Breakaway Oxidation Tests for M5 Cladding

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1. Introduction

The purpose of these tests was to determine if as-fabricated M5™ cladding would experience breakaway oxidation at ≤5000 s for oxidation temperatures in the range of 985-1000°C. The results of previous ANL studies for the breakaway oxidation of M5 cladding at 1000°C for ≤4100 s are documented in NUREG/CR-6967 [1]. The ANL criterion for breakaway oxidation is the time corresponding to 200-wppm hydrogen pickup, which is a reasonably conservative criterion for breakaway oxidation in terms of embrittlement. Based on the work of Mardon et al. [2] the breakaway oxidation time for M5 corresponding to ≈200-wppm H pickup is ≈6400 s at 1000ºC. M5 exhibits very slow growth rate of inner- and outer-surface oxide layers at 1000ºC, which may contribute to a longer breakaway-oxidation time than reported for Zry-4 (≈5400 s at 1000ºC [2]). The data published by Mardon et al. were generated by very different testing methods than the ones used at ANL. Also, breakaway-oxidation times for M5 at <1000ºC oxidation temperatures have not been reported in the open literature. In the ANL test program, all samples are oxidized in the same apparatus at similar ramp rates, hold times, and cooling rates.

2. Materials

The cladding materials used for these studies included as-fabricated M5 tubing (17×17 PWR) received from Framatome in 2003 (M5-2003) and M5 received from AREVA (formerly Framatome) in 2007 (M5-2007). ANL measured the outer diameter, wall thickness, surface roughness and hydrogen content for the test materials. Table 1 shows the comparison between M5-2003 and M5-2007. M5-2007 has a thinner wall (0.57 mm) as compared to M5-2003 (0.61 mm). Both lots are expected to have the same surface roughness and oxygen content.

Table 1 Characterization of 17x17 M5 Cladding used in the ANL Testing Program

Parameter	Outer Diameter, mm	Wall thickness, mm	OD Surface Roughness, μm	H Content, wppm	O Content, wppm
M5-2003	9.50	0.61	0.12	5	1450
M5-2007	9.50	0.57	--	17	--

3. Results

Results for M5 oxidation tests conducted at 1000ºC for ≤4100 s are reported in Ref. 1. Three additional tests were recently conducted at ≈985ºC for 5000 s.

3.1 Previous tests at 1000ºC

The thermal benchmark results for M5-2003 cladding (0.61-mm wall) are shown in Fig. 1 for 1000ºC tests. Table 2 lists the calculated and measured weight gains. For 1000ºC oxidation, M5 exhibits significantly lower weight gain and slower oxide-layer growth as compared to Zry-4 and predicted values, using the Cathcart-Pawel (CP) weight-gain correlation, for the same oxidation time. Also, above ≈10% CP-ECR (≈960 s equivalent isothermal time), weight gain does not increase in a consistent manner with oxidation time or the square root of time. All samples had lustrous black outer surfaces. The measured hydrogen pickup was also low. No breakaway oxidation was observed at 1000ºC for ≤4100 s.

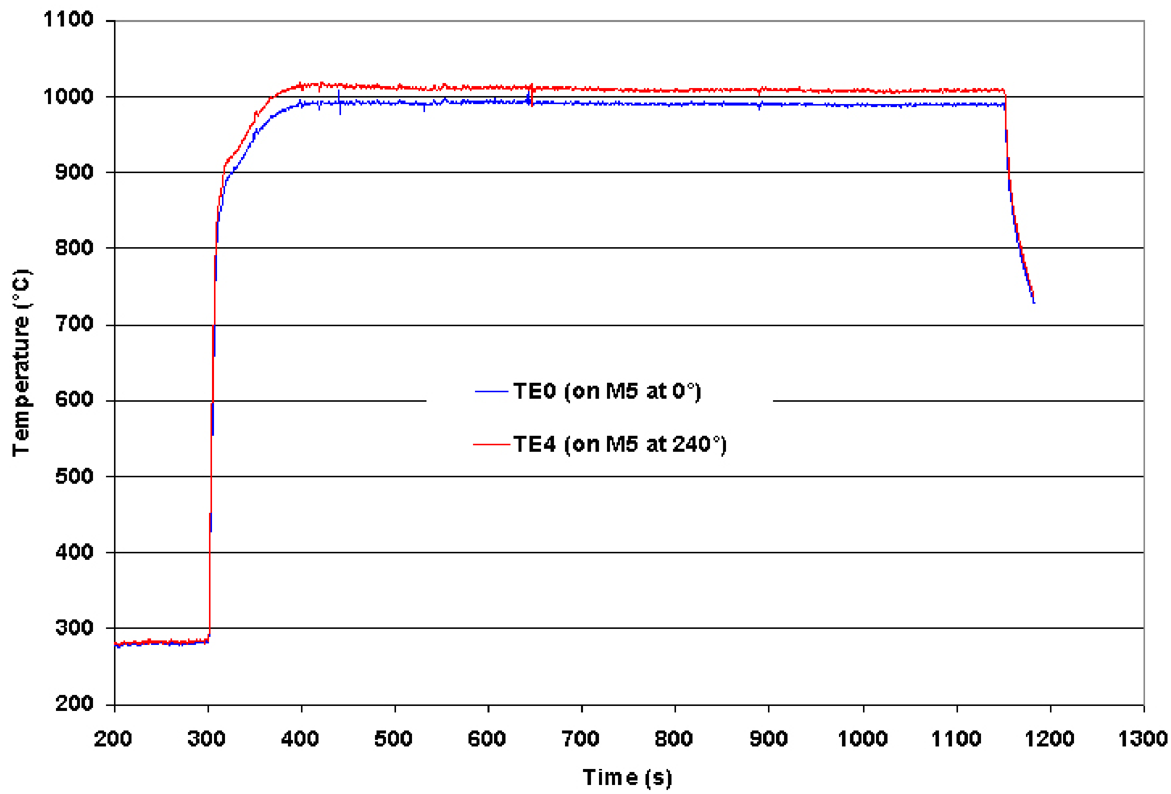

Fig. 1. Thermal benchmark results for 17×17 M5 (2003) oxidation tests at 1000ºC. The cladding OD was 9.50 mm, and the wall thickness was 0.61 mm.

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Table 2 Results of M5 Oxidation Tests at 1000ºC (see Table 1 for description of M5-2003)

Test ID	Material	Test Time[a], s	CP-predicted Weight Gain, mg/cm^2	Measured Weight Gain, mg/cm^2	LECO H-content wppm	H-pickup[b] wppm
MU#52	M5-2003	207	3.3	3.0	---	---
MU#53	M5-2003	810	6.5	5.3	---	---
MU#54	M5-2003	1880	9.8	7.4	---	---
MU#55	M5-2003	2440	11.1	8.0	---	---
MU#56	M5-2003	3380	13.1	9.2	26	22
MU#61	M5-2003	4100	14.4	8.6	13	8

[a]Time from ramp initiation at 300ºC to end of hold temperature; ramp time is ≈80 s.
[b]Hydrogen pickup is referenced to the as-fabricated sample weight.

3.2 Tests at 985ºC

During previous studies, minimum breakaway oxidation times were observed by ANL for ZIRLO™ for oxidation in the temperature range of 970-985ºC. Unlike results at 1000ºC, there was considerable scatter in hydrogen pickup vs. oxidation time within this highly sensitive temperature range. M5-2007 breakaway oxidation tests were therefore performed at ≈985ºC for 5000 s in parallel with those conducted using ZIRLO cladding.

Both ZIRLO and M5-2007 samples had the same outer-diameter (OD) and wall thickness. Therefore, the thermal benchmark temperature history determined for ZIRLO was also used for M5. The temperature history determined from a ZIRLO thermal benchmark test is shown in Fig. 2. The long-time hold temperature was 975±3ºC. Also shown in Fig. 2 are the histories of the control TC and one other TC, both welded to the sample holder. The control TC readings were only a few degrees lower than the sample readings. As it was determined that these tests would be conducted at 985ºC, the control TC was set to give an increase of 10ºC and a corresponding sample temperature of 985ºC (985±5ºC).

Table 3 lists the weight gain results for M5-2007 at a long-time hold temperature of 985ºC. No breakaway oxidation was observed for test times of 5000 s, which was confirmed by metallographic examinations (see Fig. 3). Again, M5 exhibited significantly lower weight gain and oxide-layer thickness at 985ºC than Zry-4 for the same oxidation time, which may have prolonged the time needed for breakaway oxidation. In particular, as shown in Fig. 4, both the average oxide-layer thickness and the amplitude of the scallops are relatively small (see Discussion).

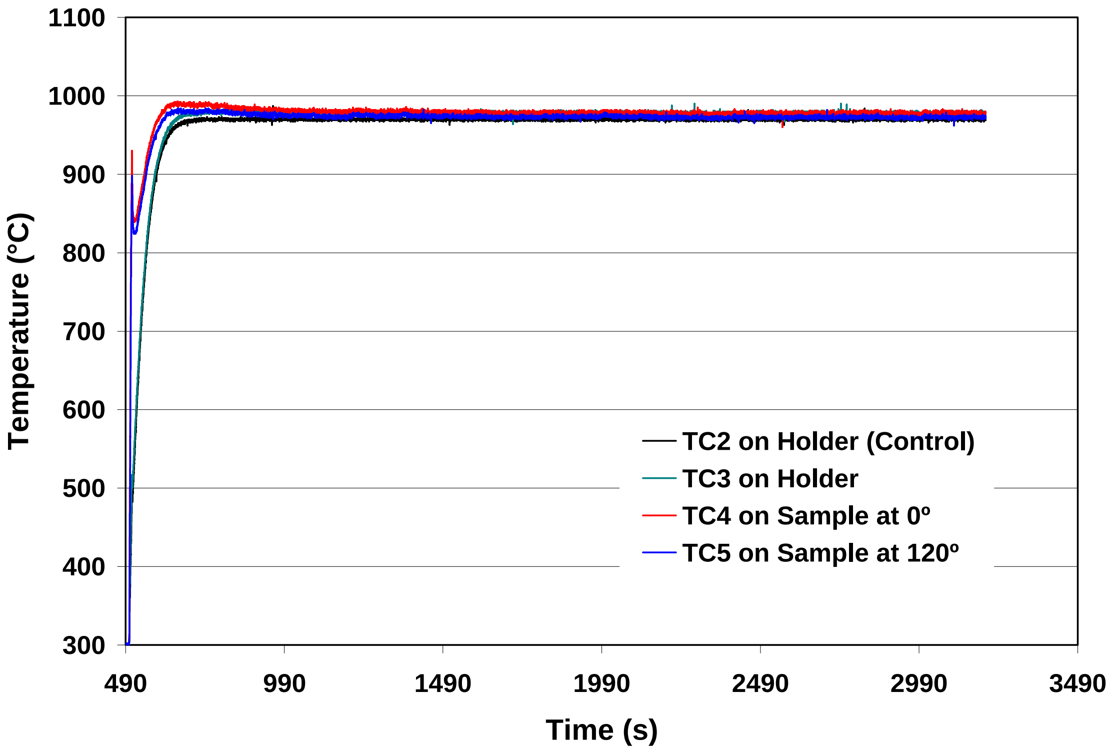


Fig. 2. Thermal benchmark results for test ZLU#132. The long-time hold temperature was 975±3ºC. The holder control temperature was increased by 10ºC for data-generating tests to give 985±5ºC.

Table 3 Results of M5 Oxidation Tests at 985ºC (see Table 1 for description of M5-2007)

Test ID	Material	Test Time[a], s	CP-predicted Weight Gain, mg/cm^2	Measured Weight Gain, mg/cm^2	LECO H-content, wppm	H-pickup[b], wppm
MU#80	M5-2007	5000	14.4	7.9	32	28
MU#83	M5-2007	5000	≈14.4[c]	7.4	---	---

[a]Time from ramp initiation at 300ºC to end of hold temperature; ramp time is ≈80 s.
[b]Hydrogen pickup is referenced to the as-fabricated sample weight.
[c]A slower ramp was used for this test as compared to the one shown in Fig. 2.

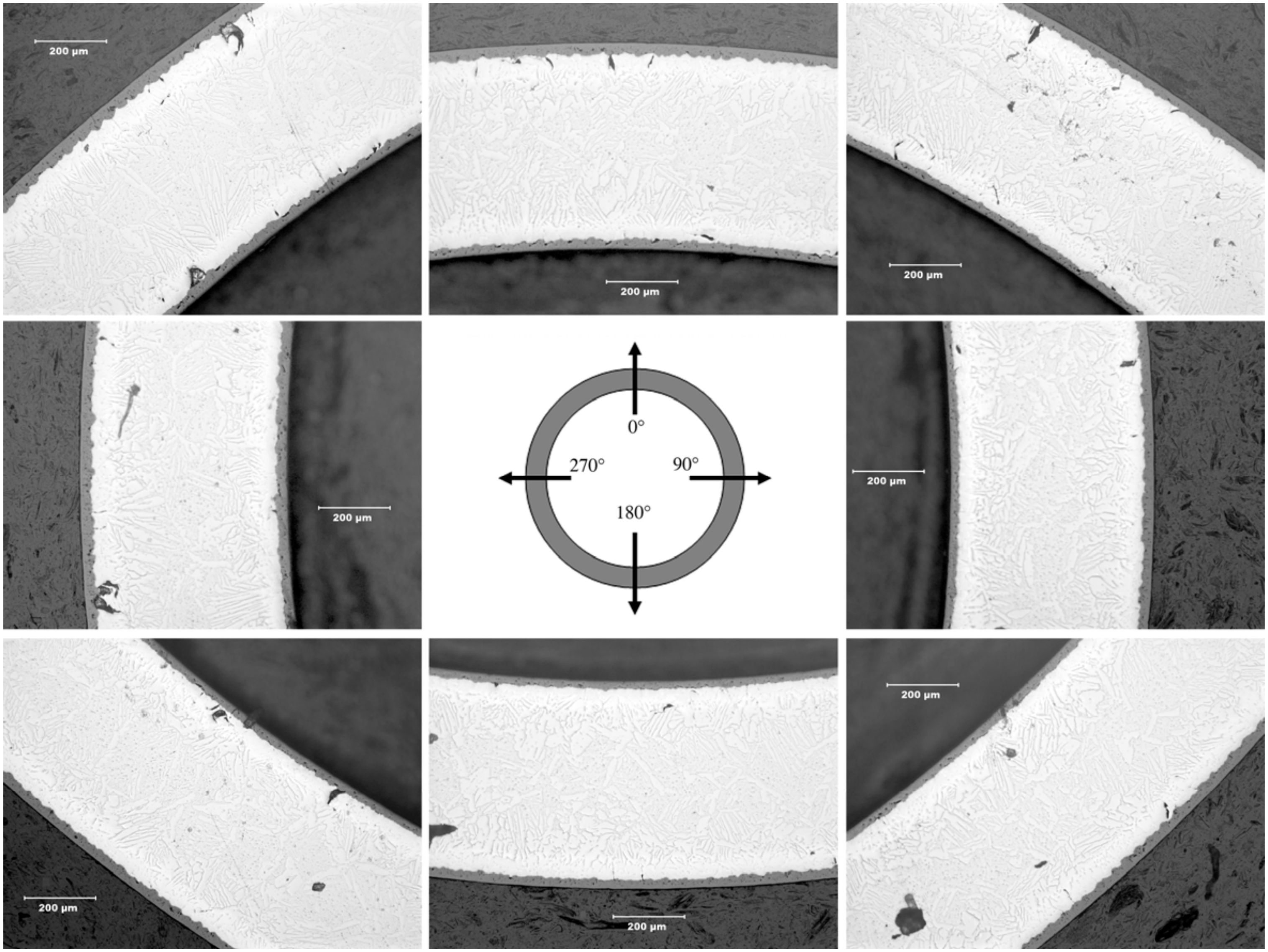


Fig. 3. Metallographic images at eight locations around the cross section of the MU#80 test sample, which show wavy interfaces between oxide and metal layers. However, no local breakaway oxidation was observed after 5000 s at 985ºC.

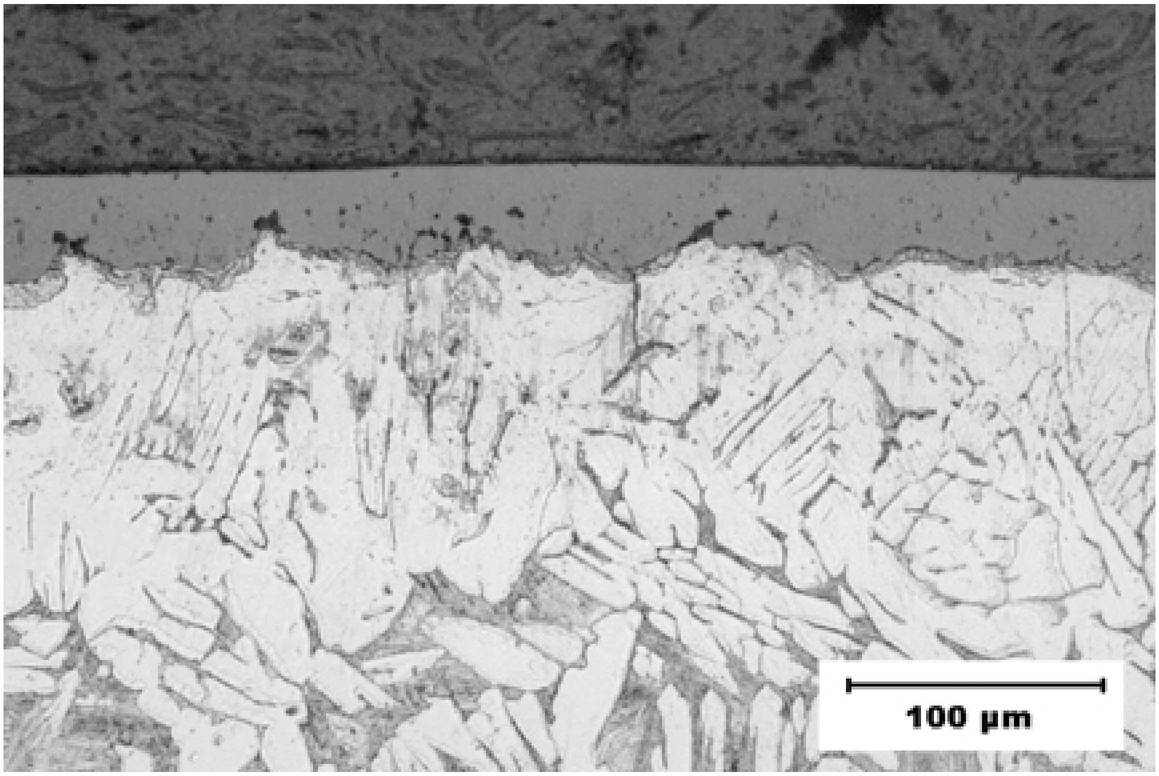


Fig. 4. Enlarged view of the metallographic image at the 12 o'clock position in Fig. 3 for the MU#80 M5 sample oxidized at 985°C for 5000 s.

3.3 Tests at 985ºC with temperature overshoot

Concurrent with breakaway oxidation studies, a test train for a shorter steam chamber was thermally benchmarked for a hold temperature of 1200ºC to conduct high-temperature embrittlement tests. It was time-consuming to switch back and forth between test trains and chambers for breakaway and high-temperature embrittlement studies. The shorter test chamber was used for the next sequence of breakaway tests, and the furnace power was scaled to give a long-time hold temperature of ≈985ºC. Three tests were run with ZIRLO samples for 3200-3400 s. Following these tests, TCs were welded onto a fresh ZIRLO sample to determine more precisely the temperature history [3]. As shown in Fig. 5, the scaling of furnace power resulted in a long-time hold temperature of 981±4ºC (≈980±5ºC). However, unlike other histories, this one had considerable overshoot early in the transient. The cladding temperature rose rapidly (18 s) to ≈1065ºC and was above 985ºC for ≈20 s. Based on the ZIRLO results [3], no effect of this excursion was expected on breakaway oxidation at long test times. In order to check the breakaway oxidation behavior of M5 cladding with temperature overshoot, Test MU#81 was run for 5000 s with M5-2007 cladding at the test conditions shown in Fig. 5. The measured sample weight gain for this test sample was 7.7 mg/cm^2, which is comparable to the M5 tests with no temperature overshoot (see Table 2). The outer surface of this sample was lustrous black. Therefore, in accordance with standardized test procedures for breakaway oxidation [4], no hydrogen analysis was performed.

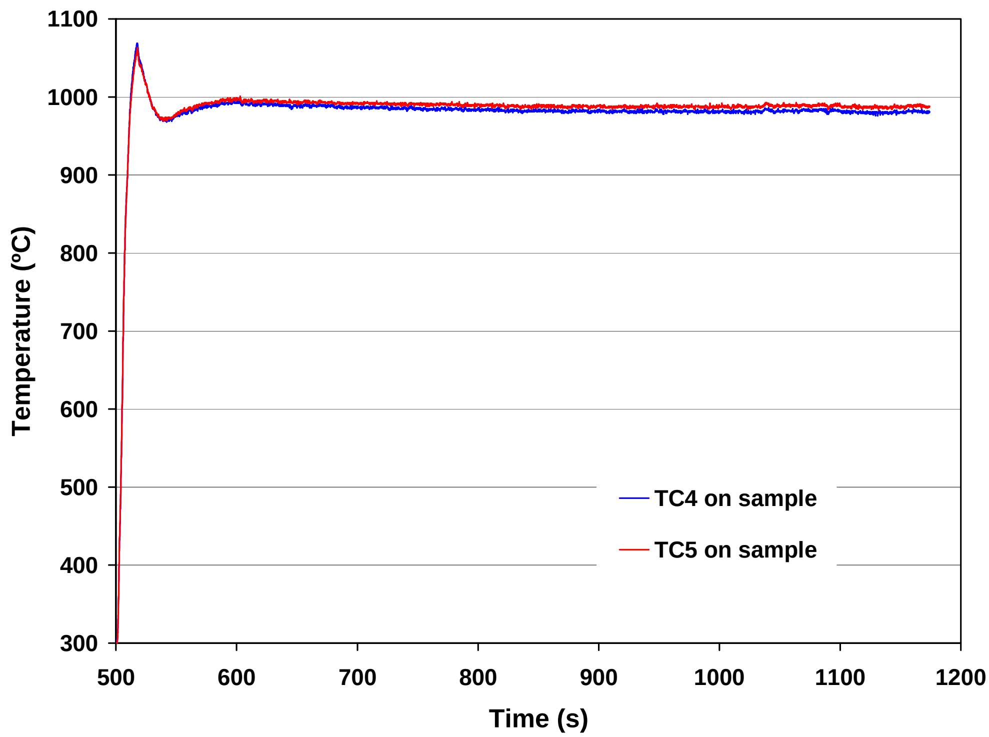


Fig. 5. Thermal benchmark results for test ZLU#129. A brief temperature excursion to ≈1065ºC occurred at the end of the heating ramp; the long time hold temperature was ≈980±5ºC.

Discussion

As shown in Table 2, M5 exhibits significantly lower weight gain as compared to the CP-predicted values at 1000ºC for the same oxidation time, as well as to the measured sample weight gains of Zry-4 tested in the same apparatus under similar test conditions. The measured sample weight gains for 17×17 M5 are compared in Fig. 6 to those measured for 17×17 Zry-4 and polished 15×15 Zry-4. For 15×15 Zry-4, only data for pre-breakaway samples are shown.

Figure 7 shows metallographic images at eight locations for the 15×15 Zry-4 sample tested (BPZ4#18) for 5000 s at a long-time hold-temperature of 986ºC. In addition to wavy (i.e., scalloped) interfaces between oxide and metal layers, local breakaway oxidation was observed in the outer-surface oxide in the area labeled as BK in Fig. 7. The hydrogen pickup (280 wppm) was just above the 200-wppm breakaway criterion. Therefore, the estimated breakaway time for this cladding material was ≈5000 s. Detailed analyses of pre-breakaway-oxidation 15×15 Zry-4 and 17×17 M5 samples, both oxidized at a long-time hold temperature of ≈985ºC for 5000 s, indicate that the lower measured sample weight gain of M5 is mainly due to slower growth of the inner- and outer-surface oxide layers. Also, the amplitude of the scallops is larger for Zry-4 than for M5 at 5000 s. Based on a few of the micrographs in Figs. 3 and 6, the differences between minimum and maximum oxide thickness were ≈15 µm for M5 and ≈30 µm for Zry-4 (see Fig. 8).

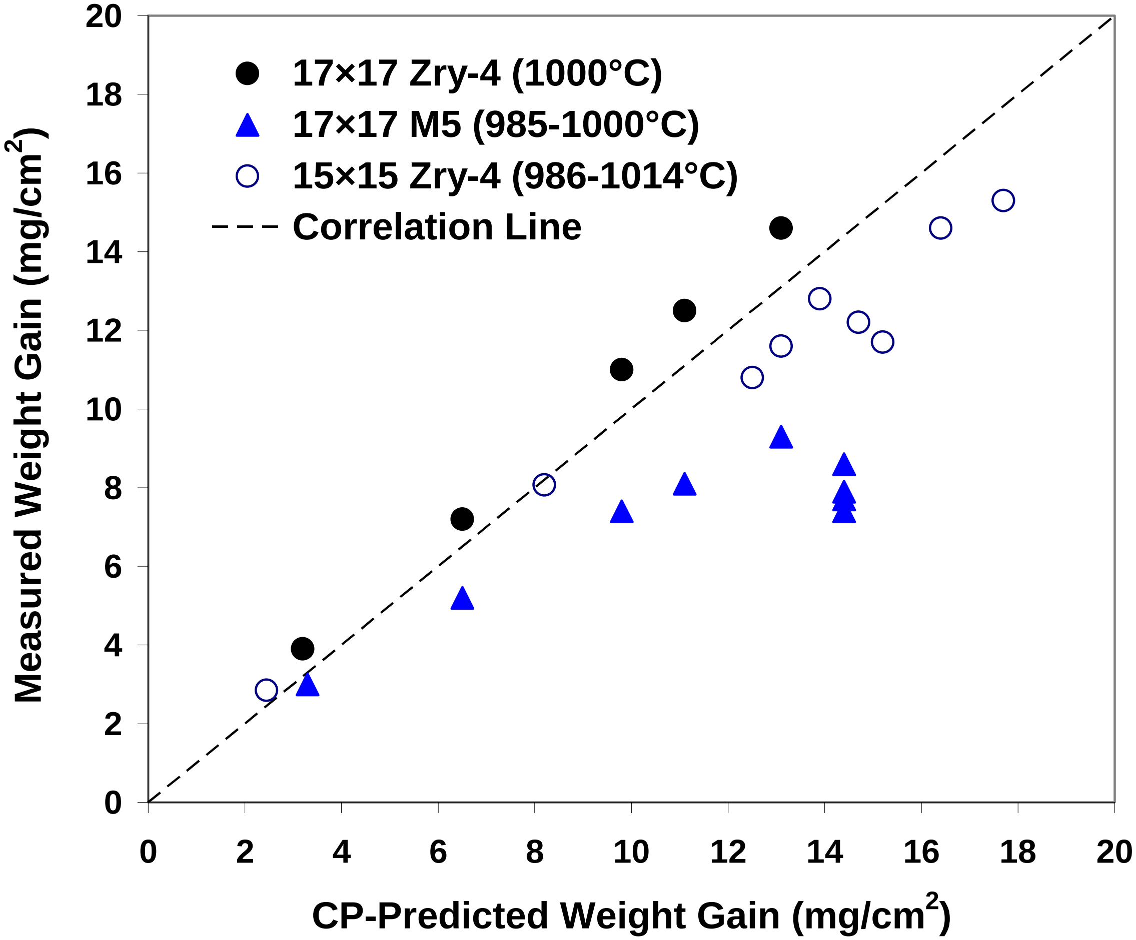


Fig. 6. Weight gain comparison for 17×17 M5, 17×17 Zry-4 and 15×15 Zry-4 at test times ≤5000 s for M5, ≤3400 s for 17×17 Zry-4, and ≤5000 s for 15×15 Zry-4.

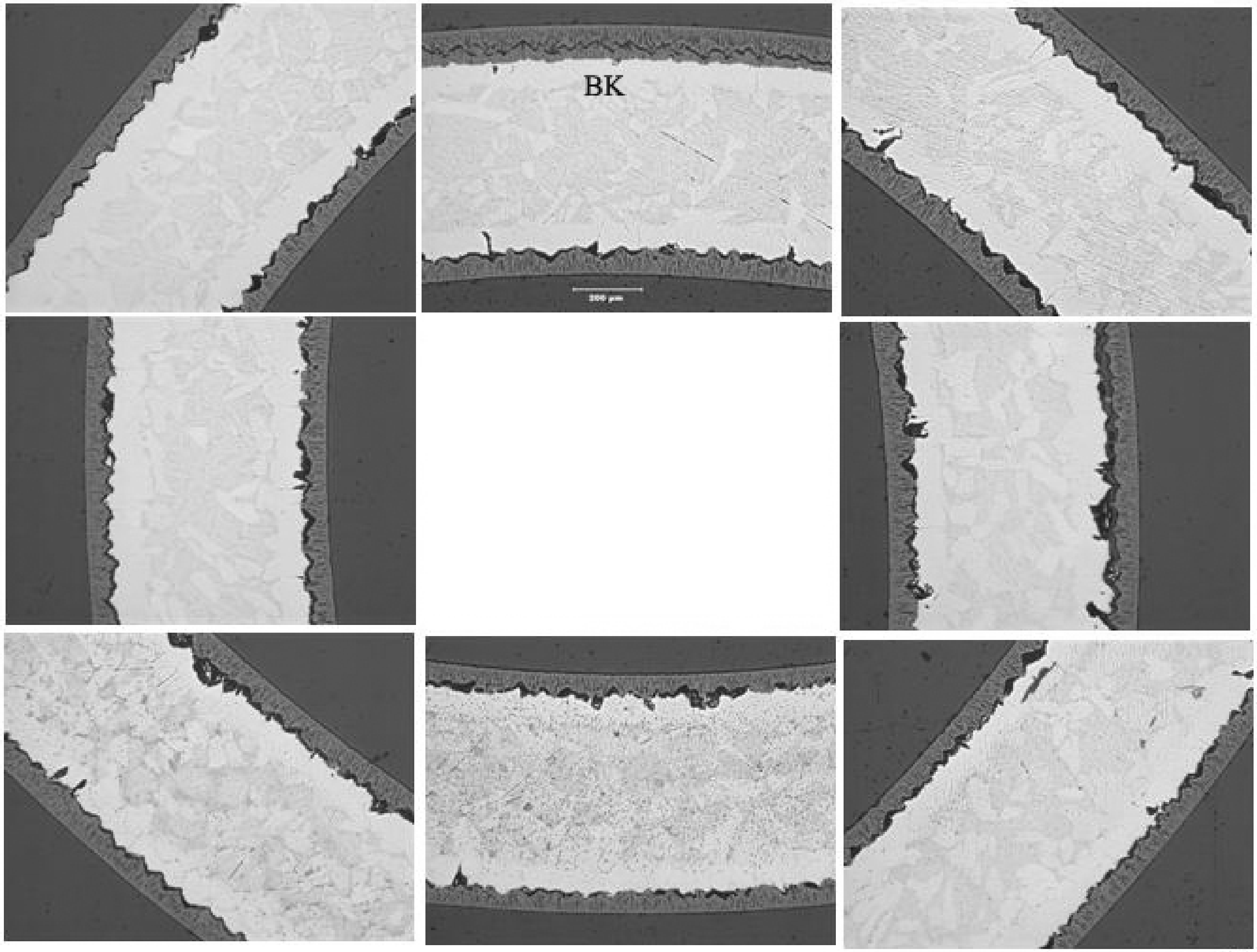
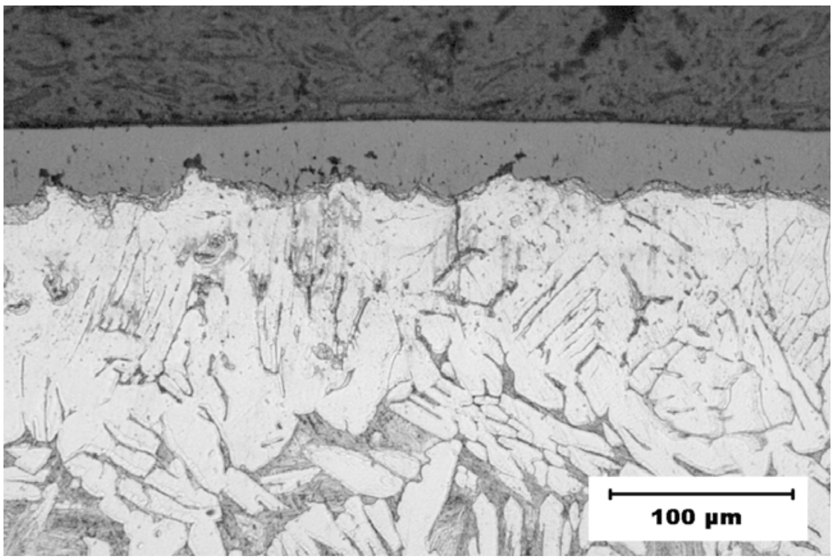
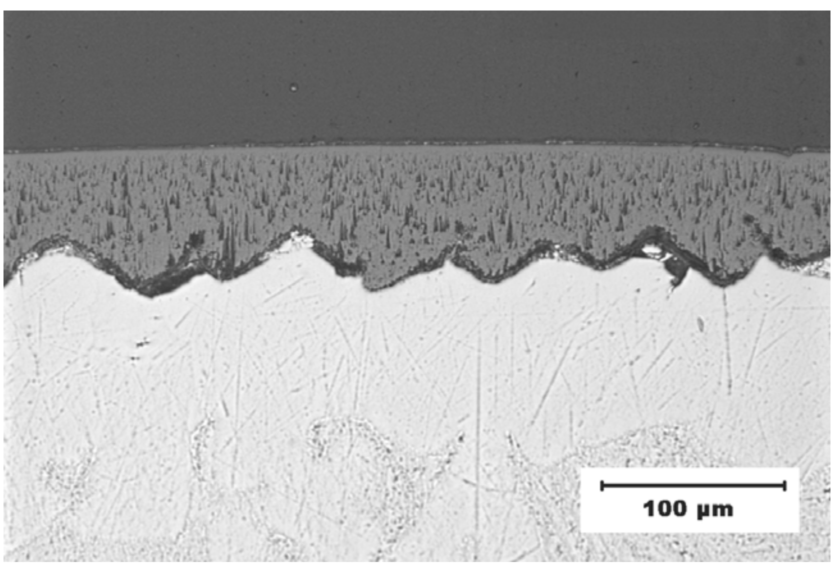


Fig. 7. Metallographic images at eight locations around the cross section of the BPZ4#18 sample tested at 1000°C for 5000 s, which show wavy interfaces between oxide and metal layers. Local breakaway oxidation was observed in Area BK.

Figure 8 shows the one-to-one comparison between M5 (a) and Zry-4 (b) outer-surface oxide layers. The small black regions at the metal-oxide interfaces are areas in which some oxide or oxygen-stabilized alpha “fell out” during grinding and polishing. More steps with finer grit would be needed to eliminate this artifact. Better surface preparation would improve the determination of the minimum oxide thickness, but not the maximum thickness. However, the quality of the micrographs is sufficiently high to determine differences in average oxide thickness and amplitude of the scallops. It is interesting to note from Fig. 6 that measured weight gains for Zry-4 are >10% lower than CP-predicted values for test times ≥3600 s. Based



(a)



(b)

Fig. 8. High magnification images of oxidation samples showing typical areas of the metal-oxide interface after 5000 s at ≈985°C for: (a) M5 and (b) Zry-4.

on these results and the scalloped region shown in Fig. 8b, it appears that the deviation from CP kinetics (parabolic) is due to suppressed local regions of oxide growth in areas where the oxide layer is thinnest. The CP-predicted value for oxide layer thickness (76 µm) is in better agreement with the measured maximum value (≈77 µm) than with average value (≈62 µm) for Zry-4 oxidized at a long-time hold temperature of 986°C for 5000 s.

Summary

Test results show that M5 exhibits very slow growth rate of inner- and outer-surface oxide layers at 985-1000ºC. The slow growth rate may also lead to slower growth of the amplitude of scallops at the metal-oxide interface. These scallops result in alternating tensile (minimum oxide thickness) and compressive (maximum oxide thickness) stresses. The regions with tensile stresses will tend to transform from tetragonal to monoclinic oxide, which will induce additional local stresses. A comparison between AREVA Zry-4 and AREVA M5 indicated that the amplitude of the scallops was twice as large at the Zry-4/oxide interface after 5000 s (breakaway time) than it was for M5 after 5000 s (no breakaway).

The new results generated for several ANL tests with and without temperature overshoot at 985°C indicate that M5 does not undergo breakaway oxidation for test times ≤5000 s. The results agree with the work of Mardon et al. [2] for which the breakaway oxidation time for M5 was interpolated to be ≈6400 s at 1000ºC based on 200-wppm hydrogen pickup.

References

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

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4. Procedure for Conducting Breakaway Oxidation Tests with Zirconium-based Cladding Alloys, Argonne National Laboratory, March 23, 2009; available online in NRC ADAMS as ML090840258 at http://www.nrc.gov/NRC/reading-rm/adams.html