Transient Temperature Breakaway Oxidation Tests

Introduction:

Based on internal discussions and comments received from public stakeholders, the staff identified three areas where further effort was needed to enhance the existing technical basis documented in NUREG/CR-6967 (ML082130389) and Research Information Letter (RIL) 0801 (ML081350225). One of these areas was breakaway oxidation behavior under transient temperature conditions. The need for additional breakaway testing was described as follows in a memorandum to the Commission dated December 19, 2008 (ADAMS ML083440156):

> *The current database on breakaway oxidation has been derived from isothermal tests. Variation in temperature profile or thermal cycling may aggravate the breakaway process and needs to be investigated.*

Technical Background:

Zirconium dioxide can exist in several crystallographic forms (allotropes). The normal tetragonal oxide that develops under Loss-of-Coolant Accident (LOCA) conditions is dense, adherent, and protective with respect to hydrogen pickup. The outer surface of this oxide has a lustrous black appearance. There are, however, conditions that promote a transformation of the oxide layer to the monoclinic phase – the phase that grows during normal operation – that 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. As this transformation results in an increase in oxidation rate, it is referred to as breakaway oxidation. Breakaway oxidation occurs in all zirconium-alloy cladding materials if the cladding is held for long times (tens of minutes) at temperatures between 650°C and 1050°C (≈1200°F and ≈1900°F). The amount of time necessary to initiate breakaway oxidation varies with temperature and is not a simple monotonic function. The temperature at which the transformation begins most rapidly is termed the "critical breakaway temperature" and it varies slightly between alloys. The critical breakaway temperature for a range of alloys was identified in Office of Nuclear Regulatory Research (RES) LOCA research program at Argonne National Laboratory by running multiple, isothermal oxidation tests to identify the minimum time to initiate breakaway oxidation for each alloy. The minimum time for breakaway oxidation at this critical temperature was found to be sensitive to the cladding outer-diameter surface finishing process, including polishing and cleaning, than to alloy type.

Objective of additional testing:

Variation in temperature profile or thermal cycling may aggravate the breakaway process. Since a working assumption is that the isothermal test at the critical breakaway temperature will result in the shortest time to breakaway, it was necessary to investigate thermal cycling scenarios which have the potential to aggravate the breakaway process. Based on knowledge of the breakaway phenomenon, three test scenarios were preformed to investigate different mechanisms which could aggravate the breakaway process.

Quick Look Results:

Oxidation tests were run on ZIRLO cladding with three transient temperature profiles. It is relevant to note that the critical temperature for breakaway oxidation reported in NUREG/CR-6967 for ZIRLO is in the range of 970-985°C. Within this range, the minimum breakaway time is 3100 ± 300 s. At the higher oxidation temperature of 1000°C, the breakaway time is longer (4000 ± 200 s).

<u>Transient #1</u>

Investigation: Will breakaway oxidation occur at a shorter time if the temperature is raised from the critical temperature during the transient to a higher temperature which would normally lead to tetragonal growth?

Transient Specifications: (single step change up) 975°C for 1500 s, 1000°C for 2500 s.

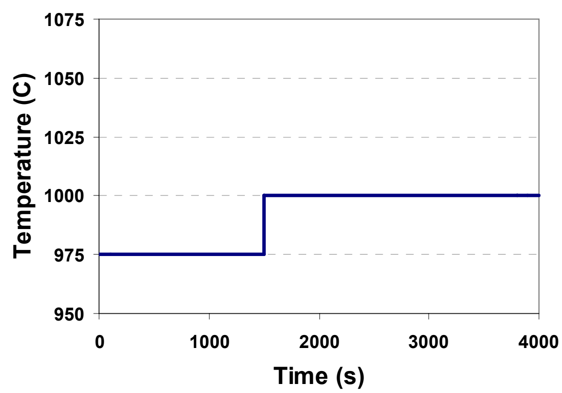

Figure 1. Approximate temperature profile for ZLU#140.

Results: There were no indications of breakaway behavior after 4000 s total oxidation time. Because the minimum time to breakaway behavior is 3100 ± 300 s under isothermal conditions at 975°C and 4000 ± 200 s at 1000°C, the results of this test indicate that this transient profile does not produce a shorter time to breakaway.

<u>Transient #2</u>

Investigation: Oxidation tests during which the furnace overshot the temperature set point suggest that this could affect the time to breakaway; therefore it was of interest to determine if this type of transient could lead to shorter breakaway times. Particularly in relation to the development of test procedures for breakaway oxidation tests, it was necessary to run a temperature transient which exceeded the critical breakaway temperature for period of time (as may occur during testing depending on the capabilities of the test furnace) and then reduced to the critical breakaway temperature.

Transient specifications: (single step change down) 1045°C for 1000 s, 980°C for 3000 s.

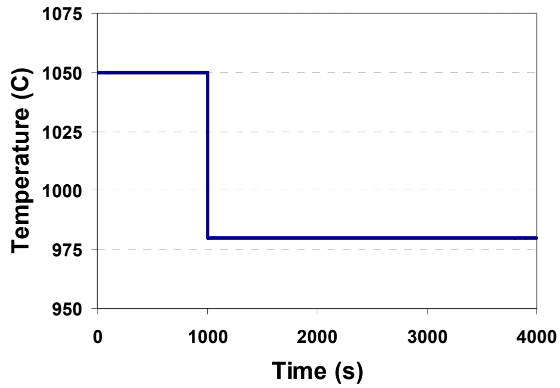

Figure 2. Approximate temperature profile for ZLU#139

Results: There were no indications of breakaway behavior after 4000 s total oxidation time. Because the minimum time to breakaway behavior is 3100 ± 300 s under isothermal conditions, the results of this test indicate that this transient profile does not produce a shorter time to breakaway.

Transient #3

Investigation: Is it possible to crack an otherwise protective oxide by passing through the critical breakaway temperature multiple times (due to thermal expansion stresses, phase transformation induced localized stresses, etc.)? To investigate this, two thermal cycling tests were run which held the cladding at the critical temperature for a period of time (either 1500 s or 2000 s) and then cycled 50°C below the critical temperature and 50°C above the critical temperature for five cycles and finally returned to the critical temperature.

Transient Specification ZLU#142: (temperature cycling) 980°C for 1500 s, then 5 cycles from 930°C to 1030°C for about 400 s, followed by 980°C for 1400s.

Results of ZLU#142: Extensive breakaway was observed for 3300 s total oxidation time. This is within data scatter for isothermal tests, and therefore this test indicates that this transient profile does not produce significantly shorter time to breakaway as compared to isothermal tests.

Transient Specification ZLU#143: (temperature cycling) 980°C for 2000 s, then 5 cycles from 930°C to 1030°C for about 400 s, followed by 980°C for 400 s.

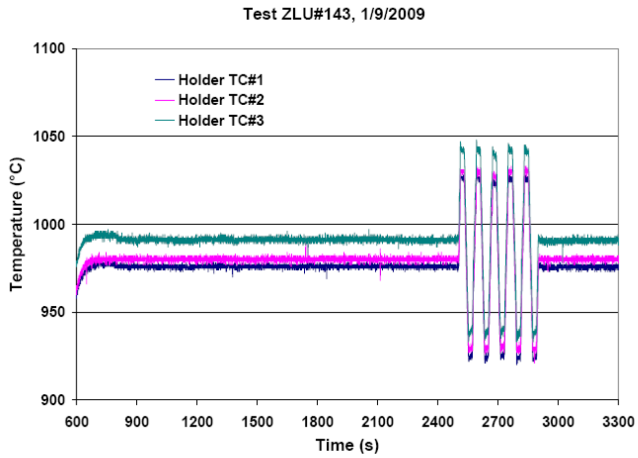

Figure 4. Thermocouple measurements for ZLU#143

Results of ZLU#143: Extensive breakaway for 2800 s total oxidation time (see Figure 5). The post-test hydrogen content of this sample was measured to be 230 ± 80 wppm. With this hydrogen content, a time to breakaway behavior of 2800 s is consistent with previous data of 3100 ± 300 s measured for ZIRLO (as-fabricated, pre-filmed and scratched).

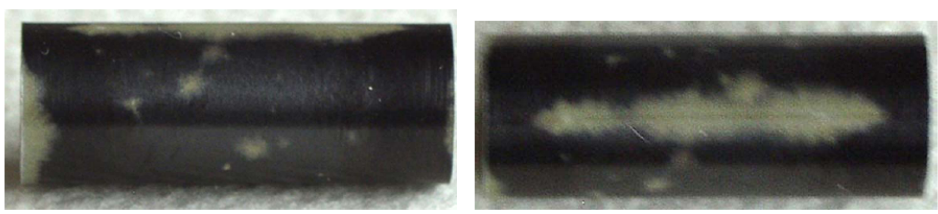

Figure 5. Images indicating breakaway oxidation following ZLU#143 test.

Conclusions:

Based on knowledge of the breakaway phenomenon, three test scenarios were preformed to investigate different mechanisms which could aggravate the breakaway process. Four transient temperature profiles were run without generating a transient that gave lower oxidation times than were observed under isothermal conditions. Therefore, no further testing was requested by NRC, nor recommended by the ANL investigators, to find a transient that might give lower breakaway oxidation times.