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Title Effect of pre-oxide and hydrogen on creep of Zircaloy-4 at 1123 K

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Highlights (85 caractères max espaces compris)

- Creep behaviour of pre-oxidized and pre-hydrided Zircaloy-4 was studied at 1123 K
- Pre-oxidation decreases creep rate depending on pre-oxide thickness and location
- Increasing the hydrogen concentration results in increasing the creep rate

Abstract

The creep behaviour of pre-oxidized and pre-hydrided Zircaloy-4 was investigated at 1123 K. Outer only and outer + inner pre-oxidation were considered in the study. The cladding creep rate decreases when the thickness of the pre-oxide layer increases and stabilizes for thicknesses higher than about 20 μm . The effect of pre-oxide is stronger in double-sided than in single-sided pre-oxidized samples and depends on the applied stress. Hydrogen increases Zircaloy-4 creep rate on both bare and pre-oxidized samples. The presence of high amounts of hydrogen, which induces the formation of significant quantities of β phase at high temperature, modifies the creep mechanism. During pre-oxidation, a network of regularly spaced radial cracks is formed on thick pre-oxide layers. At the beginning of the creep test, these cracks spread out throughout the oxide layer up to the $\alpha(\text{O})$ layer, where they stop. Finally, strain develops in the oxide-free zones.

1. Introduction

The purpose of the PERFROI project is to study the cooling of a nuclear reactor core during a Loss-Of-Coolant-Accident (LOCA), considering both the thermo-mechanical and thermohydraulic phenomena within the fuel assemblies. During this accident, the fuel assemblies of a nuclear reactor core can be partially or completely dried out. Under these conditions, the increase in fuel temperature and the pressure drop in the reactor core can lead to significant cladding strain, or even to fracture of the fuel rod cladding. The consequences of these geometry modifications on the core cooling efficiency during the injection of water by the safety systems are an important safety issue. The first axis of the PERFROI project concerns the thermo-mechanical study of the deformation and fracture of fuel rods under LOCA conditions. It includes thermo-mechanical creep and sample rupture tests (ELFE tests). The main objective of these tests is to accurately characterise the thermo-mechanical properties of the materials used in the DRACCAR data (IRSN software for the simulation of LOCA type accidents).

The deformation of the fuel rods during a LOCA transient is determined by the creep behaviour of the cladding. However, we mainly know the behaviour of bare (non-hydrided, non-oxidized) Zircaloy-4 (Zy-4) in the α and β domains. In the $\alpha+\beta$ domain, creep behaviour of bare Zy-4 is very

complex and experimental results are highly scattered. The mechanisms involved in the creep of bare Zy-4 depend on the domain considered, and on the applied stresses [1,2]:

- In the α domain at low stress (<15 MPa), creep is governed by the diffusion at the grain boundaries with an exponent n of the Norton law $\dot{\epsilon} = K(\sigma^n)$ close to 1.
- In the α domain at higher stress (> 15 MPa), the creep mechanism is sliding and dislocation climb. The values of the exponent n are in the vicinity of 5.
- In the β domain, it is the dislocation induced creep that governs the strain, with values of n in the vicinity of 4.
- In the $\alpha + \beta$ domain, the experimental data are dispersed due to the strong influence of the microstructure and the composition of the material on the mechanical behaviour. When Zircaloy is mainly in the α phase, a superplasticity mechanism by grain boundary sliding at the $\alpha - \beta$ interface accommodated by diffusion is proposed at around 1123 K for low stresses. At this temperature, the small amount of β phase (much more ductile than the α phase) forms a continuous film around the α grains, which promotes the interface sliding. When the temperature increases, the amount of β phase increases and forms grains that break the continuity around the α grains. Thus, the $\alpha - \beta$ interface sliding becomes less and less significant with a minimum ductility at around 1223 K. For high stresses, dislocation induced creep becomes dominant. The deformation laws proposed in the $\alpha + \beta$ domain relate only to low stresses with values of n close to 1.

The mechanical behaviour of zirconium alloys is highly dependent on the oxygen and hydrogen contents. Oxygen and hydrogen have opposite effects on the behaviour of Zircaloy [3-5]: the phase transformation temperatures and creep resistance increase with the amount of oxygen while they decrease with the increase in the hydrogen concentration. There are no data in the literature regarding the combined effect of both elements on the mechanical behaviour of Zy-4 in the $\alpha + \beta$ domain. This paper presents the effect of pre-oxide and hydrogen on the creep of Zircaloy-4 at 1123 K. The study is limited to one temperature but addresses the influence of other parameters as thermal and loading history, applied stress, pre-oxide thickness and location (single and double sided pre-oxide) and phase distribution on creep behaviour. Several thermal tests were also performed to characterize the changes in Zy-4 microstructure during the temperature plateau at 1123 K.

2. Materials and methods

2.1 Samples

The samples were machined from stress-relieved annealed, low-tin Zircaloy-4 cladding tubes provided by FRAMATOME (see figure 1). The outer diameter and thickness of the tubes are respectively 9.5 mm and 570 μm . The composition of the alloy is (supplier data): 1.3 wt% Sn, 0.21 wt% Fe, 0.10 wt% Cr, 0.13 wt% O, 10 wppm H.

Various states of the fuel cladding were tested:

- Bare Zircaloy;
- Pre-hydrided Zircaloy (hydrogen content \sim 130 wppm);
- Pre-oxidized Zircaloy. In service, the thickness of the inner pre-oxide formed inside the cladding in contact with the fuel can reach 10 μm , while the outer pre-oxide, formed by oxidation by

the pressurized water coolant can reach or even exceed 100 μm [6-7]. In order to limit the duration of pre-oxidation, the maximum thickness of the waterside corrosion pre-oxide has been limited to 70 μm . Two different pre-oxide configurations were studied: single-sided (SS, on external surface) or double-sided (DS, on external and internal surfaces, having similar or different thicknesses);

- Pre-hydrided (up to 1000 wppm) and pre-oxidized Zircaloy (up to 70 μm of pre-oxide thickness, both single-sided and double-sided).

Various hydriding and pre-oxidation methods were used:

- Gaseous hydriding at 693 K in a vacuum furnace;
- Pre-oxidation in dry oxygen at two different temperatures: 698 K (low temperature pre-oxidation) or 743 K (high temperature pre-oxidation). Under these conditions, the oxidation rates are respectively about 0.1 and 0.6 $\mu\text{m}/\text{day}$;
- Hydriding + pre-oxidation: gaseous hydriding followed by pre-oxidation in dry oxygen at a high temperature;
- Simultaneous pre-oxidation and hydriding: Pre-oxidation in a mixture of O_2 - 2% steam. This method allows hydrogen to be introduced into the Zircaloy during the pre-oxidation.

The materials are called Hx-Oy/z where x is the hydrogen content in ppm by mass and y and z are the thicknesses (in μm) of the outer and inner zirconia layers respectively. Thus, H400-O20/10 is a double-sided pre-oxidized Zircaloy with 20 μm (outer) and 10 μm (inner) thick pre-oxides and 400 wppm of hydrogen. x,y and z are rounded off to the nearest 10 (values lower than 150) or 100 (values higher than 150). The omission of Hx indicates a pre-oxidation in dry oxygen, with negligible hydrogen pick-up. However, few quantities of hydrogen are absorbed during pre-oxidation. The omission of z indicates a single-side pre-oxidized material. The different materials tested are presented in table 1. The standard deviations presented in the table are those of the set of samples concerned. The standard deviations of the measurements on one sample are comprised between 1 and 4 μm (for pre-oxide thicknesses) or between 2 and 26 wppm (hydrogen contents), the higher values, the higher standard deviations.

The samples are machined prior to pre-oxidation, in order to avoid damage to the oxide layer during machining. Hydriding is performed either before machining or during pre-oxidation. The pre-oxidized samples have pre-oxide layers on all surfaces (internal, external and lateral). To obtain samples with pre-oxide on the outer surface only (single-sided pre-oxide), the internal pre-oxide layer is removed by sandblasting over the reduced section. For samples with double-sided pre-oxide having different thicknesses at inner and outer surfaces (called e_{int} and e_{ext}), pre-oxidation was performed in two steps. The samples were first pre-oxidized up to obtain a first pre-oxide layer $e_{\text{ext}}-e_{\text{int}}$ thick. Then, the internal pre-oxide layer was removed by sandblasting. Finally, the samples were pre-oxidized again up to obtain an additional pre-oxide layer e_{int} thick.

2.2 Thermal test protocol

Thermal tests are carried out in a vertical resistance furnace (Model STF 15/610 from Carbolite). Segments of bare cladding and pre-oxidized cladding (10 and 50 μm of double-sided pre-oxide) are encapsulated in vacuum in quartz phials to prevent oxidation. The segments are subjected

to 2, 10 and 20 minutes thermal plateaus at 1123 K, then quenched in water. The temperature is controlled by one Type S thermocouple placed next to the furnace resistors. A second Type K thermocouple is used to measure the temperature next to the phial. At the end of the test, the phial drops into a water container placed under the furnace and is immediately fractured to allow quenching of the samples.

2.3 Tensile test protocol

Creep tests are carried out in the Figaro facility. They are performed in primary vacuum ($2 \cdot 10^{-2}$ - $5 \cdot 10^{-2}$ mbar) in a double-walled and water-cooled sealed furnace. The furnace resistors and the insulating basket are made of molybdenum. The load is applied with an electromechanical actuator with a nominal capacity of 2.5 kN. The stroke of the cylinder is 500 mm and the displacement resolution is 0.1 μm with speeds ranging between 0.001 and 500 mm/min. The applied load measurement is performed with a load cell calibrated up to 1kN in class 0.5. The expanded uncertainty ($k = 2$) of the load varies between 0.7 N (at 10 N) and 0.8 N (at 175 N).

For measuring and regulating the temperature during the creep tests, a K type thermocouple is welded onto the inner surface of the sample at mid-height of the reduced section. The temperature expanded uncertainty was estimated to be 6.0 K at 933 K and 2.9 K at 1233 K. This uncertainty is greater than the thermal gradient undergone by the sample region where the strain is measured: the axial gradient estimated to be lower than 1 K at 973 K and 1.5 K at 1273 K over 4 mm.

Marks perpendicular to the tensile axis are affixed to the external surface of the sample before the creep test. These marks, made of ceramic powder, are used for measuring the deformation during the test. The sample strain is measured without contact using a laser extensometer (Fiedler Optoelektronik brand P-50 model). The laser beam of the extensometer is focalised and reflected by marks. The system detects, over time, the position along the scanner axis of the upper and lower limits of the marks. This device enables the strain to be measured with an uncertainty lower than 0.05%.

The sample is heated at a rate of 2 K/s up to the test temperature. Once the set temperature is reached, the load is applied at a rate of 30 N/s. With the aim of saving time and material, each sample is loaded with different constant loads during one test. At the end of the test, the heating is switched off and the sample is unloaded.

The sample temperature, the applied load and the position of the boundaries of the marks placed on the sample are measured, during the test, as a function of time. If p_1 and p_2 are the positions of edges 1 and 2 respectively, the true strain between edges 1 and 2 is calculated by the formula:

$$\varepsilon_{1-2} = Ln \frac{p_2 - p_1}{p_{20} - p_{10}} \quad (1)$$

where p_{10} and p_{20} are the positions of the edges at the beginning of the test. The true strain uncertainty was estimated to be lower than 0.03% for the typical distance between marks (7 mm). The true stress (σ) is calculated assuming that the volume (V) of the deformed portion of the sample remains unchanged:

$$\sigma = \frac{F}{S} = \frac{F \cdot L}{V_0} = \frac{F \cdot L}{S_0 \cdot L_0} \quad (2)$$

F is the applied force, $L = p_2 - p_1$ is the distance between the two marks, S is the cross-sectional area of the reduced section and subscript 0 stands for initial value. For the pre-oxidized

samples, the cross-sectional areas were calculated without the pre-oxide layer. Thus the true stress is mean stress on the metal part of the sample, by removing the area occupied by the pre-oxide (considering that the pre-oxide does not support any load). The stress expanded uncertainty ($k=2$) was estimated to be between 1,4% at 10 MPa and 0.95 % at 50 MPa.

The strain rate ($\dot{\epsilon}$ or $d\epsilon/dt$) is calculated by means of the slope of the regression line strain-time ($\epsilon-t$). The associated uncertainty varies from 60% (for strains rates of about $1 \cdot 10^{-5} \text{ s}^{-1}$) to less than 6% (strain rates close to $1 \cdot 10^{-3} \text{ s}^{-1}$). To compare the results obtained at different stresses, the strain rates ($d\epsilon/dt$) were normalised in relation to the stress (σ in MPa) by $A \cdot (d\epsilon/dt)/\sigma^n$, where A ($\text{MPa}^n \cdot \text{s}$) is a constant and n depends on the stress and on the state of the material. n is equal to 1.3 for bare and single-sided pre-oxidized Zy-4 samples up to stresses close to 10 MPa and up to about 26 MPa in double-sided pre-oxidized samples (diffusion creep area in fig. 6). Otherwise, n is equal to 5 (dislocation creep area in the same figure). These stress exponents are proposed by Kaddour [2] for bare Zircaloy in the α domain. The values of constant A depend on the stress exponent and have been fixed to approach the normalized creep rates obtained with the two values of n : $A=1$ when $n=1.3$ and $A=16000$ when $n=5$.

For tests which lead to rupture of the samples, the distance between marks is measured before and after the test with a KEYENCE VHX-5000 microscope, in order to calculate the elongation after rupture, ϵ_R by the formula:

$$\epsilon_R(\%) = \frac{L-L_0}{L_0} \times 100 \quad (3)$$

L_0 and L are the distances between the marks delimitating the rupture zone (generally the central area of the sample) before and after the test. The uncertainty of ϵ_R is 0,4 %.

2.3 Sample characterization

Two segments are taken from each sample after pre-oxidation and/or pre-hydriding, as well as after testing: one for the hydrogen content measurement and the other for the metallographic examination. Hydrogen contents were determined by catharometry using a Brücker ONH mat 286 analyser. The first segment taken from the sample is cut into pieces of about 25 mg. Each piece is melted in a graphite crucible and the released hydrogen gas is then driven with the aid of a carrier gas to the measuring cell. The calibration of the device is periodically checked with certified standards. The second segment taken from the sample is embedded in resin for polishing and metallographic observation. The metallurgical observation of the samples is carried out using an optical microscope (LEICA DMR), a digital microscope (KEYENCE VHX-5000) and an electron microprobe (CAMECA SX 100) equipped with five WDS (Wavelength Dispersive Spectrometers).

The metallographic examination reveals the formation, during the creep test, of an $\alpha(\text{O})$ phase layer on the surface of the bare samples and under the oxide layer of the pre-oxidized samples. For the bare samples, it is an indication that the very small residual quantities of oxygen in the furnace are sufficient to induce some Zircaloy oxidation during the thermal transients. The thicknesses of the zirconia layers and the $\alpha(\text{O})$ phase were measured on the inner face and outer face at 4 different positions.

Chemical mapping of the samples was performed with the electron microprobe to characterize

the Fe distribution in the Zircaloy microstructure. This mapping was performed on 100x100 μm^2 surfaces with 0.25 μm steps and acquisition time of 300 ms/dot. Considering the high contrast in Fe partitioning between α and β phases, the Fe maps were transformed into binary images with the aim of measuring the β phase fraction for each sample after the tests. Nevertheless, the β phase fraction could only be estimated in samples with noticeable quantities of β phase and clearly delimited phase-boundaries, which corresponds to samples with high H-contents and thermal treatment samples subjected to 20 minutes plateaus. Oxygen concentration profiles in thermal test samples were measured by microprobe over the entire thickness of the cladding at 1 to 2 μm intervals.

3. Results

Considering the overall creep test results, the strain rates can be affected by several parameters: the oxygen and hydrogen contents, the quantity and location of the pre-oxide (single or double-sided), as well as by the thermal and mechanical history undergone by the material. All of these factors will be analysed in the following sections.

3.1 Effect of the pre-oxidation method

In order to determine the influence of the pre-oxidation process on the creep rates, Zy-4 samples were pre-oxidized by different methods. However, no differences have been observed in the microstructure or in the creep rates for similar materials pre-oxidized with the different methods. Circumferential cracks and corrugation of the pre-oxide-metal interface are observed in all types of pre-oxide (see fig 2). Conversely, the appearance of the outer surface of the samples varies depending on the thickness of the pre-oxide layer (see figure 3). The 10 μm pre-oxide surface, which is smooth and greyish, becomes light brown on pre-oxides of thickness greater than about 20 μm and crazed on pre-oxides thicker than about 28 μm .

3.2 Effect of thermal and mechanical history

Variations in the creep rate were observed as a function of the duration of the thermal plateau and the loading history. With the aim of saving time and substance, a single sample was loaded with different constant loads during the same test. In most tests, the sample was subjected to increasing and decreasing loads to check whether or not there was any loading history effect. It was observed that, in tests conducted at 1123 K and under certain conditions (detailed below), the creep rate increases when the sample has previously been submitted to high stresses. This was observed in the short-duration tests carried out on pre-oxidized Zy-4 (with low hydrogen contents), when the sample is subjected to stresses $\sigma_1 \leq 15$ MPa after plateaus at $\sigma_2 \geq 17$ MPa. Conversely, in the absence of pre-oxide, Zy-4 does not seem to be affected by an earlier loading.

Two tests were performed at 1023 K on pre-oxidized Zy-4 ($e_{\text{ZrO}_2} = 12 \mu\text{m}$) with the purpose of checking whether the effect of the loading history can also be observed in the α domain. However, the values of the creep rates measured in the increasing and decreasing load plateaus were similar.

Consequently, the Zy-4 creep in the α domain does not seem to be sensitive to the sample loading history.

The tests performed on bare Zy-4 at 1123 K showed that, in low-stress tests (which are slow), the creep rate diminishes with the duration of the test, which is an effect that is not observed at lower temperatures, or with high stresses (quick tests). In order to check whether this is still valid in the presence of pre-oxide, a test was performed at 1123 K on Zy-4 with 10 μm of single-sided zirconia. In this test, the increasing and decreasing load plateaus were applied after 30 and 60 minutes of stabilization time at 1123 K. The results of the test are presented in figure 4 and show that the creep rate diminishes with the stabilization time. The values obtained after 1 hour at 1123 K are of the order of 100 times lower than those measured without hold time.

Various creep rates are measured during each ELFE test. Thus, except for creep rates measured during the first stress plateau of each test, some time elapses between the start of the thermal plateau and the beginning of each creep rate measurement. Figure 5 shows the changes in the normalized creep rate for bare and pre-oxidized (10 μm , single-sided) Zy-4 with the time elapsed at 1123 K before the start of the measurement. As illustrated in the graph on the right, the decrease in the creep rate is negligible for plateaus lasting less than 200 s. However, as from 1800 s, it is significant (see the graph on the left in figure 5). The creep rate values affected by the thermal and mechanical history were systematically disregarded.

3.3 Effect of pre-oxide

In order to study the effect of the pre-oxide on the creep rate, tests were performed on samples with two pre-oxide configurations: single-sided (SS, with pre-oxide only on the outer surface) and double-sided (DS, with pre-oxide on the inner and outer surfaces). Figure 6 shows the creep rates obtained with both configurations and compare them with those of bare Zy-4. The creep rate decreases in the presence of pre-oxide layers and depends on the applied stress and the location of the pre-oxide. At 10 MPa, the creep rates of both kinds of pre-oxide are close and disperse. They can be up to 10 times lower than those of bare Zy-4. At 20 MPa, the decrease in the strain rate is very significant for cladding with double-sided pre-oxide, while the creep rates measured on samples with single-sided pre-oxide layers are only slightly lower than those measured for bare cladding. Beyond 30 MPa, the creep rates of double-sided pre-oxidized Zy-4 approach those of single-sided pre-oxidized and bare Zy-4. The normalised strain rate values are shown in figure 7 as a function of the pre-oxide thickness for low hydrogen samples ($[\text{H}] < 130$ wppm). As SS and DS pre-oxidized samples are not differentiated, the values are highly dispersed. As can be seen in the figure, the presence of a pre-oxide layer decreases the cladding creep rate, mainly for small pre-oxide thicknesses. As the thickness increases, this effect is mitigated and it becomes independent from the pre-oxide layer thickness for thicknesses higher than about 20 μm .

No crack was observed at the surface of non-pre-oxidized samples. However, when the samples are pre-oxidized, the pre-oxide layer is always cracked after having undergone a creep test (see figure 8). The cracks are always perpendicular to the direction of the mechanical load; however their shape depends on the initial thickness of the pre-oxide layer: they are straight on 10 μm pre-

oxides, but crooked on very thick pre-oxides (higher than about 28 μm). No difference was observed in the cracks formed on the oxide of the pre-hydrided Zy-4 relative to those formed on the non-hydrided material.

3.4 Effect of Hydrogen

The effect of low concentrations of hydrogen (~130 wppm) on the strain rate was studied for both non-pre-oxidized and single-sided pre-oxidized Zircaloy-4, while higher hydrogen contents (400-1000 wppm) were investigated for pre-oxidized samples either single-sided or double-sided. The creep rate measurements at 1123 K are illustrated in figure 9 and compared to those of non hydrided Zy-4.

The presence of around 130 wppm of hydrogen can slightly increase the Zy-4 creep rate with a stress of 10 MPa (triangles in upper graph). Conversely, small quantities of hydrogen do not seem to have any noticeable effect on the cladding strain at 20 MPa. No differences have been observed between creep rates of both SS pre-oxidized + pre-hydrided materials (H90-O10 and H700-O60, white diamonds in upper graph). Thus, at 1123 K, hydrogen content and thickness of the external pre-oxide layer seem to have little effect on strain rate for this type of material.

The effect of hydrogen on DS pre-oxidized samples is presented in the lower graph of figure 9. Despite the scattering of creep rates of DS-pre-oxidized + pre-hydrided samples (squares), it can be noticed that pre-hydriding increases creep rates for DS-pre-oxidized Zy-4, particularly at high stresses.

This apparent inconsistency between results for SS and DS pre-oxidized samples can be explained by the behaviour of hydrogen in the samples during the tests. The hydrogen contents of H700-O60 samples (single-sided pre-oxidized samples), that are around 680 wppm before the tests, halve down to around 300 wppm at the end of the tests. On the contrary, the hydrogen concentration remains rather constant in double-sided pre-oxidized samples: hydrogen contents measured after the tests are comprised between 400 wppm (in H400-O20/10 samples) and 770 wppm (in H1000-O60/10 samples). Figure 10 presents the microstructure of both materials after the creep tests. The figure shows the absence of hydrides in a zone at the vicinity of the internal surface of H700-O60 sample (the surface that is not covered by a pre-oxide layer). On the contrary, hydrides are observed under all the interfaces metal-pre-oxide near the outer surface, even where oxide spalling has occurred. The normalised strain rate values as a function of hydrogen content at different pre-oxide thicknesses are presented on figure 11. In spite of the high dispersion of the values, it can be seen that hydrogen increases the Zy-4 creep rate on both bare and pre-oxidized samples (SS and DS). It has to be noticed that for high stresses and high hydrogen contents, the effect of the creep rate due to hydridding compensates and even overcomes the decrease of the strain rate caused by pre-oxidation. This way, H1000-O60/10 samples present faster deformations than bare Zy-4 at 30 MPa (see lower graph of figure 9).

The Fe-maps of the DS-pre-oxidized + pre-hydrided samples after the creep tests are presented in figure 12 while the β phase fractions measured are presented in table 2. It can be clearly observed that the quantity of β phase measured after the tests increases with the hydrogen content in the samples: it rises from ~20 % to more than 30 % when the initial hydrogen content increases from 400 to 1000 wppm.

Only few isothermal tests were conducted until rupture. Nevertheless, these tests allow observing the effect of pre-oxidation and pre-hydriding on rupture strain (see figure 13). This figure shows that rupture strain ϵ_R , decreases when the pre-oxide thickness increases: ϵ_R is close to 200% in bare samples and decreases to about 50 % in samples with outer pre-oxide thicknesses about 60 μm . Hydrogen do not seem to affect the rupture strain under isothermal conditions. The small number of tests performed did not enable to observe if the location of pre-oxide (DS or SS) influences the rupture strain.

3.5 Evolution of the sample microstructure as a function of the high-temperature exposure time

In their initial state, before creep tests, the samples are made of Zircaloy in the α phase (with some hydrogen) either covered or not with a layer of zirconia. During high temperature exposure, oxygen and hydrogen exchanges may take place between the sample and the atmosphere of the furnace causing variations in the content of these two elements in the samples. In parallel, in the pre-oxidized samples, the oxygen contained in the oxide layer migrates toward the metal. Thus, a $\alpha\text{-O}$ layer is formed at the interface between the oxide and the metal and at the same time Zircaloy becomes enriched with oxygen. At the same time, once the $\alpha \rightarrow \alpha + \beta$ transformation temperature has been exceeded, a certain fraction of α phase is transformed progressively into β phase, and this proportion varies as a function of temperature and hydrogen and oxygen contents.

The measurements of the oxidation layer thickness and phase fraction contents are carried out after the tests and may be influenced by the atmosphere of the furnace and the cooling time. To overcome these problems and in order to measure the changes in the microstructure and the distribution of the α and β phases over time at 1123 K, some specific thermal tests were performed: segments of bare cladding and DS pre-oxidized + pre-hydrided cladding (O10/10 and H200-O50/50) were encapsulated in vacuum in quartz phials and subjected to thermal plateaus lasting 2, 10 and 20 minutes at 1123 K, and then quenched in water. No noticeable change in the zirconia thickness has been measured after these tests. Conversely, the thickness of the $\alpha\text{(O)}$ layer increases with the duration of the plateau, regardless of the thickness of the initial pre-oxide (see figure 14). On bare samples, the mass uptake is null and no oxidation layer is formed, which shows that the samples are not subjected to external oxygen sources during these specific thermal tests.

Changes in the microstructure of bare and pre-oxidized + pre-hydrided samples observed after the thermal tests as a function of the oxide thickness and of the duration of the thermal plateau are presented in figure 15. To make the figure more understandable, the microstructures of the thin pre-oxide sample (O10/10) and those obtained after 10 min are omitted. At the beginning of the thermal plateau (2 min), small β phase grains (black dots on the BSE images, white dots on the maps) precipitate homogeneously in the α phase of the bare sample. On pre-oxidized samples, the β phase also forms in the α grain boundaries (see the cavities in the BSE images): locally in the material with a fine layer of pre-oxide (O10/10) and in a more generalised way in the H200-O50/50 material. As the duration of the thermal plateau increases, the β phase migrates from the inside of the α grain towards boundaries. After 20 minutes at 1123 K, the β phase is mainly located around α grains. However, differences in the grain boundary distribution can be found: in the bare and the O10/10 samples, the

grain boundaries are partially surrounded with β phase; in H200-O50/50 samples, the β phase entirely surrounds the α grains. The β phase fractions for samples exposed during 20 min at 1123 K are presented in table 2. It can be observed that the β phase content increases with pre-oxidation + pre-hydrating treatment. As previously explained, the small size and dispersion of the β phase observed in the samples subjected to shorter thermal plateaus avoid the measurement of reliable β phase fractions.

Figure 16 shows an example of an oxygen profile measured over the cladding section in the radial direction. The dotted line indicates the exact location of the profile measurement. Three different layers can be identified inside the cladding using the oxygen profile: the pre-oxide layer at the outer surface of the cladding, with a high oxygen concentration; the metallic layer at the inner part of the cladding, with oxygen content close to the nominal content of the bare alloy (0.13 wt%); and between the two, the $\alpha(O)$ layer with an oxygen concentration ranging between 7 wt% at the $ZrO_2/\alpha(O)$ boundary and the nominal content of the metal at the $\alpha(O)/\text{metal}$ boundary. The oxygen profiles measured did not show any variation in the oxygen concentration of the metal with the duration of the thermal plateau, only the growth of the $\alpha(O)$ layer was evidenced.

5. Discussion

On pre-oxide layers with thicknesses greater than around 30 μm , a network of regularly spaced radial cracks has been observed by various authors [8-9]. This network of cracks gives the outer surface of the sample a snake-skin appearance, like that observed on the ELFE samples with 40 and 70 μm of pre-oxide (see figure 3). The cracks are caused by the creep of the metal subjected to tensile stresses generated by the oxide growth [9]. In the absence of an external mechanical load, cracks have a length shorter than the pre-oxide thickness and do not reach the metal. Thus, in pre-oxides at least 30 μm thick, some of the cracks formed during the pre-oxidation develop and propagate, during the creep test, through the pre-existing network of cracks, with the crooked appearance seen in figure 8. In 10 μm thick pre-oxides, where no crack has formed during pre-oxidation, cracks developed during the creep test are perfectly straight.

Figure 17 shows various cracks observed after a creep test on a sample with 40 μm of pre-oxide arranged from the finest opening to the largest, giving an insight into the process of formation and growth of cracks. Cracks formed on the outer surface of the pre-oxide during pre-oxidation, advance up to the $\alpha(O)$ layer where they stop. Then, the cracks open out and the edges of the cracks move parallel to the cladding surface. At the same time, the $\alpha(O)$ layer at the end of the crack is thinning. Finally, once the $\alpha(O)$ layer has practically disappeared at the front of the crack, strain continues to a level leading to rupture in zones stripped of oxide and $\alpha(O)$ layer (see the picture at the bottom of figure 17). Consequently, the strain is concentrated in the oxide-free zones. A similar mechanism has been previously observed by different authors on bare samples under steam at temperatures higher than 1273 K [10-11]. Nevertheless, it is necessary to keep in mind the fact that ELFE tests are performed in vacuum and that in the presence of an oxidizing atmosphere (steam during a LOCA) the naked crack tip should oxidize, which is likely to change the strain process (particularly during low strain rate creep).

The creep mechanisms proposed for bare Zy-4 in the α domain can be extended to pre-oxidized material at 1123 K (see figure 6): diffusion creep at low stresses (with $n \sim 1$ in the Norton law $\dot{\epsilon} = K(\sigma^n)$) and dislocation creep at high stresses (with $n \sim 5$). The large gap between the creep rate of SS and DS pre-oxidized samples at 20 MPa might be explained by the activation of the dislocation creep mechanisms in SS pre-oxidized samples, whereas the DS pre-oxidized samples remain controlled by diffusion creep.

As illustrated in figure 9, at high stresses, creep rate of DS pre-oxidized samples is more sensitive to stress when they are pre-hydrided. For H1000-O60/10 samples (orange squares), the exponent n of the Norton law is close to 10, while for H400-O20/10 materials (white squares), n ranges between 5 (DS-pre-oxide, blue circles) and 10 (H1000-O60/10). Values of n higher than 8 have been observed in dispersed phase alloys [12]. At 1123 K, Zircaloy-4 is in the $\alpha + \beta$ domain. At this temperature, the amount of β phase strongly increases with the hydrogen content while it is minimally affected by the presence of up to 2 wt% of oxygen [13]. Under equilibrium conditions, the amount of β phase formed in Zy-4 at 1123 K increases with hydrogen content from $\sim 20\%$ in bare materials [14] to $\sim 90\%$ in samples with 1000 wppm of hydrogen [15]. It has to be taken into account that, during the tests, the samples remains less than ~ 200 s at 1123 K and that β phase does not form instantaneously but progressively. According to Koo [16], the quantity of β phase formed at the end of the tests should be less than 50% of that expected at equilibrium. Consequently, the quantity and distribution of β phase evolves all along the test.

Hydrogen contents in single-sided oxidized samples (H700-O60) halve during the test while the hydrogen loss is significantly lower on pre-hydrided materials protected with double-sided pre-oxide. This change in hydrogen concentration probably explains the small effect of hydrogen on the strain rate of single-sided pre-oxidized samples compared to double-sided ones (see figure 9). ELFE tests are performed under vacuum and hydrogen can be released from the sample through the internal surface of the cladding which is not covered by a pre-oxide layer. Under vacuum, hydrogen can leave the sample in various ways:

- Mainly through the non-pre-oxidized surfaces (as the inner surface in SS pre-oxidized samples);
- To a lesser extent through the pre-oxide. The pre-oxide layer has a protective effect and the hydrogen loss diminishes in DS pre-oxidized samples;
- Small losses are also expected through the oxide-less zones after cracks propagation. In ELFE samples, hydrogen concentration increases from the edges to the center of the reduced section (which concentrates the strain of the samples). Hydrogen migrates towards the zones submitted to tensile stresses [17], as the most strained zones (under the cracks). Finally, hydrogen can leave the sample by the oxide-free surfaces on the crack tip.

Under steam, hydrogen should penetrate into the sample by similar mechanisms but in the opposite direction. However, hydrogen intake will be limited by the oxidation of oxide-free surfaces.

During the tests, variations in the creep rate were observed at constant temperature and stress, as a function of the duration of the thermal plateau and the loading history. There is no significant variation in the creep rate of non hydrided materials with the duration of the plateau at 1123 K for

periods shorter than 200 s. However, it is significant beyond 1800 s. The decrease in the creep rate over time at high temperatures for bare Zircaloy had already been observed by Garde, who explains this behaviour by the changes in the microstructure with the duration of the thermal plateau [18]. At 1123 K, the equilibrium structure of Zircaloy-4 consists in a large volume fraction of α phase and a small volume fraction of β phase, more ductile than for the α phase. Initially, β phase forms both as a continuous thin film at the α grain boundaries and within the α grains. As the hold time at high temperature increases, β phase tends to coalesce at the triple points of the α grains. When the quantity of β phase increases, continuity of the β phase film diminishes, as well as plasticity. In ELFE tests, the effect of the thermal history was observed for both bare and pre-oxidized samples. Nevertheless, oxygen and hydrogen can affect the changes in the microstructure with the duration of the thermal plateau, modifying both the phase fraction and the phase distribution. The thermal tests were performed to observe changes in the microstructure as a function of the thermal plateau duration at 1123 K. At the start of the thermal plateau, small β phase grains are precipitated uniformly in the α phase of the bare sample, while on the pre-hydrided samples small quantities of β phase form also at the α grain boundaries. As the duration of the thermal plateau increases, the quantity of β phase increases at the same time as the β phase, previously formed inside the α grains, migrates towards the grain boundaries. The presence of pre-oxide, on the contrary, does not seem to affect the distribution of the phases in the metal since no increase in the oxygen concentration was measured on the samples exposed to thermal tests, only the growth of the $\alpha(O)$ layer is observed.

For most of the tests, the pre-oxidized samples underwent increasing and decreasing loading plateaus. In some cases, the creep rate measured for decreasing plateaus can be higher than that measured on increasing plateaus for a given stress. This phenomenon is observed when the following conditions are met:

- For stresses lower than around 15 MPa. Most of the tests were performed on samples with 10 μm of SS pre-oxide, for which the boundary between the two creep regimes (diffusional creep and dislocation induced creep) is located between 10 and 20 MPa. We can thus assume that the loading history affects only the creep mechanism dominating at low stresses (grain boundary sliding + diffusion)
- For pre-oxidized samples (whether they have been pre-hydrided or not). Thus, oxygen plays a role in the creep rate increase caused by the loading history: either by the modification of the phase distribution (which can facilitate grain boundary sliding), or by the increase in the diffusion rate.
- After stresses greater than around 17 MPa, which are the typical stresses for the dislocation induced creep regime. Thus, the introduction of defects produced by this type of creep can promote diffusional creep. Another explanation could be that when the pre-strain is carried out at lower stresses, the material deforms slowly and the thermal aging can cancel out the effect of the loading history.
- In the $\alpha+\beta$ domain (at 1123 K) while the Zy-4 creep in the α domain (1023 K) does not seem to be sensitive to the sample loading history. Under these conditions, the effect is linked to the presence of the β phase.

– In short tests; when hold time at 1123 K is less than 200 s. Conversely, when pre-strain is applied after a thermal plateau of at least 1800 s, this effect is not observed and the creep rate decreases instead of increasing. Thus, the decrease in the creep rate due to hold time at high temperature dominates over the increase due to pre-strain. However, Garde observed that the effect of thermal history disappears on bare Zy-4 when pre-strain is applied before the thermal plateau (0.3% pre-strain at 973 K). He explains this fact by the introduction of defects and dislocations, which allow the precipitation of β under fine edges resulting in the limitation of the β phase coalescence and ductility maintenance after 120 minutes.

In summary, the increase in the creep rate for pre-strained cladding observed in the two-phase domain in the presence of oxygen could be explained by the introduction of defects and dislocations that promote diffusion and/or grain boundary sliding.

6 Conclusions

In order to simulate the in service corrosion of the cladding, samples have been pre-oxidized and pre-hydrided. Various pre-oxidation and pre-hydriding methods have been tested, without however revealing first order differences in the microstructure of the materials or in the creep rates of the samples obtained with different methods. Thus, the most simple and quickest method was chosen for preparing the samples: pre-oxidation at 743 K in a mixture of O_2 and steam.

The phenomenology governing the creep behaviour of Zy-4 in the two-phase domain is complex and depends on many parameters that affect the phase distribution: temperature, duration of the heat plateau, thermal and loading history, applied stress, presence of oxygen and how it is supplied (pre-oxide, test atmosphere, pre-oxide location), hydrogen content... However, the decrease in the creep rate observed in some cases appears to be related to the coalescence of the β phase at the periphery of the α grains.

The presence of a pre-oxide layer decreases the cladding creep rate. This effect is already important for small pre-oxide thicknesses, and increases for oxide thicknesses up to about 20 μm where it stabilizes. Creep rate decrease depends on the applied stress and on the location of the pre-oxide: it is stronger in double-sided than in single-sided pre-oxidized samples, in particular at stress levels close to 20 MPa.

The short duration of the tests limits the effect of pre-oxide and hydrogen on the cladding microstructure. This way, the diffusion of oxygen from the pre-oxide to the metal results only in the growth of a small $\alpha(O)$ layer at the metal/pre-oxide interface while no additional supply of oxygen is detected in the metal. In parallel, the β phase that develops and redistributes during the creep test, remains in quantities far below the values expected at equilibrium for Zy-4 with high hydrogen contents.

Two flow regimes can be distinguished in Zy-4 at 1123 K: diffusional creep at low stresses and dislocation induced creep at high stresses. Creep laws of pre-oxidized Zy-4 (both single-sided and double-sided) at 1123 K seem to follow the stress exponents proposed by Kaddour [2] for bare Zircaloy: $n=1.3$ at low stresses and $n=5$ at high stresses. The boundary between the two creep regimes, lower than 20 MPa in SS pre-oxidized cladding and bare Zircaloy-4, increases to more than

20 MPa in DS pre-oxidized samples. This fact can explain the large gap observed between the strain rates of DS and SS pre-oxidized cladding at 20 MPa.

Hydrogen increases Zy-4 creep rate on both bare and pre-oxidized samples at 1123 K. In pre-hydrided + DS pre-oxidized samples, the exponent of the Norton law at high stresses and high hydrogen contents increases up to values close to 10. The presence of high amounts of hydrogen, which induces the formation of significant quantities of β phase at high temperature, modifies the creep mechanism. This way, hydriding can compensate and overcome the decrease of the strain rate caused by pre-oxidation. Thus, H1000-O60/10 samples present faster deformations than bare Zy-4 at high stresses.

ELFE tests were performed under vacuum. In SS pre-oxidized samples, hydrogen can easily desorb from the sample through the internal surface of the cladding which is not covered by a pre-oxide layer. As a result, the apparent non-effect of hydrogen content on the strain rate of SS pre-oxidized Zy-4 is probably an artefact due to the loss of hydrogen during the creep test.

Variations in the creep rate were also observed at constant temperature and stress, as a function of the duration of the heat plateau and loading history. The creep rate shows no significant variations with the duration of the plateau at 1123 K for periods shorter than 200 s. However, these variations are significant beyond 1800 s. Consequently, it is necessary to pay attention to thermal and mechanical scenario of the tests when using the data of the bibliography.

During pre-oxidation, a network of regularly spaced radial cracks is formed on pre-oxide layers thicker than about 30 μm . During the creep tests, these cracks, which are initially located in the outer part of the oxide layer only, spread out throughout the oxide up to the $\alpha(\text{O})$ layer, where they stop. Then, the $\alpha(\text{O})$ layer at the crack tip becomes deformed. Finally, strain develops in the oxide-free zones. This mechanism is similar to that previously observed by different authors on bare cladding under steam at temperatures higher than 1273 K.

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