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Experimental study and numerical simulation of high temperature (1100–1250 °C) oxidation of prior-oxidized zirconium alloy

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ABSTRACT

Previous experiments showed that the thickness of a thick prior-oxide layer formed on Zircaloy-4 fuel cladding can decrease during the first seconds at very high-temperature, before re-growing. We confirmed these results with oxidations performed at 1200 °C on prior-oxidized Zircaloy-4. The initial reduction of the prior-oxide was explained by the balance of the oxygen fluxes at the metal/oxide interface and successfully reproduced by numerical simulations using a diffusion-reaction model. Different hypotheses were considered for the diffusion coefficients of oxygen in the different layers. This allowed discussing the effect of the prior-oxidation on the kinetics of oxygen embrittlement of the metallic substrate.

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1. Introduction

Zirconium alloys (such as Zircaloy-4) are widely used as fuel cladding tubes in nuclear Pressurized-light-Water-Reactors. In service conditions, fuel cladding tubes are in contact with the water of the primary circuit of PWR at a temperature close to 320 °C and under an isostatic pressure of 1.55.10⁷ Pa. This leads to the formation of a layer of zirconia on the external surface of the fuel cladding tubes. On Zircaloy-4 claddings, after the whole life of fuel cladding tubes (four cycles of irradiation) in a PWR, the maximum

thickness of this zirconia layer is about 100 μm. This oxide layer has to be carefully considered in safety studies, especially in the case of a hypothetical scenario of loss-of-coolant-accident. In this scenario, fuel cladding tubes could undergo a high temperature oxidation ($T \approx 1200$ °C) in water steam for a maximum duration of a few minutes [1]. This high temperature oxidation would induce the formation of a significant thickness of zirconia and the diffusion of oxygen into the fuel cladding tube [1–6]. Chuto et al. [4], Guilbert et al. [5] and Le Saux et al. [1] performed oxidation treatments at high temperature on prior-oxidized zirconium alloy. Prior-oxidized samples were chosen in order to simulate the layer of zirconia formed in-service.¹ During the first seconds of the high temperature treatment, the authors have noticed a reduction of the thickness of the prior-oxide layer, in the case of a thick prior-oxide, before the re-growth of a new additional layer of zirconia at the metal/oxide interface. This initial reduction of the thickness of prior-oxide can be explained by the oxygen flux balance at the metal/oxide interface [6]. At the beginning of the high tempera-

Abbreviations: α_{red} , $\alpha_{Zr}(O)$ phase formed by reduction of the low temperature oxide layer; Exp, experimental, i.e. data link with experimental results; EKINOX-Zr, Estimation KINetics OXidation numerical model for Zr alloys; HCP, hexagonal close-packed; HT, high temperature; HTox/HT ZrO₂, oxide layer formed at high temperature ($T \geq 1000$ °C); LOCA, loss-of-coolant-accident; LT, Low temperature, i.e. the in-service temperature of the PWR ($T \approx 320$ °C); LTox/LT ZrO₂, oxide layer formed at low temperature; Num., numerical, i.e. data link to numerical results; PBR, Pilling–Bedworth ratio; Prior- β_{Zr} , phase formed from the cooling of β_{Zr} phase stable at high temperature; PWR, pressurized-light-water-reactor.

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¹ Chuto used samples after irradiation in PWR, Guilbert et al. used samples prior-oxidized in pure oxygen at 425 °C and Le Saux et al. used samples prior-oxidized in autoclave at 360 °C and under 1.90.10⁷ Pa in water with addition of B and Li to simulate the PWR chemistry.

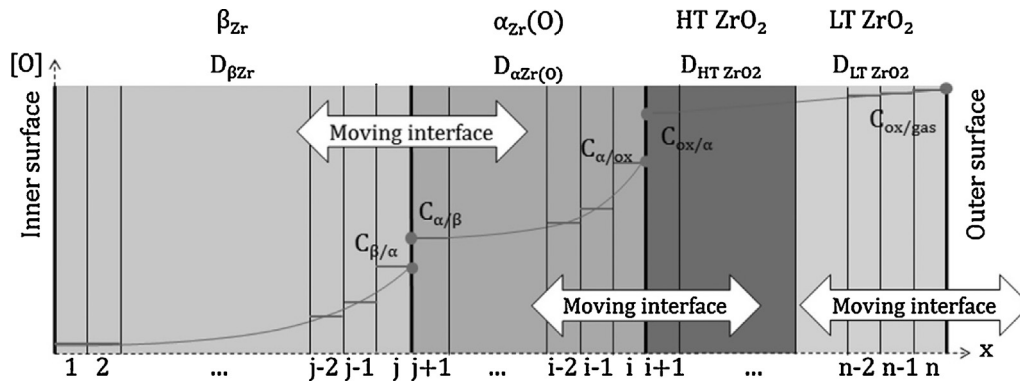


Fig. 1. Schematic of the EKINOX-Zr model.

ture treatment, because of the very high solubility of oxygen in $\alpha_{Zr}(O)$ phase at these temperatures, the gradient of the activity of oxygen in the $\alpha_{Zr}(O)$ layer is high, whereas the oxygen activity gradient is rather low in the thick layer of prior-oxide. Consequently, the inward flux of oxygen in the oxide is lower than the inward flux in the $\alpha_{Zr}(O)$ phase. Hence, the balance of the fluxes at the metal/oxide interface leads to the reduction of the prior-oxide despite the oxidizing atmosphere. This also leads to the growth of an $\alpha_{Zr}(O)$ phase at the metal/oxide interface. The flux of oxygen in the $\alpha_{Zr}(O)$ layer decreases with its thickening, i.e. with time, whereas the inward flux of oxygen in the oxide layer increases with the decrease of its thickness. Hence, after a certain time, the balance of the fluxes of oxygen at the metal/oxide interface reverses and the new oxide starts growing. In a previous work EKINOX-Zr model calculations have been used to reproduce this particular diffusion path [7]. These calculations were based on a 1D numerical resolution of diffusion-reaction equations describing the diffusion of oxygen in the $ZrO_2/\alpha_{Zr}(O)/\beta_{Zr}$ system. It was shown that the experimental data cannot be exactly reproduced by simulations done with the assumption of a unique and constant coefficient of diffusion of oxygen in each of the three phases. The aim of this paper is to understand the influence of a layer of prior-oxide² on the diffusion of oxygen in the metallic matrix during oxidation at high temperature. To do so, experiments at high temperatures were performed on prior-oxidized Zircaloy-4 samples and several hypotheses were tested using EKINOX-Zr to evaluate their validity and consequences.

2. Numerical model EKINOX-Zr

2.1. General description

The numerical tool EKINOX-Zr [6–8] was designed to simulate the oxidation at high temperature of zirconium alloys. The kinetics of growth of both the oxide scale and the layer of $\alpha_{Zr}(O)$ phase were calculated. A numerical resolution of Fick's equations with boundary conditions on moving interfaces allowed determining the profiles of diffusion of oxygen. The interfaces were considered at the local equilibrium and the thermodynamic database Zircobase [9] was used to calculate the interfacial concentrations. In the model, the fuel cladding tube was modeled as a one-dimensional planar domain. Fig. 1 presents a schematic of EKINOX-Zr model, with the

² In the rest of this article, the oxide layer formed during in-service condition will be mentioned as « prior-oxide layer » or « LT oxide layer » (LT—low temperature, i.e. in-service conditions of PWR).

assumption that one layer of each phase (ZrO_2 , $\alpha_{Zr}(O)$ and β_{Zr}) coexist from the very beginning of the simulation.

The fuel cladding tube is divided into n slabs. In each slab of metal, a concentration of oxygen X_0^p is defined. In the same way, $X_{V_0}^q$ is the concentration of anionic vacancies defined in each slab of the oxide layer. Following the Wagner's theory of oxidation [10], the transport of oxygen is calculated from slab to slab using an explicit treatment of the fluxes of oxygen in the metal (Eq. (1)) and of the fluxes of anionic vacancies in the oxide (Eq. (2)).

$$\forall p \in [1; i] \quad J_0^p = -\frac{D_0^p}{\Omega^p} \times \frac{X_0^{p+1} - X_0^p}{\frac{1}{2}(e^p + e^{p+1})} \quad (\text{metal}) (1)$$

$$\forall q \in [i + 1; n] \quad J_{V_0}^q = -\frac{(1+z)D_{V_0}^q}{\Omega^q} \times \frac{X_{V_0}^{q+1} - X_{V_0}^q}{\frac{1}{2}(e^q + e^{q+1})} \quad (\text{oxide}) (2)$$

Thus, the balance of fluxes in each slab leads to a variation of the concentration of oxygen (Eq. (3), in the metal) or of the concentration of vacancies (Eq. (4), in the oxide) in each slab.

$$\forall p \in [1; i] \quad \frac{dX_0^p}{dt} = \Omega^p \times \frac{J_0^p - J_0^{p+1}}{e^p} \quad (\text{metal}) (3)$$

$$\forall q \in [i + 1; n] \quad \frac{dX_{V_0}^q}{dt} = \Omega^q \times \frac{J_{V_0}^q - J_{V_0}^{q+1}}{e^q} \quad (\text{oxide}) (4)$$

The displacement of the metal/oxide interface is numerically achieved by introducing equations describing the variations of the thickness of the slab for the two slabs i and $i + 1$ close to the interface. These variations are governed by the difference in fluxes of oxygen at either side of the interface (Eqs. (5) and (6)). The displacement of the $\alpha_{Zr}(O)/\beta_{Zr}$ interface is calculated with the same procedure (Eqs. (7) and (8)).

$$\frac{de^{i+1}}{dt} = \frac{P\Omega}{\gamma} \times \frac{J_{V_0}^{i-1} - J_{V_0}^{i+1}}{C_{ox/\alpha_{Zr}(O)} - C_{\alpha_{Zr}(O)/ox}} \quad (5)$$

$$\frac{de^i}{dt} = -P \frac{de^{i+1}}{dt} \quad (6)$$

$$\frac{de^{j+1}}{dt} = \Omega \frac{J_0^{j-1} - J_0^{j+1}}{C_{\alpha_{Zr}(O)/\beta_{Zr}} - C_{\beta_{Zr}/\alpha_{Zr}(O)}} \quad (7)$$

$$\frac{de^j}{dt} = -\frac{de^{j+1}}{dt} \quad (8)$$

The boundary conditions are given in Eqs. (9) and (10). A mirror condition is set in the slab 1 (Eq. (10)). Hence, in order to simulate the oxidation on one side or on the two sides (inside and outside) of the fuel cladding tube, the total number of slabs is attributed to

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