Electronic supplementary information

A Mechanistic Model for Oxide Growth and Dissolution during Corrosion of Cr-Containing Alloys

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Appendix: Mathematical Derivation of Analytical Solution for Oxide Growth

A1:   Growth of a Single Phase Oxide

The metal oxidation flux can be expressed using a modified Butler-Volmer equation:

$$J_{M\#^{n+}}(t)|_{m|ox} = J_{rdx\#}^{eq} \cdot \left(exp\left(a \cdot \eta_{ox\#}(t)\right)\right) \tag{A1}$$

where $a = \frac{0.5 \cdot n \cdot F}{RT}$.

In the presence of an oxide layer, the effective overpotential is

$$\eta_{rdx\#}(t) = E_{elec}(t) - E_{ox\#}^{eq} - \Delta V_{oxide}(t) \tag{A2}$$

The potential drop across the oxide layer is assumed to be proportional to oxide thickness:

$$\Delta V_{oxide}(t) = \Delta V_{oxide}(0) + \varepsilon_{MO\#} \cdot L_{MO\#}(t) \tag{A3}$$

Under potentiostatic conditions, $E_{elec}(t) \approx$ constant with time. Substituting (A3) and (A2)

into (A1) and by separating constant terms from time-dependent terms:

$$J_{M\#^{n+}}(t)|_{m|ox} = A_J \cdot \left(exp\left(a \cdot \left(- \varepsilon_{MO\#} \cdot L_{MO\#}(t)\right)\right)\right) \tag{A4}$$

where $A_J = J_{rdx\#}^{eq} \cdot \left(exp\left(a \cdot \left(E_{elec}(t) - E_{ox\#}^{eq} - \Delta V_{oxide}(0)\right)\right)\right)$ (A5)

The oxide growth flux is:

$$J_{MO\#}(t)|_{oxide} = f_{k-MO\#}(t) \cdot J_{M\#^{n+}}(t)|_{m|ox} \tag{A6}$$

where $f_{k-MO\#}(t) = \left(\frac{k_{MO\#}(t)}{k_{MO\#}(t) + k_{diss\#}}\right)$ (A7)

$$k_{MO\#}(t) = k_{MO\#}(0) \cdot exp\left(-\frac{c_{MO\#} \cdot L_{MO\#}(t)}{RT}\right) \tag{A8}$$

This is related to the linear rate of oxide growth as:

$$\frac{dL_{MO\#}}{dt} = \upsilon_{MO\#} \cdot J_{MO\#}(t)|_{oxide} \tag{A10}$$

From (A4), (A6) to (A10),

$$\frac{dL_{MO\#}}{dt} = \upsilon_{MO\#} \cdot \left(\frac{k_{MO\#}(0) \cdot exp\left(-\frac{c_{MO\#} \cdot L_{MO\#}(t)}{RT}\right)}{k_{MO\#}(0) \cdot exp\left(-\frac{c_{MO\#} \cdot L_{MO\#}(t)}{RT}\right) + k_{diss\#}}\right) \cdot A_J$$

$$\cdot \left(exp\left(a \cdot \left(- \varepsilon_{MO\#} \cdot L_{MO\#}(t)\right)\right)\right)$$

$$\tag{A11}$$

$$\frac{dL_{MO\#}}{\upsilon_{MO\#} \cdot \left(\dfrac{k_{MO\#}(0) \cdot exp\left(-\frac{c_{MO\#} \cdot L_{MO\#}(t)}{RT}\right)}{k_{MO\#}(0) \cdot exp\left(-\frac{c_{MO\#} \cdot L_{MO\#}(t)}{RT}\right) + k_{diss\#}}\right) \cdot A_J \cdot \left(exp\left(a \cdot \left(- \varepsilon_{MO\#} \cdot L_{MO\#}(t)\right)\right)\right)} = dt$$

$$\tag{A12}$$

$$\frac{1}{\upsilon_{MO\#} \cdot A_J} \cdot \left(\frac{k_{MO\#}(0) \cdot exp\left(-\frac{c_{MO\#} \cdot L_{MO\#}(t)}{RT}\right) + k_{diss\#}}{k_{MO\#}(0) \cdot exp\left(-\frac{c_{MO\#} \cdot L_{MO\#}(t)}{RT}\right)}\right) \cdot \frac{dL_{MO\#}}{\left(exp\left(a \cdot \left(- \varepsilon_{MO\#} \cdot L_{MO\#}(t)\right)\right)\right)} = dt$$

$$\tag{A13}$$

$$\frac{1}{\upsilon_{MO\#} \cdot A_J} \cdot \left(1 + \frac{k_{diss\#}}{k_{MO\#}(0)} \cdot exp\left(\frac{c_{MO\#} \cdot L_{MO\#}(t)}{RT}\right)\right) \cdot \left(exp\left(a \cdot \varepsilon_{MO\#} \cdot L_{MO\#}(t)\right)\right) \cdot dL_{MO\#} = dt$$

$$\tag{A14}$$

$$\frac{1}{\upsilon_{MO\#} \cdot A_J} \cdot \left(exp\left(a \cdot \varepsilon_{MO\#} \cdot L_{MO\#}(t)\right) + \frac{k_{diss\#}}{k_{MO\#}(0)} \cdot exp\left(\left(\frac{c_{MO\#}}{RT} + a \cdot \varepsilon_{MO\#}\right) \cdot L_{MO\#}(t)\right)\right) \cdot dL_{MO\#}$$

$$= dt$$

$$\tag{A15}$$

The solution for the differential equation is:

$$\frac{1}{\upsilon_{MO\#} \cdot A_J} \cdot \left(\frac{1}{(a \cdot \varepsilon_{MO\#})} \cdot \left(exp\left(a \cdot \varepsilon_{MO\#} \cdot L_{MO\#}(t)\right) - 1 \right) \right.$$

$$\left. + \frac{1}{\left(\frac{c_{MO\#}}{RT} + a \cdot \varepsilon_{MO\#}\right)} \cdot \frac{k_{diss\#}}{k_{MO\#}(0)} \cdot \left(exp\left(\left(\frac{c_{MO\#}}{RT} + a \cdot \varepsilon_{MO\#}\right) \cdot L_{MO\#}(t)\right) - 1 \right) \right) = t$$

$$(A16)$$

The typical values of $\varepsilon_{MO\#}$ and $c_{MO\#}$ are such that (see Table 2 in the text):

$$\frac{c_{MO\#}}{RT} \ll a \cdot \varepsilon_{MO\#} \qquad (A17)$$

For an oxide thicker than a few angstroms:

$$exp\left(a \cdot \varepsilon_{MO\#} \cdot L_{MO\#}(t)\right) \gg 1 \qquad (A18)$$

Thus,

$$\frac{1}{\upsilon_{MO\#} \cdot A_J} \cdot \frac{1}{(a \cdot \varepsilon_{MO\#})} \cdot \left(1 + \frac{k_{diss\#}}{k_{MO\#}(0)}\right) \cdot \left(exp\left(a \cdot \varepsilon_{MO\#} \cdot L_{MO\#}(t)\right) \right) \approx t \qquad (A19)$$

By defining

$$\lambda_{MO\#} = a \cdot \varepsilon_{MO\#} = \frac{0.5 \cdot n \cdot F}{RT} \cdot \varepsilon_{MO\#} \qquad (A20)$$

$$f_{k-MO\#}(0) = \left(\frac{k_{MO\#}(0)}{k_{MO\#}(0) + k_{diss\#}}\right) \qquad (A21)$$

$$J_{MO\#}" = \upsilon_{MO\#} \cdot f_{k-MO\#}(0) \cdot A_J$$

$$= \upsilon_{MO\#} \cdot f_{k-MO\#}(0) \cdot J_{rdx\#}^{eq} \cdot \left(exp\left(\frac{0.5 \cdot n \cdot F}{RT} \cdot \left(E_{elec}(t) - E_{ox\#}^{eq} - \Delta V_{oxide}(0)\right)\right) \right) \quad (A22)$$

Taking ln of both sides of Eq. A19 yields:

$$L_{MO\#}(t) \approx \frac{1}{\lambda_{MO\#}} \left(ln(\lambda_{MO\#} \cdot J_{MO\#}") + \ln t \right) \qquad (A23)$$

A2: Conversion of Chromium Oxide to Chromite

For the conversion of chromium oxide to chromite the same derivation can be performed. The only difference is that the overpotential in this case is a function of the potential drop across the two oxide layers:

$$\eta_{rdx\#}(t) = E_{elec}(t) - E_{ox\#}^{eq} - \Delta V_{oxide}(t) \tag{A24}$$

$$\Delta V_{oxide}(t) = \varepsilon_{Cr2O3} \cdot L_{Cr2O3}(0) + (\varepsilon_{MCr2O4} - f_l \cdot \varepsilon_{Cr2O3}) \cdot L_{MCr2O4}(t) \tag{A25}$$

This change also changes the constants in Eq. A23. The thickness of chromite layer is then:

$$L_{MCr2O4}(t) \approx \frac{1}{\lambda_{MCr2O4}} (ln(\lambda_{MCr2O4} \cdot J_{MCr2O4}")) + \ln t) \tag{A23}$$

$$J_{MO\#}" = \upsilon_{MO\#} \cdot f_{k-MO\#}(0) \cdot J_{rdx\#}^{eq} \cdot \left(exp\left(\frac{0.5 \cdot n \cdot F}{RT} \cdot \left(E_{elec}(t) - E_{ox\#}^{eq} - \varepsilon_{Cr2O3} \cdot L_{Cr2O3}(0) \right) \right) \right)$$

$$\tag{A22}$$

$$\lambda_{MO\#} = \frac{0.5 \cdot n \cdot F}{RT} \cdot (\varepsilon_{MCr2O4} - f_l \cdot \varepsilon_{Cr2O3}) \tag{A25}$$