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# An approach to study oxidation-induced stresses in Zr alloys oxidized at high temperature

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## ABSTRACT

A method was elaborated to measure the deformation of Zr alloy samples *in-situ*, during oxidation at high temperature (above 900 °C typically) and subsequent cooling. In addition, a model was developed to calculate the internal stresses generated within the multiphase and multilayered material oxidized at high temperature. Comparison of simulation and experimental results confirmed the benefit of making measurements *in-situ* rather than *post-facto*. It was shown that internal stresses generated during oxidation at high temperature are potentially very different from those reported for lower temperatures, due in particular to amplified diffusion of oxygen within the metal and increased viscoplasticity.

## 1. Introduction

In some hypothetical accidental scenarios in nuclear pressurized water reactors, such as LOs of Coolant Accidents (LOCA), fuel cladding tubes made of zirconium alloys can be exposed for a few minutes to steam at High Temperature (HT, up to 1200 °C) before being cooled and then quenched in water (due to reflooding of the reactor core by the emergency core cooling systems). In such conditions, the cladding material undergoes several metallurgical evolutions. During oxidation, an oxide layer of ZrO<sub>2</sub> grows on the metal, with a tetragonal structure t<sub>ZrO2</sub> or a two-phase tetragonal and monoclinic structure t<sub>ZrO2</sub> + m<sub>ZrO2</sub>, depending on temperature in particular [1,2]. Above typically 800 °C, depending on the chemical composition of the material and the thermal history, zirconium progressively transforms from its α<sub>Zr</sub> phase with a hexagonal close-packed (hcp) structure to its β<sub>Zr</sub> phase with a body-centered cubic (bcc) structure [3]. At HT, a significant fraction of the oxygen reacting at the metal/oxide interface diffuses through the metallic substrate. Once the solubility limit of oxygen in the β<sub>Zr</sub> phase is reached, a metallic layer of oxygen-stabilized α<sub>Zr</sub> phase, called α<sub>Zr</sub>(O), grows from the interface between the oxide layer and β<sub>Zr</sub> phase substrate [3–5]. There is a strong through-thickness gradient in oxygen concentration in the α<sub>Zr</sub>(O) phase layer, from approximately 29 atomic % (at%) at the oxide/α<sub>Zr</sub>(O) interface down to 10 at% at the α<sub>Zr</sub>(O)/β<sub>Zr</sub> interface. The underlying metallic layer of β<sub>Zr</sub> phase (or two-phase α<sub>Zr</sub> + β<sub>Zr</sub> depending on temperature) has a lower oxygen concentration and a smaller through-thickness gradient, from typically 1 to 5 at%. A two-phase α<sub>Zr</sub>(O) + β<sub>Zr</sub> layer is generally observed between the “continuous” α<sub>Zr</sub>(O) layer and the β<sub>Zr</sub> phase layer. During cooling, a large

fraction of the t<sub>ZrO2</sub> phase transforms into to the m<sub>ZrO2</sub> phase [2], and the β<sub>Zr</sub> phase transforms back into the α<sub>Zr</sub> phase and forms the so-called prior-β<sub>Zr</sub> structure, with a typical Widmanstätten or parallel-lath structure morphology [7].

These evolutions cause strain fields which induce internal stresses, at both micro and macro scales. During oxidation at HT, these stresses can result from the growth of the oxide layer, oxygen diffusion through the metal, β<sub>Zr</sub> to α<sub>Zr</sub>(O) phase transformation and/or, but probably at a second order, epitaxy between zirconium and zirconia. These stresses can have an effect on the oxide structure (e.g. stabilization of t<sub>ZrO2</sub> at the expense of m<sub>ZrO2</sub>) and the oxidation kinetics of the material. The oxidation kinetics of Zr alloys in steam at HT is generally sub-parabolic or parabolic [8–10]: the oxide layer is dense and protective so that the oxidation rate is controlled by diffusion of oxygen anions through the oxide to the oxide-metal interface, where the oxidation reaction takes place; the oxidation rate decreases as the thickness of the oxide increases. But in some conditions, the oxidation regime can change. For example, a “breakaway” oxidation phenomenon is observed in Zr alloys when oxidized in steam around 1000 °C: after a certain time period (e.g. about 5000 s at 1000 °C at atmospheric pressure for Zircaloy-4 alloy [8,9,11]), the oxide layer loses its protective capability and the oxidation kinetics accelerates. Internal stresses are expected to play a role in the occurrence of this phenomenon. A review on the potential effects of stresses on the HT oxidation of metals was made by Evans [12].

Internal stresses are also generated during cooling after oxidation at HT. They are due in particular to phase transformations of both the metal and the oxide and to differences between the thermal coefficients of the different phases/layers constituting the cladding material

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oxidized at HT. These internal stresses can result in the failure of the material once it is heavily oxidized and/or hydrided [8,13]. Residual stresses after cooling may finally have some consequences on the long-term post-quenching evolution of the material.

The determination of these internal stresses is an important issue since they can affect the behaviour of the material, whose integrity is an important concern as the fuel cladding is the first barrier for retention of radioactive fission products. However, these stresses are poorly understood and quantified to date for oxidation at HT (above 900 °C).

This paper presents an approach, combining experimental characterization and modelling, developed to study internal stresses generated in Zr alloys during their oxidation at HT and subsequent cooling. In Section 2, a method to measure the deformation of Zr alloy samples *in-situ* during the thermal transient is proposed. A model taking into account the metallurgical evolutions occurring during oxidation at HT and cooling, and the thermal-mechanical properties of the material phases, is presented in Section 3. Results of calculations performed with a first set of inputs are discussed in view of the experimental data presented in Section 2. The influence of each model parameter on the development of both stresses and overall strain is then considered. Parameters having a first-order effect are determined.

## 2. *In-situ* measurement of oxidation-related macroscopic strain

### 2.1. Methods proposed in the literature

A classical way to evaluate internal stresses in oxidized materials consists in:

- measuring, on the one hand, the deformation of either a sample after having disrupted its mechanical equilibrium typically by removing a portion of the material having been homogeneously oxidized, or a sample heterogeneously oxidized;
- determining, on the other hand, the internal stresses (most of the time after cooling down to room temperature) based on a model describing the system, taking the material mechanical properties into account, and using the strains experimentally measured as either an input or a basis for comparison of the model output.

From an experimental point of view, most of the commonly used methods to indirectly evaluate internal stresses are ill-suited or difficult to apply to the case of study here. For example:

- Layer-removal method: This destructive method consists in removing a layer of the material and in measuring the induced strain. It was for example applied on zirconium and Zircaloy-2 oxidized at temperatures between 500 and 700 °C [14]. However, mechanical removal of a material layer can introduce stresses and chemical or electrochemical removal of one material phase without deteriorating the other phase appears to be tricky. Moreover, only residual stresses after cooling down to room temperature can be determined with this method.
- Deflection or curvature method: This method consists in measuring, *in-situ* or *post-mortem*, the deformation of a sample oxidized only on one side. This approach has been applied to evaluate stresses generated during oxidation of Zr alloys at temperatures up to 500 °C [15–18], but the techniques used to protect one side of the sheet sample from oxidation are not applicable to the high temperatures of interest here.
- X-ray diffraction (XRD) or Raman spectroscopy: these non-destructive methods consist in calculating stresses from micro-strains deduced from the distance between crystallographic planes. XRD has already been applied, most of the time *post-facto* but sometimes *in-situ*, to evaluate internal stresses in Zr alloys oxidized at temperatures generally between 350 and 500 °C (in air, steam or pressurized water) [19–25] or in some cases at 650–710 °C (in air) [26] or at

850 °C (in air) [27], for relatively thin oxide layers (a few microns). Raman spectroscopy was also applied for Zr alloys oxidized in pressurized water at 360 °C [28] or in air at 500–600 °C [29], 550 °C [30] or 600–900 °C [31]. However, interpretation of the results is delicate due in particular to complex effects on the diffraction patterns of the crystallographic textures of zirconium and zirconia and/or of the coarse grains obtained at HT. And implementation of such techniques in the case of HT oxidation is complicated due in particular to the thick oxide layers (several tens of microns) and to the fast oxidation kinetics involved (for example, only a few tens of seconds under steam at 1100 °C are necessary to form a 10 µm-thick oxide layer).

A fairly complete review of the data available in the literature on the residual stresses (mean values in most cases) in oxide layers formed on Zr alloys has been recently made by Guérain et al. [32]. In most cases, oxidation temperatures were between 400 and 850 °C and oxide thicknesses were of a few microns. Compressive stresses perpendicular to the oxide surface were reported in the oxide layers. It appeared that the amplitude of stresses varies from one study to another, from a few hundreds of MPa to more than 5 GPa, depending on both the conditions (alloy, atmosphere, temperature and oxide thickness) and the method used (deflection and curvature methods, XRD or Raman spectroscopy).

It was reported in several papers [33–39], for oxidations performed at various temperatures between 350 and 1110 °C, that Zr alloys significantly deform during oxidation when the oxide layer is sufficiently thick and the oxidation temperature is high enough to allow substantial metal creep. Then, it has been chosen here to take advantage of the relatively large strains expected during oxidation when it is done at HT. A method was developed to measure the deformation of cladding tube samples, *in-situ* during oxidation at HT and cooling. Indeed, *post-facto* measurements are more common and easier to implement. However, residual stresses evaluated after cooling to room temperature are not necessarily directly representative of stresses generated during oxidation or cooling. Indeed, the material can be damaged during cooling, under the effect of internal stresses, which then relax, at least partially.

### 2.2. Material and experimental procedures

The experiments presented here were made on 12 mm long, stress-relieved annealed, low tin Zircaloy-4 cladding tube samples, with an outer diameter and a thickness of 9.5 and 0.57 mm, respectively. The material's chemical composition in weight % (wt%) was 1.3% Sn, 0.22% Fe, 0.12% Cr, 0.13% O, Zr balance. The *in-situ* measurement of the oxidation-related macroscopic strain was made directly on the cladding tube samples by means of a modified Adamel-Lhomargy DT1000 quenching dilatometer.

The samples were heated at 20 °C/s up to 1100 °C under primary vacuum ( $10^{-5}$  bar), then held for 520 s at 1100 °C in a flowing mixture of 90% in volume (vol%) of He and 10 vol% of O<sub>2</sub> (flowing rate of about 5 L/min, chamber with a cross-sectional area of about 5.3 cm<sup>2</sup>, atmospheric pressure), and finally cooled down to room temperature at 1 °C/s under primary vacuum ( $10^{-5}$  bar) or at 50 °C/s under pure He (99.9999%, < 0.1 ppm by volume (vppm) of O<sub>2</sub>, < 0.5 vppm of H<sub>2</sub>O). The He-O<sub>2</sub> gas mixture was used as a surrogate for steam, excluded from use in the facility. As shown in Fig. 1, it was checked that the oxidation kinetics of Zircaloy-4 at HT under steam and under O<sub>2</sub> mixed with He are comparable. Despite an absence of hydrogen and a different enthalpy of the Zr-O reaction, the oxide formed under He-O<sub>2</sub> is expected to have properties reasonably similar to those of the oxide growing in steam. Oxidation of Zr alloys at HT is very fast at the beginning of the process and highly exothermic. Therefore, as already done in [1,2], helium was used in the mixture to increase its thermal conductivity and mitigate the increase in temperature associated with the oxidation process. It was checked that the mixture contained enough oxygen to avoid oxygen starvation.

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