A Model Addressing Effect of Growing Oxide Layer on Tritium Permeation in a High Temperature Gas-Cooled Reactor

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1. Introduction

The HTGR is one of the most promising future energy technology contributed from high efficiency, inherited passive safety features. There has been considerable work on predicting the behavior of metallic materials in HTGRs. Currently, one potential problem rising from HTGRs for co-generation application which can produce hydrogen and water is tritium permeation from the primary coolant to the end product through heat exchanger surfaces. It is, therefore, very important to predict accurate tritium penetration rates when estimating the tritium distributions and contamination levels in hydrogen and water.

Previous studies showed that the rate of tritium permeation depends on surface condition influenced by oxidation and coating thickness [1]. The trends in the permeability rapidly decrease during the early stage and thereafter the permeability decreases as the thickness or depth of the oxide increases. The permeability of the alloys can be correlated to the oxide depth, and then the depth can be related to time. Tritium permeation rates between the clean surface and the oxide surface has huge gaps. Generally speaking, tritium PRF (Permeation Reduction Factor) can vary from 10 to 1,000. Existing models, however, could not capture oxide layer growth phenomena. In this paper, the time-dependence of tritium permeation through the tubes of the heat exchangers in HTGRs was investigated in order to see the effect of the oxide layer growth.

2. Tritium Permeation model

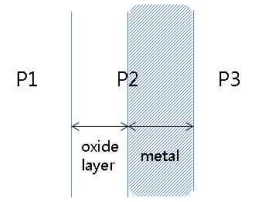

Figure 1. Schematic diagram for oxide and metal layer

The permeation rate, J_m, through the metal part can be written as

$$J_m = \frac{DK\,A}{x}(P_3^{1/2} - P_2^{1/2}) \quad (1)$$

where DK/x is the permeability of base metal at a particular temperature. A and x are the area and thickness of the material respectively. In a similar fashion the rate through the oxide(J_o) can be given as

$$J_o = \frac{EL\,A}{y}(P_2^{1/2} - P_1^{1/2}) \quad (2)$$

where EL/y is the permeability of oxide layer and y is the thickness of that layer. To simplify operations, let

$$\frac{DK\,A}{x} = g \quad , \quad \frac{EL\,A}{y} = h \quad (3)$$

At long term steady state permeation, the transfer rates through the two connected materials should be equal: ($J = J_o = J_m$).

$$g(P_3^{1/2} - P_2^{1/2}) = h(P_2^{1/2} - P_1^{1/2}) \quad (4)$$

By this relation, the metal-oxide interface pressure can be presented as follows:

$$P_2^{1/2} = \frac{gP_3^{1/2} + hP_1^{1/2}}{g+h} \quad (5)$$

Putting eqn. 5 into eqn. 2 yields

$$J = h\left(\frac{gP_3^{1/2} + hP_1^{1/2}}{g+h} - P_1^{1/2}\right) \quad (6)$$

Permeability of metal (g) is much bigger than that of oxide layer (h). Then, we have

$$J = h\left(\frac{gP_3^{1/2} - gP_1^{1/2}}{g+h}\right) \quad , g \cong g+h \quad (7)$$

$$J = h(P_3^{1/2} - P_1^{1/2}) \quad (8)$$

Then the tritium permeation rate through oxide metal can be expressed as follows:

$$J = \frac{EL\,A}{y}(P_3^{1/2} - P_1^{1/2}) \quad (9)$$

A permeation rate of tritium through a solid metal is an overall rate of transfer of the permeating species from a fluid on one side to the other side. Since this is a serial, multi-step process, the overall rate is governed by the slowest step in the transport process. This equation means that the whole flux of permeation can be expressed in terms of the oxide layer thickness and its permeability.

3. Oxide layer growth model

To describe the current model (Eq. 9), the oxide layer growth model is another important factor. A well-established model for thermal oxide growth had been proposed by Deal and Grove in the middle of the 60's. This model is assumed that the structure is one-dimensional. Therefore, the model can only be applied to oxide films grown on plane substrates. The general expression of the Deal Grove model is as follows:

$$y(t) = \frac{-A + \sqrt{A^2 + 4B(t+\tau)}}{2} \quad (10)$$

Taking the short and long time limits of the above equation reveals two main modes of operation:

$$t + \tau >> \frac{A^2}{4B} \ then \ y(t) = \sqrt{Bt} \quad (11)$$

$$t + \tau << \frac{A^2}{4B} \ then \ y(t) = \frac{B}{A}t \quad (12)$$

Let us assume that pre-oxide layer does not exist (τ=0). In the tritium permeation issue, we can accept the long time mode. Temperature dependency of parabolic constant (B) is as follows:

$$B = c_0 \exp(\frac{-E_y}{RT}) \quad (13)$$

where E_y is the activation energy and R is gas constant.

Pressure dependence of parabolic constant (B) in Eq. (10) has the following linear relation based on the reference pressure [2]:

$$B(p\ ,T) = B(p_0, T) \times \frac{p}{p_0} \quad (14)$$

Then, we have the linear parabolic model which is a function of temperature and pressure.

$$B = c_0 \exp(\frac{-E_y}{RT}) \times \frac{p}{p_0} \quad (15)$$

Let us summarize the tritium permeation model:

$$J = \frac{EL\,A}{y}(P_3^{1/2} - P_1^{1/2}) \quad (16)$$

$$EL = EL_0 \exp(\frac{-E_{EL}}{RT}) \quad (17)$$

$$y(t) = \sqrt{c_0 \exp(\frac{-E_y}{RT}) \times \frac{p_1}{p_0} \times t} \quad (18)$$

4. Model validation

A long-term experiment (>2000 hour) was conducted on Incoloy 800 at 930K with the inside of the tube continuously purged with a sweep gas of Ar/H_2O with a H_2O partial pressure of 243 torr (0.3 bar). The total pressure of the sweep gas was 675 torr (0.9 bar) [1]. The trends in the permeability rapidly decreases during the first 900 hours and is followed by a slower rate such that the logarithm of permeability becomes linear with respect to the square root of time (Figure 3). A suggested model is that the surface becomes effectively covered during the early stage, thereafter, the permeability decreases as the thickness or depth of the oxide increases.

$$EL = EL_0 \exp(\frac{-E_{EL}}{RT}) \quad (19)$$

$$y(t) = \sqrt{c_0 \exp(\frac{-E_y}{RT}) \times \frac{p_1}{p_0} \times t} \quad (20)$$

To determine each of these parameters, the following experimental data can be used. Literature survey indicates that the activation energy for hydrogen permeation through oxide coated metals is generally around 15kcal/mol [1]. Table 1 shows calculated permeabilities, pre-exponential factor based on tritium transfer rate for oxide coated Incoloy 800.

Temperature(K)	Permeability	Pre-exponential Factor (EL_0)	Activation Energy(E_{EL}) (kcal/mol)
933.15	3.9E-10	1.57679E-06	15.4
933.15	4.0E-10	1.61722E-06	15.4
933.15	5.6E-10	2.26411E-06	15.4
933.15	6.1E-10	2.46626E-06	15.4
Average	4.9E-10	1.98109E-06	15.4

Table 1. Oxide permeabilities for Incoloy 800 [1]

Yoshiaki performed experiments about high temperature behavior of Incoloy 800 in typical environment to be encountered in HTGR with particular emphasis on oxidation behavior. The activation energy was very difficult to calculate due to the scatter in the data on the Arrhenius plot. However, the value calculated using data at 1123 K and 1023 K was 197 kJ/ mol [3].

Temperature(K)	Parabolic constant(B) (mm^2s^{-1})	Pre-exponential Factor(c_0)	Activation Energy(E_y) (kcal/mol)
1023	1.13E-10	1.29343E-06	197
1123	9.26E-10	1.34766E-06	197
Average	5.20 E-10	1.32055E-06	197

Table 2. Oxide layer growth for Incoloy 800 [3]

The thickness of the oxide layer and parabolic rate constants can be taken from base data and they are summarized in Table 2. The permeation properties of the oxide layer depend on environments of its formation. Therefore, it should be careful to decide parabolic constant, pre-exponential factor and activation energy for general usages (Table 3).

variable	Description	value
EL	Permeability of oxide layer	$4.9X10^{-10}$ $\frac{cm^3(T_0,STP)\cdot mm}{cm^2\cdot min\cdot torr^{1/2}}$
y	Oxide layer thickness (at 3136 hr)	2μm
x	Metal layer thickness	1.59mm
B_1	Parabolic rate constant (at 243 torr)	$6.78X10^{-10}mm^2$/hour
B_2	Parabolic rate constant (at 714 torr)	$1.99X10^{-9}mm^2$/hour

Table 3. Parameters for tritium permeation model

The current model successfully follows a rapid decrease at early stage and shows good agreement at the latter part of the experiment. The same temperature and

2.94 times higher pressure environment was a good target to validate the current model. And it shows good agreement. (Figure3)

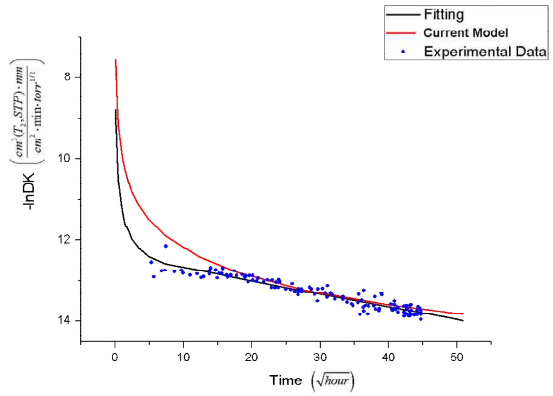

Figure 2. Comparison between current model and experimental data (Incoloy 800 at 930K with 243 torr)

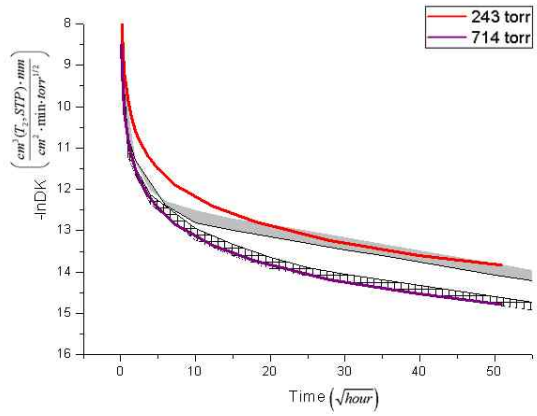

Figure 3. Comparison between current model and experimental data (Incoloy 800 at 930K with 243 torr / 714 torr)

5. Conclusion

According to the references, PRF (Permeation Reduction Factor) is about 10~1000 in case of Incoloy 800 due to the formation of the oxide layer. In this study, the permeation model including the Deal-Grove model for oxide layer formation was suggested and validated against the experimental data.

6. References

[1] J. T. Bell, J. D. Redman, and H. F. Bittner 1980. “Tritium Permeation Through Clean Incoloy 800 and Sanicro 31 Alloys and Through Steam Oxidized Incoloy 800”

[2] Liang N. Lie, Reda R. Razouk and Bruce E. Deol. 1982. “High Pressure Oxidation of Silicon in Dry Oxygen” Solid-state science and technology VoL 129, No. 12

[3] Yoshiaki Shida and Taishi Moroishi 1991. “oxidation behavior of alloy 800 in an impure helium atmosphere at high temperatures” Sumitomo Metal Industries Ltd, Advanced Technology Research Laboratories, l-3 Nishinagasu-Hondoori, Amagasaki, Japan