Development and Validation of a Code for the Oxygen Distribution of Zircaloy Cladding in Non-Isothermal Transient Steam Oxidation

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1. Introduction

Retention of an adequate level of Post-LOCA cladding ductility is a basis of the current Emergency Core Cooling System (ECCS) criteria (10 CFR 50.46). The current regulation prescribes the peak cladding temperature of 1204ºC and 17 % Equivalent Cladding Reacted (ECR) calculated by the Baker-Just correlation. The ECR correlations such as Baker-Just, Cathcart-Pawel, and Leistikow correlations were all developed with isothermal oxidation.

It is noteworthy that in reality cladding undergoes significant temperature transience during postulated Loss of Coolant Accident (LOCA). This implies that the current isothermal correlations may have limited validity for use in such rapid temperature transience. Nevertheless, those isothermal correlations are being used in safety analyses without a systematic evaluation of its predictability for ECR under rapid temperature transience.

A key limitation of isothermal correlations is that they do not conserve the thickness of each phase when temperature changes. The isothermal correlations can still be applied for transience, yet they only conserve the ECR upon any transient temperature change without a consideration of the conservation of individual phase thicknesses (α, α + β, β, and ZrO_2). Hence, the use of isothermal correlations for transience is believed to introduce prediction errors.

Recognizing such limitation of the isothermal correlation for use in safety analyses, several research efforts have been made to develop transient oxygen distribution models. DIFFOX was developed by IRSN (France) and still being updated to model transient oxygen distribution in Zircaloy [1]. Yet, it is believed that it needs to be further validated against realistically rapid LOCA transience.

In such a context, this study discusses the development and preliminary experimental validation of an in-house computer code for oxygen distribution of Zircaloy cladding in transient steam oxidation. ZrO_2(oxide), ZrO, α phase, β phase, and α + β phase are considered in the developed code.

2. Methodology

2.1 Governing Equations and Boundary Conditions

Transient oxygen diffusion in 1D radial coordinate (Eq.1) is solved with implicit finite difference method (FDM).

$$\frac{\partial C}{\partial t} = \frac{\partial}{r\partial r}(Dr\frac{\partial C}{\partial r}) \quad (1)$$

The code is developed to select either single-sided or double-sided oxidation as shown in Fig. 1.

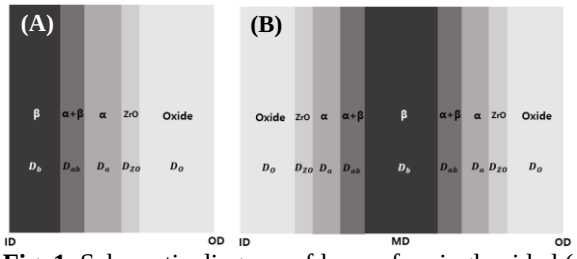

Fig. 1. Schematic diagram of layers for single-sided (A) and double-sided (B)

For double-sided oxidation, following boundary conditions were applied on inner and outer surface of the cladding.

$$C(oxide/ZrO) = C_{oxide} \text{ (at each side)} \quad (2)$$

$$\frac{\partial C(MD)}{\partial x} = 0 \quad (3)$$

Where C is the oxygen concentration. C_{oxide} is 24.58 wt% as found in the phase diagram [2].

For single-sided oxidation, following boundary conditions were applied on inner and outer surface of the cladding.

$$C(oxide/ZrO) = C_{oxide} \quad (4)$$

$$\frac{\partial C(ID)}{\partial x} = 0 \quad (5)$$

The CP oxide thickness correlation [3] was used for the oxide scale growth in the developed model.

2.1 Numerical Scheme

Eq. (1) is discretized using implicit FDM as follows

$$\frac{C_i^n - C_i^{n-1}}{dt} = D(i)\frac{C_{i-1}^n - 2C_i^n + C_{i+1}^n}{h^2} + D(i)\frac{C_{i+1}^n - C_{i-1}^n}{2*x(i)*h} \quad (6)$$

(dt : time interval, h : mesh size, x: position vector)

The diffusion coefficients are different on both sides at the interface and it applied to Eq. (7).

$$\frac{C_i^n - C_i^{n-1}}{dt} = \frac{D_{i+1}C_{i+1}^n - (D_{i+1}+D_{i-1})C_i^n + D_{i-1}C_{i-1}^n}{h^2} + \frac{D_{i+1}C_{i+1}^n - D_{i-1}C_{i-1}^n}{2*x(i)*h} \quad (7)$$

The discretized equation is then solved using Ax=b.

For each time step, the phase thickness and associated diffusion coefficients are updated. The Zr and O phase diagram was used to determine the phase thicknesses for

given oxygen distribution. Detailed calculation processes are illustrated in Fig. 2.

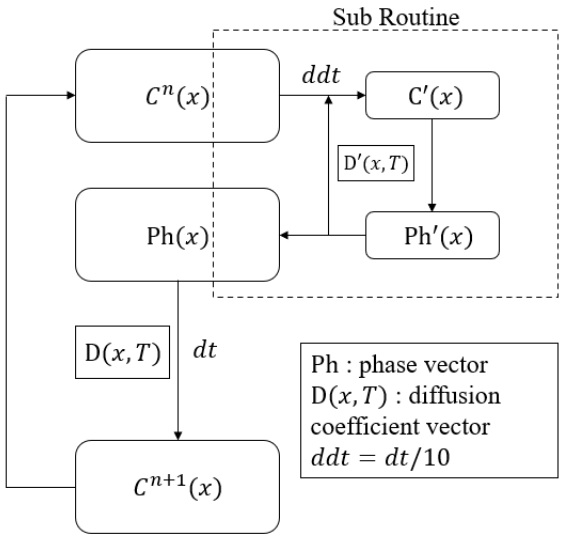

Fig. 2. Flow diagram of numerical procedure

3. Determination of diffusion coefficients

In the case of α, β, and oxide layers, the diffusion coefficients from the existing literatures [4-5] were used. For ZrO and α + β representation, simulations have been used to find pairs that can accurately match the ECR and α layer thickness of CP correlation.

ECR and α layer thickness were used as a measure of the code's predictability against the CP correlation. The diffusion coefficients of ZrO and α + β that give the best agreement with CP correlation's ECR and α layer thickness were selected. As a following step, diffusion coefficient correlations were developed by fitting the obtained diffusion coefficients over the temperature range of 900 – 1400ºC in Arrhenius plot (Fig.3).

ECR and α layer thicknesses grow parabolic over time. Therefore, after plotting each value for $\sqrt{t}$, the linear fitting slopes of obtained ($\delta_{ECR}, \delta_{\alpha}$) were compared with the values of the CP correlation. In the isothermal simulation, $D_{zo}$and D_{ab} values were changed at regular intervals, and the pair with the smallest RMS value of the error of the two coefficients was selected as the diffusion coefficient of each temperature .

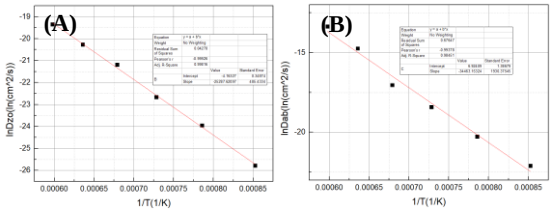

Fig. 3. Arrhenius fitting of obtained diffusion coefficient for ZrO (A) and α + β (B)

The diffusion coefficients and oxide scale growth models employed in the developed codes are summarized in Table 1.

Table 1. Summary of employed models for the developed code

	Model	**Reference**
Oxide scale thickness	$\epsilon = 0.02252\exp\left(-\frac{35890}{kT}\right)\sqrt{t}$	[3]
Diffusion coefficient of Oxide	$D_o = 0.127\exp\left(-\frac{-34510}{kT}\right)$	[5]
Diffusion coefficient of ZrO	$D_{zo} = 0.0155\exp\left(-\frac{50246}{kT}\right)$	This study
Diffusion coefficient of α	$D_{\alpha} = 3.92\exp\left(-\frac{51000}{kT}\right)$	[5]
Diffusion coefficient of α + β	$D_{ab} = 1016.5\exp\left(-\frac{68478}{kT}\right)$	This study
Diffusion coefficient of β	$D_{\beta} = 0.0248\exp\left(-\frac{28200}{kT}\right)$	[4]

By applying the obtained equations and executing the code, oxygen distribution over temperature and time can be obtained as shown in Fig.4. Also, information about the thickness and location of each phase can be obtained.

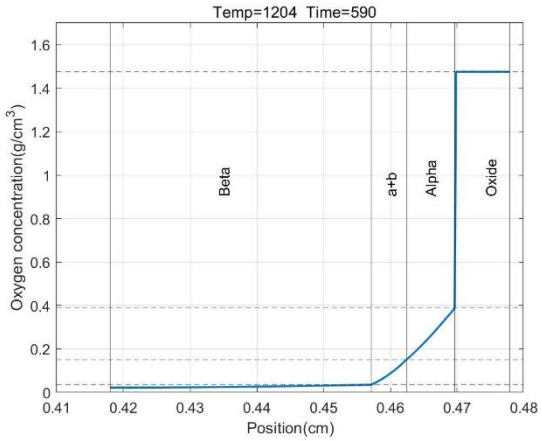

Fig. 4. Oxygen distribution of cladding at 1204 ℃ with 590 s of oxidation

As shown in the Fig.5, it is possible to obtain information on the thickness of the remaining β over time, so it can help to predict the ductility of cladding. In the early stage, the thickness decreases at a rapid rate, and the reduction rate decreases with time.

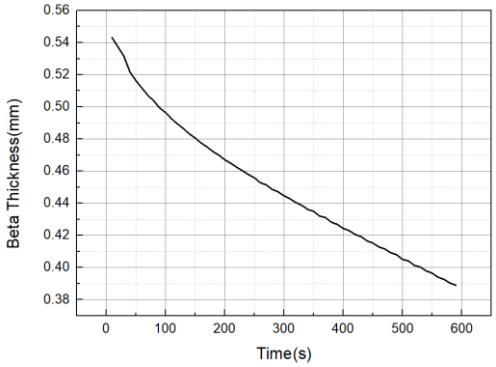

Fig. 5. β layer thickness over time when oxidized at 1204 ℃

4. Code Validation

2.1 Validation for Isothermal Oxidation

The developed code has been validated against steady-state experimental data [6]. As can be seen in Fig. 6, the developed code gives a good agreement with the experimental data.

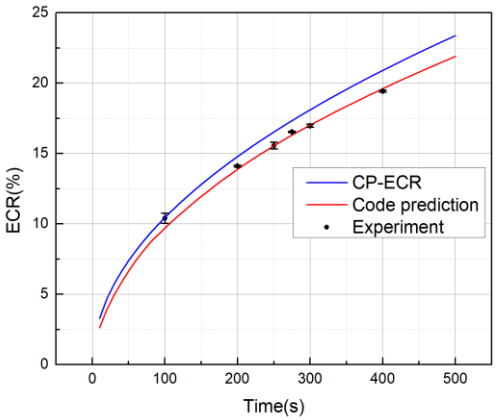

Fig. 6. Code-calculated ECR and CP-ECR over time with experiment result while oxidized at 1204℃

SEM-EDS analysis (Fig. 7) shows an acceptable level of agreement for oxygen distribution between the code result and the experiment.

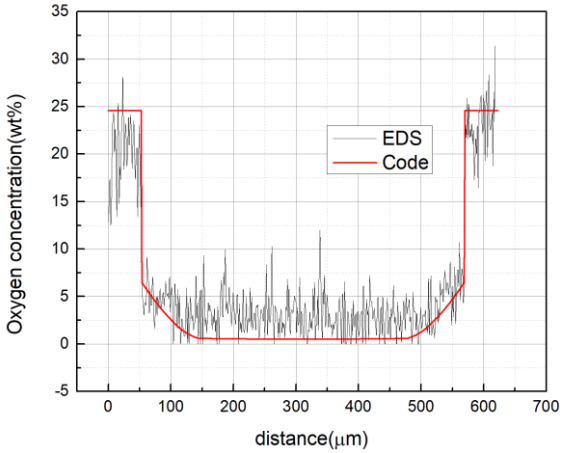

Fig. 7. Oxygen distribution data of ECR 17% sample from EDS and Code

2.2 Validation for Temperature-variant Transient Oxidation

A transient oxidation that accompanies a significant temperature variation was conducted [7] as shown in Fig. 8(A). It is noteworthy that the isothermal CP correlation does not provide an accurate prediction for the resulting ECR of this transience (error=14.5%). Considering the remarkable prediction accuracy of the CP correlation for the steady-state oxidation shown in Fig. 6, the presented error is non-negligibly high, and is a consequence of the aforementioned transient effects.

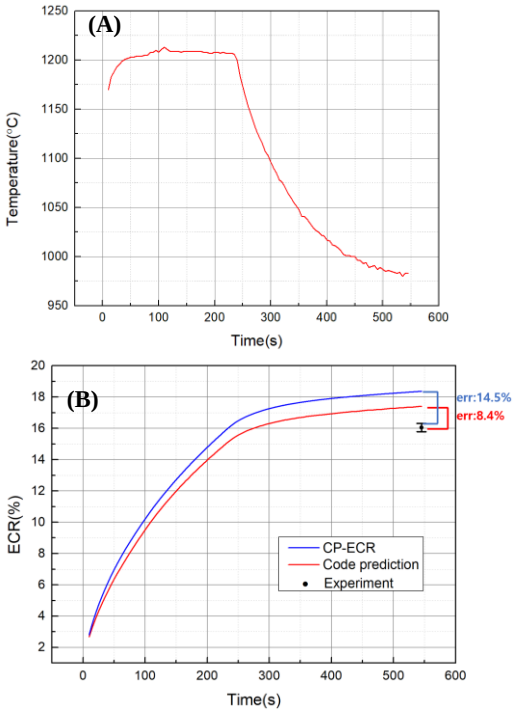

Fig. 8. Temperature profile (A) and ECR data (B) of temperature-variant oxidation

SEM-EDS analysis (Fig. 9) shows that oxide thickness was somewhat overrated (error=18%) at code result and in the bulk metal, code result and the experiment show acceptable agreement.

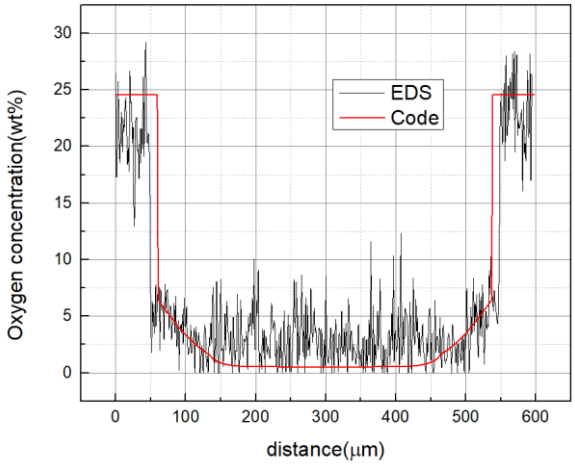

Fig. 9. Oxygen distribution data of temperature-variant oxidized sample from EDS and Code

The presented non-isothermal validation data clearly demonstrates the need for the non-isothermal consideration in Zircaloy steam oxidation simulation. It provides preliminary, yet critical, evidence that supports the sanity of the developed code.

4. Conclusion

An effort is underway to develop a DIFFOX-equivalent, yet with more rigorously validated against non-isothermal transient oxidation, computer code. A preliminary experimental validation of the code shows remarkable agreement of the code result with experimental data in both isothermal and non-isothermal transience. In the future, the effect of H uptake in the high burnup fuel and the diffusion of the z-axis through 2D expansion of the model will be added. In addition, diffusion coefficient models will be updated as comparisons with the experiments proceed.

ACKNOWLEDGEMENT

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