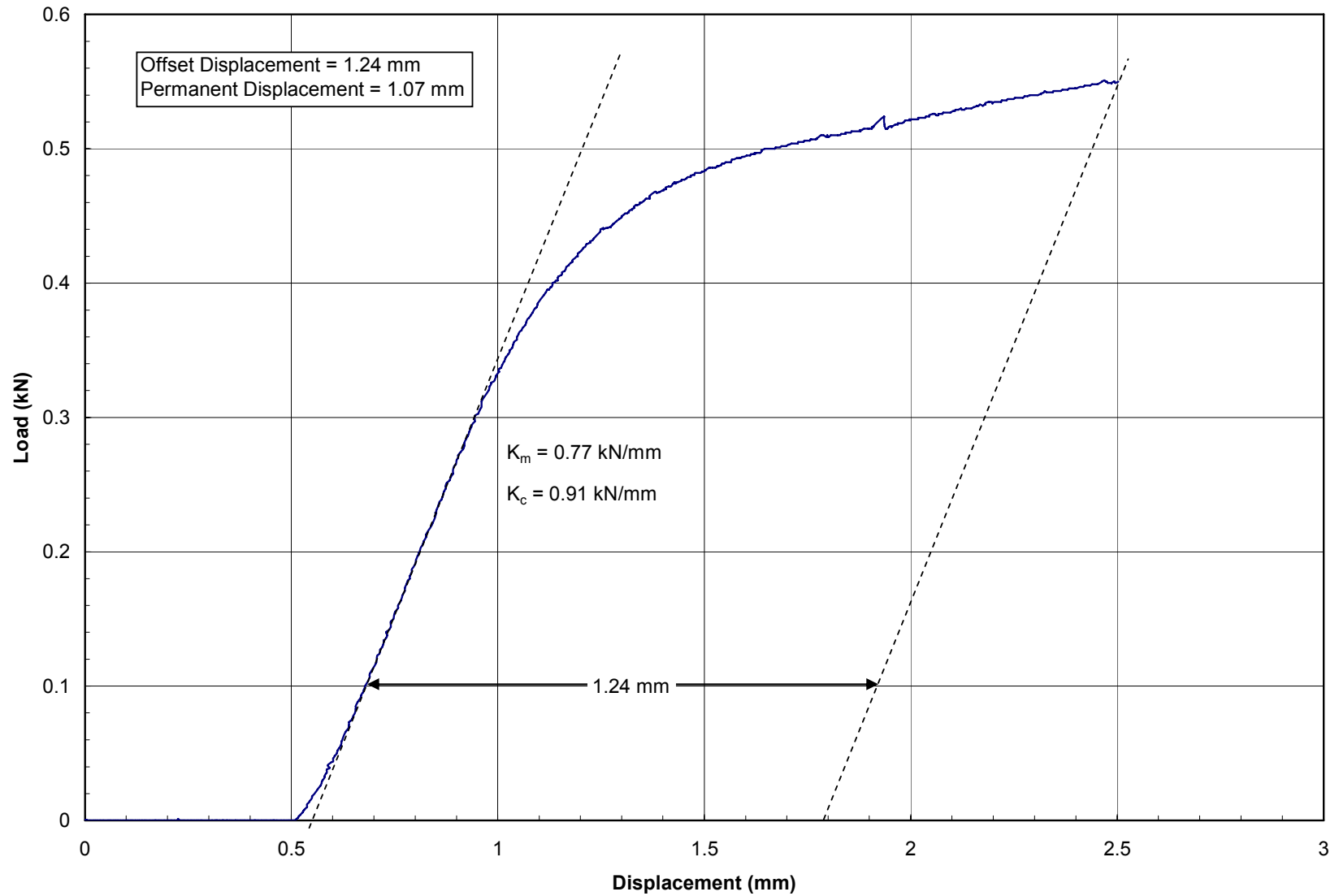


Fig. A1. Load-displacement curve for ZIRLO sample 109B1 compressed at RT and 2 mm/minute to 2-mm total displacement.

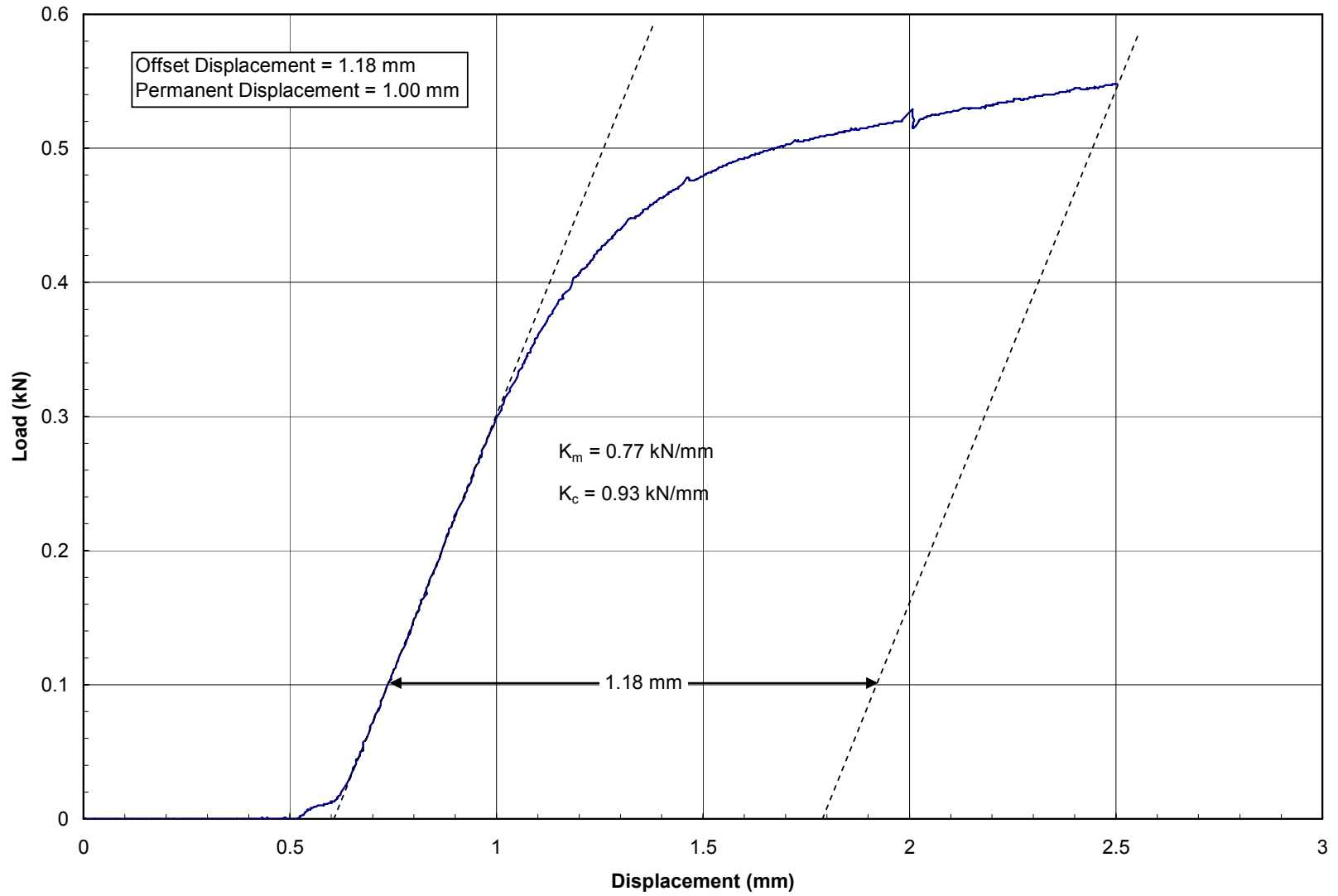


Fig. A2. Load-displacement curve for ZIRLO sample 109B2 compressed at RT and 2 mm/minute to 2-mm total displacement.

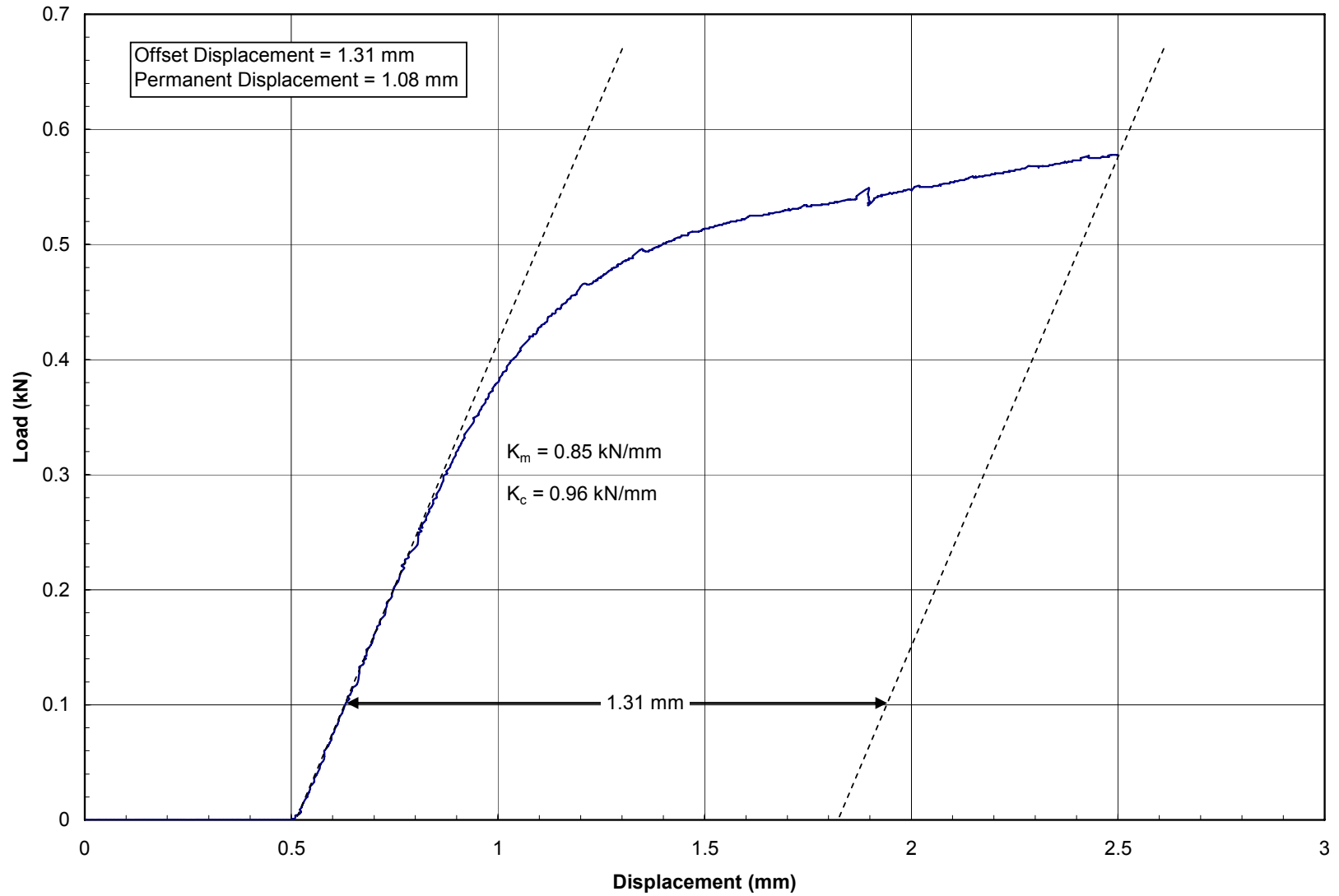


Fig. A3. Load-displacement curve for ZIRLO sample 109B3 compressed at RT and 2 mm/minute to 2-mm total displacement.

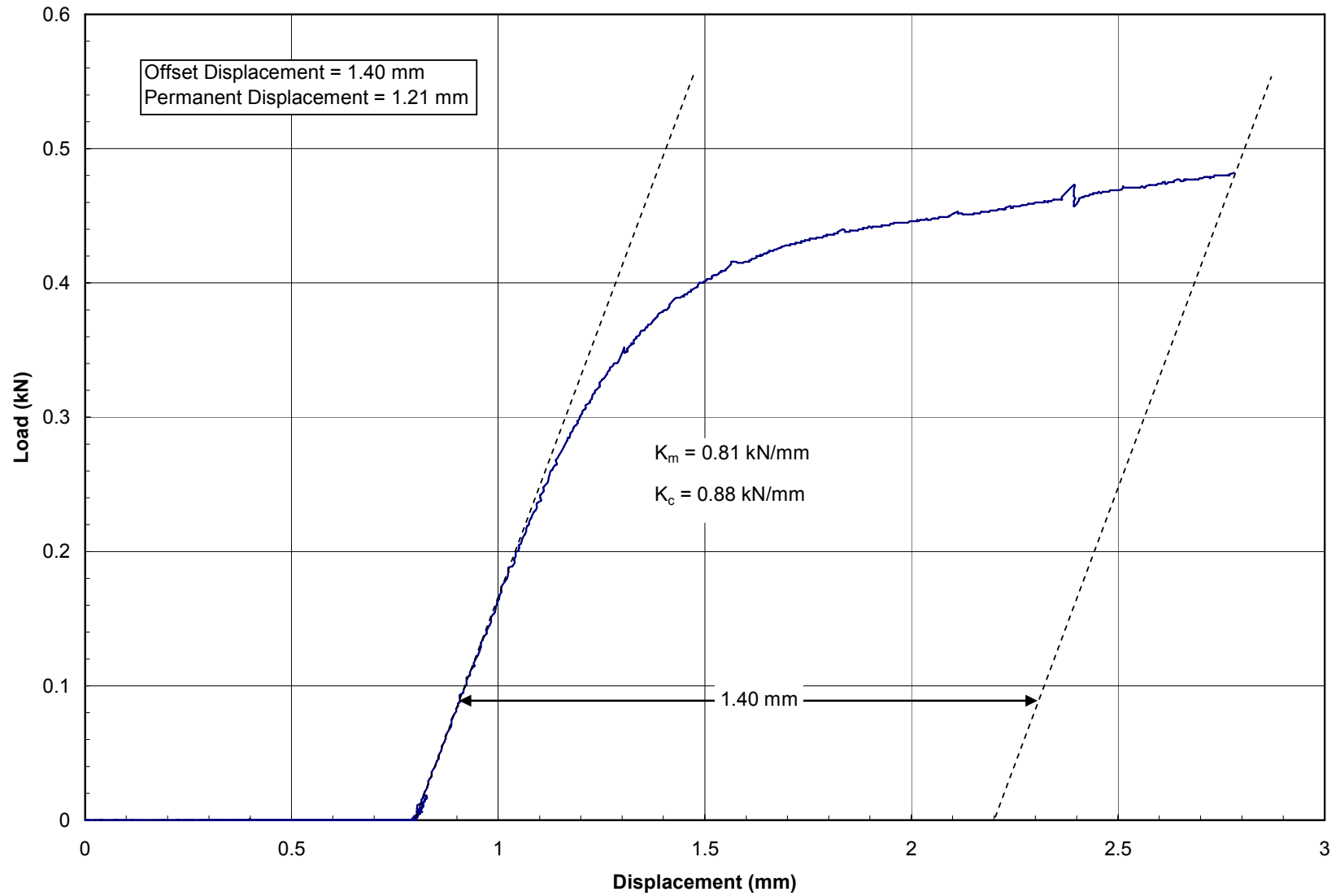


Fig. A4. Load-displacement curve for ZIRLO sample 109B4 compressed at 135°C and 2 mm/minute to 2-mm total displacement.

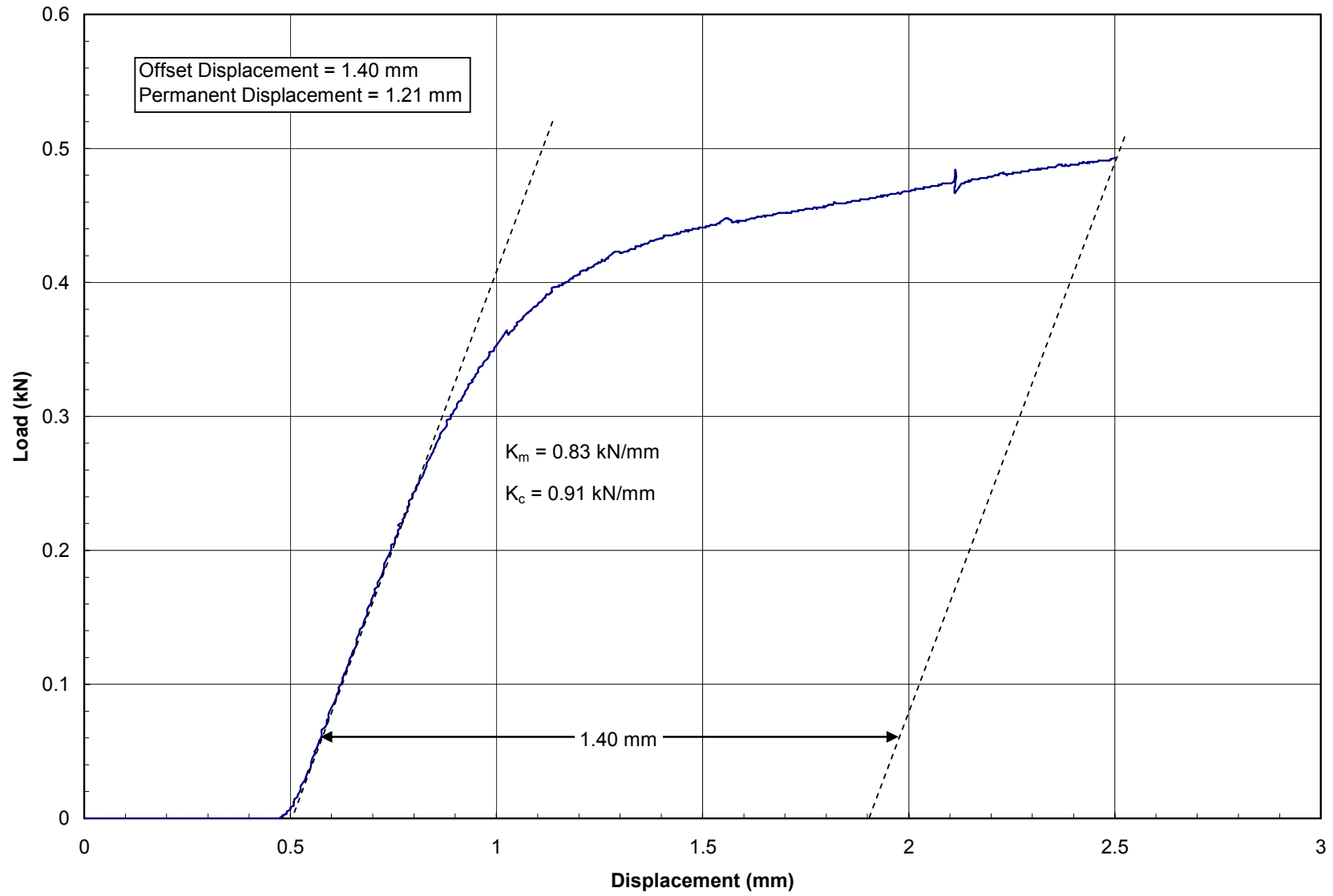


Fig. A5. Load-displacement curve for ZIRLO sample 109B5 compressed at 135°C and 2 mm/minute to 2-mm total displacement.

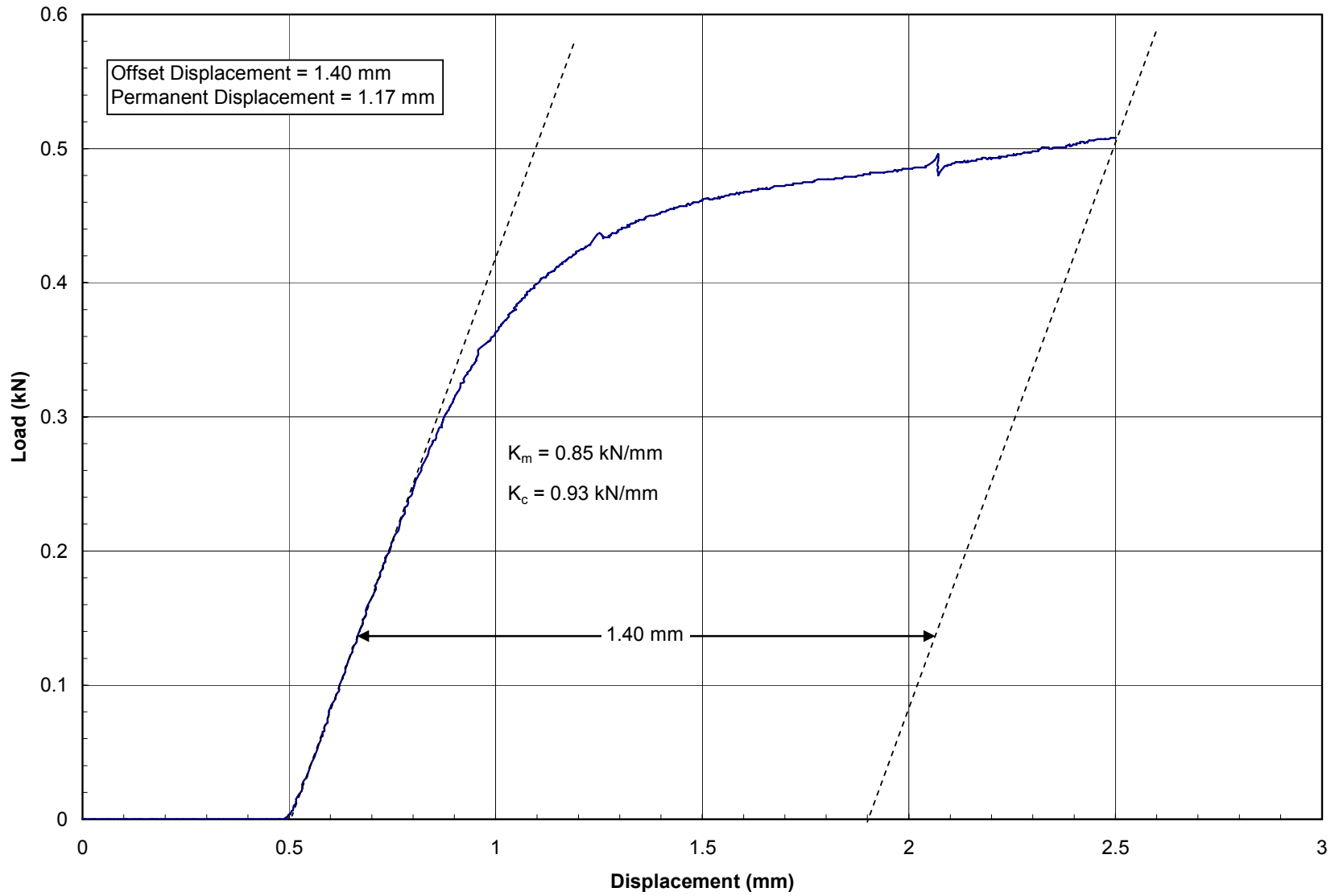


Fig. A6. Load-displacement curve for ZIRLO sample 109B9 compressed at 135°C and 2 mm/minute to 2-mm total displacement.

Appendix B

Examples of Load-displacement Curves, Offset Strains and Permanent Strains for Oxidized and Quenched Cladding Samples

Examples of load-displacement curves and offset displacements determined from these curves are shown in Figs. B1-B8. For this series of tests, prehydrided HBR-type 15×15 Zry-4 cladding samples were oxidized to 6% CP-ECR at a maximum temperature of 1200°C. As shown in Table B1 (Table 52 in Ref. 1], the quench temperature was varied from 800°C to 700°C to 600°C to slow-cooling without quench. The load-displacement curves (see Figs. B1-B6) for the quenched samples indicate that all of these samples were brittle. Based on both offset strains and permanent strains, only the slow-cooled samples retained ductility (see Figs. B7-B8). For the samples that retained ductility, the difference between the offset strains and the permanent strains was only 0.9%. For prehydrided Zry-4, the ductility criteria used in Ref. 1 were: ≥1% permanent strain and ≥2% offset strain.

Table B1 Post-quench Ductility of Prehydrided HBR-type 15×15 Zry-4 Cladding Oxidized to 6% CP-ECR at 1200°C, Cooled at 13°C/s to 800°C and Quenched (Q) at 800°C, Cooled from 800°C to 700°C at 3°C/s and Quenched at 700°C, Cooled from 700°C to 600°C at 2°C/s and Quenched at 600°C or Slow-cooled to from 600°C to RT at <2°C/s; CP-ECR calculated from beginning of ramp to end of hold time; ring-compression tests performed on ≈8-mm-long samples at 135°C and 0.0333 mm/s crosshead displacement rate

Sample and Test Conditions			ECR %		Plastic Displacement, mm		Plastic Strain, %	
Q-T, °C or SC	Test Time ^a s	H wppm	CP	Meas.	Offset	Permanent	Offset	Permanent
800	106	450	6.0	6.5	0.10	0.08	0.9	0.7
800	106	450	6.0	6.5	0.09	0.07	0.8	0.7
700	106	450	6.0	6.6	0.07	0.05	0.6	---
700	106	450	6.0	6.6	0.10	0.05	0.9	0.5
600	106	460	6.0	6.5	0.08	0.05	0.7	0.5
600	106	460	6.0	6.5	0.13	0.08	1.2	0.7
SC	106	470	6.0	6.4	0.22	0.18	2.1	1.7
SC	106	470	6.0	6.4	0.53	0.39	4.9	3.6

^aFrom beginning of ramp at 300°C to end of hold time at ≈1200°C

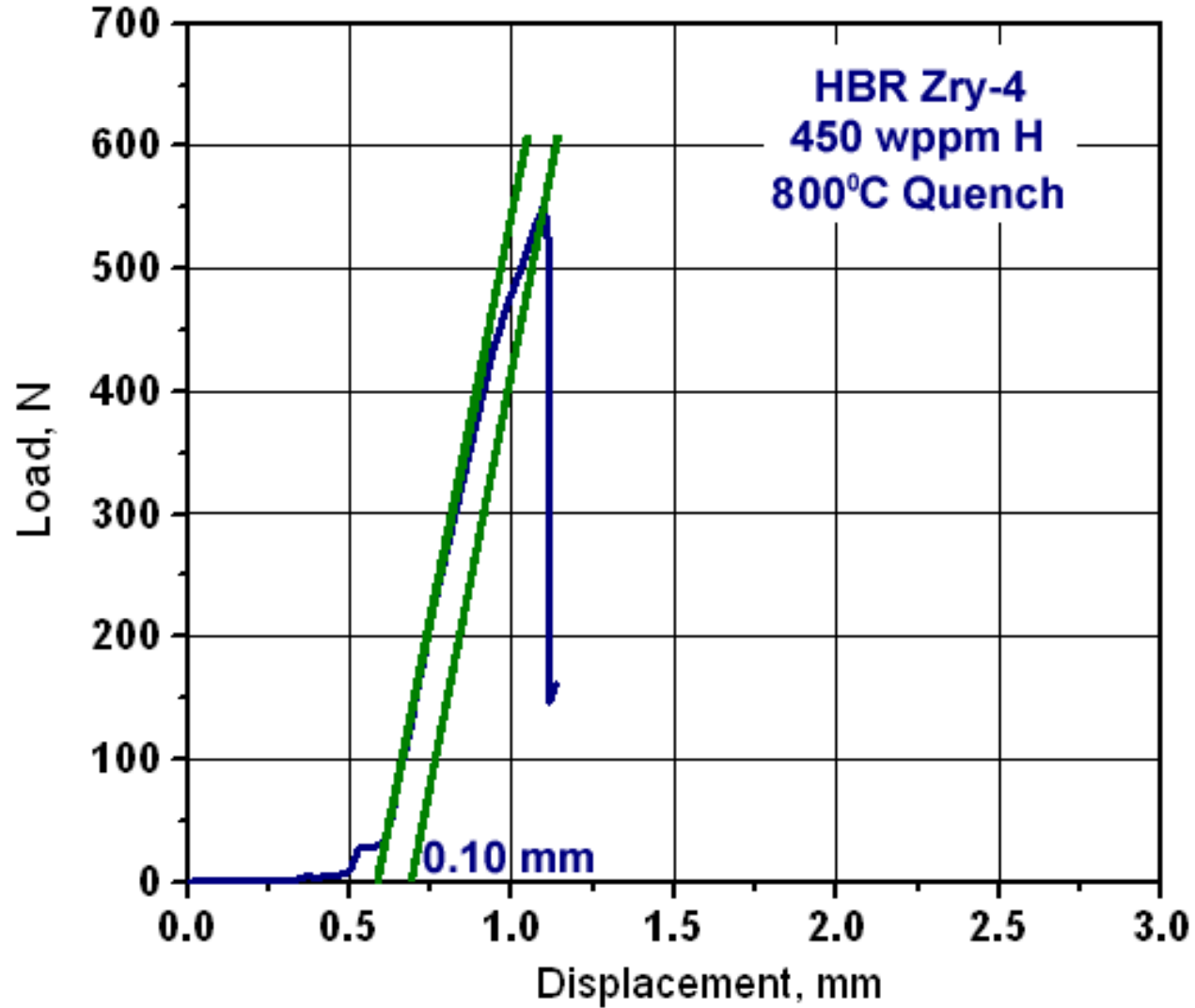


Fig. B1. Load-displacement results for ring #1 (8.12-mm long) of a prehydrided (450 wppm) HBR 15×15 Zry-4 sample oxidized to 6% CP-ECR at a maximum oxidation temperature of 1200°C and quenched at 800°C. The post-test sample had tight through-wall cracks at load and support locations. Offset and permanent displacements were 0.10 mm and 0.08 mm, respectively.

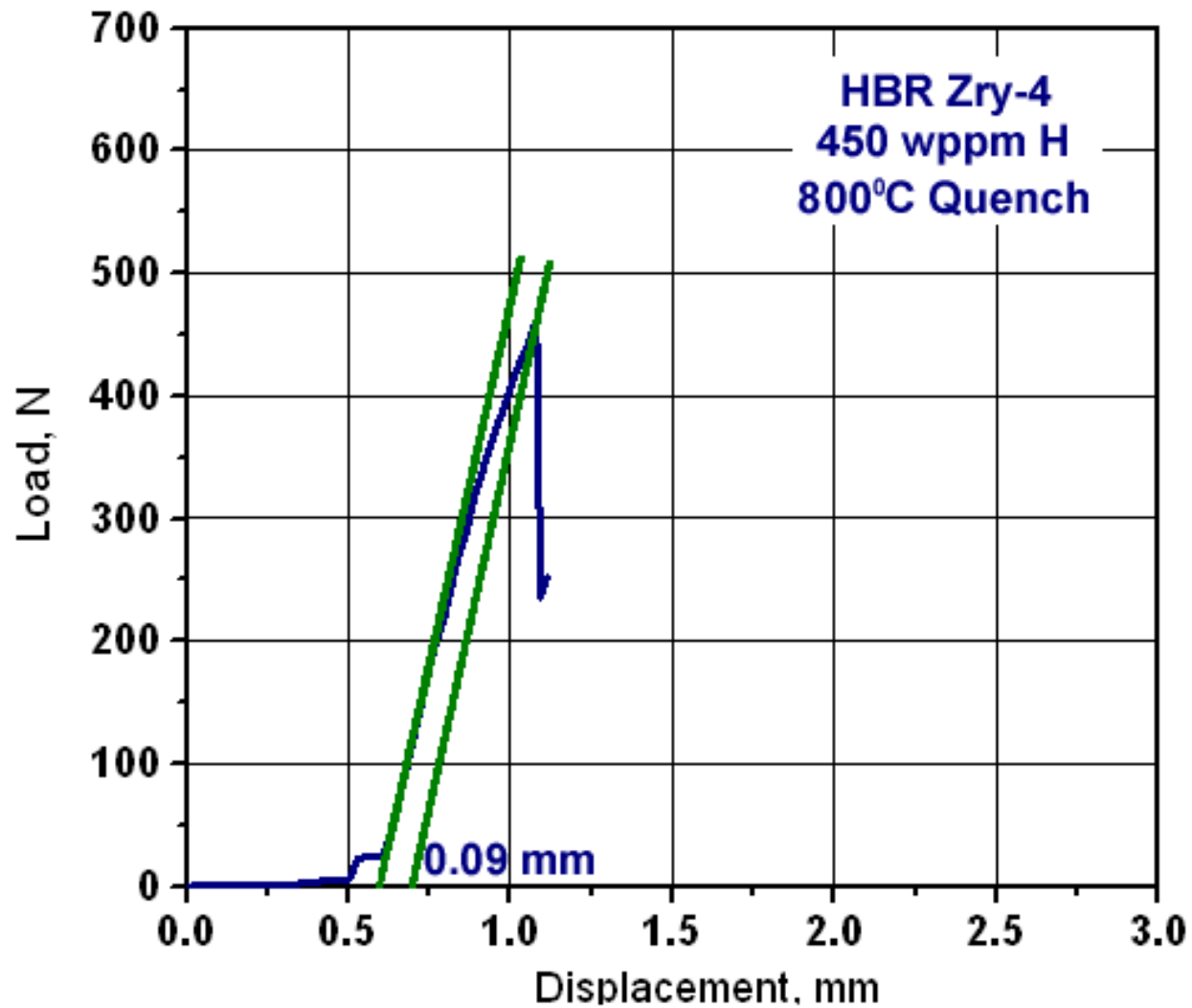


Fig. B2. Load-displacement results for ring #2 (6.84-mm long) of a prehydrided (450 wppm) HBR 15×15 Zry-4 sample oxidized to 6% CP-ECR at a maximum oxidation temperature of 1200°C and quenched at 800°C. The post-test sample had a tight through-wall crack at the support locations. Offset and permanent displacements were 0.09 mm and 0.07 mm, respectively.

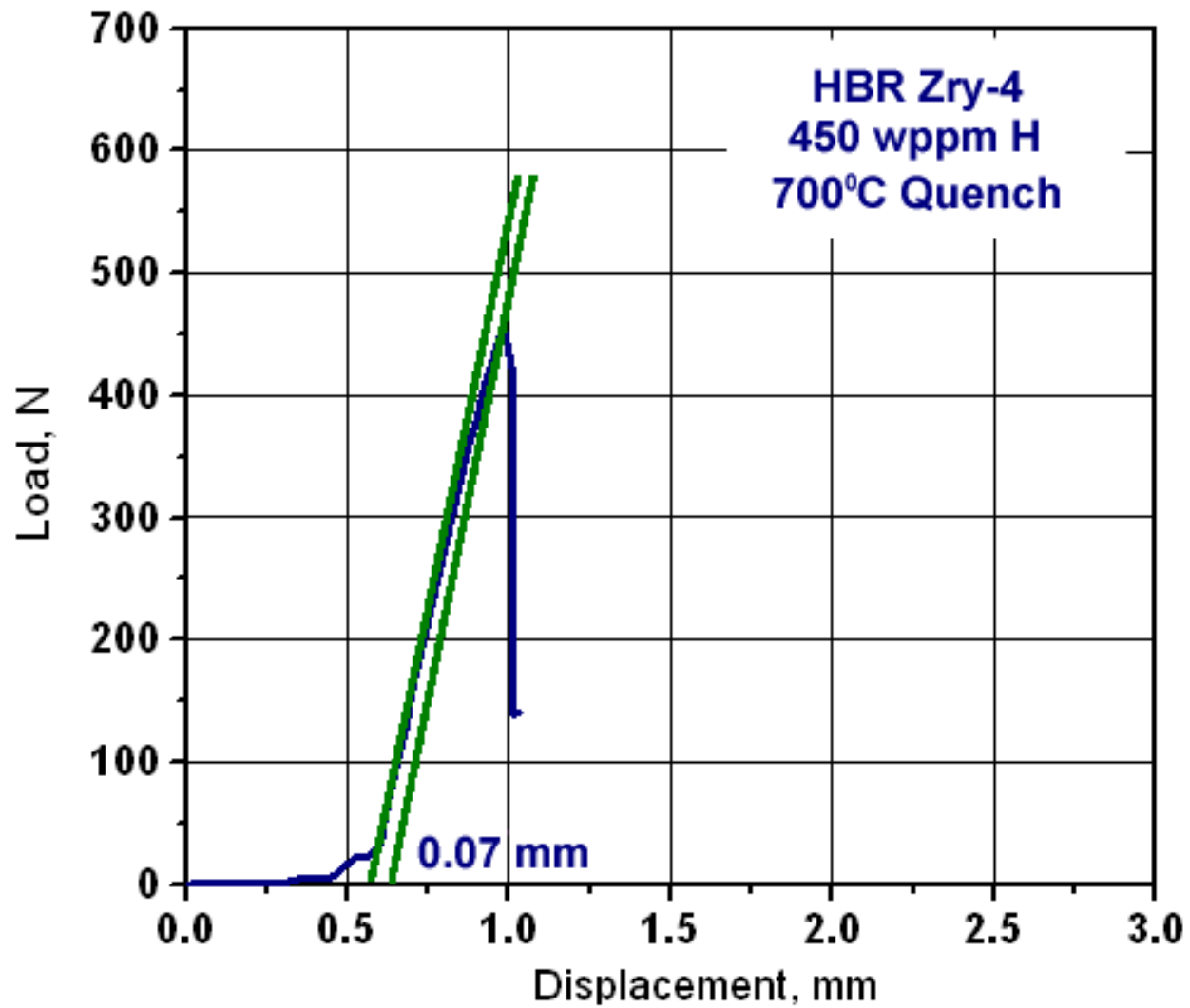


Fig. B3. Load-displacement results for ring #1 (8.08-mm long) of a prehydrided (450 wppm) HBR 15×15 Zry-4 sample oxidized to 6% CP-ECR at a maximum oxidation temperature of 1200°C and quenched at 700°C. The post-test sample had through-wall cracks at load and support locations. Offset displacement was 0.07 mm.

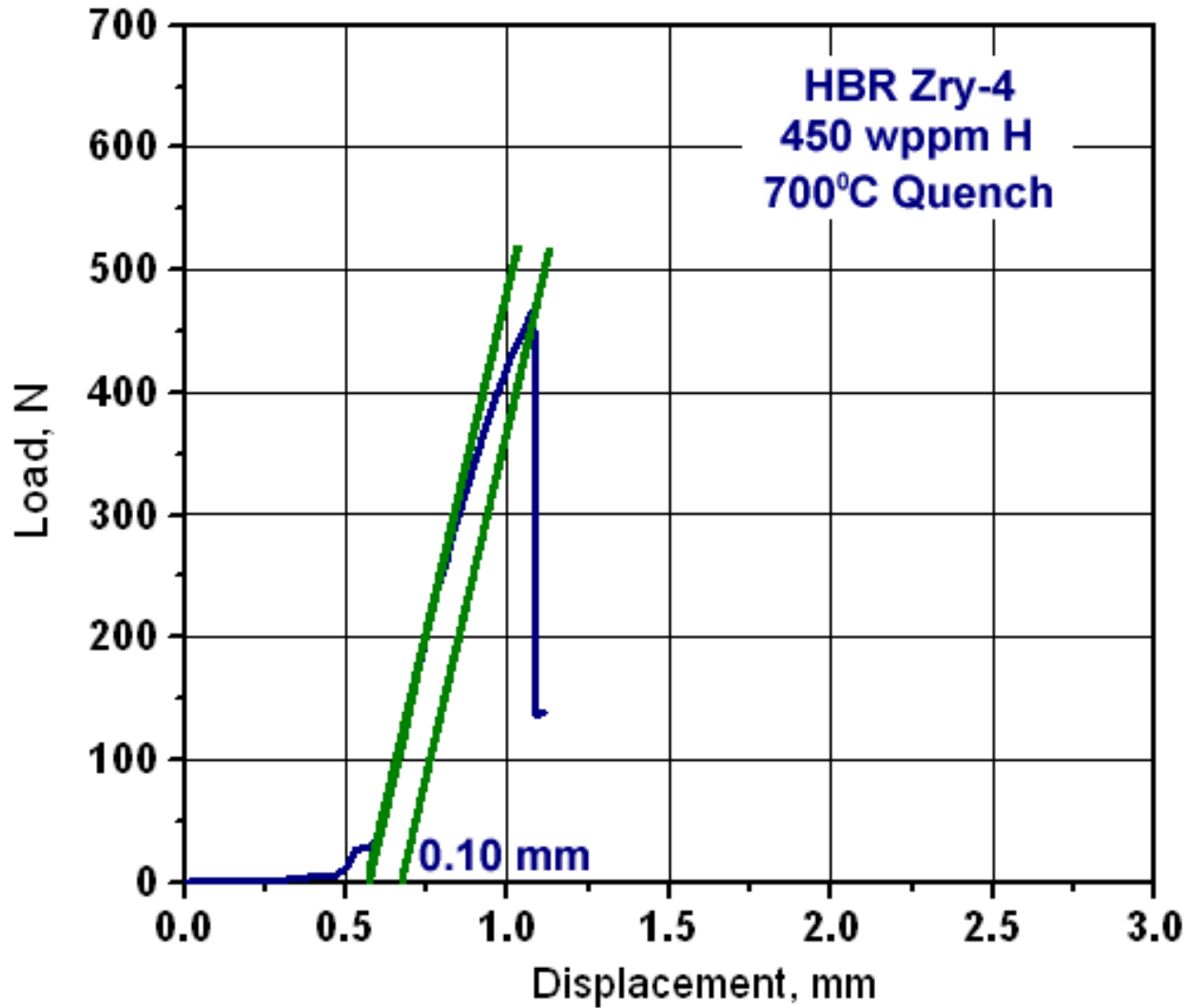


Fig. B4. Load-displacement results for ring #2 (7.30-mm long) of a prehydrided (450 wppm) HBR 15×15 Zry-4 sample oxidized to 6% CP-ECR at a maximum oxidation temperature of 1200°C and quenched at 700°C. The post-test sample had tight through-wall cracks at load and support locations. Offset and permanent displacements were 0.10 mm and 0.05 mm, respectively.

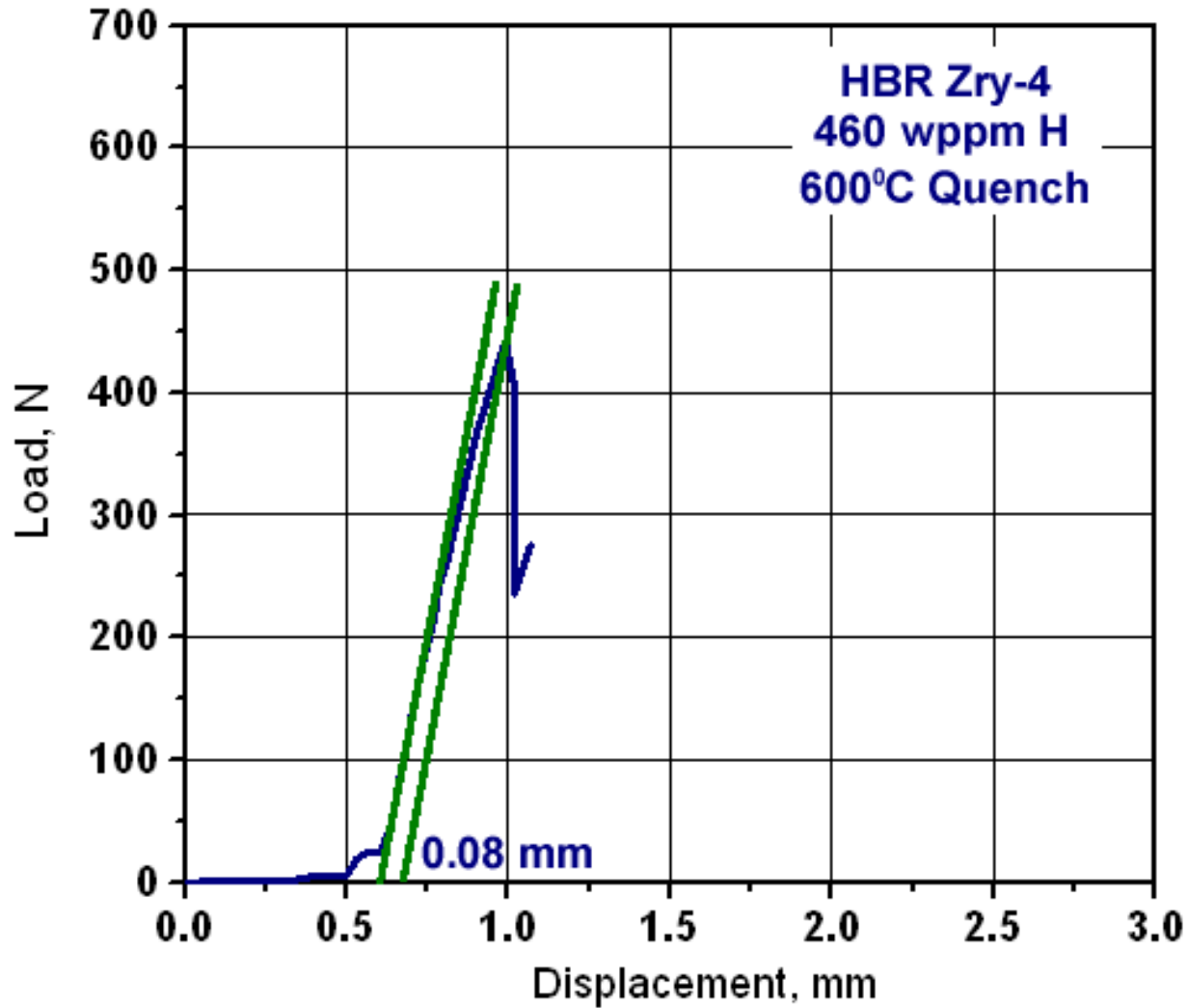


Fig. B5. Load-displacement results for ring #1 (7.93-mm long) of a prehydrided (460±30 wppm) HBR 15×15 Zry-4 sample oxidized to 6% CP-ECR at a maximum oxidation temperature of 1200°C and quenched at 600°C. The post-test sample had a tight through-wall crack at the support location. Offset and permanent displacements were 0.08 mm and 0.05 mm, respectively.

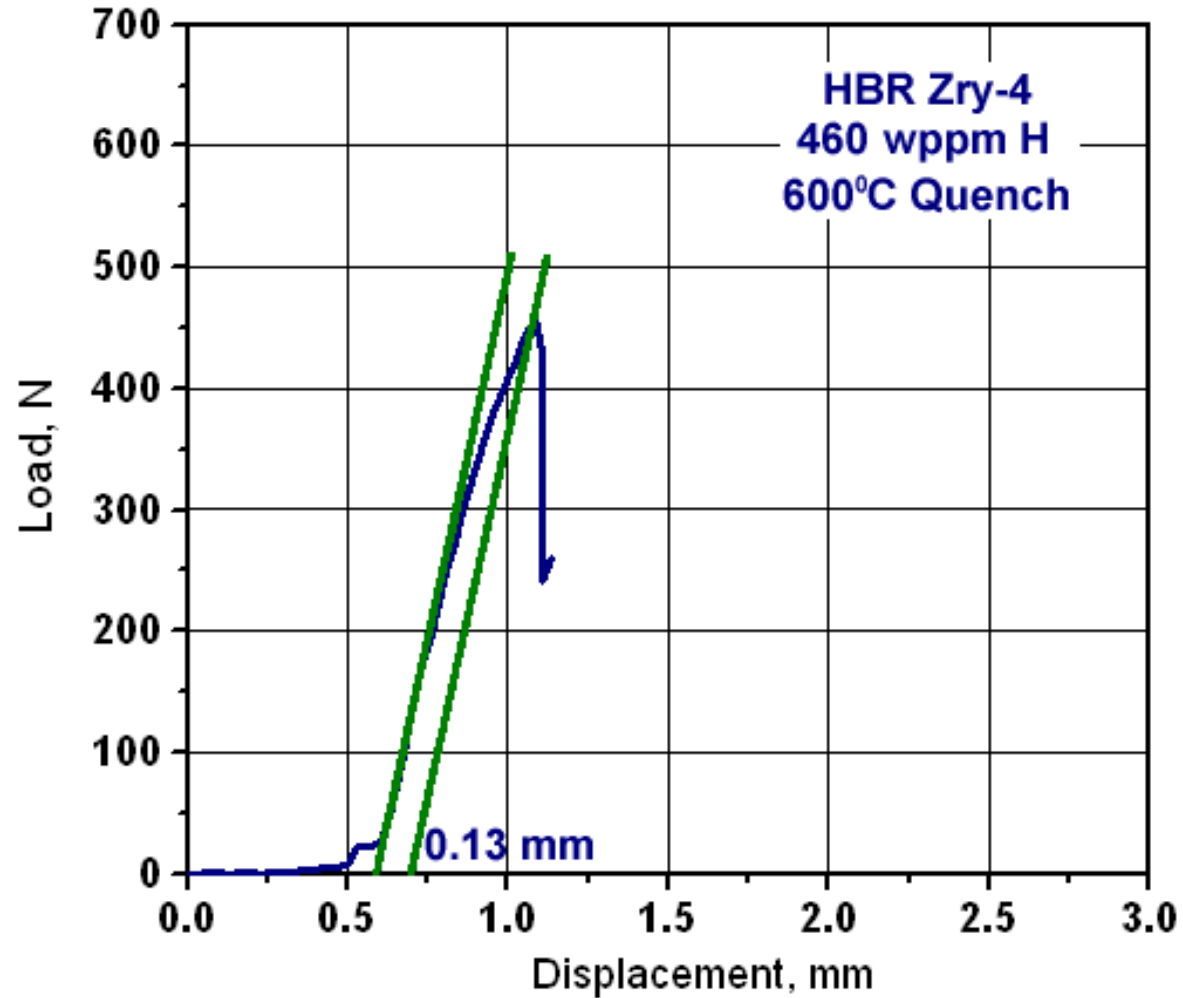


Fig. B6. Load-displacement results for ring #2 (7.05-mm long) of a prehydrided (460±30 wppm) HBR 15×15 Zry-4 sample oxidized to 6% CP-ECR at a maximum oxidation temperature of 1200°C and quenched at 600°C. The post-test sample had a through-wall crack at the loading location. Offset and permanent displacements were 0.13 mm and 0.08 mm, respectively.

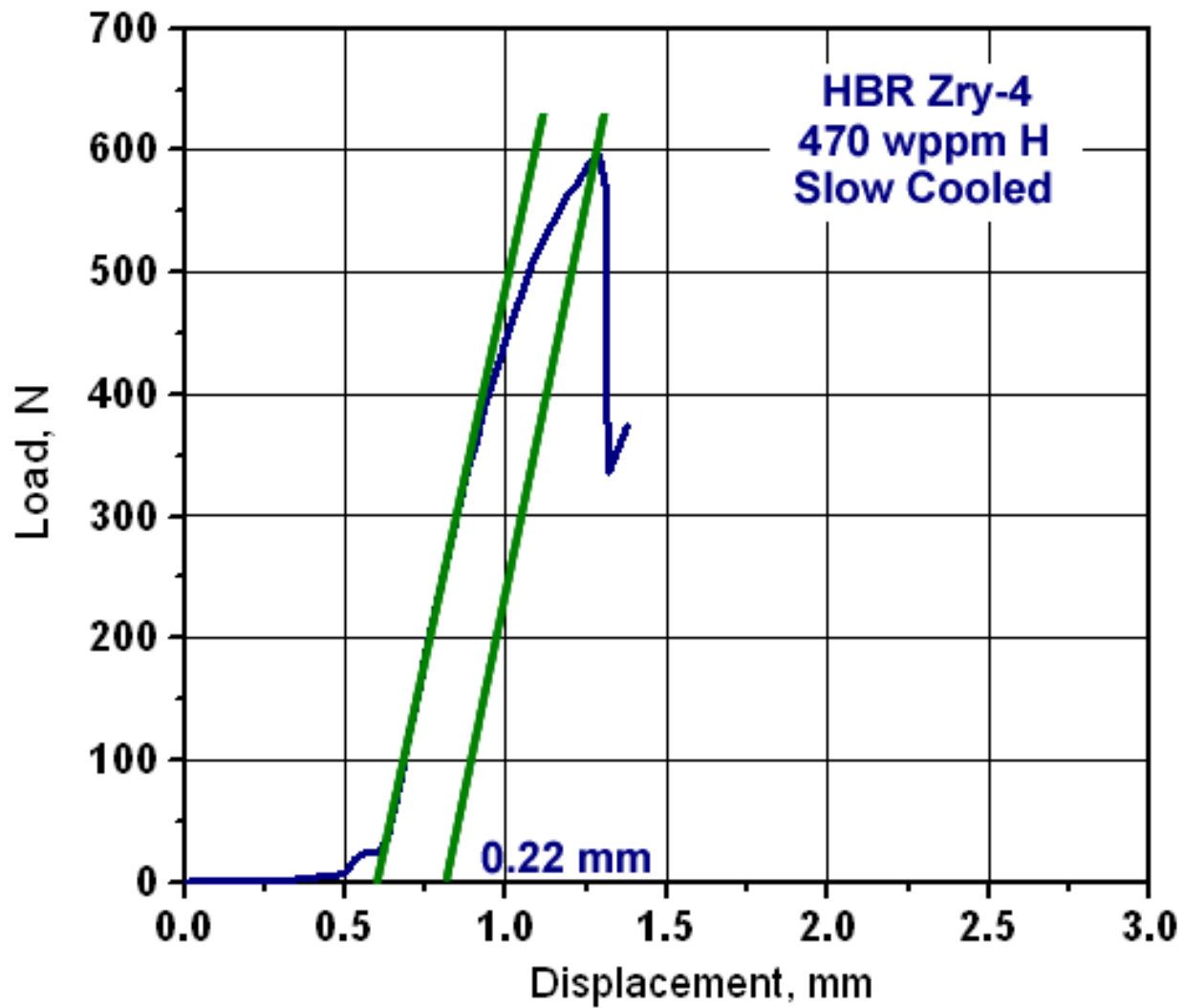


Fig. B7. Load-displacement results for ring #1 (8.04-mm long) of a prehydrided (470 ± 30 wppm) HBR 15×15 Zry-4 sample oxidized to 6% CP-ECR at a maximum oxidation temperature of 1200°C and cooled to RT without quench. The post-test sample had a tight through-wall crack at the support location. Offset and permanent displacements were 0.22 mm and 0.18 mm, respectively.

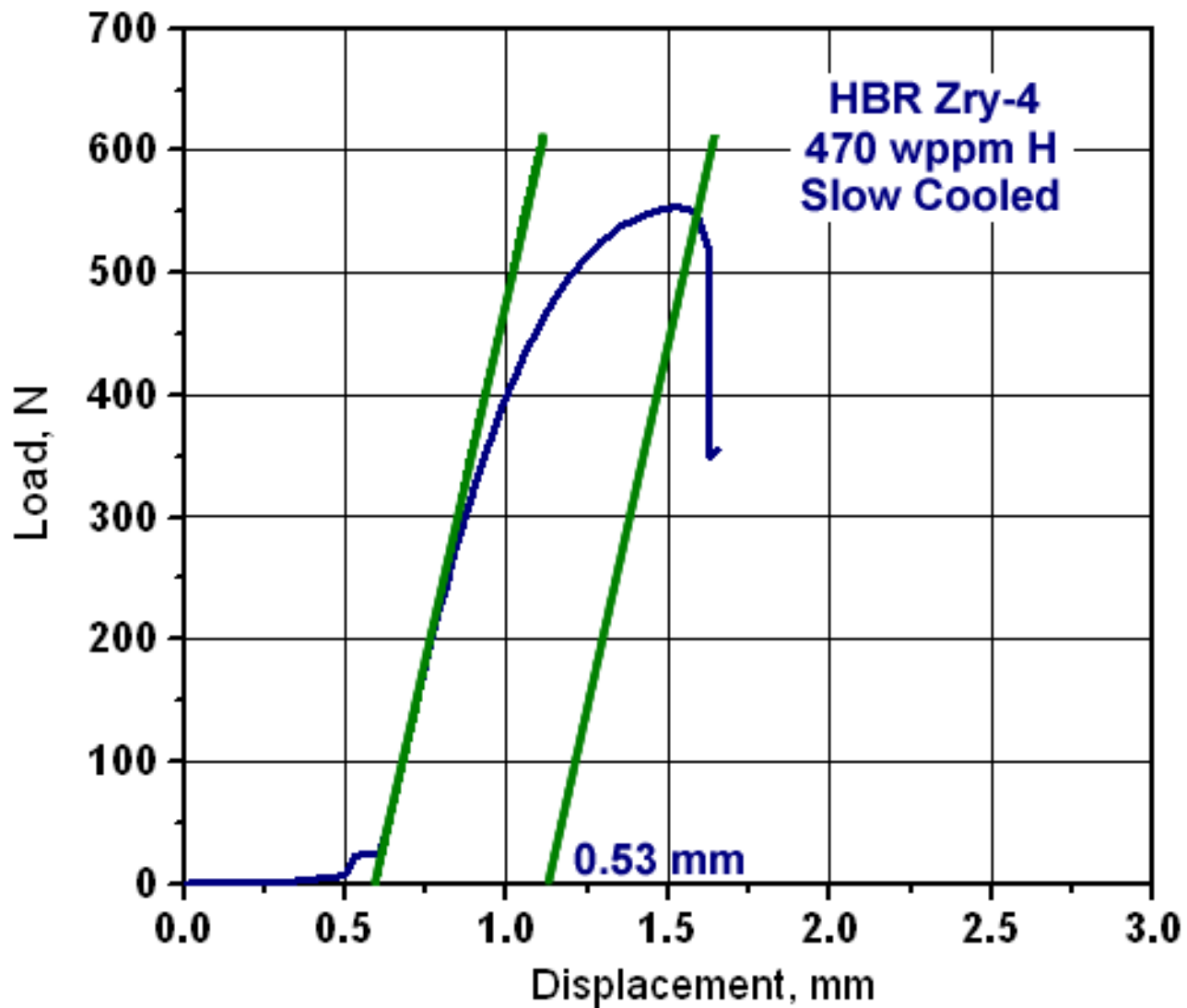


Fig. B8. Load-displacement results for ring #2 (7.05-mm long) of a prehydrided (470 ± 30 wppm) HBR 15 \times 15 Zry-4 sample oxidized to 6% CP-ECR at a maximum oxidation temperature of 1200°C and cooled to RT without quench. The post-test sample had a tight through-wall crack at the loading location. Offset and permanent displacements were 0.53 mm and 0.39 mm, respectively.

Appendix C

Relationship between Offset Strain and Permanent Strain

For as-fabricated cladding compressed at 135°C at 0.033 mm/s to a total displacement of 2 mm, the difference between offset displacement and permanent displacement is ≤ 0.2 mm, which corresponds to a strain difference of $\approx 2\%$. For as-fabricated and prehydrided cladding oxidized at $\leq 1200^\circ\text{C}$, the difference depends on the magnitude of the permanent displacement. For material with high ductility, the difference in displacements can be as high as 0.5 mm. For material with essentially no ductility, both the offset displacement and the permanent displacement values are in the "noise" and their difference can be as low as 0.01 mm.

However, what is relevant to the determination of the ductile-to-brittle transition oxidation level is the error in offset strain as determined by the difference between offset (δ_p/D_o in %) and permanent (d_p/D_o in %) strains for permanent strains in the range of 0.8-2.3%. Figure C1 summarizes the data reported in Ref. 1, as well as in Figs. 1 and 2 of this procedure. The data are plotted as a function of CP-ECR. Low values of permanent strain at low CP-ECR levels (e.g., 5-10%) are from prehydrided Zry-4 and high-burnup Zry-4 and ZIRLO samples. Low values of permanent strain at intermediate CP-ECR levels (10-18%) are from high-burnup ZIRLO and M5 samples. Low values of permanent strain at high ECR values (15-20%) are from as-fabricated cladding materials. The best linear fit to the Zry-4 data is given by:

$$\delta_p/D_o - d_p/D_o = 0.60 + 0.0534 \text{ CP-ECR} \quad (\text{C1})$$

The few data points for ZIRLO and M5 appear to be within the scatter of the many data points for Zry-4. Equation C1 gives the difference in offset and permanent strains as 0.9% at 5% CP-ECR and 1.7% at 20% CP-ECR.

If permanent displacement and strain are not available because tests are not interrupted immediately after the first significant load drop, then the permanent strain criterion can be derived from Eq. C1 by setting the permanent strain (d_p/D_o) to 1%:

$$\delta_p/D_o \geq 1.60 + 0.0534 \text{ CP-ECR} \quad (\text{C2})$$

For multiple data points, the one-sigma lower bound should be used in Eq. 2 for the offset strain.

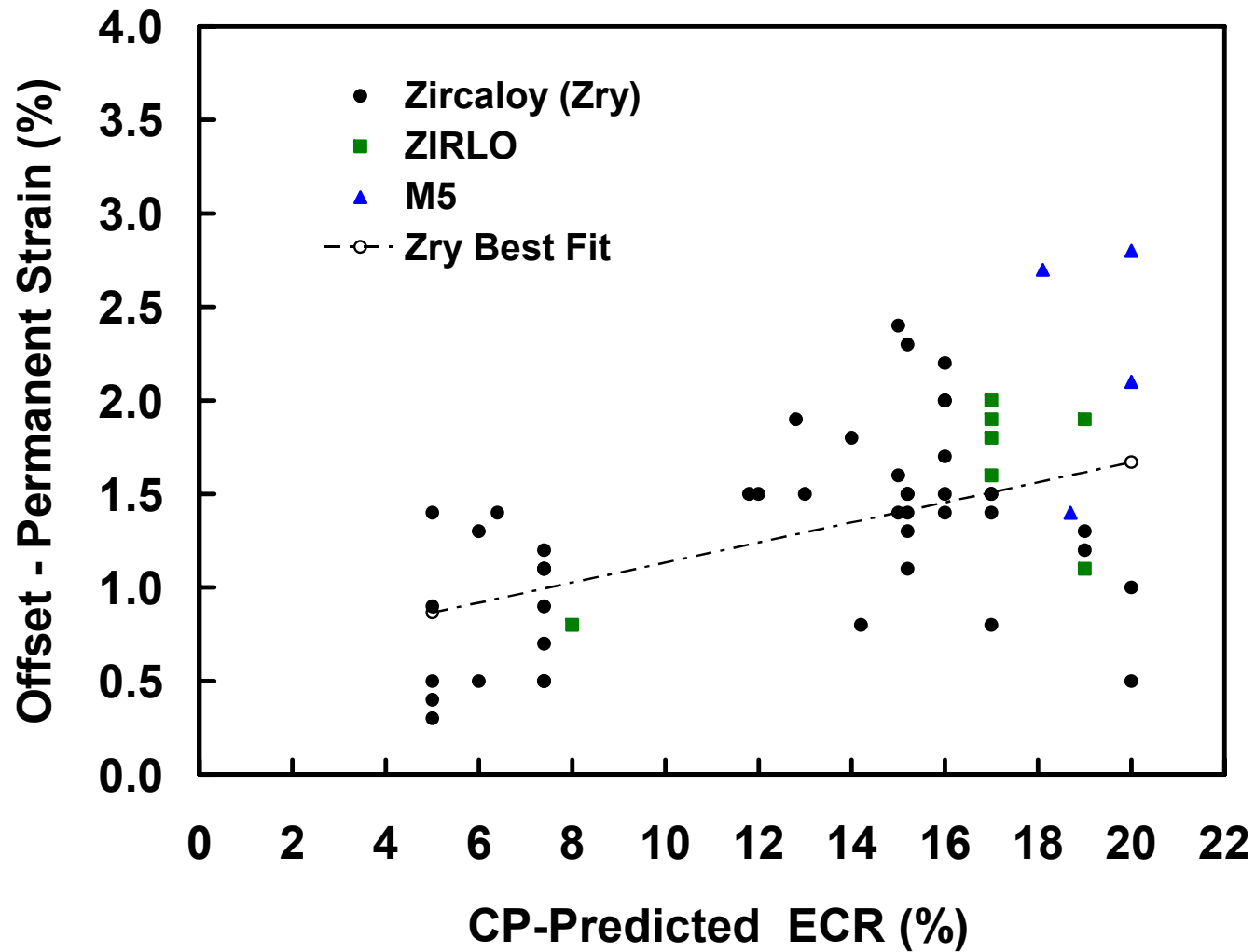


Fig. C1. Difference in offset strain and permanent strain as a function of calculated oxidation level (CP-ECR) near the embrittlement threshold for as-fabricated, prehydrided and high-burnup cladding alloys oxidized at 1200°C and ring-compressed at 135°C and 0.033 mm/s.