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Hydrogen motion in Zircaloy-4 cladding during a LOCA transient

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Abstract. Hydrogen and oxygen are key elements influencing the embrittlement of zirconium-based nuclear fuel cladding during the quench phase following a Loss Of Coolant Accident (LOCA). The understanding of the mechanisms influencing the motion of these two chemical elements in the metal is required to fully describe the material embrittlement. High temperature steam oxidation tests were performed on pre-hydrided Zircaloy-4 samples with hydrogen contents ranging between 11 and 400 wppm prior to LOCA transient. Thanks to the use of both Electron Probe Micro-Analysis (EPMA) and Elastic Recoil Detection Analysis (μ-ERDA), the chemical elements partitioning has been systematically quantified inside the prior-β phase. Image analysis and metallographic examinations were combined to provide an average oxygen profile as well as hydrogen profile within the cladding thickness after LOCA transient. The measured hydrogen profile is far from homogeneous. Experimental distributions are compared to those predicted numerically using calculations derived from a finite difference thermo-diffusion code (DIFFOX) developed at IRSN.

1. Introduction

During a LOCA transient, the fuel cladding tubes are subjected to high temperature steam oxidation before core reflooding. During this type of accident, metallurgical evolutions due to α-β phase transformations and partitioning of oxygen/hydrogen but also of the main alloying elements is observed in the material. These phenomena have a strong influence on the material mechanical properties [1]. The microstructure results in a complex distribution of oxygen and hydrogen within the cladding thickness. At 1200°C, the hydrogen has low affinity for α(O) and an excellent solubility in the β-phase. During high temperature oxidation, most of the hydrogen moves towards the β-phase and is expected to remain in the prior β-phase after quenching [1, 2, 3]. The understanding of the mechanisms influencing the motion of these two chemical elements is required to fully describe the post-quenched embrittlement.

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This study aims at determining oxygen and hydrogen concentrations in cladding materials after a LOCA transient. Several 70 mm long Zircaloy-4 samples are pre-hydrided with hydrogen contents ranging between the as-received content (~ 10 wppm) and 400 wppm. The samples are then steam oxidized at high temperature (1200°C), to simulate LOCA conditions, and quenched in a water bath at room temperature. The microstructure of the material, especially the phase distributions within the cladding thickness, is systematically characterized by metallography. Local oxygen and hydrogen distributions are specifically investigated using Electron Probe Micro-Analysis (EPMA) and micro Elastic Recoil Detection Analysis (μ-ERDA). Image analysis and metallographic examinations are combined to provide average oxygen profile as well as hydrogen profile within the cladding thickness after LOCA transient. Experimental average radial distributions are then compared to those predicted numerically using calculations derived from the DIFFOX code developed at IRSN [4].

2. Materials and methods

2.1. Materials

The specimens investigated in this study have been cut from low tin 17x17 SRA Zircaloy-4 fuel cladding tubes provided by AREVA-NP. The tubular samples are 70 mm long, have a 9.5 mm outer diameter and a 570 μm thickness respectively. Chemical composition of the tested material is detailed in Table 1.

Table 1. Chemical composition of the tested Zircaloy-4

Sn (wt %)	Fe (wt %)	Cr (wt %)	O (wt %)	H (wppm)
1.3	0.21	0.10	0.13	10

2.2. Experimental process

2.2.1. Hydrogen gaseous charging. The hydrogen gaseous charging of the 70 mm long cladding tubes is performed at the École Centrale de Paris. Each Zircaloy-4 sample is inserted in a quartz tube under high vacuum heated by a furnace at 420°C. Pure hydrogen is injected into the quartz tube. The charging temperature is chosen sufficiently low to avoid cladding recrystallization while permitting homogenous distribution of hydrogen in the sample. The sample is then slowly cooled down at 20°C/h to obtain large circumferential hydrides and uniformly distributed across the sample thickness. After gaseous charging, tubes are cut into 20 mm long segments for the oxidation. Thin samples are also cut for hydrogen measurements and metallographic analysis.

2.2.2. High temperature oxidations. Two-sided steam oxidations are performed in a vertical furnace at 1200°C in a mixture of argon and steam. The argon and steam flow rates are respectively 10Nl.min-1 and 500g.h-1 (50 vol% argon and 50 vol% steam) in order to prevent steam starvation and limit hydrogen pick-up. Oxidation durations are adjusted to reach ECR (Equivalent Clad Reacted) values of 15, 20 and 25%. The ECR is assessed using Cathcart-Pawel correlation assuming inner and outer wall oxidation [5]. Oxidation is interrupted by dropping the sample into a water bath at room temperature. The hydrogen content is also measured after oxidation for each sample by hot extraction. The microstructure of the material, especially the phase distributions within the cladding thickness, is characterized by metallography. Oxygen profiles are systematically measured using EPMA on each radial cut.

2.3. Samples characterizations

2.3.1. Hydrogen content measurement

The hydrogen content of the samples is measured using a Brücker ONH mat 286 by melting the sample at 1500°C in the presence of a carrier gas (argon). The hydrogen is then released in the device. The hydrogen content is determined by catharometry comparing the conductivity of the mixture with the one of pure argon. For 70 mm long tube samples, four axial locations are systematically

characterized. A minimum of four analyses at each axial location are performed to check the homogeneity of hydrogen content.

2.3.2. Metallography examination

After oxidation, two cross sections are cut are at each end for all the tested samples for metallography. The thicknesses of the oxide and □(O) layers are systematically measured at four different angular locations at both outer and inner surfaces on each metallographic radial cut. The phase distribution of the samples is estimated by image analysis based on a half ring metallography reconstruction. The metallography is first transformed into a binary image of the two phases in the metal. This binary image is then used to determine the radial profile of α (O) phase fraction. An illustration is shown in Figure 1.

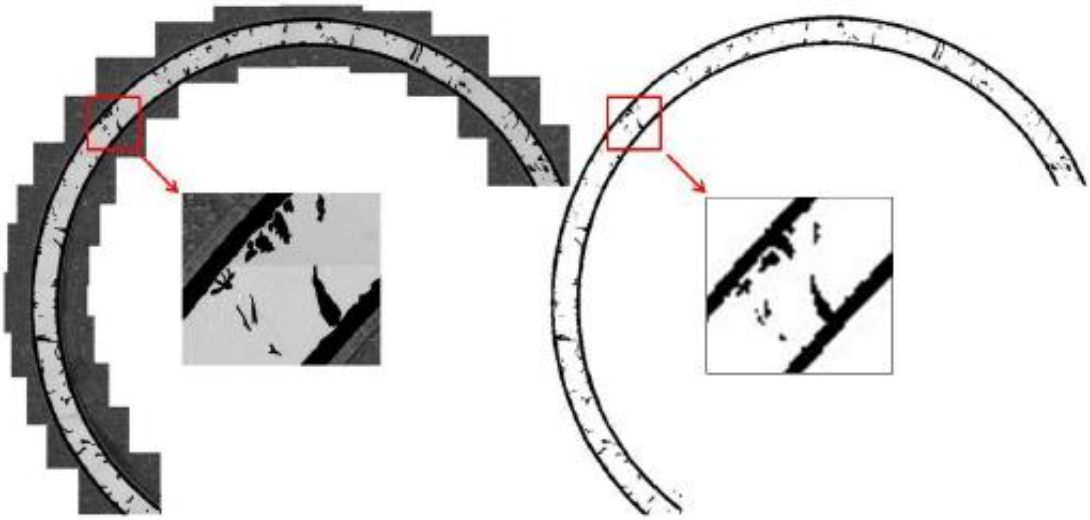

Figure 1. Example of the reconstruction and the binarisation of the optical microscopies (H66-7)

2.3.3. Electron Probe Micro-Analysis (EPMA)

Each radial cross section of the samples is embedded in a conductive resin with an as-received Zircaloy-4 sample. A mechanical polishing and then a chemical etching with a fluohydric acid solution is performed before introduction in the microprobe vacuum chamber. Oxygen K□ line is measured with a W/Si multi-layer synthetic crystal. Zircaloy-4 standards with homogeneous and known oxygen contents are used to perform oxygen calibration. The oxygen measurement uncertainty is estimated to ± 0.2 wt%. All the profiles are measured within the thickness with 1 µm stage displacement step in each phases and 250 nm stage displacement step at the zirconia/α(O) and α/prior-β interfaces. Points analysis are also performed in the α(O) inclusions, the α(O) layer and in the prior-β-phase.

2.3.4. Elastic Recoil Detection Analysis (ERDA)

The hydrogen distribution and quantification within each phase of the material are quantitatively measured at a microscopic scale using micro Elastic Recoil Detection Analysis (µ-ERDA). A 3 MeV 4He+ incident beam with an intensity of 500 pA is focused on the sample at a glancing angle of 15° with respect to the sample surface. Hydrogen atoms ejected by elastic collision are collected with a Si surface barrier detector placed symmetrically, with a 15° grazing angle. The energy of recoil hydrogen atoms is related to the depth from which they are scattered to the surface (the deeper hydrogen is located, the higher is the energy loss). Measurements are performed using a 3x2 µm² beam size and a 1x1 µm surface scanned step. Due to the grazing incidence, the actual beam size increases by a factor 4 according to the horizontal axis. Scan durations are about 4 to 5 hours to obtain 400x100 µm² maps.

The hydrogen measurement uncertainty is estimated to ± 10%. A homogeneously hydrided Zircaloy-4 sample is used to determine the accuracy of ERDA analysis. The hydrogen contents measured by sample fusion and by ERDA of this sample are respectively 190 ± 43 wppm and 207 ± 20 wppm.

3. Results and discussions

3.1. Chemical elements partitioning

Alloying element segregation within the cladding samples are systematically analyzed using EPMA. During the high temperature oxidation, some strong partitioning of the chemical elements occurs within the thickness of the cladding tube due to the oxygen diffusion and the associated progressive transformation of the β-phase into an oxygen stabilized α(O) layer [6, 7]. Typical illustration of the concentration profiles for alloying compounds obtained using EPMA are presented in Figure 2. The residual prior-β phase is enriched in iron and chromium consistently with their β-stabilizing properties. On the contrary, oxygen is segregated into the α phase. The chromium concentration follows a diffusion-like profile whereas tin is uniformly distributed into the two phase region without any noticeable segregation.

Experimental oxygen distributions are compared to the predictions of a 1-D finite-difference code developed by IRSN to model the oxygen diffusion equations [4]. The calculations accurately determine the α-layer thickness but strongly underestimate the oxygen content within the α(O) inclusions in the α(O)+β regions. EPMA indicates that in the α(O) inclusions and in the prior-β phase, the oxygen content is constant but different in each of the two phases. Consequently, using the α(O)-phase radial distribution, it is possible to determine the equivalent averaged oxygen radial profile. A rather continuous oxygen profile is obtained between the α(O) layer and the two-phase region. Experimental and calculated profiles are illustrated in Figure 3.

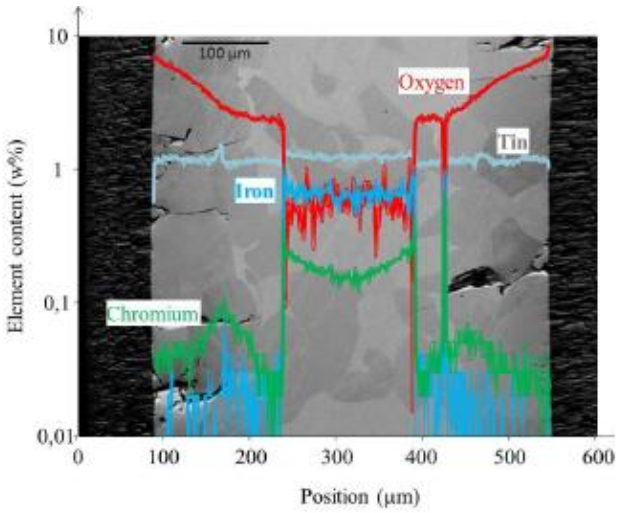

Figure 2. Typical concentration profiles in chemical elements alloy obtained by EPMA after oxidation at 1200°C during 624s

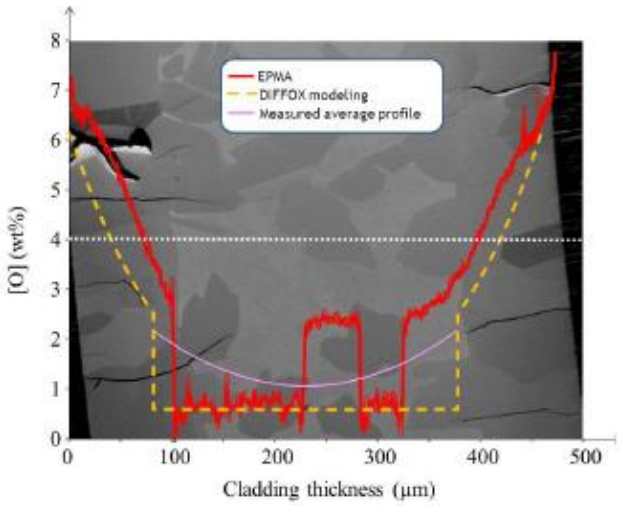

Figure 3. EPMA oxygen profiles versus Diffox modeling and measured average profile taking into account phases distribution

3.2. Local hydrogen quantification

Electron Recoil Detection Analysis (ERDA) has been performed on some oxidized samples to determine the hydrogen distribution within the cladding material. A typical map obtained by ERDA is illustrated in Figure 4. A hydrogen enrichment of the β-phase and depletion of the α(O) phase is evidenced. A local hydrogen enrichment is also observed around the α(O) grains in the beta side in agreement with Rapsaet study [2]. Far from α(O)-prior β grain boundaries, the hydrogen is

homogenously distributed and its local content is close to equilibrium concentration. ERDA measurement was further used to determine hydrogen diffusion profile normal to grain boundaries from α(O) layer to the homogeneous prior-β phase. The hydrogen enriched layer is about 25 µm thick in the beta phase. A typical hydrogen diffusion profile derived from the hydrogen content analyses normal to a grain boundary is illustrated in Figure 5.

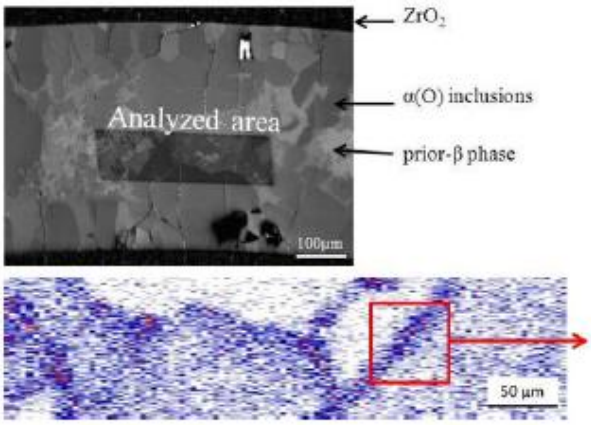

Figure 4. Hydrogen distribution measured by ERDA after oxidation at 1200°C during 624s

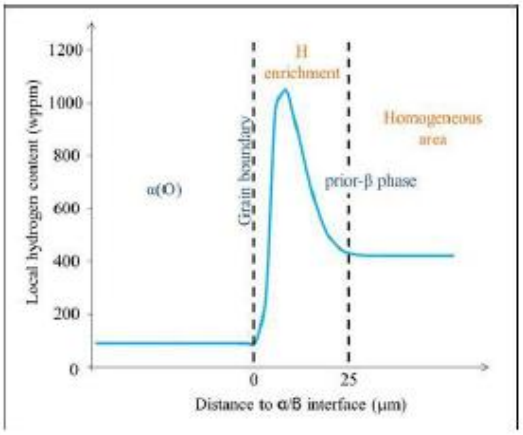

Figure 5. Hydrogen diffusion profile measured by ERDA in the red area

As for oxygen content, an assessment of the averaged hydrogen content along the radial direction is obtained by combining the α(O)-phase radial distribution assuming equilibrium concentrations in each of the two co-existing phases. The measured average hydrogen profile shows continuity at α(O) layer and two-phase region. This profile is plotted in Figure 6. Hydrogen follows a complex profile within the cladding thickness controlled by the inclusion distribution in the two-phase domain. Hydrogen migrates from hydrogen depleted regions towards hydrogen rich regions implying that its motion is not governed by usual concentration gradients but most probably by more complex processes.

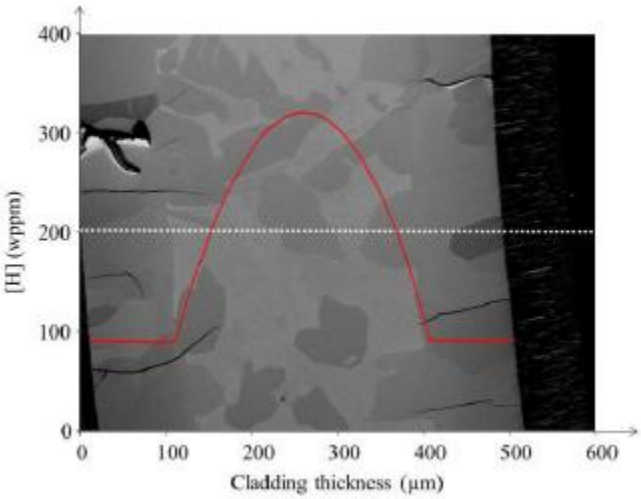

Figure 6. Hydrogen measured average profile taking into account phases distribution

4. Conclusions and perspectives

The present study addresses oxygen and hydrogen average contents in a Zircaloy-4 cladding after a LOCA steam oxidation transient. Within the samples, special attention was paid to the region with co-existing α(O)+βphases. This region is not homogenous and considering 1-D diffusion modeling, a special data treatment has to be performed to compare experimental data to modeling results.

Using ERDA and EPMA measurements, the distribution of the main alloying elements within the steam-oxidized cladding samples was thoroughly characterized. The main chemical compounds are close to equilibrium except far from α/β grain boundaries. At these locations, Cr and H are locally not homogeneously distributed whereas other elements like oxygen and iron are rather homogeneously distributed in each phase, without any measurable local enrichment for these two last elements. Additionally, the α(O)-phase radial profile was derived from metallographic analysis.

Considering these experimental observations and assuming that the phase contents are uniform, radial profiles of oxygen and hydrogen have been determined. The oxygen profile is compared to diffusion simulations using the DIFFOX code. The code prediction shows that improvements are necessary to better model the diffusion of both oxygen and hydrogen in the mixed phase region.

5. Acknowledgment

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