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A thermogravimetric comparative study of the high temperature steam oxidation of bare and pre-oxidized Zircaloy-4, M5_{Framatome} and Optimized ZIRLOTM

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ABSTRACT

For LOCA analysis, high temperature oxidation kinetics in steam of Zircaloy-4 and the two Nb-bearing alloys used in French Pressurized Water Reactors (PWRs), $M5_{Framatome}^{1}$ and Optimized ZIRLO^{TM 2}, have been studied with the thermogravimetric technique, in the 900-1200°C temperature range. A specific test protocol for fast heating of the specimens in a high steam flow rate has been used. For as-received claddings, at 1100°C and above, oxidation kinetics is comparable and close to parabolic for the 3 alloys. Below 1100°C, significant deviation from the parabolic kinetic regime is observed and M5 _{Framatome} oxidizes slower than Zircaloy-4 and Optimized ZIRLO. The influence of pre-oxidation, simulating corrosion in normal reactor operation, has been investigated for Zircaloy-4 and M5_{Framatome}. A strong protective effect is observed below 1200°C, while at 1200°C the pre-oxidation layer appears to be much less protective, possibly because of the monoclinic to tetragonal zirconia transformation.

INTRODUCTION

In a Loss Of Coolant Accident (LOCA), oxidation in steam at high temperature of the cladding material is accompanied by strong heat production, contributing to the temperature escalation, and by massive gaseous hydrogen release, an important safety concern. The oxidation reaction also contributes to cladding weakening and can lead to rods rupture, massive fuel dispersion and finally loss of coolable geometry. Furthermore, the oxidation reaction. High temperature oxidation kinetics of the Zr nuclear grade alloys was therefore studied since the 50's, first for the Zircaloys family. Oxidation tests were initially performed with as-received materials, and the Emergency Core Cooling Systems (ECCS) acceptance criteria defined in 1973 [1] were based on oxidation tests campaigns using fresh Zircaloy-4 (the historical Zr-alloy for PWR), see ref. [2] for an exhaustive review of these experimental data. Later, the influence of the zirconia corrosion scale formed on the claddings during normal operation has been taken into account, either by using laboratory prepared pre-oxidized specimens [3-8] or with "true" irradiated defueled rods [9-12].

Most of the Zr-alloys high temperature oxidation tests are isothermal interrupted tests, where the weight gain, assumed to be due to oxygen uptake, is determined by weighting the specimen before and after a given exposure duration. A rather high number of tests is therefore required to establish a complete kinetic curve. For well controlled isothermal conditions, the heating and cool-down rate should be high. For this reason heating systems having low thermal inertia have often been used: laser heating [13], infrared lamp furnaces [9-12], and electromagnetic induction heating [3, 14]. Resistive furnaces, however, lead to easier temperature control and better homogeneity. For fast heating, the specimen can be maintained in a cold zone while the furnace is heated, inserted in the hot zone for a given duration, and finally extracted from the hot zone for fast cooldown, a protocol that has been used in many laboratories [3, 14],[15],[16],[7, 8, 17, 18]. For faster cooldown, the specimen may be quenched in water after extraction [7, 8, 17, 18]. Heating and cooldown rate achieved with this protocol are on the order of 100°C/s.

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² Optimized ZIRLO is a trademark or registered trademark of Westinghouse Electric Company LLC, its affiliates and/or its subsidiaries in the United States and may be registered in other countries throughout the world. All rights reserved. Unauthorized use is strictly prohibited. Other names may be trademarks of their respective owners.

An attractive alternative to the interrupted test protocol is the Thermogravimetric Analysis (TGA) technique, allowing online measurement of the specimen weight change during its reaction. A complete oxidation curve is obtained within a single experiment, and the reaction rate is straightforwardly derived by time derivation of the weight increase signal and can be analysed in term of oxidation regimes. TGA has been used in our laboratory and in others for cladding oxidation studies related to Spent Fuel Pool LOCA (SFP-LOCA) [19],[20, 21], [22],[23],[24], for which the temperature domain of interest is somewhat lower than for core large break LOCA. One of the limitations of the TGA technique is its low heating rate, few tenth °C/min for commercial, resistive furnace-based apparatus. For isothermal tests, the reactive gas thus must be injected after a heating phase under inert atmosphere. For high temperature oxidation tests, a question arises regarding possible alteration of the specimen during the slow and rather long (compared to the oxidation duration) heating phase. Specifically, with pre-oxidised cladding specimens, at least partial dissolution of the low temperature zirconia scale may occur during heat-up. Low permissible gas flow rates are a second limitation of commercial TGA apparatus. This can be a serious drawback for LOCA studies, due to the high oxidation rates of zirconium alloys at high temperature [19, 25]. This is probably the main reason explaining why this technique has been barely used in this domain. Few rather recent oxidation studies covering the temperature range of interest for in-reactor large break LOCA using the TGA technique have nevertheless been published [26-32]. In Refs. [29], [30] and [31], however, the steam flow rates used are low, and steam starvation conditions have to be suspected, as revealed for [29] and [30] by the high hydrogen concentrations incorporated in the metal during the oxidation tests, in conditions where they were not expected (away from the breakaway domain). The use of a low steam flow rate can have a significant impact on the oxidation process and its kinetics, as will be discussed in the present paper.

For the present study, sets of TGA steam oxidation tests have been performed with the Zircaloy-4, $M5_{FRAMATOME}$ and Optimized ZIRLO alloys (respectively referred to as Zy4, M5 and OZ in what follows) in the 900-1200°C temperature range. A commercial SETARAM thermobalance have been modified to accept high steam flow rates and a specific test protocol has been used to achieve high heating and cooling rates. Comparison is made between the three alloys and with results from interrupted tests. The influence of a low temperature pre-oxidation layer simulating in reactor corrosion is subsequently evaluated and discussed.

1. EXPERIMENTAL

1. Material

20 mm long tube specimen were cut from 17x17 PWR cladding tubes. The Zircaloy-4 tubes were provided by AREVA. For M5, two batches were used, provided by AREVA (now Framatome) (batch 1) and by Framatome (batch 2). Zy4 and M5 batch 1 were used for as-received and pre-oxidized specimens, M5 batch 2 for pre-oxidized specimens only, and OZ for as-received specimens only.

	Fab. year	Nb (%)	Sn (%)	Fe	Cr	O (%)	C (ppm)	Si (ppm)	S (ppm)	H (ppm)
Zy4 SRA	2000	<40 ppm	1.29-1.31	0.21-0.22 %	0.11 %	0.127-0.137	149-163	89-94	13-23	≤ 3
M5 batch 1	2004	0.99-1.01	< 30 ppm	303-328 ppm	41-44 ppm	0.139-0.149	22.26	<10	14-18	≤ 3
M5 batch 2	2019	0.97-1.00	< 25 ppm	345-390 ppm	< 50 ppm	0.130-0.140	70-80	<10	14-23	≤ 4
OZ	2021	0.9-1.0	0.65-0.70	0.10-0.12	56-69 ppm	0.113-0.124	<60	43-50	<25	<10

Table 1: Ingots mass composition (data from vendors)

2. Pre-oxidation

The objective of pre-oxidation is to form a zirconia layer on the cladding surface simulating, as far as possible, the waterside corrosion layer that grows on the cladding outer surface during normal in-reactor operation. As for previous studies [7, 33], cladding specimens were pre-oxidized in a resistive furnace at 425° C in a flowing O₂ + steam mixture. Depending on the alloy, the steam partial pressure was

adjusted to try to have similar amounts of hydrogen incorporated in the metal as the ones measured after waterside corrosion in PWRs. Table 2 gives the pre-oxidation conditions and main features of the different pre-oxidized batches prepared for this study: steam partial pressures of the furnace atmosphere, pre-oxidation durations, mean zirconia scale thicknesses (calculated from the weight gain assuming 97% dense zirconia and measured from radial cross sections when available), growth rates, hydrogen contents measured by hot extraction and equivalent hydrogen pick-up fraction (HPUF). This parameter is calculated assuming that only steam contributes to the oxidation. This is obviously not true, but as so the HPUF parameter is a measurement of the amount of hydrogen incorporated per amount of ZrO_2 formed, and gives a comparison point with the HPUF observed for in-reactor corrosion (17-18% for Zy4, 7-10% for M5). Note that because our pre-oxidations are double side, a given HPUF will result in a 2 times higher hydrogen incorporation than for single side corrosion. For M5, a first series was produced under 150 hPa steam partial pressure, leading to excessive hydrogen incorporation. For the second series the steam partial pressure was lowered to 12 hPa leading to hydrogen amounts closer to expectation. For two batches of this second series however, the hydrogen amounts incorporated were too high, likely because of misfunctioning of the steam flow controller. Figure 1 shows examples of cross section SEM images of pre-oxide scales grown on Zv4 and M5 cladding substrates.

	P _{H2O} (hPa)	Duration (day)	Mean pre-ox scale thickness from mass gain (µm)	Growth rate (µm/day)	Mean pre-ox scale thickness from metallography	H content (wppm)	HPUF (%)
Zy-4	150	256	26.5 - 32	0.1 - 0.125		300 - 360	8 - 9
M5 _{Framatome} 1st series	150	258	18 - 23	0.07 - 0.09		200 - 250	10 - 12
M5 _{Framatome} 2nd series	12	47	5.03	0.18	4.7 ± 1	30	4.2
	12	117	13.7	0.12	12.15 ± 1	45	2.3
	?	147	8.9	0.06	8.9 ± 1.1	80	7.2
	12	167	20.9	0.125	19.2 ± 2.0	50	1.8
	?	172	21.5	0.125	19.5 ± 1.3	170	7.2

Table 2: Main characteristics of pre-oxidized cladding batches



3. TGA Apparatus

A SETARAM single furnace thermobalance was used for the high temperature steam oxidation tests. A 30% steam + 70 % argon mixture was injected from the bottom of the furnace while a helium counterflow protect the balance measurement head from steam condensation. A type B thermocouple was point welded on each specimen for measurement of its temperature. It also serves as a convenient suspension device, suppressing the need of drilling holes in the tubes. As illustrated in Figure 2, different configurations were used: the thermocouple wires were welded on the lateral external face for asreceived specimens (Figure 2a). For pre-oxidized specimens, the thermocouple wires were welded on the upper end section, in two different points (Figure 2b) or in a single point (Figure 2c). Because the SETARAM furnace can achieve only moderate heating rates, the following test protocol was used: the furnace is first heated to the desired temperature, the steam + mixture is injected and after temperature stabilization the sample is lowered down into the hot zone. The resulting heating rate, as measured by the welded thermocouple, depends on the furnace temperature and the specimen initial state (as received or pre-oxidized). It varies between 15 and 100°C/s (Table 3). With as-received tubes, a temperature overshoot is observed due to the heat produced by fast oxidation of the bare material (see Figure 3). At 1200°C, the effect is quite strong (up to 160°C overshoot), but it lasts less than 20s. No such overshot was observed for pre-oxidized tubes.



Figure 2: a. Thermocouple welded on the lateral face (as received specimens). b and c. thermocouple welded on the upper-end face (pre-oxidized specimens).

T (°C)	Heating rate for as-received cladding (°C/s)	Temperature overshoot (°C)	Heating rate with pre-ox tubes (°C/s)
900	15-16	No overshoot	14-16
1000	35-41	25-30	24-29

T (°C)	Heating rate for as-received cladding (°C/s)	Temperature overshoot (°C)	Heating rate with pre-ox tubes (°C/s)	
1100	59-60	60-85	38-41	
1200	80-100	100-160	50	

Table 3: Heating rates and temperature overshoots



Figure 3: Heating temperature profiles for as-received and pre-oxidized specimens

4. Steam flow rate

Considering the test protocol used in the present study, where the experiment starts with the furnace opened, a high steam flow rate (FR) is required to avoid any air counterflow and undesired nitriding. Furthermore, due to the high oxidation rate of zirconium-based cladding materials at high temperature, fast renewal of the atmosphere around the sample surface is needed, which requires a high gas flow rate. Easy access of the gas phase to the sample surface, including the inner surface, is also a prerequisite. Under steam, away from any breakaway influence, that is for short exposure time or above 1050°C [14, 30], the oxide scale formed remains dense and hydrogen pick-up is not expected [34]. A high hydrogen content in the sample after oxidation would then be an indication of insufficient steam supply, because steam depletion and hydrogen enrichment of the atmosphere seen by the downflow part of the specimen surface would induce hydrogen incorporation there. Oxidation kinetics would be affected, because of slower oxidation of the parts of the surface that experience oxygen starvation conditions. This effect had sometimes been called "Hydrogen blanketing effect" [35]. Strong hydrogen picks-up were indeed reported after thermogravimetric oxidation tests by Steinbruck [29] as well as by Zino [30]. In Ref. [29], high hydrogen contents (up to 1500 wppm) were measured after the oxidation tests at 1100°C (the highest temperature investigated), for the four alloys studied (Zy-4, M5, E110, ZIRLO). The atmosphere was steam-reach (100% steam) and the flow rate was rather high (5 g/h), however a difficult access of the steam to the inner surface of the tubes may be suspected, due to the balance configuration (the specimens are not suspended but laid on a ceramic plate). In Zino's work [30], a SETARAM thermobalance was used whose configuration is close to the one used in the present study, however the steam flow rates were very low (< 0.5 g/h). For the two alloys studied and for a rather low temperature (1000°C), hydrogen pick-up were reported (up to 1000 wppm), in the beginning of the steam exposure [36]. The effect of low steam flow rate is illustrated in Figure 4 for the M5 alloy at 1000°C: TGA kinetic curves (i.e. derivative of the weight gain) from Zino [30], obtained for various flow rates in the range 0.09 - 0.45 g/h are compared to a test of the present study, obtained for a 58 g/h steam flow rate. A much higher oxidation rate peak is observed for the IRSN test and later, from about 100-200s, the rate becomes lower for the IRSN test. Plotting the rate as a function of the mass gain (or as a function of the

scale thickness calculated from the mass gain assuming a fully dense oxide), the influence of the steam flow rate is even more visible. Above about 10 μ m scale thickness, the oxidation rates measured by Zino are significantly higher than the one determined from the present study, suggesting that the hydrogen picked-up at the beginning of the tests may later affect the zirconia scale microstructure, resulting in a less passivating layer. However, we also have to keep in mind that a low steam FR will favor a nonhomogeneous scale growth, which may complicate the interpretation. A high steam FR is therefore required for non-biased kinetic measurements at high temperature. However, high FRs have been observed to have a negative impact on the temperature homogeneity inside the small thermobalance furnace. Finally, a compromise was chosen and most of the tests in the present study were performed with a 14.5 g/h steam FR. A comparison at 1200°C between tests performed at 100 g/h and 14.5 g/h steam FR is presented in Figure 5, showing similar mass gain rate between the two tests. From the point of view of the oxidation kinetics, a 14.5 g/h steam FR is therefore acceptable.



Figure 4: Influence of the steam flow rate (FR). TGA oxidation tests at 1000°C on as-received M5_{Framatome}. Mass gain rate plotted as a function of time (left) or as a function of mass gain and equivalent ZrO₂ thickness (right).



Figure 5: TGA tests on as-received M5 at 1200°C for two different steam FR

Hydrogen content after high temperature oxidation has been measured by hot extraction (LECO) on selected Zy4 and M5 samples, corresponding to oxidation conditions for which H pick-up is not

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expected. The results are presented in Table 4. Most of the specimens have very low H content, confirming the absence of hydrogen pick-up during the HT oxidation. Samples oxidized at 1200°C with a 14.5 g/h steam flow rate however show non negligeable amount of hydrogen incorporation. It means that this flow rate is insufficient to avoid steam starvation in the downstream part of the 20 mm long cladding tubes. However, the hydrogen contents remain moderate and below the 200 wtppm US-NRC breakaway criteria [34]. Most importantly, the consequence of the starvation on the oxidation kinetics is negligeable (Figure 5). These results, furthermore, show that none of the selected specimens have passed the breakaway transition.

Alloy	Oxidation temp. (°C)	Steam flow rate (g/h)	Duration (min)	H (wtppm)
Zy4	900	14.5	60	16 ± 5
	1000	14.5	60	36.5 ± 10
	1000	14.5	60	24.5 ± 7
	1100	14.5	30	17 ± 5
	1200	14.5	15	$\textbf{184.5} \pm 25$
	1200	14.5	15	101 ± 15
M5	900	58	30	4.5 ± 3
	1000	58	60	8.5 ± 3
	1000	58	60	5 ± 4
	1100	58	30	14 ± 5
	1100	14.5	30	15.5 ± 5
	1200	100	15	11.5 ± 4
	1200	14.5	15	$\textbf{128.5} \pm 40$

Table 4: Hydrogen content after HT oxidation.

2. TGA RESULTS

As received alloys

As received Zircaloy-4 was investigated first to validate the experimental protocol. In Figure 6, our thermogravimetric data are compared to results obtained from interrupted tests (samples weighted before and after oxidation) obtained at JAEA [9], KFKI [16], CEA [5, 37], and at our lab at IRSN [7, 38], all performed with low tin Zy-4 material. A globally good agreement between TGA tests and interrupted test is observed. It is worthwhile noticing the very good reproducibility of the TGA tests (5 tests performed at 1000°C and 3 tests at 1200°C) while significantly higher scattering is observed for interrupted tests. Figure 6 also depicts the predictions, for temperatures of 1000, 1100 and 1200°C, made with the Cathcart-Pawel correlation, derived from tests using high tin Zircaloy-4 [39]. The predictions tend to overestimate the TGA data and appears to be an upper bound of the interrupted tests.



Figure 6: Results on as-received Zy-4. TGA data compared to interrupted test results from JAEA [9], KFKI [16], CEA [5, 37] and IRSN [7, 38].

Same type of comparative work has been performed with as-received M5. In Figure 7 our TGA curves are compared with results of interrupted tests obtained at CEA [5], JAEA [40], and in our lab, as well as with thermogravimetric data from KIT [29]. Note that KIT TGA curves have been corrected before plot: in Fig. 2 of Ref. [29], a steep increase at t=0 when steam is injected in the thermobalance can be systematically observed on all weight gain curves at 900, 1000, 1100 and 1200°C. It is believed to be due to a hydrodynamic effect and have been subtracted from the published original curves. Again, a good reproducibility of our weight gain measurements is observed (2 tests are plotted at 1000, 1100 and 1200°C), and a good agreement with data points from interrupted tests can be observed. The differences between KIT and IRSN TGA curves can likely be attributed to the different test protocols and steam flow rates.



Figure 7: Results on as-received M5. TGA data compared to interrupted data points from CEA [5] and JAEA [40], and to TGA data from KIT [29].

For the present study, high temperature oxidation of as-received Optimized ZIRLO was investigated in greater details than for Zy4 and M5 because less data are available in the open literature for this alloy.

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Specifically, longer tests were performed, and additional temperatures were investigated around 1000°C, where breakaway oxidation is expected. TGA curves obtained with OZ specimens are plotted in Figure 8. Again, the good reproducibility of the data can be emphasized (tests were doubled at 950, 975, 1000, 1050 and 1100°C). For the duration investigated, breakaway transitions were observed at 975, 1000, 1025 and 1050°C. Breakaway times were determined from the minimum of the time derivative of the weight gain curves, leading to unambiguous and accurate values. Results are plotted in Figure 9. Breakaway time remains unchanged for the two tests doubled at 975 and 1000°C. Results are consistent with data found in the open literature for ZIRLO and confirm that the minimum breakaway time does occur at about 1000°C, as generally observed for other zirconium alloys.



Figure 8: Weight gain curves obtained with as-received Optimized ZIRLO specimens.



Figure 9: Breakaway time for Optimized ZIRLO (present study) and for ZIRLO (NUREG 6967 (2008) [41], Kim (2010) [32], Steinbrück (2011) [29]).

TGA weight gain curves obtained with as-received specimens are compared for the three alloys in Figure 10, for time <3600s. At 1100 and 1200°C, all the curves merge, showing that there is no oxidation kinetics difference between the alloys.

In contrast, at 1000°C, the weight gains vary very significantly from one alloy to another, in the following order: Zy4 > OZ > M5. In the present study, due to earlier breakaway for Optimized ZIRLO (2000 s) than for Zy-4 (3800 s), weight gain for OZ becomes higher than for Zy4 for exposure times > 4500 s. The same behavior had been observed by Steinbrück et al. with ZIRLO. However, this has not to be considered as a general conclusion because breakaway time for a given alloy may depend on many parameters (batch composition, surface state, steam flow rate, etc ...). Breakaway time at 1000°C ranging from 1500 to 5700 s were reported for Zy4 [36]. For M5, no breakaway transition was reported with recent batches, up to very long exposure (10000 s [5] or even 16000 s [36]). In the present study, no breakaway transition for M5 has been observed at 1000°C up to a test duration of 10000 s. At 900°C, TGA curves merge for Zy-4 and Optimized ZIRLO while the kinetics are slightly slower for M5. The better behavior of M5 over Zy-4 at intermediate temperature, earlier mentioned in [42] is confirmed.

For all temperature investigated and for the three alloys, experimentally measured mass gains are always lower than mass gains calculated from the Cathcart-Pawel correlation [43]. In other terms, the Cathcart-Pawel correlation is concluded to be a conservative approach to calculate zirconium alloy oxidation kinetics in steam at high temperatures.



Figure 10: Comparison of Weight gain curves obtained with as-received Zircaloy-4, M5 and Optimized ZIRLO at 1200, 1100, 1000 and 900°C. At each temperature, the Cathcart-Pawel (CP) correlation [43] is also plotted (black lines).

Pre-oxidized specimens

For pre-oxidized specimens, only the lateral inner and outer surfaces are covered with an oxide layer. The end surfaces are bare, either because the 20 mm samples were cut from longer pre-oxidized tubes, or, in the case of samples cut to 20 mm before pre-oxidation, because the end faces were polished after pre-oxidation to weld the thermocouple. As the mass measurements were intended to be representative of pre-oxidized surfaces, the measurements were systematically corrected for the contribution of the end faces, using the mass gain results obtained for as-received samples:

 $(\Delta m/S)_{corr} = [\Delta m_{exp} - (\Delta m/S)_{as-received} * S_{ends}]/S_{lat}$

where Δm_{exp} is the experimentally measured weight gain, $(\Delta m/S)_{as\text{-received}}$ is the weight gain per area unit for as-received samples, calculated from $(Kt)^{1/n}$ fits (see the discussion section) S_{ends} is the area of both end faces S_{lat} is the area of lateral inner and outer surfaces Furthermore, for tests at 1000 and 1100°C on 30 μ m pre-oxidized Zy4, a fairly marked edge effect was observed (Figure 11), reflecting initiation of the high-temperature oxidation at the tube edges, followed by axial propagation of the oxidation under the pre-oxide layer [33]. This effect is also clearly visible in the metallography. For these tests, the mass measurements were corrected for this effect, considering: i) axial propagation from the edges at constant speed, V. By measuring the axial extension of the affected zone at the end of the test (Figure 12b), V was estimated to be 0.22 μ m/s at 1000°C and 0.35 μ m/s at 1100°C; ii) in the zone reached by this propagation, oxidation kinetics corresponds to those of as received samples, calculated from (Kt)^{1/n} fits (see the discussion section). Thus, the contribution of the edge effect to the mass gain, which must be subtracted from the measured mass gain, is given by:

$$\Delta m_{edge \ effect} = 2 * V * \pi (D_{in} + D_{out}) \int_0^t k t^{1/n} dt \tag{1}$$

where D_{in} and D_{out} are the inner and outer diameters of the cladding tubes, respectively.

Finally, for the tests at 1000 and 1100°C with pre-oxidized Zy4, the measurements have to be corrected twice, from the contribution of the end surfaces and from the edge effect:

$$(\Delta m/S)_{corr} = [\Delta m_{exp} - (\Delta m/S)_{as\text{-received}} * S_{ends\text{-}} \Delta m_{edge\ effect}]/S_{lat}$$

These corrections, for end faces and edge effects contributions, lead to significant changes of the raw measurements, as shown in Figure 12. In particular, the edge effect correction becomes significant for long oxidation times. To test the validity of the correction calculated via Eq. (1), the volume of oxide formed at high temperature beneath the pre-oxide layer at the ends was assessed from metallography performed on an axial section of one specific specimen. The volume of the high temperature oxide was estimated from the area of the triangles drawn in red in Figure 12b, and the mass of this HT oxide was then subtracted from the final mass, giving the point shown in green in Figure 12a. The result confirms the validity of the correction by Eq. (1). For M5 specimens, despite a slight color change at the ends of the samples, metallographic cuts show that the edge effect was week and needs no correction.



Figure 11: pre-oxidized specimens after high temperature oxidation and metallographic cross sections of selected specimens.



Figure 12: a- TGA mass gain curves for a Zy-4 pre-oxidized specimen oxidized at 1000°C, showing the end faces and edge effect corrections. b- Metallographic cross section of the specimen from which the mass of high temperature oxide formed by edge effect was estimated.

TGA results obtained with pre-oxidized specimens are plotted as dotted lines in Figure 13 and Figure 14, for Zv4 and M5 respectively. Comparisons are made with TGA curves obtained on as-received specimens (full lines) as well as with data points obtained by interrupted tests on the OHTAVA furnace with pre-oxidized specimens, published in [7] for Zy4, not previously published for M5. For Zy4, 30 μ m thick pre-oxide have been tested with TGA, and the strong protective influence of a 30 μ m thick pre-oxide scale already observed throughout the interrupted test is confirmed. The protective effect is lower at 1200°C. A good agreement between TGA and interrupted tests is observed. For M5, the situation is more complex because different pre-oxide thicknesses and different pre-oxidation conditions have been tested. There is again a protective influence of the pre-oxidation layer, which increases as the pre-oxide thickness increases, but which also depends on the pre-oxidation conditions: for the highest steam partial pressure pre-oxidation conditions, where rather high hydrogen amounts were incorporated during the pre-oxidation, the protective influence of the pre-oxide scale is weaker. No clear explanation of this effect is proposed because no obvious difference between the microstructures of the pre-oxidation scales was observed on SEM images. Specimens having incorporated low hydrogen amounts are believed to be more representative of in-reactor corrosion. Interrupted tests were performed with specimens pre-oxidized with the lower steam partial pressure conditions, resulting in low hydrogen amount incorporated (30, 45 and 60 wtppm for 5, 10 and 20 µm pre-oxide scale thickness respectively) and should therefore be compared to TGA tests performed with same type of specimens. The agreement appears satisfactory.



Figure 13: TGA weight gain curves for 30 µm pre-oxidized Zy4 specimens (dotted lines) compared to the curves for as-received Zy4 (full lines). Data points obtained from interrupted tests with 30 µm pre-oxidized Zy4. Black lines calculated from Eq. (3), see the discussion section.



Figure 14: TGA weight gain curves for pre-oxidized M5 specimens (dotted lines) compared to the curves for as-received M5 (full lines). Data points obtained from interrupted tests with pre-oxidized M5. Black lines calculated from Eq. (3), see the discussion section.

DISCUSSION

Kinetic analysis of the pre-breakaway regime for as-received claddings

It is well established that oxidation of Zr alloys is an internal oxidation process (i.e. the new oxide forms at the M/O interface side) and is controlled by oxygen diffusion through the growing zirconia scale, as far as the zirconia remains dense, that is away from breakaway oxidation. The oxidation kinetics of Zr alloys at high temperature are often considered to be parabolic. However significant deviations from the parabolic regime have been reported in previous studies [26, 36, 44] and the kinetic regime can be better described using a variable n exponent rather than equal to 2 in the following equation:

 $\Delta m/S = (K t)^{1/n}$ (2)

where K is a constant depending on the temperature

Our weight gain curves have been fitted to Eq. (2) using the Excel solver. The datapoints for the first 100 s were discarded from the fit considering that the temperature at the beginning of the tests was not fully stabilized. As the shorter breakaway time was 2000 s (at 1000°C for OZ), the fits were for consistency initially limited to a 1800 s maximum time for all three alloys. However, for OZ, the results at 1000°C were observed to vary significantly if the maximum time considered is decreased to 1200 s. Finally, to be sure to avoid any influence of the breakaway transition on the n and K parameters, a 100-1200s time range was chosen for the fits. The time range was 100-900 s for tests at 1200°C.

Examples of fits at 1000°C are plotted in Figure 15 for the three alloys. For Zy4 and OZ, when approaching the breakaway transition, occurring at 2000 s for OZ and at 3800 s for Zy4, a rather strong deviation from the fit extrapolation is observed, reflecting a significant slowdown of the mass gain rate before the breakaway transition occurs. Such slowdown has already been reported for ZIRLO by Lee

and coworkers, and they have proposed that the formation of porosities at the metal/oxide interface is responsible of the slowdown [45]. We indeed observe voids at the M/O interface after 3600 s oxidation at 1000°C for Zy-4 (Figure 16a). Voids distribution seems to be correlated to the M/O interface undulation: voids are mostly found where the oxide scale is the thinner, suggesting that they limit the oxide inward progression and that they may be responsible of the weight gain slowdown. Such voids are not observed for M5 after 3600 s at 1000°C (Figure 16b), no breakaway transition was observed for the longer test duration (10000 s) and the experimental mass gain curve deviates only slightly from the (K t)^{1/n} fit. No such metallographic image is available for OZ as no test at 1000°C was interrupted before the breakaway transition.



Figure 15: TGA weight gain curves and fits with Eq. (2) for tests at 1000°C.



Figure 16: Cross sections of Zy4 and M5 specimens after 3600 s oxidation at 1000°C.

Values of the parameters n and K derived from the fits are given in table 5. The values of n are plotted in Figure 18 and compared with literature values derived from TGA experiments, and with values from interrupted tests performed on M5 at IRSN as well [46]. Considering that the experimental conditions may differ across studies, the steam flow rate in particular, and that the fit output depends on the time range considered for the fit, agreement between literature data and values from the present study is judged satisfactory. Roughly, we observe that n values are close to 2 at high temperature while at lower temperature, the n exponent tends to be higher, reaching values in the 2.5 - 3 range. The transition from a sub-parabolic (n>2) to a close to parabolic (n \approx 2) regime when the temperature increases seems to occur rather sharply, thus our data were fitted with an arctangent type function (Figure 17):

$$n = n_{min} + \left(\frac{n_{max} - n_{min}}{2}\right) \left(1 - 2\pi \arctan\left(\frac{T - T_0}{\beta}\right)\right) \qquad \text{Eq. (3) see Figure 17}$$

Where n_{max} and n_{min} are the max and min n values

T the temperature

 T_0 the temperature at which the transition occurs

 2β (in K) is the width to go from 25 to 75% of the $n_{min} - n_{max}$ interval.



Figure 17: Arctangent function used to fit n = f(T) data

The fits, plotted as dotted lines in Figure 18, tend to indicate that the transition from a sub-parabolic (n>2) to a close to parabolic (n \approx 2) regime occurs latter (that is above 1000°C) for the Nb-bearing alloys compared to Zircaloy-4.

Alloy	T (°C)	K (g ⁿ m ⁻²ⁿ s ⁻¹)	n
Zy4	900	3.64	2.61
	1000	8.03	2.18
	1000	8.46	2.20
	1000	8.96	2.20
	1000	7.88	2.16
	1000	8.44	2.18
	1100	24.04	2.13
	1200	426.39	2.50
	1200	330.38	2.43
	1200	145.86	2.27
M5	900	3.26	2.82

	1000	20.85	2.64
	1000	17.02	2.58
	1100	8.88	1.93
	1100	29.00	2.17
	1200	78.68	2.14
	1200	84.86	2.15
OZ	900	4.93	2.69
	950	17.29	2.74
	950	21.67	2.80
	950	15.50	2.69
	950	25.52	2.80
	975	11.53	2.49
	975	11.11	2.49
	1000	33.25	2.63
	1000	27.44	2.58
	1025	12.10	2.21
	1050	18.10	2.20
	1050	17.57	2.20
	1075	15.05	2.09
	1100	19.66	2.10
	1100	24.16	2.13
	1200	74.58	2.15

 Table 5: K and n values inferred from fitting experimental weight gain data to Eq. (1) in the 100-1200s time range



Figure 18: Exponent n inferred from Eq. (1) and fits with Eq. (2). Comparison with TGA data from Nagase et al. [44], Baek et al. [27], Kim et al.[32] and Zino [36], and from interrupted tests conducted at IRSN [46]. Dotted lines are fits of our data points with eq. (3)

Alloy	n min	n max	<i>Т</i> ₀ (К)	<i>β</i> (K)
Zy4	2.13	2.75	1250	10
M5	2.12	2.88	1287	10
OZ	2.15	2.74	1281	5.7

Table 6: n_{min} , n_{max} , T_0 and β parameters derived from fits of n values with eq. (2)

Theoretically, the so-called parabolic kinetic regime (n=2) means that the oxygen diffusivity in zirconia is constant over time [47]. Deviation from the parabolic regime below 1000°C was earlier observed for Zy4 [25] and later confirmed by many authors [26, 44, 48]. A n>2 exponent likely means that the oxygen diffusivity decreases over time while the scale is growing, but there is no consensus on the root causes of the decrease. Compressive stresses as well as the tetragonal to monoclinic phase transformation of zirconia are often cited as possible causes of the deviation from the parabolic regime, and these two effects may be coupled. Several studies have indeed evidenced that, due to the rather high Pilling-Bedworth ratio of the Zr/ZrO₂ system, compressive stresses develop in thermally grown zirconia scales (readers could refer to the review paper [49]). Even if most of these studies relates to normal operation temperatures, the few studies referring to higher temperature conditions [50, 51] confirm the existence of compressive stresses in thermally grown zirconia. Spatially resolved measurement techniques tend to show that a stress gradient exists across the scale, the compressive stresses being maximum close to the metal/oxide interface [51-54]. Compressive stresses are known to stabilize the t-ZrO₂ form of zirconia [52, 55] below its stability temperature domain (~1205-2377°C for stoichiometric zirconia [56]). Substoichiometry, i.e. oxygen vacancies in the anion sublattice, is also known to contribute to $t-ZrO_2$ stabilization at low temperature [57]. Therefore, as sometime evidenced by Raman investigations [51, 52], below 1200°C t-ZrO₂ will tend to form close to the M/O interface, where both the compressive stress level and the deviation from stoichiometry are high. While the oxide scale grows, the t- ZrO_2 grains formed at the interface move away from the interface and will tend to convert into m-ZrO₂. Then it can be understood that the proportion of t- ZrO_2 in a scale will decrease in relation to m- ZrO_2 as the scale is growing, and this has been well established by in-situ XRD studies [58-60]. As the oxygen diffusivity is several orders of magnitude lower for m-ZrO₂ [61, 62] than for t-ZrO₂ [63, 64], this would give rise to a decrease with time of the apparent mean oxygen diffusivity of the scale and therefore to a n>2 value. Zino and coworkers, using Zircaloy-4 substrate, have reported that above 1000° C, the t-ZrO₂ fraction remains constant with time, which is consistent with a $n \approx 2$ exponent.

Effect of pre-oxidation

All the TGA curves obtained with pre-oxidized specimens show that mass is gained as soon as the sample is heated and that the mass gain rate is continuously decreasing with time, for all temperatures investigated and for both Zy4 and M5. While this behavior is consistent with the growth of a protective layer on bare alloys, it is a priori surprising for pre-oxidized cladding specimens. Indeed, at least for the pre-oxidation conditions investigated in this study, the pre-oxidized scales formed have been observed to be mostly stoichiometric [7]. Therefore, one would have expected to observe an initial phase with null or very low mass gain rate at the beginning of the high temperature stage, corresponding to the time required to establish a gradient of oxygen vacancies across the pre-oxide layer, a gradient necessary to allow new oxygen diffusion towards the M/O interface and incorporation. On the contrary, the TGA data prove that oxygen is incorporated right from the start of the high temperature plateau. At first sight, one may propose a fast oxygen gas phase transport process through open porosities of the pre-oxidized layer. This is, however, contradictory to the clearly lower mass gain rate for pre-oxidized specimens compared to bare ones. This is also not consistent with data previously obtained at 850°C in our lab using ¹⁸O as a diffusion tracer, showing limited contribution from the porosity network in the preoxidized layer to the oxygen transport [65]. Instead, we should have in mind that oxygen diffusion from the pre-oxidized layer to the metal underneath and interlinked growth of a thick α -Zr(O) layer occur when the temperature rises. Oxygen vacancies are then created in the oxide close to the metal, eventually inducing oxide to metal conversion [7, 33]. Therefore, fast diffusion of vacancies and establishment of a gradient of oxygen vacancies across the pre-oxidized scale would explain incorporation of new oxygen from the gas phase right from the beginning of the high temperature stage.

Discussing the role of a pre-oxidized layer on high temperature oxidation, one also must consider the role of crystallographic phases of zirconia. Zirconia layers grown at 425°C have been observed to be mostly consist of the monoclinic phase, at least after cool down to room temperature, where Raman mapping took place [7, 65]. Contrarily, at high temperature, the tetragonal phase is predominant and above 1100°C only t-ZrO₂ grains form [58, 59]. As the oxygen diffusivity is several orders of magnitude lower for m-ZrO₂ compared to t-ZrO₂, the crystallographic composition (at high temperature) of both the pre-existing low temperature zirconia layer and the growing high temperature scale should have an impact on the high temperature oxidation kinetics. To gain insight on this aspect, we have calculated

what would have been the mass gain rate if the pre-oxidized layer offers the same passivation effect as a high temperature oxide scale having the same δ thickness. Using the kt^{1/n} adjustments of the TGA curves obtained on as-received samples, the mass gain rate would be:

$$[\Delta m/S) (t) = [K(t+t_1)]^{1/n} - [Kt_1]^{1/n}$$
 Eq. (3)

where t_1 is the time needed to form at high temperature a scale of thickness δ

This calculation has a physical meaning only if the oxygen diffusion coefficient remains constant as the oxide thickness increases, that is if the kinetics is parabolic. It was then performed at 1100°C and 1200°C only, where the n coefficient was close to 2. Curves calculated by Eq. (3) have been plotted as black lines in Figure 13 and Figure 14. At 1200°C, these calculated curves appear to correspond fairly well with experimental data obtained with pre-oxidized specimens, meaning that the pre-oxidized layer has the same protective effect as a scale of the same thickness formed at 1200°C. In other terms, oxygen diffusion through the two, low temperature and high temperature layers can be described by the same apparent diffusivity. Incidentally, it also tends to indicate that the porosity of the pre-oxidized layer (evaluated from SEM images to be about 5%, mainly due to the cracks between the sublayers and still present after high temperature oxidation [7, 65]) has no or minor influence on the oxygen transport. This is consistent with data obtained at 850°C in our lab using the ¹⁸O as a diffusion tracer, that seemed to indicate no oxygen ingress through porosities of the pre-oxidized layer [65]. At 1100°C on the contrary, experimental TGA curves are well below the calculated ones, showing that the passivation effect of the low temperature pre-oxidized layer is much stronger than the one of a high temperature scale. The explanation could be that the pre-oxidized layer remains mostly monoclinic at 1100°C and transforms into the tetragonal phase when heated to 1200°C. This is coherent with the Zr-O phase diagram, indicating a m to t-ZrO₂ phase transformation at 1205°C [56]. At 900 and 1000°C, even if curves calculated from Eq. (3) have not been plotted, it is clear that the protective influence of the pre-oxidized layers is also strong. Therefore, for LOCA oxidation modelling purposes and as a simplified approach, it is suggested that the effect of pre-oxidation could be calculated considering the 1200°C temperature as a threshold below which oxygen diffusion through the pre-oxidized scale is simulated using $m-ZrO_2$ diffusivity values and above which t-ZrO₂ diffusivity is preferred.

CONCLUSIONS

Thermogravimetric analysis (TGA) has seldom been used for LOCA cladding oxidation studies because the steam flow required for sufficient oxygen supply to the sample surface is high and generally incompatible with commercially available thermobalances. Analysis of the few studies available in the literature using this technique indeed shows that kinetic results can be significantly affected by steam starvation. Furthermore, slow heating rates of TGA apparatus require that the rather long heating phase has to be carried out in inert atmosphere. Such test protocol is, however, not suitable for measurements on pre-oxidized samples, since the pre-oxidized layer may be reduced, both chemically and in thickness, during the heating phase [7].

For the present study, steam oxidation tests have been performed in the 900-1200°C temperature range for three alloys, Zircaloy-4, $M5_{Framatome}$ and Optimized ZIRLO, first with as-received tubes then Zy4 and M5 specimens pre-oxidized at 425°C to simulate a pre-transient in reactor corrosion. A commercial SETARAM thermobalance was modified to facilitate high steam flow rates. A thermocouple welded on the cladding specimen was used as a suspension device to minimize the impact on the steam flow and for better control of the sample temperature. A test protocol including insertion of the sample in the hot furnace enabled the sample to rapidly reach isothermal conditions. Tests were highly reproducible and comparison with literature data and with data from interrupted oxidation tests have validated the test procedure.

For the as-received specimens, significant oxidation rate differences were observed between the three alloys in the low temperature range (1000°C and below), with a better behavior of the M5 alloy. At 1000°C, when approaching the breakaway transition, a marked slowdown of the kinetics was observed for Zy4 and Optimized ZIRLO. It was interpreted as being caused by the formation of porosities at the metal/oxide interface, which can be a precursor to the transition. No breakaway transition was observed for M5 up to long duration. Away from the breakaway transition regime, at 1100°C and above, the

alloy's composition seems to have no influence on the oxidation rate and the kinetic curves merge for the three alloys.

With pre-oxidized specimens, the protective influence of a zirconia layer, formed at low temperature, against high temperature oxidation is confirmed. Due to the stoichiometry of the zirconia, the pre-oxidized layer was initially expected to be non-conductive and a zero mass gain rate period was envisaged at beginning of the steam exposure. In contrast, the oxygen pick-up was observed to start immediately, likely meaning that a gradient of oxygen vacancies rapidly establishes across the pre-oxidized layer. Although the underlying physics require further studies, , the protective properties of the pre-oxidized layer is effective, and the mass gain rate is much lower than for bare claddings up to 1100°C. At 1200°C, the protectiveness becomes weak, probably because of the monoclinic to tetragonal zirconia transformation.

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FIGURE CAPTIONS

Figure 1: SEM cross sections of pre-oxide scales grown at 425°C in O2 + H2O. a. Zy4, 256 days; b. M5, 167 days
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