EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** High temperature in-situ time resolved quantitative study of internal stresses evolution during the oxidation of zirconium alloys	**Experiment number**: 20170247
Beamline: BM02	**Date of experiment**: From 2017, Sept. 29 to Oct. 3 and 2018, Jan. 26 to Jan. 29	**Date of report**: Feb., 2018
Shifts: 15	**Local contact(s)**: Nils Blanc	*Received at ESRF:*

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Objective & expected results (less than of 10 lines):

In hypothetical accidental situations in a nuclear pressurized water reactor, fuel cladding tubes made of zirconium alloys can be exposed to steam at high temperature up to 1200°C, before cooling down to room temperature by water quenching. In such conditions, the cladding material undergoes several structural and metallurgical evolutions (growth of zirconia, oxygen diffusion through the metal, phase transformation of both the metal and the oxide…) causing internal stresses (at micro and macro scales). The objective of the present experiments was to follow *in situ* the oxidation process of one zirconium alloy (Zircaloy-4) at high temperatures, up to 1200 °C, and to determine the evolution of the structure and microstructure of zirconia layers as a function of temperature, time and oxidizing atmosphere. The stable phase of pure zirconia below 1170 °C is the monoclinic one ($P2_1/c$ space group), nevertheless the tetragonal phase of zirconia ($P4_2/nmc$ space group) can be stabilized at lower temperatures by stresses or when the crystal size is in the nanometric range.

Results and conclusions of the study:

On the experimental point of view, we had to follow simultaneously the evolution of the monoclinic to tetragonal phases volume fraction, the mean size, and the elastic strain of the crystals in the two structural forms, during heating, isothermal holding and cooling. One of the tricky aspects was that a strict control of the temperature, atmosphere (injection of flowing helium as a neutral gas and of a mixing of helium and oxygen as an oxidizing gas), and oxidation process, was needed. All the experiments have been realized thanks to the QMAX furnace which is available on the BM02 beamline. This prototype furnace has been already used during other experiments at temperatures as high as 1700°C, nevertheless during our experiment in September 2017 we were not able to reach in a convenient manner the expected temperatures, and we had to face many technological problems with the heating resistor. Thus the beamline manager allocated us 12 additional shifts at the end of January 2018. The results presented in this report have been obtained during this last experimental session.

According to the literature in the range from 700 °C to 1200 °C, the kinetics of the oxidization process is strongly depend of temperature. Very fast process was expected at high temperature and our aim was to follow the formation of the oxide with a time resolution of 1 sec. All the diffraction patterns have been recorded using the XPAD-WOS 2D detector which allows recording a part of the Debye-Scherrer rings. The detector was fixed on the 2θ goniometer arm at a distance of 850 mm from the specimen. The energy of the X-ray beam was fixed at 17.6 keV, just below the zirconium K-edge. Temperature measurement in another tricky part of the experiment. It was monitored during the experiment via two thermocouples, one fixed on the heating resistor, and one spot-welded directly on the specimen surface. Accurate temperature was also determined after the experiment by following the evolution of the diffraction peak positions of the NIST α-alumina powder placed onto the sample. Typical diffraction images recorded before and after oxidation are shown in Fig. 1. One image was acquired every second. All the diffraction rings corresponding to zirconium, monoclinic and tetragonal zirconia, and alumina are clearly evidenced. With the used setup, diffraction rings do not overlap.

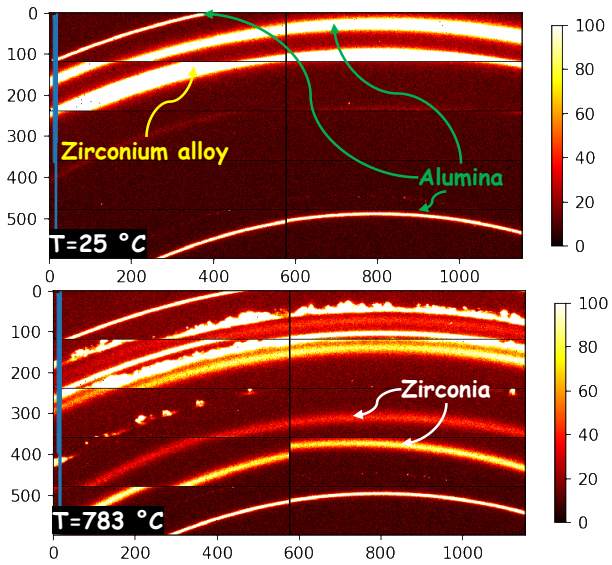


Fig. 1. Diffraction images recorded before and after oxidation.

We first followed the oxidation of one sample as a function of temperature under flowing He-O_2 with a relatively low oxygen partial pressure. Patterns recorded at room temperature and at 800°C are reported in Fig. 2. Zircaloy-4 and alumina diffraction peaks are clearly identified on the pattern recorded at room temperature. The mains diffraction peaks are observed for both monoclinic and tetragonal phases of zirconia. Thanks to a convenient choice of the setup parameters (X-ray beam energy, detector size and position) these peaks are located between the alumina and Zircaloy peaks without any overlapping. All the patterns have been recorded after careful optimization of the primary beam which was nearly-parallel (horizontal and vertical focalization far away after the detector). One of the noticeable points is that although the use of a 2D detector and a data reduction process through azimuthal integration, the obtained instrumental function is symmetric and exhibits a small full width at half maximum (FWHM) close to 0.03°. As evidenced in Fig. 2c, the FWHM of zirconia peaks is significantly higher. This is due to microstructural effects.

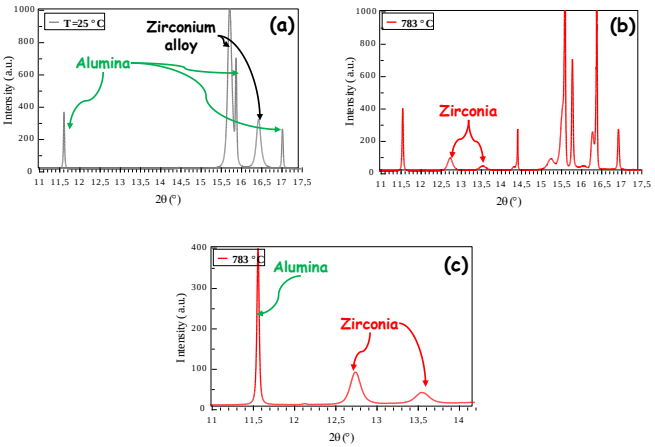
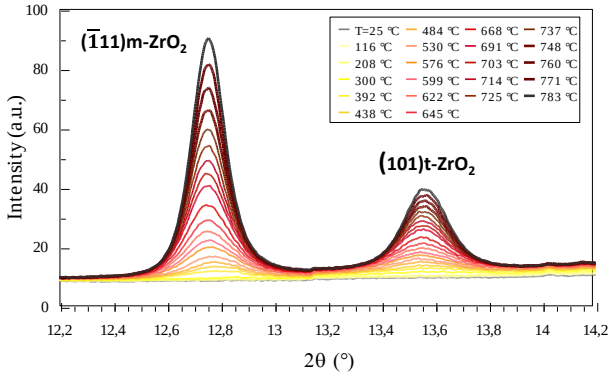


Fig. 2. Diffraction patterns at room temperature and at 783 °C. Due to the nanometric size of the zirconia crystals, the zirconia peaks are roughly 5 times wider than the alumina one.

On Fig. 3 we reported a direct illustration of the oxidation process during heating of the sample, performed under an atmosphere containing oxygen. The intensities of the two zirconia diffraction peaks are continuously growing. It seems that increasing the temperature induces a decrease of the relative amount of tetragonal zirconia compared to monoclinic zirconia. Moreover, the FWHM of the peaks is continuously decreasing. This is related to the crystals growth process.



(b)

Fig. 3. Illustration of the oxidation process during heating at 20 °C/min.

A second part of the experiment was devoted to the determination of the coupling between crystals growth kinetics for both monoclinic and tetragonal zirconia phases and the variation of the relative amount of these two phases. This aspect was studied through isothermal treatments at various temperatures. As an illustration, the evolution as a function of time of the mean size of the monoclinic crystals during isothermal oxidation at 700 °C is reported in Fig. 4. We were able to determine this mean crystal size for each pattern recorded every second. As a consequence very smooth evolution was observed. By using such results and the evolution of zirconia phases volume fractions, we will be able to evidence the main characteristics of the Zircaloy-4 oxidation process at high temperature. Strain evolution (not shown here) will be also considered.

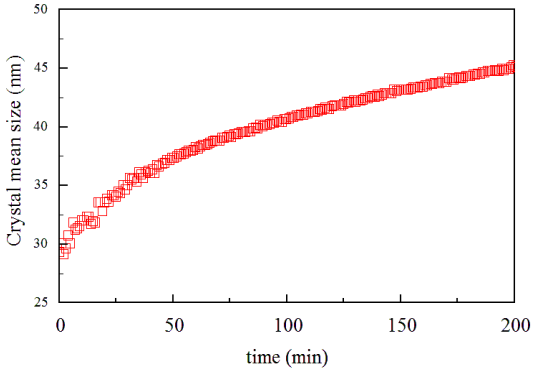


Fig. 4. Evolution of the mean size of the monoclinic crystals during an isothermal treatment at 700 °C, evaluated from line broadening.

Justification and comment about use of beamtime (5 lines)

The realization of such measurements is quite tricky on the experimental point of view. Thanks to an accurate control of the gas flow into the furnace we were able to introduce oxygen at a chosen moment. The BM02 diffraction setup associated to the QMAX furnace is very well-suited for such *in situ* measurements. We were thus able to realize time resolved measurements of the oxidation process of Zircaloy-4 at high temperature, with a good control of temperature and atmosphere, with a time resolution of 1 sec.