

PREDICTION OF TRANSIENT PASSIVE FILM
GROWTH ON ALLOY C-22

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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 given by Equations (2) and (3).

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

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

where

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

$a = \Omega k_3^0 e^{\alpha_3(1-\alpha)\chi\gamma} e^{-\alpha_3\chi\beta\gamma pH}$, $b = \alpha_3\chi\epsilon\gamma$, 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.

Equations (2) and (3) were used to calculate the transients in film thickness and current for Alloy C-22 upon stepping the applied voltage over the cycle $0.5 V_{scc} \rightarrow 0.6 V_{scc} \rightarrow 0.3 V_{scc} \rightarrow 0.0 V_{she} \rightarrow 0.3 V_{she} \rightarrow 0.6 V_{she}$ in a solutions of $pH = 6$ at $25^\circ C$ and $90^\circ C$. The transients are being used to define the conditions under which the corrosion of high-level nuclear waste (HLNW) canisters may be predicted using quasi steady state models and for assessing whether the Point Defect Model is capable of providing quantitative prediction of accumulated damage.

An important finding of this work is the identification of the processes that lead 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 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, 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. Calculation 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 observed². However, as the film thickens, the potential drop across the film increases, due to the constant field strength¹, and hence 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.

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