Journal of Nuclear Materials 385 (2009) 346–350

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Microprobe analysis of neutron irradiated and autoclaved zirconium niobium claddings using synchrotron-based hard X-ray imaging and spectroscopy

A. Froideval [a,*], S. Abolhassani [a], D. Gavillet [a], D. Grolimund [a,b], C. Borca [a,b], J. Krbanjevic [c], C. Degueldre [a]

[a] *Paul Scherrer Institut, Nuclear Energy and Safety, 5232 Villigen PSI, Switzerland*
[b] *Paul Scherrer Institut, Swiss Light Source, 5232 Villigen PSI, Switzerland*
[c] *Ecole Polytechnique Fédérale de Lausanne, Centre de Recherches en Physique des Plasmas, Lausanne, Switzerland*

ARTICLE INFO

PACS:
28.41.Qb
78.40.Kc
61.80.Hg
61.05.cj
68.37.Yz

ABSTRACT

Two zirconium alloys (Zr–2.5%Nb) – one oxidized in a pressurized water reactor, the other oxidized in autoclave and used as reference – are analyzed by combining synchrotron-based scanning transmission and fluorescence X-ray microscopy and micro-X-ray absorption spectroscopy (micro-XAS). Two-dimensional zirconium distribution maps recorded on the neutron irradiated and the non-irradiated autoclaved Zr–2.5%Nb alloys clearly allow the localization of the oxide and the metal parts of the interface with a micrometer spatial resolution. Micro-XAS investigations make possible the determination of the speciation of zirconium and niobium both in the oxide and the metal parts of the interface for the irradiated and non-irradiated samples. The coordination environment and/or the valency of zirconium and niobium in the metal and the oxide parts of the interface have been determined for both materials, and interpreted on the basis of comparison with metal and oxide reference compounds.

1. Introduction

Zirconium-based alloys are extensively used as materials for fuel claddings, pressure tubes in CANDU reactors and to a certain extent for other structural components such as fuel channels, in various types of operating nuclear reactors. The properties of zirconium alloys depend on the chemical composition and the heat treatment of the alloy for each type of reactor. It has been demonstrated by several studies that the variation of the chemical composition of the alloys such as the addition of niobium can considerably improve the corrosion resistance of the claddings materials [1–5]. The structure and composition of oxides formed on different zirconium alloys have been subject of several investigations in the past e.g. [6–13]. One of the requirements of the cladding being its resistance to corrosion, the aim of these examinations is to correlate the oxidation behaviour of the alloys to the structure and composition of the oxide layers formed at the surface of the alloys in different oxidation environments. The oxidation state, e.g. the oxidation state of different secondary phases present in the oxide layer, is one parameter which has been investigated. Certain precipitates (e.g. $Zr(Fe,V)_2$ Laves phases in Zr-based alloys) [9] have been observed to remain metallic in the oxide in the vicinity of the interface. Niobium containing alloys have also shown a similar behaviour. As an example, studies performed on autoclaved materials [10] as well as on irradiated materials [11] have revealed Nb-rich metallic phases in the vicinity of the metal–oxide interface in the oxide layer. The oxidation state of the niobium in autoclaved materials has been studied in detail in Zr–2.5%Nb as well as in Zr–20%Nb alloys by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [10]. These authors have demonstrated that the β-Nb and Nb-rich phases show a delayed oxidation and remain metallic in the vicinity of the metal–oxide interface in the zirconium oxide matrix. They ultimately oxidize to form an amorphous oxide. The same behaviour is observed for irradiated Zr–Nb alloys examined by TEM [11,14]. As the oxidation state of different atoms can be determined on an averaged scale by X-ray absorption spectroscopy (XAS), effort is made to use this technique to further examine the speciation of zirconium and niobium in Zr–Nb alloys. The present study concerns the spectroscopic investigations of a zirconium niobium alloy with a niobium concentration of 2.5 wt.%. The analysis of the formal valency and/or the coordination environment of zirconium and niobium both in the oxide and the metal sides of the metal–oxide interface for an irradiated and non-irradiated Zr–2.5%Nb alloys is performed by means of micro-XAS. The results are discussed and interpreted on the basis of comparison with spectroscopic data recorded on metal and oxide reference compounds.

---

* Corresponding author. Tel.: +41 56 310 44 48; fax: +41 56 310 35 65.
E-mail address: annick.froideval@psi.ch (A. Froideval).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.12.022

2. Experimental

2.1. Description of materials

A Zr–2.5%Nb cladding segment of a fuel rod irradiated in a pressurized water reactor (PWR) and a non-irradiated Zr–2.5%Nb tube section oxidized in an autoclave have been used for this study.

The irradiated fuel rod was exposed for three reactor cycles at 600 K under a pressure of 15 MPa and had an average burn up of 41.4 MW d kg^{-1}. The neutron fluence of the segment studied has been estimated to be approximately of 8.3×10^{21} cm^{-2} ($E > 0.821$ MeV). The oxide thickness of the segment has been determined by scanning electron microscopy (SEM). The details of the microstructure of this neutron irradiated sample are already provided in [11]. Briefly, the material shows a Nb-rich phase which has precipitated in the form of platelets. The Nb-rich regions can be observed both in the metal and the oxide, and they show a delayed oxidation with respect to the zirconium matrix in the vicinity of the metal–oxide interface. The autoclaved Zr–2.5%Nb alloy used as reference material has been oxidized at 620 K under a pressure close to 10 MPa. This sample has also been analyzed by SEM in order to determine the thickness of its oxide layer. Additional compounds such as NbO, NbO_2 and Nb_2O_5 niobium oxides purchased from Alfa Aesar and Aldrich as well as a niobium metal sample have been used as reference materials in this study.

2.2. Sample preparation

Both the neutron irradiated and the autoclaved reference Zr–2.5%Nb materials have been prepared by focused ion beam (FIB). The used 'NVision 40' workstation from Carl Zeiss (Germany) is equipped with an electron column (GEMINI SEM) having a high resolution field emission gun and a zeta FIB system. This system allows high speed sputtering of the material for the early stages of sample preparation. The samples are milled and continuously imaged by SEM during preparation.

A small tube segment of 1 mm × 2 mm, is mounted on the holder, with the oxide layer perpendicular to the ion beam, in order to create a small thinned window for spectroscopic measurements. A window with 30 μm in axial, and 20 μm in circumferential orientations is milled using a gallium ion beam. The acceleration voltage for the sputtering has been of 30 kV and the beam current has been of 45 nA for fast sputtering and removal of material, and of 80 pA for final polishing. The final thickness of the small window cut in the irradiated sample is experimentally determined from the SEM image to be close to 10 μm. Both irradiated and non-irradiated autoclaved samples are prepared under similar conditions and geometry.

2.3. High resolution 2D images and X-ray absorption spectra

The microscopic and spectroscopic measurements conducted on the FIB manufactured Zr–2.5%Nb samples have been carried out at the micro XAS beam line of the Swiss Light Source (SLS, Villigen, Switzerland) [15]. This analytical facility is the unique SLS beam line allowing for the investigation of radioactive materials by means of high intensity hard X-ray synchrotron radiation with a micro-focused X-ray beam. In the present work, the micro XAS beamline has been set up in order to deliver monochromatic X-rays tuned to the photon energy of either Zr or Nb K-edge for elemental selectivity by means of a double crystal monochromator using a pair of Si (1 1 1) crystals. The final X-ray spot size at the sample surface is close to 1 μm × 1 μm. A specific specimen holder, on which the samples are mounted at 90° with respect to the incident photon beam to minimize the X-ray spot size at the sample surface, is positioned on a 3 axis-motion manipulator. This manipulator allows an accurate positioning of the sample with respect to the photon beam.

The element-resolved speciation of zirconium atoms in the irradiated and in the autoclaved Zr–2.5%Nb materials have been investigated using the following two-step measurement strategy: (i) two-dimensional ~40 μm × 50 μm high resolution scanning map recorded at 18.2 keV, i.e. above the Zr K-edge, in transmission detection mode with a micrometer spatial resolution; and (ii) absorption spectra recorded at the Zr K-edge using a micron-focused hard X-ray beam for two sample positions (one in the metal and one in the oxide parts of the interface). The data have been recorded by measuring the incoming and the transmitted signals detected by two Ar-filled ionization chambers at ambient pressure. For each position in the oxide and in the metal sides of the metal–oxide interface, good measurement statistics have been achieved by recording a unique extended X-ray absorption fine structure (EXAFS) spectrum in the range of 17 900–18 700 eV. The Athena and Artemis softwares [16] which are part of the Ifeffit program [17] have been used to process and to fit the experimental XAS data. Phase and amplitude have been generated by the FEFF code [18], for the zirconium metal and zirconia [19,20] model compounds.

A similar two-step measurement strategy has been applied at the Nb K-edge to investigate the element-resolved speciation of niobium atoms in the same samples; the measurements have been carried out in fluorescence mode using a Ketek Si detector. To obtain reasonable measurement statistics, five absorption spectra recorded at the Nb K-edge have been merged and then smoothed using 10 iterations. A standard niobium foil has been used to calibrate the experimental data in energy.

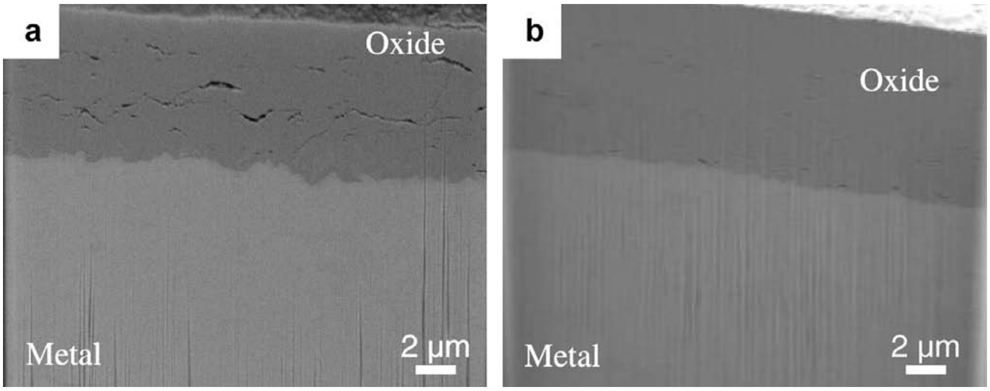

Fig. 1. SEM images which zoom in the metal–oxide interface of (a) the neutron irradiated and (b) the non-irradiated autoclaved reference Zr–2.5%Nb materials (sample preparation: Focused Ion Beam).