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Theoretical Modeling of Protective Oxide Layer Growth in Non-isothermal Lead-Alloys Coolant Systems: Quarterly Progress Report (01/01/05- 03/31/05)

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Task 21: Theoretical Modeling of Protective Oxide Layer Growth in Non-isothermal Lead-Alloys Coolant Systems

Quarterly Progress Report
01/01/05- 03/31/05

UNLV-AAA University Participation Program

Principle Investigator: Yitung Chen
Co-Principle Investigators: Huajun Chen, Jinsuo Zhang, and Jichun Li

Purpose and Problem Statement

The goal of the proposed research project is to provide basic understanding of the protective oxide layer behaviors and to develop oxide layer growth models of steels in non-isothermal lead-alloys (lead or lead-bismuth eutectic) coolant systems. It is widely recognized that the corrosiveness of the lead-alloys is a critical obstacle and challenge for which it can be safely used or applied in the nuclear coolant systems. Active oxygen control technique can promote the formation of the "self-healing" oxide films on the structural material surface, drastically reducing steel corrosion and coolant contamination. Many experiments of steels exposed to flowing lead-alloys have been carried out to study the protective oxide layer behaviors. However, the experimental data are still very incomplete at present and can not provide the dependence of the oxide behaviors on the system operating temperature, temperature profiles along the lead-alloys loop, oxygen concentration, flow velocity, etc. In addition, oxygen distribution in a non-isothermal lead-alloys coolant system is not well understood. Precise studies and simulations of all hydrodynamics with thermal conditions encountered in practical coolant loop systems by use of different flowing conditions in the laboratory are difficult and expensive, if not impossible. Therefore it is important and necessary to develop theoretical models to predict the protective oxide layer behaviors at the design stage of a practical lead-alloys coolant system, to properly interpret and apply experimental results from test loops, and to provide guidance for optimization in lead-alloys nuclear coolant systems. The research project, therefore, is aimed at filling the gaps of protective oxide layer growth and the oxygen concentration level before lead-alloys nuclear coolant is ready for programmatic implementations and industrial applications.

Personnel

Principle Investigator:

- Dr. Yitung Chen (Mechanical Engineering)

Co-Principle Investigators:

- Dr. Huajun Chen (Mechanical Engineering)
- Dr. Jinsuo Zhang (LANL)
- Dr. Jichun Li (Mathematics)

Graduate Students:

- Mr. Taide Tan, Ph.D Graduate Student, (Mechanical Engineering)
- Ms. Xianfang Tan, M.S. Graduate Student, (Mechanical Engineering)

National Laboratory Collaborators:

- Dr. Ning Li, LBE Team Leader, LANL

Management Progress

Budget Issues:

- N/A

Student Issues:

- N/A

Management Problems

No management problem issues at this time.

Technical Progress

(1) An improved kinetic model has been developed to predict the mass transfer controlled corrosion/precipitation in non-isothermal LBE pipe/loop systems. One journal manuscript based on this model has been prepared and submitted to "Journal of Nuclear Science and Technology" for the publication.

In this mass transfer model, a turbulent core region and a laminar sub-layer region have been considered separately to the total mass transfer to the transferring corrosion product from the wall. Two sets of mass transfer equations have been solved separately both in the turbulent core region and sub-layer region. Following the model development, the local corrosion/precipitation rate is calculated and a parametric study has been made to illustrate the effects of the axial temperature profile in details. The obtained solutions can also be extended to the more general problems of mass transfer in the developed turbulent wall-bounded shear flows.

The improved model has been applied to the DELTA loop at Los Alamos National Laboratory [1]. The DELTA loop is a non-isothermal closed loop and is used to study the corrosion of various materials in the flowing LBE system. The temperature profile is shown in Figure.1. The following parameters are used in the analysis: Loop/pipe length $L = 29.92$ m, hydraulic diameter $d = 0.0525$ m, kinematic viscosity of LBE $\upsilon = 1.5 \times 10^{-7}$, Liquid LBE velocity $V = 0.5$ ms^{-1}, oxygen concentration in LBE $c_O = 0.01$ ppm, and the diffusion coefficient of iron in LBE is approximately estimated as $D = 10^{-9}$ m^{2}s^{-1}[1].

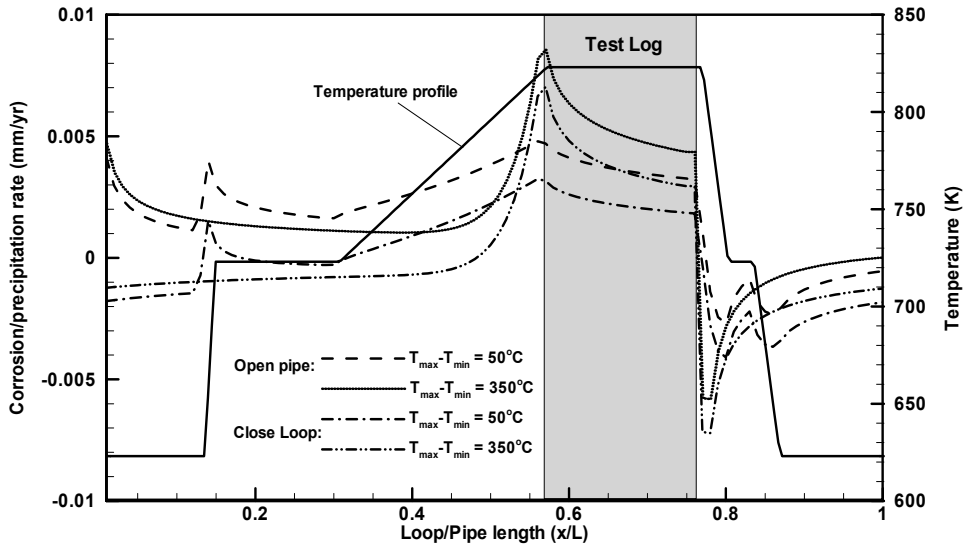


Figure 1 Corrosion rate under different axial temperature distribution
($T_{\max} = 550^0$, $c_w = Min(10^{6.01-4380/T}, c_o^{-4/3} 10^{11.35-(12844/T)})$, c_o is the oxygen concentration)

Figure 1 shows the predicated corrosion/precipitation rate by the present model in the pipe/loop flow in the DELTA Loop. From this figure, one can find that there also exists a precipitation region in the open pipe case and this precipitation region occurs beside the highest temperature region because of the large axial temperature difference.

(2) Numerical analysis of the coupled natural convection and corrosion product transfer in a two-dimensional circular loop was made to study the corrosion product under the active oxygen controlled model.

In our simulation, it is assumed that the wall temperature distribution changes along the wall and the oxygen concentration almost keep the same value. According to the oxygen control technology [2], the concentration of iron (the main corrosion product) is a function of oxygen and axial temperature. And it can be calculated by the following equation

$$c_w = \mathrm{Min}(10^{6.01-4380/T}, c_O^{-4/3} 10^{11.35-(12844/T(\theta))})$$

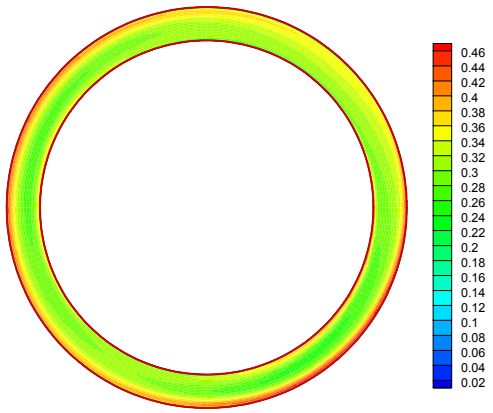
where c_O is the oxygen concentration in LBE liquid , $T(\theta)$ is the absolute wall temperature in Kelvin, θ is the angle in axis direction.

The following parameters are used in this numerical procedure: Circular Loop radius L = 1 m, hydraulic diameter d = 0.2 m, kinematic viscosity of LBE $\upsilon = 1.5 \times 10^{-7}$ m^2s^{-1}, density of LBE ρ=10084 kgm^{-3} ms^{-1}, heat capacity $C_p = 146.26$ J $kg^{-1}K^{-1}$, thermal expansion coefficient $\beta = 1.514 \times 10^{-4}$, oxygen concentration in LBE c_o=0.01ppm, the difference between maximum and minimum temperature ΔT =350°, and the diffusion

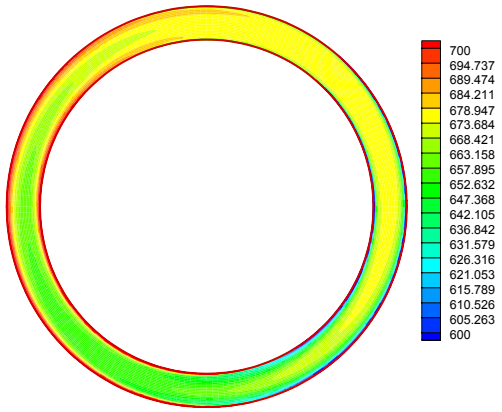
coefficient of corrosion product in LBE $D = 10^{-9}$ m^2s^{-1}. The temperature profile of the circular loop can be found in Ref.[1].

Figure 2 shows the distributions of velocity magnitude (Figure 2a), temperature (Figure 2b), and corrosion product concentration (Figure 2c) in the circular loop. Due to the existence of temperature difference, the liquid LBE flows clockwise due to the effect of the buoyancy. As shown in Figure 2a, the maximal velocity magnitude locates near the outer wall due the effect of curvature of circular loop. From Figure 2b, it can be found the downstream effect on temperature distribution is very evident. For the liquid LBE, the Prandtl number is very small, which makes the temperature in the bulk flow almost uniform. Since the diffusion coefficient of corrosion product (iron) in liquid LBE is very small, the Schmidt number for corrosion product becomes very large, which makes the mass diffusion boundary layer becomes very thin. To show the variation of corrosion product along the loop clearly, here we take the diffusion coefficient as 5×10^{-5}. Similar to the distribution temperature distribution, the downstream effect on corrosion product is also very evident. Figure 3 shows the corrosion/precipitation rate along the loop for the inner wall and outer wall. The figure indicates the corrosion/precipitation rate in the outer wall is larger than that in the inner wall due to effect of the curvature.

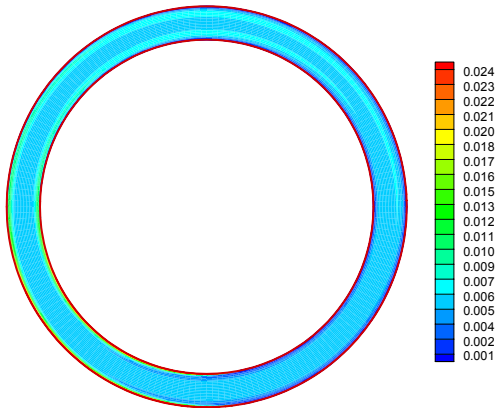
Next, we will study the transport mechanism of oxygen in the nature convective LBE loop.



(a)Velocity magnitude (m/s)



(b)Temperature distribution (K)



(c)Corrosion product concentration distribution (ppm)

Figure 2 Distributions of velocity magnitude, temperature, and corrosion product concentration in the circular loop

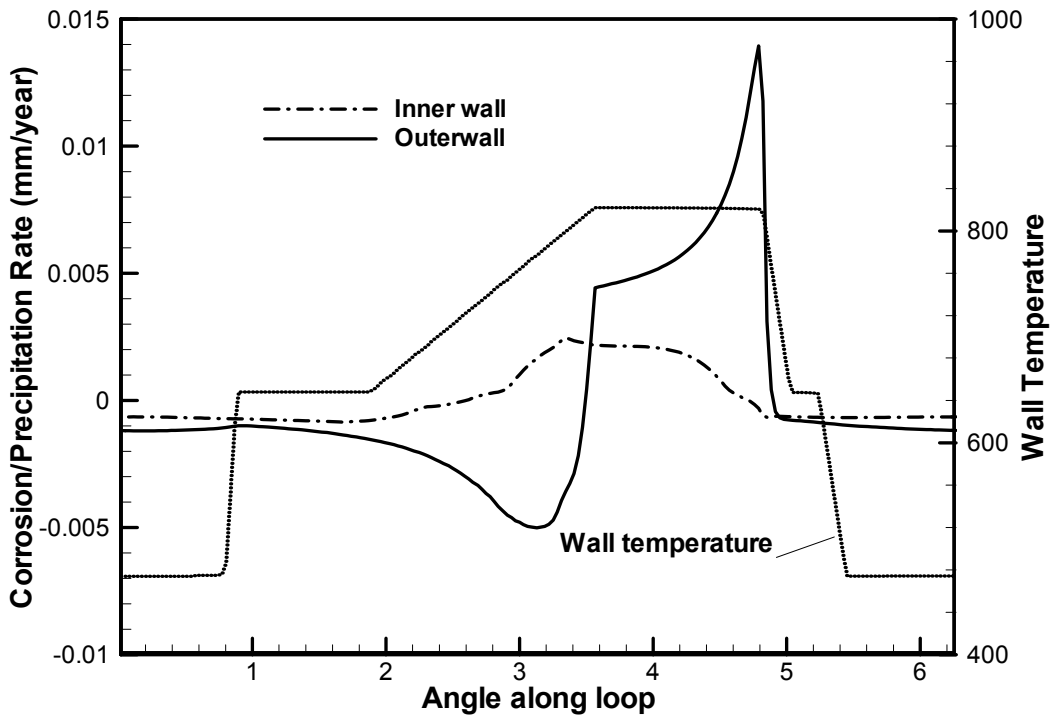


Figure 3 Corrosion/Precipitation Rate along the loop

(3) A kinetic oxide growth model in Liquid LBE has been developed for the pure iron exposed liquid LBE with oxygen controlled.

The schematic plot is shown in Figure 4. The oxide (Fe_3O_4) layer grows toward both in internal side (II surface) and external side (III surface). The assumptions have been made as follow:

1. The interfaces are local equilibrium and the processes do not affect the kinetics of oxidation.
2. The growth of the oxide (Fe_3O_4) is limited by the diffusion of iron
3. The diffusion of oxygen anion is neglected.
4. The oxide layer growth and the consumption of metal obey the Wagner's parabolic law.
5. The interfaces are flat plat.

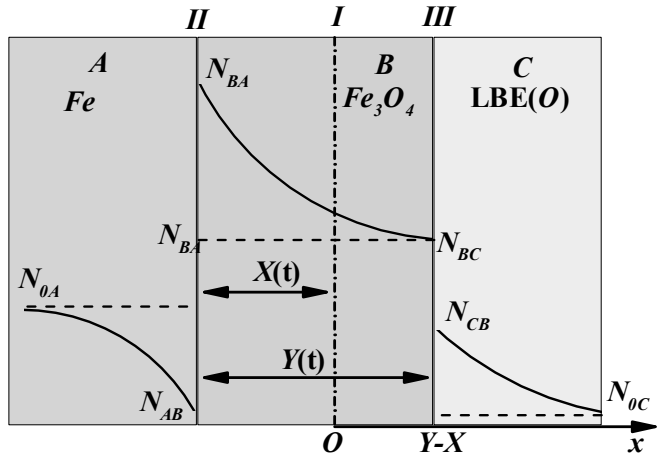


Figure 4 Schematic plot of the structure of pure iron exposed to LBE with oxygen controlled. A region: Metal Fe; B region: Metal oxide Fe_3O_4; C region: Liquid LBE with oxygen; I: Original metal surface; II: Metal-oxide Interface; III: Oxide-LBE interface. X : Depth of metal consumption; Y: Width of Oxidation Layer.

According to the Wagner's parabolic law, depth of metal consumption X and width of oxidation layer Y can be written as follow:

$$X = 2\gamma_1 (D_B t)^{1/2}, \; Y = 2\gamma_2 (D_B t)^{1/2} \tag{1}$$

where D_B is the diffusion coefficient of iron through the oxide layer, γ_1 and γ_2 are parabolic constant, and t is the time.

The diffusion of iron in A, B, and C phases are determined by the Fick's secondary Law as follow:

$$\text{In phase A:} \quad \frac{\partial N_A}{\partial t} = D_A \frac{\partial^2 N_A}{\partial x^2} \tag{2.a}$$

$$\text{In phase B:} \quad \frac{\partial N_B}{\partial t} = D_B \frac{\partial^2 N_B}{\partial x^2} \tag{2.b}$$

$$\text{In phase C:} \quad \frac{\partial N_C}{\partial t} = D_C \frac{\partial^2 N_C}{\partial x^2} \tag{2.c}$$

with the initial and boundary conditions:

$$N_A = N_{0A} \;\; \text{at} \;\; x = -\infty; \tag{3.a}$$

$$N_{AB} = K_{AB}(N_{BA} - N_C) \text{ and } D_A \frac{\partial N_A}{\partial x} = D_B \frac{\partial N_B}{\partial x} + (N_{BA} - N_{AB}) \frac{dX}{dt} \tag{3.b}$$

$$\text{At } x = -X(t)$$

$$N_B = N_{BC}, \; N_C = N_{CB} \;\; \text{at} \;\; x = Y(t) - X(t) \tag{3.c}$$

$$N_C = N_{0C} \;\; \text{at} \;\; x = \infty \tag{3.d}$$

A general solution diffusion in the multiphase diffusion can be written as

$$N_i = \alpha_i + \beta_i erf\left(\frac{x}{2\sqrt{D_i t}}\right) \quad i = A, B, C \tag{4}$$

The constant α_i and β_i can be calculated by considering the boundary condition (3). And the parabolic constant γ_1 and γ_2 can be derived by considering consummation of metal in the whole oxide layer and the mass balance equation in the surface III (the interface between oxide and LBE).

The consummation of the metal in Δt must equal in summation of increase of metal in the oxide and diffusion into the LBE, that is

$$\rho_{Fe}\frac{dX}{dt} = \rho_{Fe_3O_4}\frac{m_{Fe}}{m_{Fe_3O_4}}\frac{dY}{dt} - D_c m_{Fe}\left.\frac{dN_C}{dx}\right|_{x=Y-X} \tag{5}$$

The mass balance equation at the surface III (the interface between oxide and LBE) can be expressed as

$$D_C\left.\frac{\partial N_C}{\partial x}\right|_{x=Y-X} = D_B\left.\frac{\partial N_B}{\partial x}\right|_{x=Y-X} + (N_{BC} - N_{CB})\frac{d(Y-X)}{dt} \tag{6}$$

This model is applied with using the following parameters: N_{0A}=0.2×10^{-4} mol/cm^3, K_{AB}= 2.5, N_{0C} = 0 mol/cm^3, N_{CB} = 2×10^{-10} mol/cm^3, N_{BC} = 0.6×10^{-4} mol/cm^3, D_A = 1×10^{-18} m^2/s,D_B= 5.8×10^{-20} m^2/s, D_C = 1×10^{-9} m^2/s. Figures 5-7 show the distributions of iron in the three-phase system. As the time of holding increases, the depths of the diffusion zones in the phase A (steel) and in the phase C (liquid LBE) increases. The iron concentration in the oxide layer almost keeps the linear. From Figure 7, it can be found the diffusion of iron through the oxide film is very small. Figure 8 shows the time dependence of increments in the thickness of oxide layers. From Fig.8, we can find the oxide growth toward to the inner side is considerable.

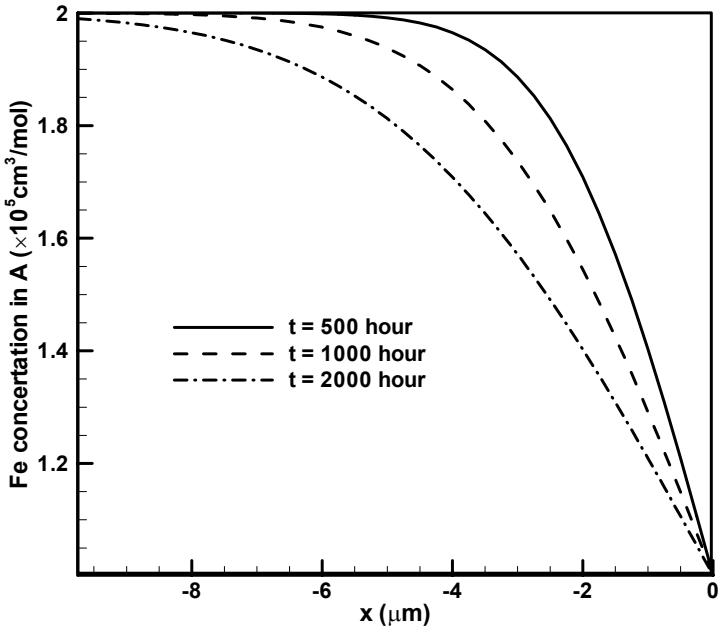


Figure 5 Iron concentration in phase A (steel)

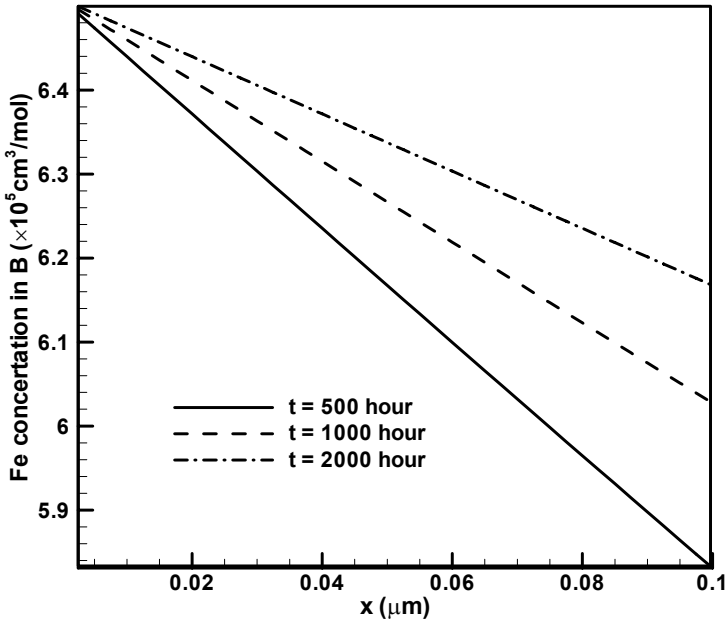


Figure 6 Iron concentration in phase B (Oxide layer)

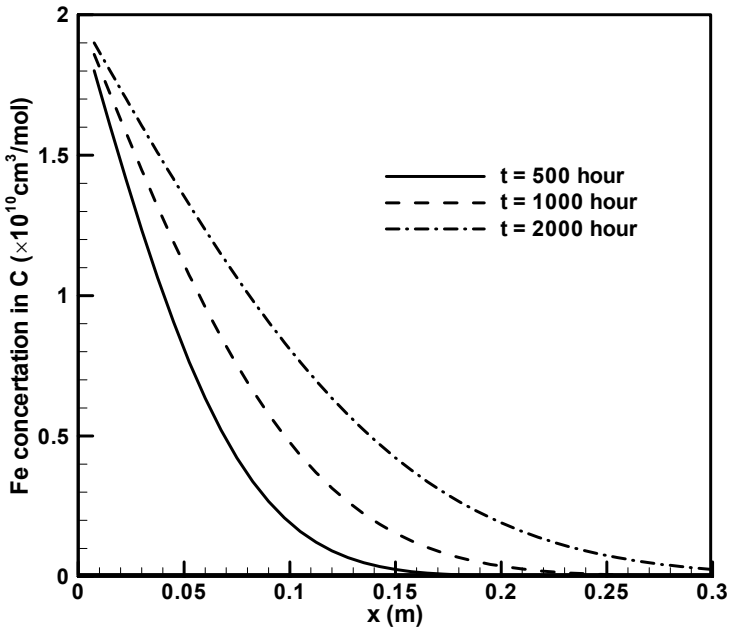


Figure 7 Iron concentration in phase C (Liquid LBE)

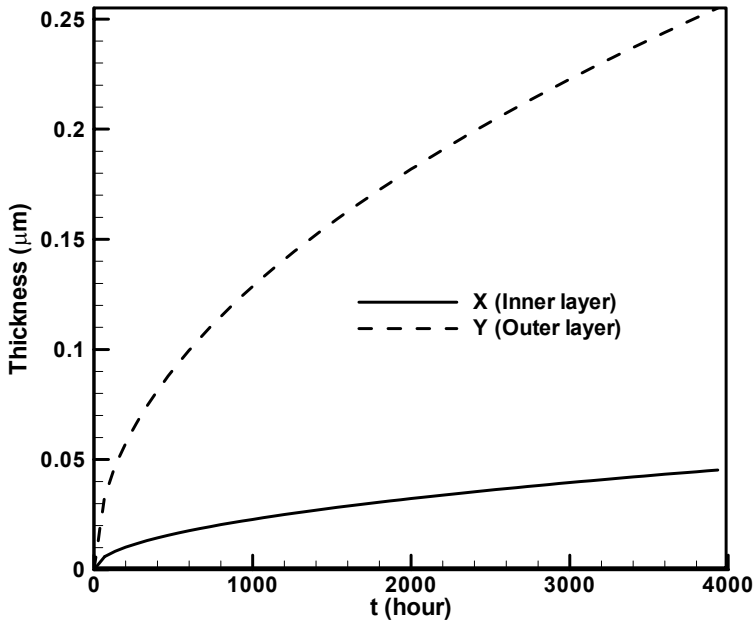


Figure 8 Time dependence of increments in the thickness of oxide layers

[1] J. Zhang, N. Li, J. Nucl. Mater. 321 (2003) 184.
[2] N. Li, J. Nucl. Mater. 300 (2002) 73.