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Method for describing the Zircaloy-4 oxidation using the analytical solution of the oxygen diffusion equation

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Abstract

The oxidation of the Zircaloy-4 fuel element sheath at high temperature transients is treated as a moving boundary one-dimensional diffusion problem. It is usually solved by numerical methods. A method is provided in this work to analytically solve the oxygen diffusion equations. The temperature transient has been approximated as a stepwise function of time, $\{T_i, (t_{0i}, t_i)\}_{i=1,n}$. The main assumption was that in the beginning of the ith step of the temperature transient the oxide grown during the previous steps, x_{0i}, could be considered as being formed at a constant temperature, T_i, but during another time interval, named equivalent time interval Δt_{eq}. Calculations have been made with a routine, OXCON, developed using this model. The results approach well the predictions of validated corrosion codes, FROM and PRECIP-II, which solve the diffusion equations using numerical methods.

1. Introduction

The development of models to describe zirconium alloys oxidation is important in order to improve the thermo-mechanical description of the nuclear fuel element behavior during in-reactor operation.

At temperatures corresponding to normal in-reactor operation the oxygen diffusion in the fuel cladding is negligible. It has been demonstrated that the growth of the oxide is not a limiting factor for the life time of the in-reactor fuel element even at high burnups. The oxidation of the cladding becomes a problem when the fuel element is subjected to accident conditions where the temperature in the cladding reaches high variable values.

It is assumed that the oxygen diffusion is the rate controlling process. There are two types of models for the corrosion of the fuel element sheath. (I) Semi-empirical models use the rate theory and are based on correlations giving the thickness of the reaction layer (or the weight gain) as a function of time and temperature. The constants in the correlations were calculated by fitting a proposed mathematical description to experimental data both for normal [1,2] or accidental [3] conditions of in-reactor operation. (II) Theoretical models treat the oxidation problem as a moving boundary one-dimensional diffusion problem. These models are based on the analytical [4–7] or numerical [8–11] solution of the oxygen diffusion equation in the reaction layers. Theoretical models provide not only the weight gain and the reaction layers thickness but also the oxygen concentration dependence on the spatial coordinate.

Knowledge of the oxygen concentration profile is extremely important in establishing the fuel damage criteria and this is the reason for describing the high temperature oxidation of zirconium alloys using theoretical models.

Studying the oxidation of the fuel element sheath and its consequences on the whole behavior of the nuclear fuel element we have developed a computer routine, OXCON, based on a theoretical oxidation model. The routine was requested to be

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simple in structure in order to be implemented in a more complex code which describes the fuel element behavior during accident conditions. To meet this requirement we have chosen to analytically solve the oxygen diffusion equations, carefully observing the applicability range of these solutions. To that end, the temperature transients were approximated by a succession of isothermal steps and we have adopted the concept of 'equivalent time' which is detailed in Section 2.

In Section 2 we present the mathematical model for analytically solving the oxidation of the Zircaloy-4 fuel element sheath as a moving boundary one-dimensional diffusion problem in a semi-infinite medium. Section 3 presents the results obtained using the model compared with the predictions of similar validated codes. A discussion of the results and of the model limits together with final conclusions and directions for further studies are contained in Section 4.

2. The mathematical model

The theoretical treatment for the oxidation of zirconium and its alloys was proposed by Debuigne and Lehr [5] and improved by Leclercq [4]. Physical models have been developed [6,9] based on these models to describe the oxidation of zirconium alloys. As the curvature of the reaction layers is small, it is sufficient to solve the diffusion equation in the radial direction only [9]. The diffusion is considered to take place in a semi-infinite medium due to the relatively large thickness of the cladding compared to the penetration depth of the oxygen provided that the oxidation time is short enough.

We take the space coordinate normal to the coolant/oxide interphase with its origin located at this interface. This axis represents the direction of the oxygen diffusion. If the oxide and the metal are assumed to have the same density, the oxide/metal interphase is located at the abscissa ξ and its displacement in the time interval dt is $d\xi$. Actually, the zirconium oxide density is different to that of the zirconium metal, $\rho_{Zr}/\rho_{ZrO_2}=f\neq 1$. The oxide volume is larger than that of the metal which reacted with the coolant to form it. This volume increase is reflected as an increase of the radial dimension and in this case the coolant/ oxide interphase is located at ξ'. When the oxide metal interface displacement is $d\xi$, the oxide thickness grows by $d\xi'=f d\xi$. Consequently the formation of an oxide with a density different to that of the metal causes, in the reference system described above, the rigid motion of the α-phase by a speed $(1-1/f)d\xi'/dt$ [7].

When the reaction layers are the oxide and the α-Zr only, the oxygen diffusion equations are, respectively (the second Fick's law)

$$D_1\frac{\partial^2 C_I}{\partial x^2}=\frac{\partial C_I}{\partial t};\quad C_I=\begin{cases}C_1 & \text{for } x=0\\ C_2 & \text{for } x=\xi'\end{cases},$$

$$D_2\frac{\partial^2 C_{II}}{\partial x^2}=u_x\frac{\partial C_{II}}{\partial x}+\frac{\partial C_{II}}{\partial t};\quad C_{II}=\begin{cases}C_3 & \text{for } x=\xi'\\ 0 & \text{for } x=\infty\end{cases}, \tag{1}$$

where D_1 and D_2 are the oxygen diffusion coefficients in oxide and in α-Zr; $u_x=(1-1/f)d\xi'/dt$ is the velocity of the rigid displacement of the α-Zr phase; $C_I=C_I(x,t)$ and $C_{II}=C_{II}(x,t)$ are the oxygen concentrations in the oxide and α-Zr respectively; C_1 is the oxygen concentration on the coolant/ oxide interface, C_2 and C_3 are the oxygen concentrations at the oxide/ α-Zr in oxide and in the α-Zr phase respectively.

When the reaction layers are the oxide, α-Zr and β-Zr, the oxygen diffusion equations are obtained writing adequately the second Fick's law:

$$D_1\frac{\partial^2 C_I}{\partial x^2}=\frac{\partial C_I}{\partial t};\quad C_I=\begin{cases}C_1 & \text{for } x=0\\ C_2 & \text{for } x=\xi'\end{cases},$$

$$D_2\frac{\partial^2 C_{II}}{\partial x^2}=u_x\frac{\partial C_{II}}{\partial x}+\frac{\partial C_{II}}{\partial t};\quad C_{II}=\begin{cases}C_3 & \text{for } x=\xi'\\ C_4 & \text{for } x=\xi_1'\end{cases}, \tag{2}$$

$$D_3\frac{\partial^2 C_{III}}{\partial x^2}=u_x\frac{\partial C_{III}}{\partial x}+\frac{\partial C_{III}}{\partial t};\quad C_{III}=\begin{cases}C_5 & \text{for } x=\xi_1'\\ 0 & \text{for } x=\infty\end{cases},$$

where ξ_1' is the position of the α-Zr/β-Zr interface in the considered reference system, D_3 is the oxygen diffusion coefficient in β-Zr, $C_{III}=C_{III}(x,t)$ is the oxygen concentration in β-Zr; C_4 and C_5 the oxygen concentrations at the α-Zr/β-Zr interface in the α-Zr and β-Zr phases respectively.

Diffusion equations have been solved using the Neumann method: for each differential equation a particular solution was found and constants in these solutions were calculated using the corresponding boundary conditions [7,11,12].

For the case when the reaction layers are the oxide and the α-Zr phase, the oxygen concentrations in both phases which satisfy Eq. (1) are given by

$$C_{\mathrm{I}}(x,t) = C_1 + \frac{C_2 - C_1}{\mathrm{erf}\,\gamma'}\mathrm{erf}\frac{x}{2\sqrt{D_1 t}} \quad \text{for } 0 \le x \le \xi', \tag{3}$$

$$C_{\mathrm{II}}(x,t) = \frac{C_3}{\mathrm{erfc}(\gamma'\Phi/f)}\mathrm{erfc}\left(\frac{x}{2\sqrt{D_2 t}} - \gamma'\Phi(1 - 1/f)\right) \quad \text{for } x > \xi', \tag{4}$$

where $\Phi = (D_1/D_2)^{1/2}$ and $\gamma' = \xi'/(2\sqrt{D_1 t})$ is a constant for the given temperature.

For the case of the oxide, α-Zr and β-Zr phases as reaction layers, the solutions of the oxygen diffusion Eq. (2) are

$$C_{\mathrm{I}}(x,t) = C_1 + \frac{C_2 - C_1}{\mathrm{erf}\,\gamma'}\mathrm{erf}\frac{x}{2\sqrt{D_1 t}} \quad \text{for } 0 \le x \le \xi', \tag{5}$$

$$C_{\mathrm{II}}(x,t) = \frac{C_4\,\mathrm{erf}(\gamma'\Phi/f) - C_3\,\mathrm{erf}[\gamma_1' - \gamma'\Phi(1-1/f)] + (C_3 - C_4)\mathrm{erf}\left(\left(x/\left(2\sqrt{D_2 t}\right)\right) - \gamma'\Phi(1-1/f)\right)}{\mathrm{erf}(\gamma'\Phi/f) - \mathrm{erf}[\gamma_1' - \gamma'\Phi(1-1/f)]}, \tag{6}$$

$$C_{\mathrm{III}}(x,t) = \frac{C_5\,\mathrm{erfc}\left(\left(x/\left(2\sqrt{D_3 t}\right)\right) - \gamma'\Phi\Phi_1(1-1/f)\right)}{\mathrm{erfc}(\gamma_1'\Phi_1 - \gamma'\Phi\Phi_1(1-1/f))}, \tag{7}$$

where $\Phi_1 = (D_2/D_3)^{1/2}$ and $\gamma_1' = \xi_1'/2(D_2 t)^{1/2}$ is a constant for the given temperature.

To evaluate the coordinates ξ' and ξ_1' for the separation surfaces of the reaction layers we have to consider the movement of the interphase boundaries. The origin of this movement is the difference between incoming (J_{in}) and outgoing (J_{out}) fluxes. Considering that the fluxes are given by $J = -D(\partial C/\partial x) + u_x C$, we obtain, corresponding to each interphase boundary,

$$\frac{\mathrm{d}\xi'}{\mathrm{d}t} = -\frac{D_1}{fC_2 - C_3}\left.\frac{\partial C_{\mathrm{I}}}{\partial x}\right|_{\xi'} + \frac{D_2}{fC_2 - C_3}\left.\frac{\partial C_{\mathrm{II}}}{\partial x}\right|_{\xi'} + \mu_x C_{\mathrm{I}}|_{\xi'} - \mu_x C_{\mathrm{II}}|_{\xi'} \tag{8}$$

and

$$\frac{\mathrm{d}\xi_1'}{\mathrm{d}t} = -\frac{D_2}{C_4 - C_5}\left.\frac{\partial C_{\mathrm{II}}}{\partial x}\right|_{\xi_1'} + \frac{D_3}{C_4 - C_5}\left.\frac{\partial C_{\mathrm{III}}}{\partial x}\right|_{\xi_1'} + \mu_x C_{\mathrm{II}}|_{\xi_1'} - \mu_x C_{\mathrm{III}}|_{\xi_1'}. \tag{9}$$

Below the α–β transformation temperature, using Eq. (8) and replacing the corresponding derivatives of C_{I} and C_{II} given immediately from Eqs. (3) and (4) we obtain

$$\frac{1}{f}\gamma' = \frac{C_1 - C_2}{fC_2 - C_3}\frac{\exp(-\gamma'^2)}{\sqrt{\pi}\,\mathrm{erf}\,\gamma'} - \frac{C_3}{fC_2 - C_3}\frac{\exp\left[-(\gamma'\Phi/f)^2\right]}{\Phi\sqrt{\pi}\,\mathrm{erfc}\,(\gamma'\Phi/f)}. \tag{10}$$

In a similar manner, the equations for γ' and γ_1' can be obtained in the case where the reaction layers are oxide, α-Zr and β-Zr:

$$\begin{cases} \dfrac{1}{f}\gamma' = \dfrac{C_1 - C_2}{fC_2 - C_3}\dfrac{\exp(-\gamma'^2)}{\sqrt{\pi}\,\mathrm{erf}\,\gamma'} + \dfrac{C_3 - C_4}{fC_2 - C_3}\dfrac{\exp[-(\gamma'\Phi/f)^2]}{\Phi\sqrt{\pi}\,\{\mathrm{erf}(\gamma'\Phi/f) - \mathrm{erf}[\gamma_1' - \gamma'\Phi(1-1/f)]]\}} \\ \gamma_1' = \gamma'\Phi(1-1/f) - \dfrac{C_3 - C_4}{C_4 - C_5}\dfrac{\exp(-[\gamma_1' - \gamma'\Phi(1-1/f)]^2)}{\sqrt{\pi}\,(\mathrm{erf}(\gamma'\Phi/f) - \mathrm{erf}[\gamma_1' - \gamma'\Phi(1-1/f)])} - \dfrac{C_5}{C_4 - C_5}\dfrac{\exp\{-[\gamma_1' - \gamma'\Phi(1-1/f)]^2\Phi_1^2\}}{\Phi_1\sqrt{\pi}\,\mathrm{erfc}\{[\gamma_1' - \gamma'\Phi(1-1/f)]\Phi_1\}} \end{cases} \tag{11}$$

We obtain the weight gain in each reaction layer by integrating in the spatial coordinate the solutions of the diffusion equation on the corresponding domain. Then, below the α/β transition temperature the weight gain in the oxide and the α-Zr phase are, respectively,

$$W_{\mathrm{ox}}(t)=2\sqrt{D_1 t}\left[C_2\gamma'+\frac{C_2-C_1}{\sqrt{\pi}}\frac{\exp(-\gamma'^2)}{\operatorname{erf}\gamma'}\right] \tag{12}$$

and

$$W_{\alpha}(t)=2\sqrt{D_2 t}\,C_3\left(\frac{\exp\left[-(\gamma'\Phi/f)^2\right]}{\sqrt{\pi}\operatorname{erfc}(\gamma'\Phi/f)}-\frac{\gamma'\Phi}{f}\right). \tag{13}$$

Above the α/β transition temperature the weight gain in the oxide, α-Zr and β-Zr phases are, respectively,

$$W_{\mathrm{ox}}(t)=2\sqrt{D_1 t}\left[C_2\gamma'+\frac{C_2-C_1}{\sqrt{\pi}}\frac{\exp(-\gamma'^2)}{\operatorname{erf}\gamma'}\right], \tag{14}$$

$$W_{\alpha}(t)=2\sqrt{D_2 t}\times\frac{(C_4-C_3)\left[\exp\left[-(\gamma'\Phi/f)^2\right]-\exp\left\{-\left[\gamma_1'-\gamma'\Phi(1-1/f)\right]^2\right\}\right]+C_4\left[\gamma_1'-\gamma'\Phi(1-1/f)\right]-C_3\gamma'\Phi/f}{\sqrt{\pi}\left\{\operatorname{erf}(\gamma'\Phi/f)-\operatorname{erf}\left[\gamma_1'-\gamma'\Phi(1-1/f)\right]\right\}}, \tag{15}$$

$$W_{\beta}=2C_5\sqrt{D_3 t}\left\{\frac{\exp\left\{-\Phi_1^2\left[\gamma_1'-\gamma'\Phi(1-1/f)\right]^2\right\}}{\sqrt{\pi}\operatorname{erfc}\left\{\Phi_1\left[\gamma_1'-\gamma'\Phi(1-1/f)\right]\right\}}-\Phi_1\left[\gamma_1'-\gamma'\Phi(1-1/f)\right]\right\}. \tag{16}$$

Using a large number of oxidation experiments on fuel element claddings, the temperature dependence of the oxygen diffusion coefficients have been established [9] for oxide, α-Zr and β-Zr:

$$\begin{cases} D_1=1.57\times10^{-5}\exp(-17685/T)\ \mathrm{m^2/s} \\ D_2=4.11\times10^{-4}\exp(-25682/T)\ \mathrm{m^2/s}. \\ D_3=2.64\times10^{-6}\exp(-14107/T)\ \mathrm{m^2/s} \end{cases} \tag{17}$$

where T is the temperature in K.

Calculations performed assuming equal densities ($f=1$) for oxide and metal [12] in comparison with experimental data obtained in INR have shown the applicability of these coefficients in describing the oxidation of INR fuel cladding during high transient temperatures.

As the oxygen concentrations on separation surfaces have been assumed to be equal to the corresponding equilibrium concentrations, we have used the most recent values found in literature [13]:

$$C_1=1511\ \mathrm{Kg/m^3}, \tag{18}$$

$$C_2=5631\frac{16X}{91.22(100-X)+16X}\ \mathrm{Kg/m^3}\quad X=66.3-8.6\times10^{-4}T. \tag{19}$$

$$C_3=1118.6\frac{Y}{1-Y}\ \mathrm{Kg/m^3}\quad Y=\begin{cases}0.3 & T<1473\ \mathrm{K}\\ 5.833\times10^{-8}T^2-1.652\times10^{-4}T+0.4167 & 1473\ \mathrm{K}\le T<2173\ \mathrm{K}\end{cases} \tag{20}$$

$$C_4=64.9\left(-0.2263+\sqrt{\frac{T}{63.385}-16.877}\right)\ \mathrm{Kg/m^3}\quad T\ge1073. \tag{21}$$

$$C_5=\begin{cases}64.9\left(-0.00428+\sqrt{\frac{T}{392.46}-3.1417}\right)\ \mathrm{Kg/m^3} & 1233\ \mathrm{K}<T<1373\ \mathrm{K}\\ 64.9\frac{T-1081.7}{491.159}\ \mathrm{Kg/m^3} & T\ge1373\ \mathrm{K}\end{cases}. \tag{22}$$

These values also proved to be adequate when used for describing the oxidation behavior of the INR fuel element sheath [12].

In order to use the analytical solutions for the oxygen diffusion equations in describing the oxidation behavior of the Zircaloy-4 fuel element sheath during high temperature transients we considered the following assumptions.

1. the temperature distribution in the cladding is uniform;
2. the temperature transient can be considered as a stepwise function of time, $\{T_i, (t_{0i}, t_i)\}_{i=1,n}$ with $t_i = t_{0i} + \Delta t_i$;
3. for any given step of the considered temperature transient, corresponding to the time interval (t_{0i}, t_i), for which the temperature is T_i, the oxygen concentrations at the interphase surfaces are given by the equilibrium temperature–composition phase diagram;
4. in the beginning of the ith step of the temperature transient the oxide layer thickness grown during the previous steps, x_{0i}, can be regarded as being formed at a constant temperature, T_i, during the equivalent time interval Δt_{eq}. The equivalent time interval can be evaluated using the definition for γ' with $\xi' = x_{0i}$:
$$\Delta t_{eq} = (x_{0i}/\gamma')^2/4D_1. \tag{23}$$
γ' is a constant for a given temperature and can be evaluated by numerically solving Eq. (10) or system Eq. (11) when T_i is below or above the α–β transition temperature respectively;
5. the oxidation during the first $(i-1)$ steps of the temperature transient can be considered as having the same consequences (reaction layers thickness, oxygen profiles, weight gains) as an isothermal oxidation proceeding at the temperature of the current step, T_i, during the equivalent time
$$t_{eq} = \Delta t_{eq} + \Delta t_i. \tag{24}$$

The assumption on the equivalent time enables us to treat the oxidation of the fuel element sheath during temperature transients as if it were isothermal and proceeding after a modified time scale. In this way we are enabled to use the analytical solutions for the corresponding diffusion equations.

3. Results

We have developed a computer routine, OXCON, based on the model described in the previous section for the oxidation of the fuel element cladding during high temperature transients.

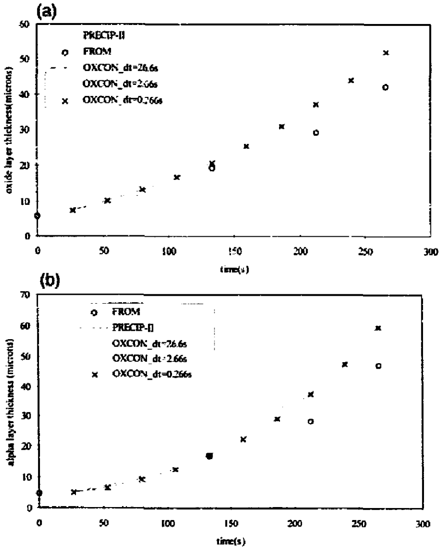

Fig. 1. Time dependence of the thicknesses of (a) oxide and (b) α-Zr corresponding to heating from 1200 K to 1600 K at a rate of 1.5 K/s.

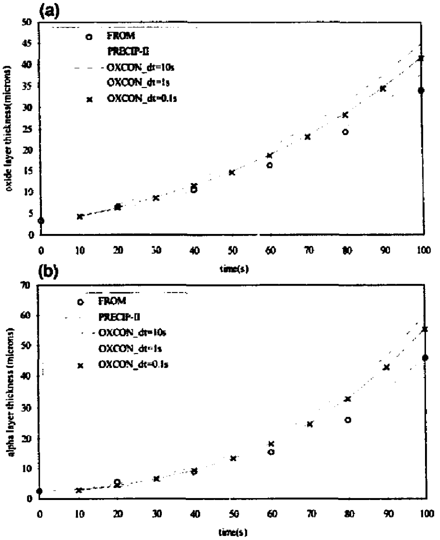

Fig. 2. Time dependence of the thicknesses of (a) oxide and (b) α-Zr corresponding to heating from 1200 K to 1700 K with a rate of 5 K/s.

To prove the ability of our OXCON routine to predict the time dependence of the reaction layers thickness we have chosen, for this work, to compare its results to those of Canadian (FROM) [9] and Japanese (PRECIP-II) [10] oxidation codes. These codes solve the uni-dimensional diffusion equations for semi-infinite media using numerical methods with

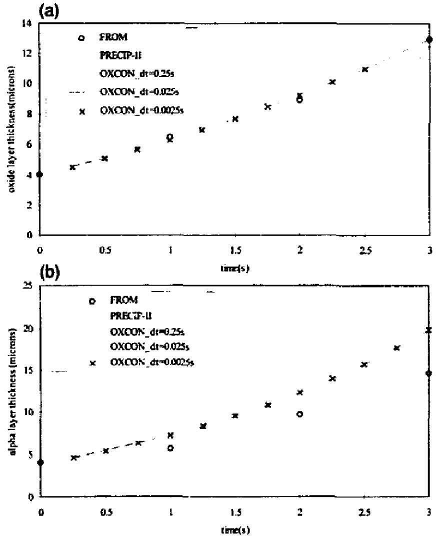

Fig. 3. Time dependence of the thickness of (a) oxide and (b) α-Zr corresponding to heating from 1500 K to 1800 K with a rate of 100 K/s.

finite difference schemes and have been verified by their authors against experimental data. Both codes' predictions have shown good agreement with experimental data. A set of such experimental data used in the FROM code verification consisted of values of the reaction layers thickness at different moments during heat up ramps. We possess information about the predictions of the FROM code from figures in Ref. [9] only but the PRECIP-II code is available in INR.

OXCON and PRECIP-II have been run for three different temperature transients corresponding to heat up at constant rates of 1.5 K/s, 5 K/s and 100 K/s, respectively. The thickness of the oxide and α-Zr layers have been calculated and are displayed together with the corresponding FROM predictions in Figs. 1–3.

In OXCON we have considered the step functions approximating the temperature transients so that for each considered step, i, $\Delta t_i = \Delta t$. For each heat up ramp three different values for the Δt have been used in OXCON and they were mentioned on the plots as dt.

It is evident from Figs. 1–3 that for each heating rate the OXCON predictions of oxide and alpha layer time evolutions are very close to the PRECIP-II predictions, slightly overestimating them and both agree quite well with those of the FROM code.

When the Δt value was higher the OXCON overprediction was higher. Using for Δt values so that the temperature variation from one step to another be less than 5 K, the OXCON predictions became nearly independent of Δt.

4. Discussion and conclusions

The method based on the analytical solution of the diffusion equation proposed in this paper is simpler in structure than the codes based on numerical methods. Our method gives results similar to those of the numerical oxidation codes.

Calculations have shown that the routine based on the model developed in this work gives predictions for the oxide layer thickness very close to those of the finite difference oxidation codes PRECIP-II and FROM on the entire considered computational experiment, slowly overestimating them. We plan to continue studying the predictions of OXCON for more complex temperature transients, containing also cooling periods.

We have assumed that the oxygen concentrations at interfaces are identical to those given by the Zr–O phase diagram, so we have considered that instantaneous local equilibrium holds [13] but the validity of this assumption still requires verification.

The predictions of the oxidation model developed here have to be verified against experimental data and versus the predictions of the other oxidation codes, in order to enlarge the applicability of OXCON over more general temperature histories containing also cooling periods. To describe the α-Zr incursions (α-fingers) which form in β-Zr during cooling periods, the further study of the thermodynamic aspects of the zirconium alloys oxidation process seems to be adequate.

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