Semi-Empirical Corrosion Model for Zircaloy–4 Cladding

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Abstract

The Zircaloy-4 cladding tube in Pressurize Water Reactors (PWRs) bears corrosion due to fast neutron flux, coolant temperature, and water chemistry. The thickness of Zircaloy-4 cladding tube may be decreased due to the increase in corrosion penetration which may affect the integrity of the fuel rod. The tin content and inter-metallic particles sizes has been found significantly in the magnitude of oxide thickness.

In present study we have developed a Semi-empirical corrosion model by modifying the Arrhenius equation for corrosion as a function of acceleration factor for tin content and accumulative annealing. This developed model has been incorporated into fuel performance computer code. The cladding oxide thickness data obtained from the Semi-empirical corrosion model has been compared with the experimental results i.e., numerous cases of measured cladding oxide thickness from UO_2 fuel rods, irradiated in various PWRs.

The results of the both studies lie within the error band of 20μm, which confirms the validity of the developed Semi-empirical corrosion model.

***Key words**:* Corrosion, Zircaloy-4, tin content, accumulative annealing factor, Semi-empirical, PWR.

1. Introduction

Study related to the corrosion of Zircaloy cladding in Pressurized Water Reactor PWRs fuel assembly has been important due to the following reasons:

- Higher fuel discharge burnup to reduce fuel cycle costs
- Higher coolant inlet temperature to increase plant thermal efficiency
- increase of coolant pH and lithium concentration to reduce plant radiation levels.

There are various factors to determined the corrosion rate i.e., fast neutron flux, alloy composition, metallurgical conditions of cladding during fabrication, water chemistry, and coolant temperature. Among all of the above said factors, tin content of Zircaloy-4 cladding was found to have very important effect on the prediction of oxide magnitude at all burnups as well as Intermetallic particles size have also significantly effects on the predictions of oxide magnitude. Therefore, cumulative corrosion rate can be primarily controlled with the tin content and metallurgical structure of cladding.

In present study we have developed a Semi-empirical corrosion model by modifying the Arrhenius equation of corrosion for Zircaloy–4 cladding as a function of acceleration factor by considering tin contents in the cladding alloy as well the metallurgical structure of cladding. Developed model after incorporating into fuel performance code, was verified by forty five cases of measured cladding oxide thickness data from UO_2 fuel rods irradiated in five different PWRs.

The thermodynamics of Zr-O system as an oxide film indicates that oxygen is more stable when dissolved in metal phase. Due to this reason, first half monolayer of oxygen have been react with clean Zirconium surface and converted into subsurface or thin film. Afterward this process continues to formed a thin oxide layer.

The weight gain kinetics for Zircaloy-4 have been fall in two periods referred as pre- and post-transition. The pre transition period has been characterized by decreasing rate of weight gain, which is closer to a cubic growth kinetic curve. When the magnitude of oxide have been reached a thickness of about 2μm, the oxidation rate increased to a post-transition, approximately linear rate. The developed oxide layer in pre–transition is very compact and protective, its structure is a tetragonal and having black or lustrous color. Whereas after pre–transition it has a friable and gray monoclinic structure.

PWR cladding have the fast neutron flux (ϕ) of order of 10^{13} to 10^{14} neutron/cm^2-s. Garzarolli[1] have studied and concluded that high neutron flux effects either or both the crystal structure of the oxide film or the chemistry within pore in oxide.

The main metallurgical factors, size and distribution of second phase particles, have been correlate with the corrosion resistance of Zircaloy. The alloying elements (Fe, Cr and Ni) have less solubility in α Zirconium. Therefore, these alloying elements are always present at operational temperatures. The particle size and distribution depends on the details of cladding after beta phase homogenization, annealing temperatures and time after cold working. In 1984, Steinberg et al.[2] studied and concluded an accumulated annealing parameter, that contain all applied heat temperatures in alpha phase region of zirconium during fabrication.

$\Sigma Ai = \Sigma (t_i * \exp(-Q/R*Ti))$

Where: Activation energy (Q) = 80000 Cal/mole, Real gas constant (R), Effective time of annealing (ti), Step (i), Temperature (Ti) and Annealing parameter (A). In-pile measurements of oxide thickness and corrosion rates could be reasonably well correlated directly or indirectly with the A parameter.

2. Development of Semi–Empirical Corrosion Model

To increase the fuel performance and reliability in the PWRs fuel assembly, a semi-empirical corrosion model for Zircaloy–4 cladding has been developed. In the corrosion model, tin contents in the cladding composition and Annealing Parameter are additional acceleration factors.

The Zircaloy corrosion process which is a diffusion–controlled reaction. The developed model can be utilized to determined or estimated the oxidation process of Zircaloy cladding by using semi–empirical correlations divided by pre–transition and post–transition kinetics.

The Zircaloy oxidation kinetics has been determined using the Arrhenius equation as a function of temperature, activation energy and additional acceleration factors.

The following Arrhenius equation has been used to find the corrosion rate in the pre–transition regime.

$$\frac{d\delta^3}{dt} = K_{pre} \cdot \exp\left(-\frac{Q_{pre}}{R \cdot T_i}\right) \qquad (\text{mm}^3/\text{day})$$

$$K_{pre} = F_{Sn} \cdot F_A \cdot \cdot F_{pre}$$

The following Arrhenius equation has been used to find the corrosion rate in the post–transition regime.

$$\frac{d\delta}{dt} = K_{post} \cdot \exp\left(-\frac{Q_{post}}{R \cdot T_i}\right) \qquad (\text{mm/day})$$

$$K_{post} = F_{Sn} \cdot F_A \cdot F_{\phi} \cdot F_{post}$$

where

δ = Oxidation thickness [mm]

t = Time [day]

R = Universal gas constant, 1.986 [cal/mol–K°]

T_i = Metal/oxide interface temperature [K°]

K_{pre} = Frequency factor for pre–transition regime, 1.89 × 10^{10} μm^3/ d

K_{post} = Frequency factor for post–transition regime 804 × 10^{07}μm/ d

Q_{pre} = Activation energy for pre transition, 32,269 cal/mol

Q_{post} = Activation energy for post transition, 27,150 cal/mol

F_{Sn} = Tin content enhancement factor

F_A = Annealing parameter enhancement factor

F_{ϕ} = Fast neutron enhancement factor

In the present study we have enhanced the Zircaloy corrosion model by improving the following acceleration effects:

- Tin contents in Zircaloy composition
- Accumulated annealing parameter

The differential equation of oxide thickness has been solved numerically by a fourth order Runge–Kutta integration formulae.

3. Tin Effect

It has been observed that by minimizing the tin concentration (SN) in the Zircaloy-4 cladding, with in the ASTM specified ranges, significantly increased the corrosion resistance. Initially corrosion behavior of standard Zircaloy-4 in different PWRs have been determined through statistical method. Through this method it have been found that variations in the alloy chemistry has been cause of the scatter observation as well as the alloying element Sn influenced the corrosion behavior as shown in Fig.1[3].

Low concentration of tin in the ranges1.2% and 1.4% in the Zircaloy-4 have been irradiated up to higher burn-up more that, 50 MW.d/kgU at PWR plant[4]. A significant reduction of scatter in corrosion behavior has been achieved by chemistry modification. Under normal operation conditions, standard Zircaloy-4 cladding will reach an oxide thickness of 100μm at a burnup of 45-55 MW.d/kgU, while improved low tin Zircaloy-4 may reach that value at a higher burnup range of 50-60 MW.d/kgU or higher.

Therefore, the Tin effect may be expressed by a multiplicative coefficient included in the frequency factor.

$F_{Sn} = (-0.2557 + 0.6666 * SN)/0.8$

Where F_{Sn} is a linear function of tin content.

4. Annealing Parameter Effect

The accumulated annealing parameter has been defined in the correlation between the size of intermetallic precipitates and the applied annealing conditions[5]. The mean particle of the intermetallic precipitates in Zircaloy-4 correlates with the accumulated annealing parameter ΣA_i, at activation temperature Q/R of 40000 K as illustrated in Figure 2.

This correlation is independent of the number and the sequence of the annealing in alpha-range and is also not effected by intermediate cold-working steps. Figure 2. shows that the increase of the particle size starts at the ΣA_i value of 10^{-18} h. Using this annealing parameter, this correlation can be used to determine mean size of intermetallic precipitates in Zircaloy-4.

The metallurgical property due to which Zircaloy-4 corrosion occurred is defined as the growth of intermetallic phase present as precipitates as shown in Figure 3.[6].

The Figure 3 shows that corrosion rate depends on the average precipitate diameter. The annealing parameter factor, $F_{\Sigma A}$ is the representative of the growth of precipitates at different heat treatment and corrosion rate on intermetallic precipitate size.

$F_{\Sigma A}$=[1.01425 + (1962.28/ (0.15767*(SQRT(3.14/2.0)))* exp((-2. * (MPS +0.29483)^2.)/ (0.15767^2)))] /1.015452

Where MPS is mean precipitate size given as

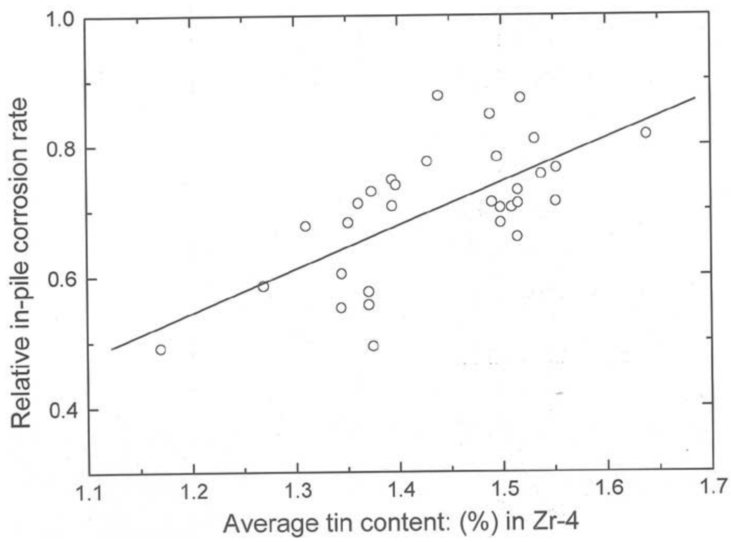

Figure 1. Tin effects

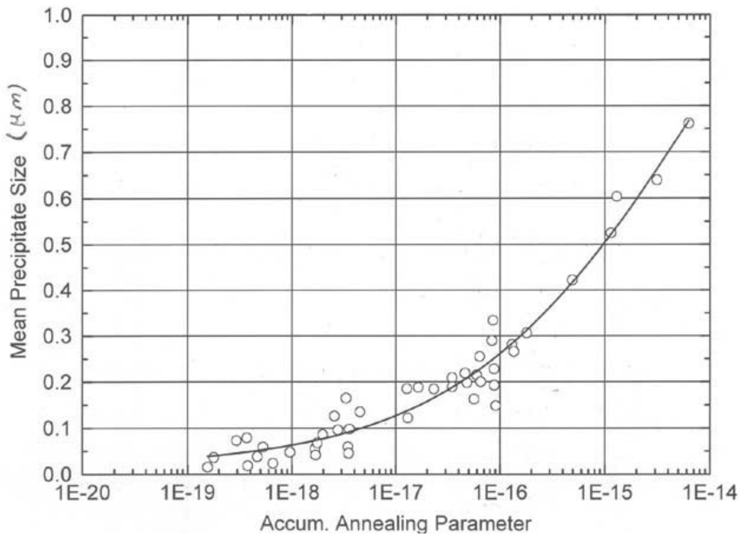

Figure 2. Accumulative annealing parameter effects

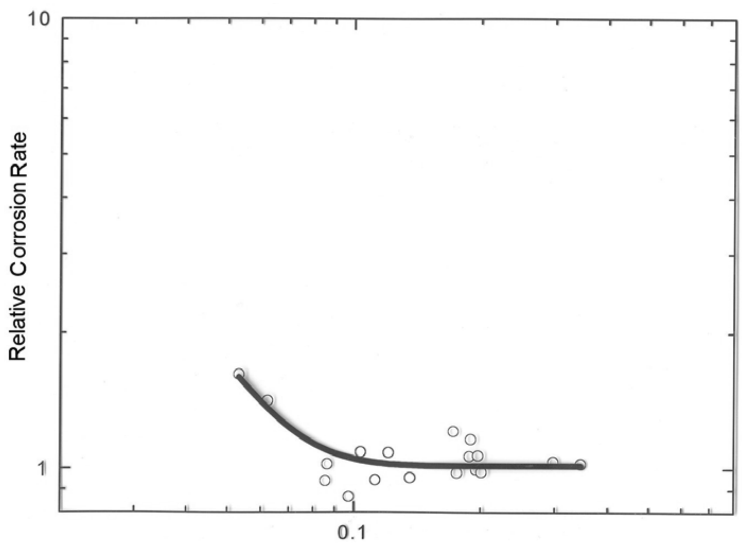

Figure 3. Average diameter of precipitates effects on the corrosion rate.

$$MPS = ((0.01484-1.58827)/(1.0+(\Sigma A_i/7.8818E-15)^{0.38504}))+1.58827$$

ΣA_i is accumulative annealing parameter.

5. Verification of Developed Model and Discussion

i. The datab ase consists of 45 fuel rods taken from five different PWRs. Each reactor designated as A, B, C, D and E. All selected fuel rods have been irradiated at high burnup for one to five cycles. Detailed of each reactor and its distinguished characteristics are summarized in table 1.

ii. Results obtained from the semi-empirical corrosion model are compared with the experimental results of the Plant A,B,C,D and E and all these results are plotted in Figure 4.

Table 1. Population and characteristics of reactors

Plant	Fuel Rods	Distinguished characteristics
A	6	High temperature PWR, high tin content rods
B	16	High time integrated LiOH exposure
C	5	Medium tin content rods
D	12	High as well as low tin content rods
E	6	High temperature PWR, different intermetallic particle size distribution.

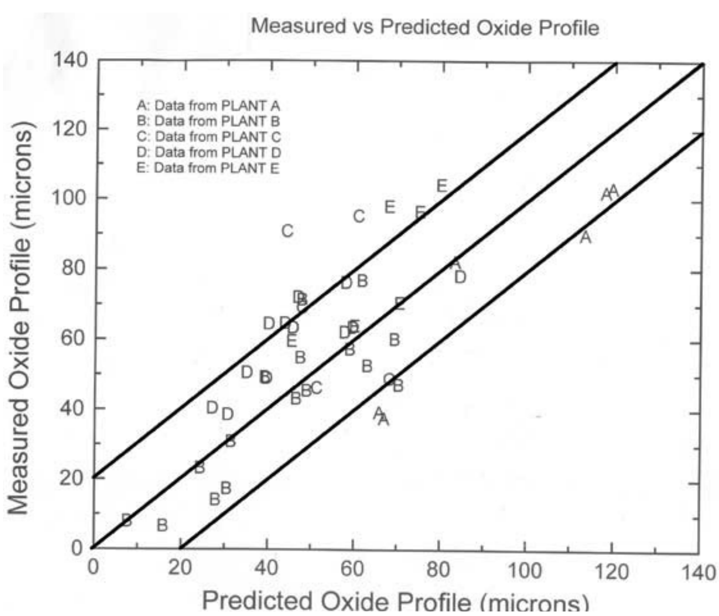

Figure 4. Result comparison between calculated and experimental

iii. Plant A is characterized by its high coolant temperature and high tin content. 06 fuel rods have been irradiated. The results obtained from the both studies ,Calculated and experimental, are plotted in Figure 4. The results obtained from the both study at Plant A are comparable and show good agreement.

iv. Plant B fuel rods contained high time integrated lithium concentration, LiOH. 16 fuel rods have been irradiated. In previous studies related with Zircaloy-4 corrosion LiOH has been considered for high corrosion rate but it's not validated through the experimental investigation. Therefore LiOH has not incorporated in this semi-empirical corrosion model.

v. Zr-4 cladding used for plant C fuel rods have medium tin content. 05 fuel rods have been irradiated. Large difference is observed between predicted and measured oxide profiles on most of the fuel rods, and difficult to explain. Although results at fuel rod No.5, have excellent agreement between predicted and measured oxide profile.

vi. Zr-4 cladding used for plant D fuel rods have high tin content as well as low. 12 fuel rods have been irradiated. The results obtained from the both studies, Calculated and experimental, are shown in Figure 4. The results obtained from the both study at Plant D are comparable and show good agreement.

vii. Fuel rod of Zircaloy-4 added in the Plant E contained high temperature, different intermetallic particle size distribution. The distinguished characteristic of Plant E rods is that different precipitate sizes were intentionally used to verify the effect of intermetallic precipitate on corrosion of Zr-4. Predicted behaviour of plant E rods is similar to those of Plant D. Although predicted corrosion thickness is comparable to that of measured corrosion and show good agreement.

viii. It is observed that maximum oxide thickness difference between both studies (predicted and experimental) is found at peak oxide thickness. Therefore, the results obtained from the both studies are comparable and error found in the range of 10μm to 20μm on all the fuel rods (45) of reactor A-E.

6. Conclusion

It is concluded that after a detailed study related with the corrosion thickness of the Zircaloy-4 cladding by considering the effects of Tin and accumulative annealing parameters. The effect of Tin on corrosion rate is dominant and increases linearly with increase in tin content. Whereas, accumulative annealing parameter becomes important when its value is very low.

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