

TRANOX: Mechanistic Model for Non-Isothermal Steam Oxidation of Zircaloy Cladding

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1. Introduction

Zirconium-based nuclear fuel cladding used in commercial nuclear reactor is oxidized at high temperature in Design-Based Accidents such as Loss of Coolant Accident (LOCA) and Reactivity Insertion Accident (RIA). High-temperature oxidation results in the formation of zirconium oxide (ZrO_2), ZrO , α - $Zr(O)$, and prior- β phases in descending order of the oxygen amount (Fig. 1 (a)). The innermost region (prior- β) is the basis of residual ductility and ductility of the prior- β layer is dependent on its oxygen content [1]. In that regard, predicting the thickness and oxygen content of the prior- β is important to assure an adequate level of post-accident residual ductility.

In isothermal steam oxidation, resulting thickness and oxygen concentration of the prior- β are correlated with Equivalent Cladding Reacted (ECR), the total amount of oxygen uptake. Therefore, current Emergency Core Cooling System (ECCS) criteria (10 CFR 50.46) is based on ECR calculated by isothermal correlations such as Baker-Just, Cathcart-Pawel (CP), and Leistikov correlations.

On the other hand, all accidents are non-isothermal transients and isothermal relations between prior- β and ECR are not valid in the accident condition. Isothermal ECR correlations can be limitedly applied to non-isothermal conditions by assuming quasi-isothermal conditions at each time step. ECR could be conserved during temperature change but the thickness of each phase is not preserved under such assumption (Fig. 1 (b)).

In such a context, this study discusses the development and experimental validation of a mechanistic model for oxygen concentration distribution in Zr-alloy for both isothermal and non-isothermal conditions. Furthermore, the limited hydrogen effect on oxygen distribution was analyzed through this model.

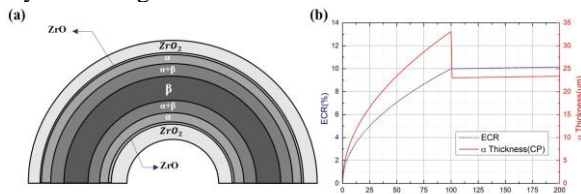


Fig. 1. (a) Phase development of steam-oxidized cladding. (b) Incoherent α - $Zr(O)$ thickness prediction based on CP-ECR correlation upon the change of temperature from 1200 to 1000°C at $t=100$ s (ECR is consistently maintained in relation to time).

2. Code Development

The presented model is named TRANOX (TRANsient Oxidation) and it solves the radial diffusion equation

$(\frac{\partial C}{\partial t} = \frac{\partial}{\partial r}(Dr \frac{\partial C}{\partial r}))$ using Finite Difference Method (FDM) with spatial phase transformation for each time step.

2.1 Governing equation and Numerical scheme

The 1-D radial diffusion equation is discretized with position interval h and time interval dt (Eq. (1)). D_i and C_i are diffusion coefficient and oxygen concentration of i^{th} node, respectively.

$$\frac{C_i^n - C_i^{n-1}}{dt} = \frac{D_{i+1}C_{i+1}^n - (D_{i+1} + D_{i-1})C_i^n + D_{i-1}C_{i-1}^n}{h^2} + \frac{D_{i+1}C_{i+1}^n - D_{i-1}C_{i-1}^n}{2*r(i)*h} \quad (1)$$

Cladding is divided into 40000 radial meshes and each mesh is classified into one of ZrO_2 , ZrO , α - $Zr(O)$, and prior- β phases according to the employed hydrogen-accounted phase diagram (Fig. 2).

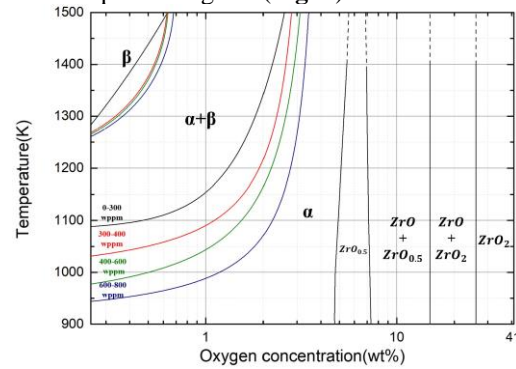


Fig. 2. Employed hydrogen-accounted Zr-O Phase diagram of TRANOX. Dashed lines indicate extrapolation [2].

A detailed numerical procedure is illustrated in Fig. 3. For given initial conditions (temperature, content of hydrogen, and oxygen), TRANOX calculates the thickness of the oxide layer using CP correlation [3]. Afterward, the phase of each mesh is determined according to the phase diagram and the diffusion coefficient is calculated through phase type and temperature. The discretized equation is then implicitly solved using the Thomas algorithm [4].

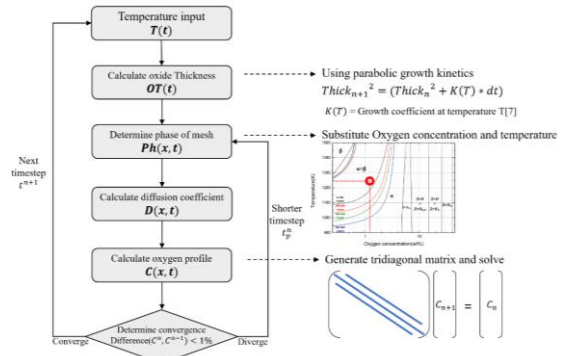


Fig. 3. Flow chart of the integrated numerical scheme employed in TRANOX.

2.2 Determination of diffusion coefficient

The diffusion coefficient of each phase was determined as a combination that gives the best agreement with isothermal steam oxidation experimental data (ECR and α -Zr(O) thickness) over 1000-1250°C. Diffusion coefficients were fitted as Arrhenius form as shown in **Fig. 4 (a)-(c)**. The diffusion coefficient of the $\alpha+\beta$ equilibrium phase is determined as linear combination of diffusion coefficients of α -Zr(O) and prior- β . Among the diffusion coefficients, ZrO was the smallest, and prior- β was the largest (**Fig. 4 (d)**), consistent with the order of the literature[5,6]. Diffusion coefficients of each phase were assumed as hydrogen-unaffected.

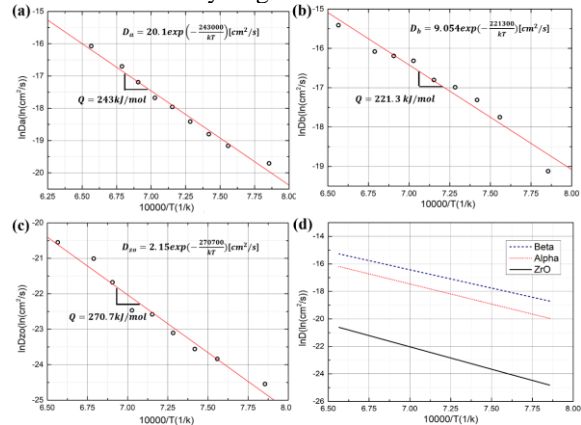


Fig. 4. Arrhenius plot of diffusion coefficients: (a) α -Zr(O) layer. (b) prior- β layer. (c) ZrO layer. (d) All diffusion coefficients used in the model.

3. Code Validation

High-temperature steam oxidation of Zircaloy-4 specimens was conducted to validate the developed model. Each specimen was cut into 1 cm and thermocouple was attached to measure the temperature directly. Both isothermal and non-isothermal steam oxidation tests were conducted (**Fig. 5 (a)-(b)**).

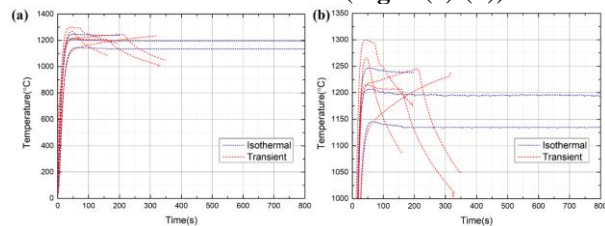


Fig. 5. Measured temperature profile: (a) Overall profile. (b) Magnified (1000~1300°C).

The rate of temperature change in the presented experiments and typical nuclear accidents are summarized in **Table. 1**. The temperature change is close to LOCA but quite smaller than RIA, which is the fastest transient among nuclear accidents.

Table. 1. Temperature changing rate of transient temperature oxidation.

	LOCA	RIA	Experiment
Maximum Heating Rate(K/s)	110	3300	100

Maximum Cooling Rate(K/s)	-10	-50	-100
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3.1 Existence of each phase

The existence of phases employed in the TRANOX (ZrO_2 , ZrO, α -Zr(O), $\alpha+\beta$, and prior- β) was evaluated by SEM (EM-30AX) and TEM (JEM-F200) analyses. **Fig. 6 (a)** is the SEM image of the cross-section of steam-oxidized Zircaloy-4 cladding and ZrO_2 , α -Zr(O), $\alpha+\beta$, and prior- β are present. **Fig. 6 (b)** and (c) are the SAED patterns for ZrO_2 and α -Zr(O), respectively.

There was no clear evidence of the existence of ZrO, a tens of nanometer layer between ZrO_2 and α -Zr(O). Even so, this study presumes ZrO layer with low diffusion coefficient to model a sharp concentration gradient at the metal/oxide interface.

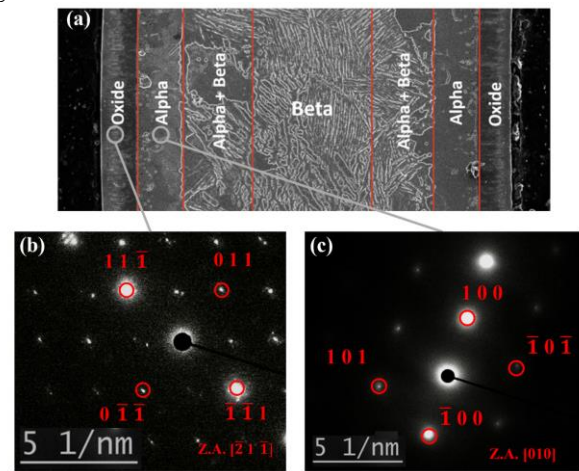


Fig. 6. SEM image and TEM SAED pattern: (a) Cross-sectional SEM image of Zircaloy-4 cladding oxidized to ECR 17% at 1200°C. (b) SAED pattern of the oxide scale (monoclinic ZrO_2). (c) SAED pattern of α -Zr(O).

3.2 Oxygen distribution

The oxygen distribution of oxidized specimen was measured by EPMA (JXA-8530F). The measured and predicted values showed very high agreement that unbiased according to isothermal and non-isothermal (**Fig. 7**).

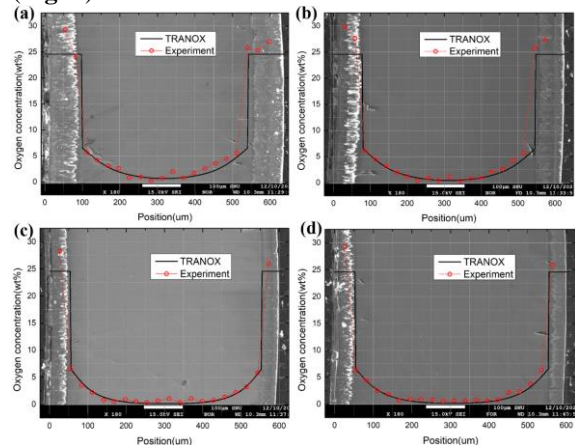


Fig. 7. TRANOX-to-Experiment (EPMA) comparisons of oxygen distribution: (a) Isothermally oxidized at 1150°C for 1600 s (ECR = 27%). (b) 1200°C for 600 s (ECR =22%). (c) Non-isothermal oxidation with heating rate of 57°C/s, cooling rate of 64°C/s, peak cladding temperature of 1240°C (ECR = 15.6%). (d) Non-isothermal oxidation with heating rate of 100°C/s, cooling rate of 84°C/s, peak cladding temperature of 1300°C (ECR = 15.7%).

3.3 Phase thickness and ECR

Fig. 8 (a) was the prediction result and measured data of ECR, and it shows TRANOX predicts ECR accurately. This result is based on an accurate prediction of the thickness of the oxide layer (**Fig. 8 (b)**), which occupies about 80% of the total ECR. **Fig. 8 (c)** and **(d)** are the prediction result of the thickness of α -Zr(O) and prior- β , respectively. TRANOX accurately predict the thickness of both layer and measurement error of prior- β layer is relatively smaller because it is thicker. It is noteworthy that there was no biased accuracy for both isothermal and non-isothermal transients.

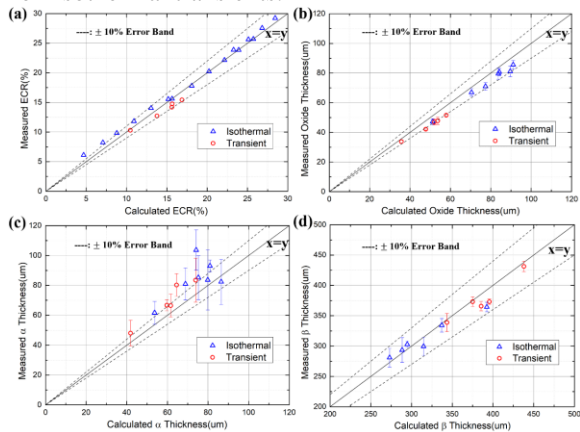


Fig. 8. Model-to-data comparison: (a) ECR. (b) Oxide layer thickness. (c) α layer thickness. (d) β layer thickness.

Additionally, high-accuracy CP correlation and TRANOX were compared in terms of prediction of ECR and thickness of prior- β . **Fig. 9 (a)** is the prediction result of ECR and both models showed high accuracy. In the case of prior- β , the accuracy of the two models was similar under isothermal conditions, but the accuracy of TRANOX was higher for non-isothermal transients.

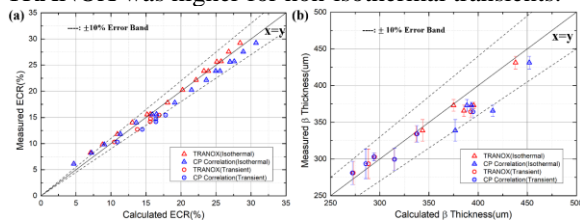


Fig. 9. Model-to-Experimental comparison of Cathcart-Pawel correlation and TRANOX: (a) ECR. (b) Prior- β layer thickness.

3.4 Hydrogen effect on oxygen distribution

According to the phase diagram (**Fig. 2**), hydrogen changes the equilibrium concentration of each phase. However, in the presence of hydrogen, the overall

distribution of oxygen in the cladding was almost identical with as-received cladding (**Fig. 10 (a)**) and it is in accord with existing literature [7]. TRANOX reproduces this hydrogen-insensitive oxygen distribution (**Fig. 10 (b)**). Despite the similar oxygen distribution, the thickness of α -Zr(O) layer slightly changes by hydrogen and there was an apparent increase in diffusion coefficient (**Fig. 10 (c)**).

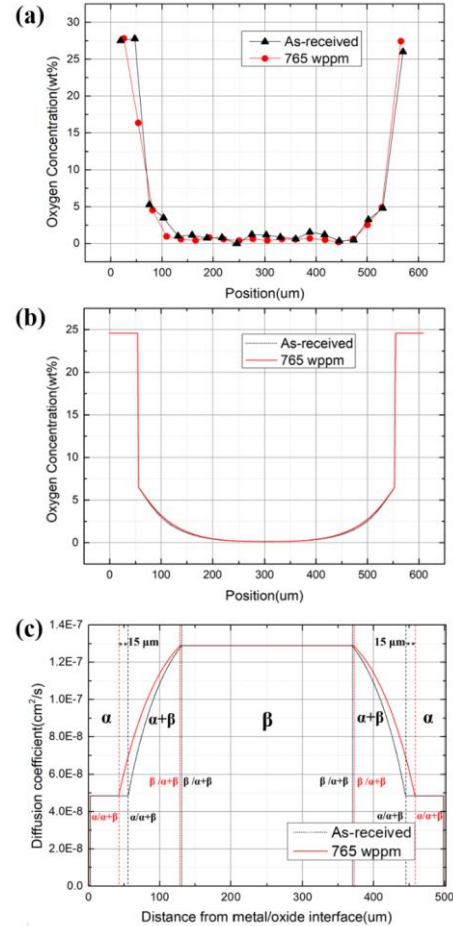


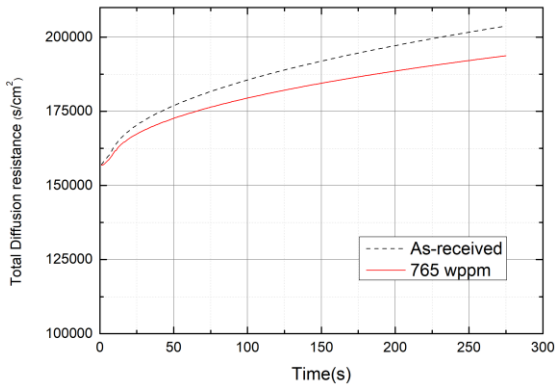
Fig. 10. Oxygen distribution of as-received and pre-hydrided (H:765wppm) Zircaloy-4 oxidized for 275 s at 1204°C to ECR 15.9% (pre-hydrided) and 15.7% (as-received): (a) Calculated with TRANOX. (b) Experiment result. (c) Diffusion coefficient distribution.

To explain hydrogen-insensitive oxygen distribution, the concept of diffusion resistance was introduced to compare oxidation resistance between hydride and as-received specimen. Total diffusion resistance (R_{total}) is calculated by summing up local resistance (R_i) (**Eq. (2)**). D_i is the diffusion coefficient and r_i is the radial position of i^{th} node.

$$R_{total} = \sum R_i = \frac{\ln \left(\frac{r_{(i+1)}}{r_i} \right)}{2\pi D_i} \text{ [s/cm}^2\text{]} \quad (2)$$

Fig. 11 shows a comparison of total diffusion resistance over time of Zircaloy oxidized at 1204 °C. It is almost identical in the initial stage and the difference increases by 5% as oxidation progresses. Since the oxidation kinetics follows parabolic law [3], negligible resistance difference in the early stage, which oxidation took fast,

leads to hydrogen-insensitive oxygen distribution.



4. Conclusion

In this study, 'TRANOX', a code that calculates oxygen distribution at given temperature transience, was developed and validated to predict the integrity of the cladding when nuclear fuel cladding is oxidized in accidents including LOCA. TRANOX predicts the oxidation of Zircaloy (ECR, thickness of each phase, and oxygen distribution) accurately for both isothermal and non-isothermal transience. In addition, it gives explanation for hydrogen-insensitive oxygen distribution through the diffusion resistance concept.

Acknowledgments

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REFERENCES

- [1] Hobson, D.O., Ductile-brittle behavior of Zircaloy fuel cladding (CONF-730304--1), United States, (1972).
- [2] Séverine Guilbert-Banti, Pauline Lacote, Gaëlle Teraud, Pascal Berger, Jean Desquines, Christian Duriez, Influence of hydrogen on the oxygen solubility in Zircaloy-4, Journal of Nuclear Materials, Volume 469 (2016), 228-236.
- [3] R.E. Pawel, The Kinetics of Oxidation of Zircaloy-4 in Steam at High Temperatures, Journal of The Electrochemical Society, 126 (1979), 1105-1111.
- [4] W T Lee. Tridiagonal Matrices: Thomas Algorithm. MS6021, Sci. Comput. Univ. Limerick, pages 1–3, November 2011.
- [5] Michael Reyes, Asghar Aryanfar, Sun Woong Baek, Jaime Marian, Multilayer interface tracking model of zirconium clad oxidation, Journal of Nuclear Materials, Volume 509 (2018), 550-565.
- [6] R. E. Pawel, Oxygen Diffusion in the Oxide and Alpha Phases during Reaction of Zircaloy-4 with Steam from 1000 to 1500 °C, J. Electrochem. Soc. 126 (1979), 1111-1118.
- [7] Kyunghwan Keum, Youho Lee, Effect of cooling rate on the residual ductility of Post-LOCA Zircaloy-4 cladding, Journal of Nuclear Materials, Volume 541 (2020), 152405.