



## Chemical and microstructural characterization of a 9 cycle Zircaloy-2 cladding using EPMA and FIB tomography



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### HIGHLIGHTS

- The composition of the material changed extremely after 9 cycles.
- Hydrides in the metal are depleted in Fe and Ni compared to that of the matrix.
- The micro-crack structure of a formed oxide does not change with irradiation.
- Crack volume fraction in the oxide increases considerably with increasing cycles.
- Hydride oxidation could be a cause of the increasing H-uptake at high burnups.

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### ABSTRACT

A high burn-up Zircaloy-2 cladding is characterised in order to correlate its microstructure and composition to the change of oxidation and hydrogen uptake behaviour during long term service in the reactor. After 9 cycle of service, the chemical analysis of the cladding segment shows that most secondary phase particles (SPPs) have dissolved into the matrix. Fe and Ni are distributed homogeneously in the metal matrix. Cr-containing clusters, remnants of the original  $Zr(Fe, Cr)_2$  type precipitates, are still present. Hydrides are observed abundantly in the metal side close to the metal-oxide interface. These hydrides have lower Fe and Ni concentration than that in the metal matrix.

The three-dimensional (3D) reconstruction of the oxide and the metal-oxide interface obtained by Focused Ion Beam (FIB) tomography shows how the oxide microstructure has evolved with the number of cycles. The composition and microstructural changes in the oxide and the metal can be correlated to the oxidation kinetics and the H-uptake. It is observed that there is an increase in the oxidation kinetics and in the H-uptake between the third and the fifth cycles, as well as during the last two cycles. At the same time the volume fraction of cracks in the oxide significantly increased. Many fine cracks and pores exist in the oxide formed in the last cycle. Furthermore, the EPMA results confirm that this oxide formed at the last cycle reflects the composition of the metal at the metal-oxide interface after the long residence time in the reactor.

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### 1. Introduction

Zirconium based alloys have been used as the fuel cladding in light water reactors (LWR), mainly due to their resistance to

degradation in the reactor environment as well as their low cross section of neutron capture [1,2]. However, oxidation of the cladding, uptake of the released hydrogen and the irradiation induced chemical and microstructural changes contribute to the

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deterioration of the performance of the cladding [2,3], and are the main factors that limit the life time of the cladding. As the oxidation of the cladding proceeds, hydrogen progressively enters the underlying metal and once its solubility limit at the service temperature is reached, it precipitates in form of hydrides [4]. This precipitation changes the microstructure of the cladding and modifies its mechanical properties, with deleterious effects on its ductility. Although the oxidation and H-uptake have been extensively studied both in reactor [5–10], and in the autoclave [11–14], the mechanisms involved are not yet fully understood. For example, it is not clear why the oxidation and hydrogen uptake rates of some cladding alloys dramatically change after a certain residence time in the reactor [9,15]. Furthermore, most studies were carried out on the cladding materials under autoclave condition without irradiation, and the role of irradiation needs to be examined on irradiated materials.

Neutron irradiation in reactors has significant effect on the microstructure and also chemistry of the cladding materials. For instance, dissolution (and to a certain extent the amorphization) of secondary phase particles (SPPs), due to irradiation, may lead to an overall change of the composition of the cladding, please refer to [16,17], and references therein. These SPPs play a protective role against rapid corrosion [18]. Therefore their dissolution reduces the oxidation resistance of the material. The role of the SPP dissolution on the H-uptake is still not fully understood. It is suggested that the dissolved alloying elements will be redistributed and could increase the uptake acting even as a catalytic agent [6].

It is generally agreed that the oxidation of Zr is governed by the microstructure of the oxide in the vicinity of the metal-oxide interface and the protective quality of this layer at the metal-oxide interface; the role of interface microstructure on the H pickup behaviour is less evident, although a similar behaviour should be expected [14,19–24].

In a previous study in Paul Scherrer Institut the behaviour of the LK3/L type cladding from a Boiling Water Reactor (BWR) has been examined [9]. As an example, in the series of samples studied, it has been observed from destructive tests that the hydrogen content at the same elevation of the cladding doubled between the third and the fifth cycles, as well as during the last two cycles of its service and the oxide thickness also increased drastically. It has been also shown that the hydrogen pickup fraction at the same elevation gradually increased with the number of cycles.

The aim of this study is to search for microstructural changes at the metal-oxide interface and in the oxide, which combined with the chemical changes could explain the modifications of behaviour at high burnups and long residence times.

In this paper, a detailed chemical analysis is performed by means of EPMA and subsequently the microstructure of the oxide at different regions and in the vicinity of the metal-oxide interface is studied by 3D FIB. Many published studies applying 3D FIB tomography are available from recent years, both on the investigation of the Zr based cladding materials [10,25,26], and also on different types of materials [27–32]. The aim here will be to use this methodology to observe in 3D and quantify the micropore structure of the oxide at different cycles.

## 2. Materials and methods

A Zircaloy-2 material with LK3/L grade, from Westinghouse Electric was studied. The designation “/L” indicates that the fuel cladding has an inner liner to enhance the Pellet-Cladding Interaction (PCI) resistance [33]. The fuel rod had a special irradiation scheme, meaning that it has been irradiated for 6 cycles, after which it has been stored in the pool side for one cycle, and subsequently irradiated for 3 further cycles, in the BWR

“Kernkraftwerk Leibstadt” (KKL), in Switzerland (each cycle is 11 months and the reactor being down for service for approximately one month per year) [34]. The composition of the LK3/L material is provided in Table 1, the corresponding data for heat treatment is already described in Ref. [9]. The average burnup of the rod is 78.7 MWd/kgU. The mean oxide thickness is  $46 \pm 2.5 \mu\text{m}$  at 2039.5 mm elevation, and the total hydrogen content was measured to be 595 ppm at 2045 mm elevation [9]. In this study a segment from the elevation of 2039 mm has been examined. It must be mentioned that rods with such long residence times are produced very rarely to examine the material behaviour in extreme conditions [34].

### 2.1. Electron probe microanalysis

For chemical measurements the Electron Probe Micro-Analyzer (EPMA), a JEOL JXA-8500F EPMA with field emission gun (FEG) was used. The sample was embedded in resin followed by polishing and decontamination. A schematic drawing of the cross-section of the whole sample, the procedure of the sample preparation, and the overview of the cladding segment showing the different orientations are provided in Appendix A. All measurements were obtained using the  $K_{\alpha}$  signal of O, Cr, Ni, Fe, and  $L_{\alpha}$  signal of Zr and Sn. Table A2 in Appendix A shows the detailed parameters of the crystals used for the detection of different elements. All regions, including the crud<sup>1</sup>-oxide and metal-oxide interfaces as well as bulk metal were studied with the acceleration voltage of 15 kV. The point measurements for local information (e.g. point measurements in the hydrides) and the measurements in the oxide part have been carried out using the smallest beam size at 15 kV acceleration voltage and at 240–260 nA probe current while 5  $\mu\text{m}$  beam diameter has been used for the rest of the point measurements (e.g. line scans in the metal). The spatial resolution of the elemental maps is 200–300 nm. Beam current between 240 and 260 nA was used during all elemental maps. Quantitative point analyses were performed in the metal and in the oxide (precision of the analysis is given in Appendix A). The maps provide only qualitative analysis to represent the distribution information about each element in the material. Therefore, it is worth mentioning that different maps cannot be compared on a quantitative basis. All point analyses are quantitative and the results are normalized.

As in BWRs the burnup is asymmetric along the rod, measurements at different orientations of the cladding segment were carried out.

### 2.2. Focused Ion Beam tomography

A Zeiss NVision40 dual beam FIB-SEM was used to characterize the inner structure of the oxide and metal in 3D. Automatic slice-and-view was employed. Before the start of the procedure, the region of interest was protected by deposition of a layer of platinum and the surrounding material was removed with decreasing ion beam currents (for details please refer to Appendix B). ImageJ 1.50 and its plugin, TrakEM2 have been used to process the images acquired. The alignment of the collected images was performed partly by automatic and partly by manual adjustments. During the reconstruction, manual and semi-automatic labelling methods

<sup>1</sup> Crud (Chalk River Unidentified Deposit) is the deposit on the surface of cladding during the service.

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