

Analysis of Transient Passive Film Growth on Zirconium
in High Temperature Aqueous Solutions

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According to the Point Defect Model (PDM)¹, the rate of change in thickness of the barrier layer of the passive film can be written as

$$\frac{dL}{dt} = a.e^{-bL} - c \quad (1)$$

where the parameters are as previously defined². Equation (1) is readily integrated for a step in voltage to yield the transients in anodic oxide film thickness and current density given by Equations (2) and (3).

$$L(t) = L_0 + \left(\frac{1}{b}\right) \ln \left[\left(\frac{a'}{c}\right) e^{-bL_0} (e^{bct} - 1) + 1 \right] - ct \quad (2)$$

$$i = \chi F k_3^0 e^{\alpha_3 V} e^{-c_3 pH} X + (\delta - \chi) F k_7^0 e^{\alpha_7 V} e^{c_7 pH} (C_{H^+} / C_{H^+}^0)^n \quad (3)$$

respectively, where

$$X = \frac{c e^{-b_3 L_0}}{a' e^{-b_3 L_0} - (a' e^{-b_3 L_0} - c) e^{-bct}} \quad (4)$$

$a = \Omega k_3^0 e^{\alpha_3(1-\alpha)\chi V} e^{-\alpha_3\chi\beta\gamma pH}$, $b = \alpha_3\chi\epsilon\gamma$, and $c = \Omega k_7(C_{H^+} / C_{H^+}^0)^n$, with other parameters being defined elsewhere². Note that c is the dissolution rate at voltage $V + \Delta V$, and that $a' = k_3^0 e^{\alpha_3(1-\alpha)\gamma(V+\Delta V)} e^{-\alpha_3\beta\gamma pH}$. Note also that Equations (2) and (3) apply strictly to an oxygen ion conducting film, although it is believed (but not proven) that the theory is also applicable to cation interstitial conducting barrier layers as well.

Equations (2) and (3) are being used to analyze the transients in film thickness and current for anodic film growth on zirconium upon stepping the applied voltage over the cycle $0.5 V_{sce} \rightarrow 0.6 V_{sce} \rightarrow 0.3 V_{sce} \rightarrow 0.0 V_{she} \rightarrow 0.3 V_{she} \rightarrow 0.6 V_{she}$ in a solution of $pH = 7.06$ at $250^\circ C$. The transients are being used to derive values for important parameters in the Point Defect Model, which is now being used to describe the growth of oxide films on zirconium and Zircaloy fuel sheathing in water-cooled nuclear reactors.

Equations (2) and (3) make important predictions with regard to film growth and thinning in response to positive and negative potential steps, respectively. Thus, on stepping the potential in the positive direction, only part of the potential ($\alpha\Delta V$) appears as an additional potential drop across the film (barrier layer)/solution (f/s) interface, whereas an additional potential drop of $(1-\alpha)\Delta V$ appears across the metal/film (m/f) interface, where α is the polarizability of the f/s interface¹. The additional potential drop at the m/f interface enhances the rate of

production of oxygen vacancies, thereby leading to enhanced growth of the film into the metal. If the film dissolution reaction is not an electrochemical process (as is likely for zirconium), the additional potential drop at the f/s interface (i.e., $\alpha\Delta V$) does not enhance the rate of film dissolution, so that the film thickens. Theory indicates that film thickening is very fast; a phenomenon that has been noted elsewhere². Upon stepping the potential in the negative direction [negative $(1-\alpha)\Delta V$], the first term in Equation (1) becomes very small and the film thickness is predicted to decrease at a constant rate, which has also been observed for tungsten². However, as the film thickens, the potential drop across the film increases, due to the constant field strength¹, and the additional potential drop across the m/f interface becomes smaller. At some point, the first term on the right side of Equation (1) again contributes to film growth and eventually equals the dissolution rate, c . At this point, the film is in a steady state condition.

In the present work, the film thickness is being measured using high frequency capacitance methods, while the thickness changes over the voltage cycle. The current is measured simultaneously. The PDM, through Equations (2) and (3), is then optimized on both sets of data to yield the desired parameter values. Comparison of the parameter values derived from $L(t)$ and $i(t)$ provides a means of assessing the success of the theory.

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