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Scientific Notebook No. 304: Passive Current Densities in Cr-Mo-Ni Alloys (01/29/1999 through 07/19/2002)

CENTER FOR NUCLEAR WASTE
REGULATORY ANALYSES

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TITLE: PASSIVE CURRENT DENSITIES IN Cr-Mo-Ni ALLOYS

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OBJECTIVE: MODEL THE OXIDE ON Cr-Mo-Ni ALLOYS TO PREDICT THE PASSIVE CURRENT DENSITY. THIS PASSIVE CURRENT DENSITY WILL BE USED TO ESTIMATE THE LIFE OF WASTE PACKAGE MATERIALS.

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Notation: Assume an oxide of A of stoichometry $AO_{\chi/2}$

A in oxide site: A_A

O in oxide site: O_O

Missing A: $V_A^{\chi'}$ is A-vacancy $A_A = [A^{\chi+} + V_A^{\chi'}]$

Missing O in lattice: $V_O^{\cdot\cdot}$ → means +2

Assume the presence of a defect $B^{\gamma+}$ in site $V_A^{\chi'}$: $[B^{\gamma+} + V_A^{\chi'}] = B_A^{\gamma-\chi}$

I will assume that other defects are less likely; for example

$[A^{\chi+} + V_O^{2+}] = A_O^{\chi+2}$

It may be argued that these defects increase the electrostatic energy, and therefore are less likely; i.e., $A^{\chi+}$ and V_O^{2+} repel each other.

Assume a A-B alloy with an oxide of the following structure

metal	oxide 1	oxide 2	solution
A-B	$AO_{\chi/2}$	$BO_{\psi/2}$	

Metal / oxide 1 interface reactions

$A + V_A^{\chi'} \xrightarrow{K_1} A_A + V_A + \chi e'$ A injection into $AO_{\chi/2}$

$B + V_A^{\chi'} \xrightarrow{K_2} B_A^{\gamma-\chi} + V_B + \gamma e'$ Formation of $B_A^{\gamma-\chi}$ defects

$A \xrightarrow{K_3} A_A + \frac{\chi}{2} V_O^{2+} + \chi e'$ Film formation, creation of $\frac{\chi}{2} V_O^{2+}$ defects

oxide 1 / oxide 2 interface

$A_A + V_B^{\psi'} \xrightarrow{K_4} A_B^{\xi-\psi} + V_A^{\chi'} + (\xi-\chi)e'$

$B_A^{\gamma-\chi} + V_B^{\psi'} \xrightarrow{K_5} B_B + V_A^{\chi'} + (\gamma-\chi)e'$

$\psi A O_{\chi/2} + \chi B_A^{\gamma-\chi} + \chi(\gamma-\chi)e' \xleftrightarrow{K_6} \chi B O_{\psi/2} + \psi A_B^{\xi-\psi} + \psi(\xi-\psi)e'$

→ oxide 2 / solution interface

$A_B^{\xi-\psi} + \phi \xrightarrow{\text{nothing}} A^{\delta+} + V_B^{\psi'} + (\delta-\psi+\psi-\xi)e'$

$B_B \longrightarrow B^{\delta+} + V_B^{\psi'} + (\delta-\psi)e'$

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oxide 2 / solution interface

$V_O^{2+} + H_2O \xrightarrow{K_9} O_O + 2H^+$

$BO_{\psi/2} + \psi H^+ \longrightarrow B^{\delta+} + \frac{\psi}{2} H_2O + (\delta-\psi)e'$

Metal | oxide 1 | oxide 2

$A + V_A^{\chi-} \xrightarrow{K_1} A_A + V_A + \chi e^-$

$B + V_A^{\chi-} \xrightarrow{K_2} B_A^{\gamma-\chi} + V_B + \gamma e^-$

$A \xrightarrow{K_3} A_A + \frac{\chi}{2} V_O^{2+} + \chi e^-$

$A_A + V_B^{\psi-} \xrightarrow{K_4} A_B^{\xi-\psi} + V_A^{\chi-} + (\xi-\chi)e^-$

$B_A^{\gamma-\chi} + V_B^{\psi-} \xrightarrow{K_5} B_B + V_A^{\chi-} + (\psi-\gamma)e^-$

$\psi AO_{\frac{\chi}{2}} + \chi B_B^{\gamma-\chi} + \chi(\gamma-\chi)e^- \xrightarrow{K_6} \chi BO_{\psi/2} + \psi A_B^{\xi-\psi} + \psi(\xi-\psi)e^-$

$AO_{\chi/2}$ $BO_{\psi/2}$

$BO_{\psi/2}$ | solution

$A_B^{\xi-\psi} \xrightarrow{K_7} A^{\delta+} + V_B^{\psi-} + (\delta-\xi)e^-$

$B_B \xrightarrow{K_8} B^{\delta+} + V_B^{\psi-} + (\delta-\psi)e^-$

$V_O^{2+} + H_2O \xrightarrow{K_9} O_O + 2H^+$

$BO_{\psi/2} + \psi H^+ \xrightarrow{K_{10}} B^{\delta+} + \frac{\psi}{2} H_2O + (\delta-\psi)e^-$

Assume steady-state

$V_A^{\chi-}$ consumption: $J_{V_A^{\chi-}} = -a_A a_{V_A^{\chi-}} K_1 - a_B a_{V_A^{\chi-}} K_2$

$= -a_{V_A^{\chi-}} (a_A K_1 + a_B K_2)$

a_A and a_B → activity of A and B respectively

$V_A^{\chi-}$ production: $J_{V_A^{\chi-}} = -a_{V_B^{\psi-}} (a_{A_A} K_4 + a_{B_A} K_5)$ $a_{A_A} \approx 1$

$V_B^{\psi-}$ consumption: $J_{V_B^{\psi-}} = -a_{V_B^{\psi-}} (a_{A_A} K_4 + a_{B_A} K_5) = J_{V_A^{\chi-}}$

$V_B^{\psi-}$ production: $J_{V_B^{\psi-}} = -a_{A_B} \theta K_7 + \theta(-a_{B_B}) K_8$

V_O^{2+} production: $J_{V_O^{2+}} = \frac{\chi}{2} a_A K_3$

V_O^{2+} consumption: $J_{V_O^{2+}} = a_W a_{V_O^{2+}} \theta K_9$

CONT P4

$AO_{\frac{x}{2}}$, Rate of film formation $\propto a_A K_3$

Rate of film dissolution $\propto a_{B_A} K_6$

At steady-state $a_A K_3 = a_{B_A} K_6$

$BO_{\frac{\psi}{2}}$, Rate of film formation $\propto \frac{x}{\psi} a_{B_A} K_6$

Rate of film dissolution $\propto K_{10} C_{H^+}^{n}$

At steady-state $\frac{x}{\psi} a_{B_A} K_6 = K_{10} C_{H^+}^{n} \theta$

Consequently $a_A K_3 = a_{B_A} K_6 = \frac{\psi}{x} K_{10} C_{H^+}^{n} \theta$

Steady-state relationships

$$a_{V_A^{x-}} (a_A K_1 + a_B K_2) = a_{V_B^{\psi-}} (a_{A_A} K_4 + a_{B_A} K_5) \quad [1]$$

$$a_{V_B^{\psi-}} (a_{A_A} K_4 + a_{B_A} K_5) = \theta (a_{A_B} K_7 + a_{B_B} K_8) \quad [2]$$

$$\frac{x}{2} a_A K_3 = a_W a_{V_o^{2+}} K_9 \theta \quad [3]$$

$$a_A K_3 = a_{B_A} K_6 = \frac{\psi}{x} K_{10} C_{H^+}^{n} \theta \quad [4]$$

From [1] and [2]

$$a_{V_A^{x-}} (a_A K_1 + a_B K_2) = a_{V_B^{\psi-}} (a_{A_A} K_4 + a_{B_A} K_5) = \theta (a_{A_B} K_7 + a_{B_B} K_8)$$

From [3] and [4]

$$a_A K_3 = a_{B_A} K_6 = \frac{\psi}{x} K_{10} C_{H^+}^{n} \theta = \frac{2}{x} a_W a_{V_o^{2+}} K_9 \theta$$

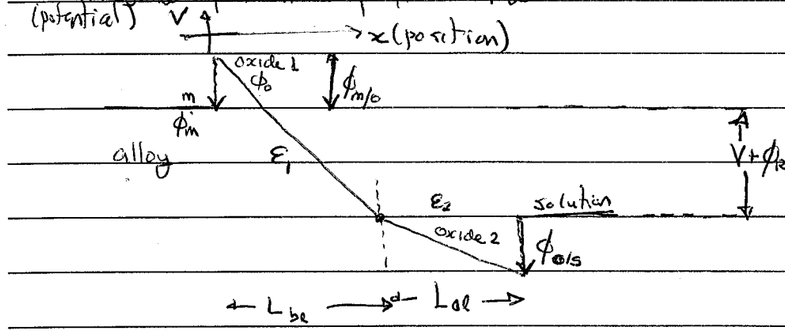
2/1/99 CPJ

The total current density is given by

$$\begin{aligned} i = F \{ & x a_A a_{V_A^{x-}} K_1 + \tau a_B a_{V_A^{x-}} K_2 + x a_A K_3 \\ & + a_{A_A} a_{V_B^{\psi-}} K_4 (\xi - x) + (\psi - \tau) a_{B_A} a_{V_B^{\psi-}} K_5 \\ & + a_{B_A} \left[\xi - \psi + \frac{x}{\psi} (\tau - x) \right] K_6 \\ & + a_{A_B} (\delta - \xi) K_7 \theta + a_{B_B} (\rho - \psi) \theta K_8 + K_{10} a_{H^+}^{n} \theta (\rho - \psi) \} \end{aligned}$$

CONT BY

Assume potential profile like



$\phi_{m/o} = \phi_m - \phi_{oxide}$ = potential drop at alloy/oxide interface.

$\phi_{o/s} = \phi_o - \phi_s$ = potential drop at oxide/solution interface

$$(V + \phi_R) - \phi_{m/o} - \phi_{o/s} = \varepsilon_2 L_{ol} + \varepsilon_1 L_{bl}$$

$$\phi_{m/o} = V + \phi_R - \phi_{o/s} - \varepsilon_2 L_{ol} - \varepsilon_1 L_{bl}$$

According to the Point Defect Model

$$\phi_{o/s} = \phi_{o/s} = \alpha V + \beta pH + \phi_{o/s}^{\circ}$$

$$\phi_{m/o} = (1-\alpha) V + \phi_R - \phi_{o/s}^{\circ} - \beta pH - \varepsilon_2 L_{ol} - \varepsilon_1 L_{bl}$$

Let $\varepsilon \equiv \frac{\varepsilon_1 L_{bl} + \varepsilon_2 L_{ol}}{L_{bl} + L_{ol}}$ and $L \equiv L_{bl} + L_{ol}$

then $\phi_{m/o} = (1-\alpha) V + \phi_R - \phi_{o/s}^{\circ} - \beta pH - \varepsilon L$

Potential dependence of K_3:

$$K_3 = K_3^{\circ} \exp\left(g_3 \frac{F}{RT} \phi_{m/o} \right)$$

Potential dependence of K_{10}

$$K_{10} = K_{10}^{\circ} \exp\left[g_{10} (\rho - \psi) \frac{F}{RT} \phi_{o/s} \right]$$

Since $a_A K_3 = \frac{\psi}{x} K_{10} a_{H^+}^{n} \theta = a_{B_A} K_6^{\circ}$

Since I am assuming that there is not any potential drop between the two oxides $K_6 = K_6^{\circ}$; i.e., K_6 is not potential dependent.

$$K_3 = \frac{\psi}{x} \frac{K_{10} a_{H^+}^{n} \theta}{a_A}$$

$$K_3 = \frac{\Psi}{\chi}\frac{K_{10}\,a_{H^+}^n\,\theta}{a_A} = K_3^\circ\, e^{\alpha_3\gamma x\phi_{m/o}}$$

$$\alpha_3\gamma x\phi_{m/o} = \ln\left(\frac{\Psi}{\chi}\frac{K_{10}\,a_{H^+}^n\,\theta}{K_3^\circ\,a_A}\right)$$

$$\phi_{m/o} = \frac{1}{\alpha_3\gamma x}\ln\left(\frac{\Psi}{\chi}\frac{K_{10}\,a_{H^+}^n\,\theta}{K_3^\circ\,a_A}\right) = \frac{1}{\alpha_3\gamma x}\ln\frac{\Psi K_{10}^\circ\,a_{H^+}^n\,\theta}{K_3^\circ\,a_A} + \frac{\alpha_{10}\gamma(\beta-\psi)\,\phi_{o/s}}{\alpha_3\gamma x}$$

$$pH = -\mathrm{Log}\,a_{H^+} \qquad 10^{-pH} = a_{H^+} = e^{-\ln 10\,pH} = a_{H^+}$$

$$\ln a_{H^+} = -\ln 10\,pH$$

$$\phi_{m/o} = \frac{1}{\alpha_3\gamma x}\ln\frac{\Psi K_{10}^\circ\,\theta}{K_3^\circ\,a_A} + \frac{1}{\alpha_3\gamma x}\,n(-\ln 10\,pH) + \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x}\,\phi_{o/s}$$

$$\phi_{m/o} = \frac{1}{\alpha_3\gamma x}\ln\frac{\Psi K_{10}^\circ\,\theta}{K_3^\circ\,a_A} - \frac{n\ln 10}{\alpha_3\gamma x}\,pH + \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x}\,\phi_{o/s}$$

On the other hand

$$\phi_{m/o} = V + \phi_R - \phi_{o/s} - \mathcal{E}L$$

Consequently $\mathcal{E}L = V + \phi_R - \phi_{o/s} - \frac{1}{\alpha_3\gamma x}\ln\frac{\Psi K_{10}^\circ\,\theta}{K_3^\circ\,a_A} + \frac{n\ln 10}{\alpha_3\gamma x}\,pH - \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x}\,\phi_{o/s}$

$$\mathcal{E}L = V + \phi_R - \left(1 + \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x}\right)\phi_{o/s} - \frac{1}{\alpha_3\gamma x}\ln\frac{\Psi K_{10}^\circ\,\theta}{K_3^\circ\,a_A} + \frac{n\ln 10}{\alpha_3\gamma x}\,pH$$

If $\phi_{o/s} = \alpha V + \beta\,pH + \phi_{o/s}^\circ$ then

$$\mathcal{E}L = \left[1 - \left(1 + \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x}\right)\alpha\right]V + \left[\frac{n\ln 10}{\alpha_3\gamma x} - \left(1 + \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x}\right)\beta\right]pH + \phi_{13} - \left(1 + \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x}\right)\phi_{o/s}^\circ - \frac{1}{\alpha_3\gamma x}\ln\frac{\Psi K_{10}^\circ\,\theta}{K_3^\circ\,a_A}$$

$\mathcal{E}L = c_1 V + c_2\,pH + c_3^\circ$ → it has the same assumed form for $\phi_{o/s}$

Note that $\mathcal{E}L = V_{ox}$ is the potential drop within the oxide. Is there some means of measuring such potential drop as function of the applied voltage?

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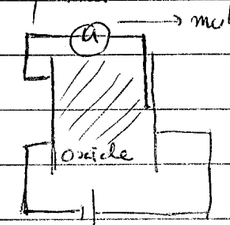
$$\phi_{o/s} = \alpha V + \beta\,pH + \phi_{o/s}^\circ \qquad (1)$$

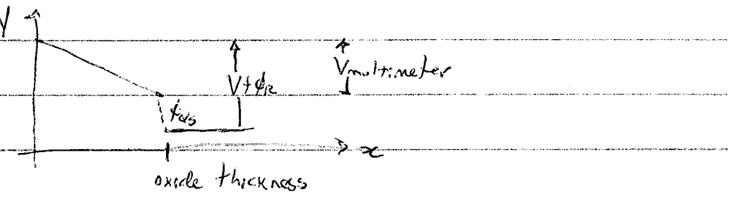
→ This is an open problem. How feasible is this equation, and how can be measured the potential drop at the oxide/solution interface?

Can we design an experiment for measuring that?

Thought experiment:



Potential profile:



$$\phi_{o/s} = V + \phi_R - V_{multimeter}$$

If we do this experiment there are several issues that render its conclusions invalid:

1) stoichiometry, 2) structure, 3) thickness

Points 1), 2), and 3) are variable for an oxide grown in situ. That is to say, a comercial oxide is not necessarily equivalent to an oxide formed in situ.

Certainly Equation (1) is a strong assumption. Its validity depends more on the accuracy of the predictions than anything else.

We will take Equation (1) for granted, but in case of obtaining wrong conclusions, we should try alternative functions to define $\phi_{o/s}$.

2/1/99 CRP

SUMMARY

Important equations:

$$\phi_{mlo} = \frac{1}{\alpha_3 \gamma x} \ln \frac{\psi K_{10}^\circ \theta}{K_3^\circ a_A} - \frac{n \ln 10}{\alpha_3 \gamma x} pH + \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x} \phi_{ols}$$

$$EL = C_1 V + C_2 pH + C_3^\circ$$

$$C_1 = \left[1 - \left(1 + \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x}\right)\alpha\right]$$

$$C_2 = \frac{n \ln 10}{\alpha_3 \gamma x} - \left(1 + \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x}\right)\beta$$

$$C_3^\circ = \phi_R - \left(1 + \frac{\alpha_{10}(\beta-\psi)}{\alpha_3 x}\right)\phi_{ols}^\circ - \frac{1}{\alpha_3 \gamma x} \ln \frac{\psi K_{10}^\circ \theta}{K_3^\circ a_A}$$

$$I = F\{x a_A a_{V_H^{x-}} K_1 + \tau a_B a_{V_A^{x-}} K_2 + x a_A K_3 + a_{A_A} a_{V_B^{\psi-}} K_4 (\xi - x)$$
$$+ (\psi - \tau) a_{B_A} a_{V_B^{\psi-}} K_5 + a_{B_A} [\xi - \psi + \tfrac{x}{\psi}(\tau - x)] K_6$$
$$+ a_{A_B} (\delta - \xi) K_7 \theta + a_{B_B} (\beta - \psi) \theta K_8 + K_{10} a_{H^+}^n + \theta (\beta - \psi)\}$$

Steady-state equations

$$a_A K_3 = a_{B_A} K_6 = \frac{\psi}{x} K_{10} a_{H^+}^n \theta = \frac{z}{x} a_W a_{V_0^{x+}} K_9 \theta$$

$$a_{V_H^{x-}} (a_A K_1 + a_B K_2) = a_{V_B^{\psi-}} (a_{A_A} K_4 + a_{B_A} K_5) = \theta (a_{A_B} K_7 + a_{B_B} K_8)$$

RATE CONSTANTS AT THE METAL/OXIDE INTERFACE

$$K_j = K_j^\circ e^{\alpha_j z_j \gamma \phi_{mlo}} = K_j^\circ \exp\left[\frac{\alpha_j z_j \gamma}{\alpha_3 \gamma x} \ln \frac{\psi K_{10}^\circ \theta}{K_3^\circ a_A}\right] \exp\left[\frac{n \alpha_j z_j \gamma}{\alpha_3 \gamma x} \ln a_{H^+}\right] \chi$$

$$\exp\left[\frac{\alpha_j z_j \gamma \alpha_{10}(\beta-\psi)}{\alpha_3 x} \phi_{ols}\right]$$

$$K_j = K_j^\circ \left(\frac{\psi K_{10}^\circ \theta}{K_3^\circ a_A}\right)^{\frac{\alpha_j z_j \gamma}{\alpha_3 \gamma x}} a_{H^+}^{\frac{n \alpha_j z_j}{\alpha_3 x}} \exp\left[\frac{\alpha_j z_j \alpha_{10}(\beta-\psi)}{\alpha_3 x} \gamma \phi_{ols}\right]$$

If $\phi_{ols} = \alpha V + \beta pH + \phi_{ols}^\circ$, then

$$\exp\left[\frac{\alpha_j z_j \alpha_{10}(\beta-\psi)}{\alpha_3 x} \gamma (\alpha V + \beta pH + \phi_{ols}^\circ)\right] = e^{\frac{\alpha_j z_j \alpha_{10}(\beta-\psi)}{\alpha_3 x} \gamma \alpha V} a_{H^+}^{-\frac{\alpha_j z_j \alpha_{10}(\beta-\psi)\gamma\beta}{\alpha_3 x \ln 10}} e^{\frac{\alpha_j z_j \alpha_{10}(\beta-\psi)\gamma\phi_{ols}^\circ}{\alpha_3 x}}$$

$$e^{\frac{\alpha_j z_j \alpha_{10}(\beta-\psi)}{\alpha_3 x} \gamma \left(-\frac{\beta \ln 10\, pH}{\ln 10}\right)} = a_{H^+}^{-\frac{\alpha_j z_j \alpha_{10}(\beta-\psi)}{\alpha_3 x \ln 10} \gamma \beta}$$

Then

$$K_j = K_j^\circ \left(\frac{\psi K_{10}^\circ \theta}{K_3^\circ a_A}\right)^{\frac{\alpha_j z_j}{\alpha_3 x}} a_{H^+}^{\frac{\alpha_j z_j}{\alpha_3 x}\left[n - \frac{\alpha_{10}(\beta-\psi)\gamma\beta}{\ln 10}\right]} e^{\frac{\alpha_j z_j \alpha_{10}(\beta-\psi)\gamma\alpha V}{\alpha_3 x}} e^{\frac{\alpha_j z_j \alpha_{10}(\beta-\psi)\gamma\phi_{ols}^\circ}{\alpha_3 x}}$$

2/2/99 CRP

Since we are assuming that no potential drop occurs at the oxide1/oxide2 interface $K_4 = K_4^\circ$, $K_5 = K_5^\circ$, and $K_6 = K_6^\circ$, i.e, the dissolution rates do not depend on the applied voltage. It is reasonable to expect $a_{A_A} = a_{A_A}^\circ$ and $a_{B_A} = a_{B_A}^\circ$. The reason is that a_{A_A} and a_{B_A} are defined at the oxide1/oxide2 interface. By definition, such region may be defined as the place where $a_{A_A} = a_{A_A}^\circ$ and $a_{B_A} = a_{B_A}^\circ$, where $a_{A_A}^\circ$ and $a_{B_A}^\circ$ are given values.

Then

$$a_{V_B^{\psi-}} = \frac{\theta (a_{A_B} K_7 + a_{B_B} K_8)}{a_{A_A}^\circ K_4^\circ + a_{B_A}^\circ K_5^\circ}$$

$a_{V_B^{\psi-}}$ is computed at the oxide1/oxide2 interface, and it is potential dependent

On the other hand

$$a_{V_A^{x-}} = \frac{\theta (a_{A_B} K_7 + a_{B_B} K_8)}{a_A^\circ K_1 + a_B^\circ K_2}$$

By definition $a_A = a_A^\circ$ and $a_B = a_B^\circ$

$$I = F\left\{\frac{x a_A^\circ K_1 + \tau a_B^\circ K_2}{a_A^\circ K_1 + a_B^\circ K_2} \theta (a_{A_B} K_7 + a_{B_B} K_8) + x \frac{\psi}{x} K_{10} a_{H^+}^n \theta \right.$$
$$+ \frac{(\xi - x) a_{A_A}^\circ K_4^\circ + (\psi - \tau) a_{B_A}^\circ K_5^\circ}{a_{A_A}^\circ K_4^\circ + a_{B_A}^\circ K_5^\circ} \theta (a_{A_B} K_7 + a_{B_B} K_8)$$
OPR 2/2/99
$$+ a_{B_A}^\circ [\xi - \psi + \tfrac{x}{\psi}(\tau - x)] \tfrac{\psi}{x} K_{10} a_{H^+}^n \theta + (\beta - \psi) K_{10} a_{H^+}^n \theta$$
$$\left. + a_{A_B} (\delta - \xi) K_7 \theta + a_{B_B} (\beta - \psi) \theta K_8 \right\}$$

$$I = F\theta \left\{ (a_{A_B} K_7 + a_{B_B} K_8) \left[\frac{x a_A^\circ K_1 + \tau a_B^\circ K_2}{a_A^\circ K_1 + a_B^\circ K_2}\right]_{\text{OPR 2/4/99}} + \left[\frac{(\xi - x) a_{A_A}^\circ K_4^\circ + (\psi - \tau) a_{B_A}^\circ K_5^\circ}{a_{A_A}^\circ K_4^\circ + a_{B_A}^\circ K_5^\circ}\right]_{\text{OPR 2/4/99}} \right.$$
$$\left. + a_{A_B} (\delta - \xi) K_7 + a_{B_B} (\beta - \psi) K_8 + K_{10} a_{H^+}^n \left[\psi + \tfrac{x}{\psi}\left[\xi - \psi + \tfrac{z}{x}[\tau - x]\right] + \beta - \psi\right] \right\}$$

2/2/99

We know (or believe) that the oxide that forms on the alloy is Cr_2O_3. We will continue with our analysis assuming that the outer layer is made of NiO_2 or NiO. We will assume that the dissolved species are Ni^{2+} and Cr^{3+}

Metal oxide interface:

$Cr + V_{Cr}^{3'} \xrightarrow{k_1} Cr_{Cr} + V_O + 3e'$ $\quad x=3$

$Ni + V_{Cr}^{3'} \xrightarrow{k_2} Ni_{Cr}^{-} + V_{Ni} + 2e'$ $\quad \tau=2$

$Cr \xrightarrow{k_3} Cr_{Cr} + \frac{3}{2} V_O^{2+} + 3e^-$

oxide 1 / oxide 2 interface Cr_2O_3 / NiO interface

$Cr_{Cr} + V_{Ni}^{2-} \xrightarrow{k_4} Cr_{Ni}^{+} + V_{Cr}^{3-}$ $\quad \zeta=3,\ \psi=2,\ \chi=3,\ \tau=2$

$Ni_{Cr}^{-} + V_{Ni}^{2-} \xrightarrow{k_5} Ni_{Ni} + V_{Cr}^{3-}$

$2CrO_{\frac{3}{2}} + 3Ni_{Cr}^{-} + 3(-1)e^- \xrightarrow{k_6} 3NiO_{\frac{2}{2}} + 2Cr_{Ni}^{+} + 2e^-$

$2CrO_{\frac{3}{2}} + 3Ni_{Cr}^{-} \xrightarrow{k_6} 3NiO + 2Cr_{Ni}^{+} + 5e^-$

NiO / solution interface

$Cr_{Ni}^{+} \xrightarrow{k_7} Cr^{3+} + V_{Ni}^{2-}$ $\quad \delta=3$

$Ni_{Ni} \xrightarrow{k_8} Ni^{2+} + V_{Ni}^{2-}$ $\quad \delta=2$

$V_O^{2+} + H_2O \xrightarrow{k_9} O_O + 2H^+$ $\quad \delta=\psi=2$

$NiO + 2H^+ \xrightarrow{k_{10}} Ni^{2+} + H_2O$

2/3/99 Rate constants at the metal/oxide interface

$$K_j = K_j^\circ \left(\frac{\psi K_{10}^\circ \Theta}{K_3^\circ a_A}\right)^{\frac{\alpha_j z_j}{\alpha_3 \chi}} a_{H^+}^{\frac{\alpha_j z_j n}{\alpha_3 \chi}} \qquad \chi=3$$

Darell Dunn has experimental evidence that the passive current density is independent of pH. Very likely $n \approx 0$, and K_j is a constant

$$E_L = (1-\alpha)V + \left(\frac{n \ln 10}{\alpha_3 \gamma \chi} - \beta\right) pH + \phi_R - \phi_{fs}^\circ - \frac{1}{\alpha_3 \gamma \chi} \ln \frac{\psi K_{10}^\circ \Theta}{K_3^\circ a_A}$$

2/3/99

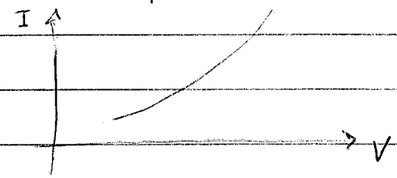
The current density then becomes

$$I = F\Theta \left\{ (a_{AB} K_7 + a_{B_\beta} K_8) \frac{3 a_O^\circ K_1 + 2 a_\beta^\circ K_2}{a_O^\circ K_1 + a_\beta^\circ K_2} + \frac{1}{3} K_{10} a_{H^+}^n \right\}$$

$K_{10} = K_{10}^\circ \exp[\alpha_{10}(\delta-\psi)\gamma \phi_{o/s}] = K_{10}^\circ$

$K_7 = K_7^\circ \exp[\alpha_7 \delta \gamma \phi_{o/s}] = K_7^\circ e^{3\alpha_7 \gamma \phi_{o/s}}$

$K_8 = K_8^\circ \exp[\alpha_8 \delta \gamma \phi_{o/s}] = K_8^\circ e^{2\alpha_8 \gamma \phi_{o/s}}$



Darell Dunn also found that the passive current density is function of the $[Cl^-]$. How is that included in the above description?

2/4/99

$-|C_{m/f}|-|C_f|-|C_{f/s}|-|C_d|-$ capacitors connected in series

$\frac{1}{C} = \frac{1}{C_{m/f}} + \frac{1}{C_f} + \frac{1}{C_{f/s}} + \frac{1}{C_d}$ $\quad C_d \rightarrow$ capacitance of diffusive layer

More likely $C_{m/f}$ and $C_{f/s} \rightarrow \infty$, then $\frac{1}{C} \approx \frac{1}{C_f} + \frac{1}{C_d}$

In D.D. Macdonald, K.M. Ismail, and E. Sikora, J. Electrochem. Soc., 145, 3141-3147 (1998) No. 9, September 1998

The thickness of the oxide is measured via C. C is measured via impedance experiments as function of the frequency. This approach is not quite correct, since the capacitance detected by impedance devices

CONT. P. 12

2/4/99 AFJ

is the differential capacitance, and not the geometric capacitance. This mistake is done quite often. We need to find some other means to measure the capacitance.

$$I = F\theta \left\{ \left(a_{A_B} K_7 + a_{B_B} K_8\right) \frac{3a_A^\circ K_1 + 2a_B^\circ K_2}{a_A^\circ K_1 + a_B^\circ K_2} - \frac{1}{3} K_{10} a_{H^+}^n \right.$$

Darrell found that I is pH independent, therefore $n \approx 0$, $\beta \approx 0$

If $I \propto V$

Consequently $K_{10} \approx 0$ and $a_{A_B} \approx 0$

$$I \approx F\theta\, a_{B_B} K_8 \frac{3a_A^\circ K_1 + 2a_B^\circ K_2}{a_A^\circ K_1 + a_B^\circ K_2} = F\theta a_{B_B} \frac{3a_A^\circ K_1 + 2a_B^\circ K_2}{a_A^\circ K_1 + a_B^\circ K_2} K_8^\circ e^{2\alpha_8 \gamma \alpha V} e^{2\alpha_8 \gamma \phi_{is}^\circ}$$

$$\ln I = 2\alpha_8 \gamma \alpha V + \ln\left[F\theta a_{B_B} \frac{3a_A^\circ K_1 + 2a_B^\circ K_2}{a_A^\circ K_1 + a_B^\circ K_2} K_8^\circ e^{2\alpha_8 \gamma \phi_{is}^\circ}\right]$$

$$\frac{d \ln I}{dV} = 2\alpha_8 \gamma \alpha$$

→ may be a function of $[Cl^-]$

Darrell is observing high dissolution rates at higher $[Cl^-]$ concentrations. Is $\frac{d \ln I}{dV}$ independent of $[Cl^-]$? It should be. Maybe not

We need to do experiments in a wider potential range. Current experiments span from 200 mV to 400 mV_{SCE}. Above these potentials active dissolution is observed. I am interested in observing what happens at lower potentials.

The model developed so far presumes the existance of two phases. I will change the approach, and analyze one single phase with plenty of defects.

2/5/99 AFJ

2nd Model

Alloy	Film	Solution
(1) $A + V_A^{x-} \xrightarrow{k_1} A_A + V_A + xe^-$		(4) $A_A \xrightarrow{k_4} A^{\delta+} + V_A^{x-} + (\delta - x)e^-$
(2) $B + V_A^{x-} \xrightarrow{k_2} B_A^{\tau-x} + V_B + \tau e^-$		(5) $B_A^{\tau-x} \xrightarrow{k_5} B^{\delta+} + V_A^{x-} + (\delta - \tau)e^-$
(3) $A \xrightarrow{k_3} A_A + \frac{x}{2} V_O^{2+} + xe^-$		(6) $AO_{x/2} + xH^+ \xrightarrow{k_6} A^{\delta+} + \frac{x}{2} H_2O + (\delta - x)e^-$
		(7) $V_O^{\cdot\cdot} + H_2O \xrightarrow{k_7} O_O + 2H^+$

V_A^{x-} consumption: $J_{V_A^{x-}} = -k_1 a_A a_{V_A^{x-}} - k_2 a_B a_{V_A^{x-}}$

V_A^{x-} creation: $J_{V_A^{x-}} = -K_4 a_{A_A} \theta - K_5 a_{B_A} \theta$ θ = surface active sites

V_O^{2+} creation: $J_{V_O^{2+}} = k_3 a_A$

V_O^{2+} consumption: $J_{V_O^{2+}} = a_w a_{V_O^{2+}} \theta$

Film formation $\propto a_A K_3$

Film dissolution $\propto \theta K_6 a_{H^+}^n$

Steady-state relationships:

$$K_1 a_A a_{V_A^{x-}} + K_2 a_B a_{V_A^{x-}} = K_4 a_{A_A} \theta + K_5 a_{B_A} \theta$$

$$K_3 a_A = a_w a_{V_O^{2+}} \theta$$

$$K_3 a_A = K_6 a_{H^+}^n \theta$$

Current:

$$I = F\left\{ x K_1 a_A a_{V_A^{x-}} + K_2 a_B a_{V_A^{x-}} \tau + K_3 a_A x + (\delta - x) a_{A_A} K_4 \theta + (\delta - \tau) a_{B_A} K_5 \theta + (\delta - x)\theta a_{H^+}^n K_6 \right\}$$

OPR 2/5/99

$$a_A K_3^\circ e^{x\alpha_3 \gamma \phi_{m/f}} = K_6 a_{H^+}^n \theta$$

$$x\alpha_3 \gamma \phi_{m/f} = \ln \frac{K_6 a_{H^+}^n \theta}{a_A K_3^\circ} \qquad \phi_{m/f} = \frac{1}{x\alpha_3 \gamma} \ln \frac{K_6 a_{H^+}^n \theta}{a_A K_3^\circ}$$

At m/f interface

$$K_j = K_j^\circ e^{z_j \gamma \phi_{m/f}} = K_j^\circ \exp\left[\frac{\alpha_j}{x\alpha_3} \ln \frac{K_6 a_{H^+}^n \theta}{a_A K_3^\circ}\right] = K_j^\circ \left(\frac{K_6 a_{H^+}^n \theta}{a_A K_3^\circ}\right)^{\frac{\alpha_j z_j}{\alpha_3 x}}$$

$$K_j = \left(\frac{K_6 a_{H^+}^n \theta}{a_A K_3^\circ}\right)^{\frac{\alpha_j z_j}{\alpha_3 x}} = \left(\frac{K_6}{a_A K_3^\circ}\right)^{\frac{\alpha_j z_j}{\alpha_3 x}} a_{H^+}^{\frac{\alpha_j z_j n}{\alpha_3 x}}$$

2/5/99

$$I = F\theta \left\{ \frac{\chi K_1 a_A + \tau K_2 a_B}{a_A K_1 + a_B K_2} (K_4 a_{A_A} + K_5 a_{B_A}) + \cancel{+} K_6 a_{H^+}^{n} + (\delta-\chi) a_{A_A} K_4 \cancel{+} (\beta-\tau) a_{B_A} K_5 + (\delta-\chi) a_{H^+}^{n} K_6 \right\}$$

For the Cr–Ni case, most likely $\delta = \chi = 3$

$\beta = \tau = 2$

$$I = F\theta \left\{ \frac{\chi K_1 a_A + \tau K_2 a_B}{a_A K_1 + a_B K_2} (K_4 a_{A_A} + K_5 a_{B_A}) + \cancel{+} K_6 a_{H^+}^{n} \right\}$$

Which is basically equivalent to the equation derived for the bilayer system, which is almost equivalent to the equation derived by Macdonald.

Now I have to talk with Gustavo and Darell and see what they think.

Darell believes that the passive current density is not only independent of pH, but also of the applied voltage.

I have computed so far equations for the passive current density that are quite similar with those computed with the PDM in its original form.

ORIGINAL PDM

(1) $m + V_M^{x\prime} \xrightarrow{K_1} M_M + V_m + \chi e'$ (3) $M_M \xrightarrow{K_3} M^{\delta+} + V_M^{x\prime} + (\delta-\chi) e'$

(2) $m \xrightarrow{K_2} M_M + \left(\frac{\chi}{2}\right) V_O^{\cdot\cdot} + \chi e'$ (4) $V_O^{\cdot\cdot} + H_2O \xrightarrow{K_4} O_O + 2H^+$

(5) $MO_{\chi/2} + \chi H^+ \xrightarrow{K_5} M^{\delta+} + \frac{\chi}{2} H_2O + (\delta-\chi) e^-$

Consumption of $V_M^{x\prime}$: $J_{V_M^{x\prime}} = -a_{V_M^{x\prime}} K_1$

Creation of V_M^{x-} : $J_{V_M^{x-}} = -\theta K_3$

Creation of $V_O^{\cdot\cdot}$: $J_{V_O^{\cdot\cdot}} = \frac{\chi}{2} K_2$

Consumption of $V_O^{\cdot\cdot}$: $J_{V_O^{\cdot\cdot}} = a_W \theta a_{V_O^{\cdot\cdot}} K_4$

Film creation $\propto K_2$ $\xrightarrow{\text{at steady-state}}$ $K_2 = K_5 a_{H^+}^{n} \theta$

Film dissolution $\propto K_5 a_{H^+}^{n} \theta$

Total current density:

$$I = F\left\{ \chi a_{V_M^{x-}} K_1 + \chi K_2 + (\delta-\chi)\theta K_3 + (\delta-\chi) K_5 a_{H^+}^{n} \theta \right\}$$

Assuming that the charge transport is due mainly to oxygen vacancies ($V_O^{\cdot\cdot}$), then $K_1 \approx 0$, $K_3 \approx 0$. It is more appropriate to say that $K_1, K_3 \ll K_2$.

In such a case

$$I \approx F\{\chi K_2 + (\delta-\chi) K_5 a_{H^+}^{n} \theta\}$$

In the case $\delta = \chi$

$$I = F\chi K_2$$

"Evidently" I is not dependent on pH.

The expression for I is perfectly valid, regardless of whether or not steady-state is attained, provided that transport is indeed due to the motion of oxygen vacancies.

IF V_M^{x-} are the main charge carriers, then $K_2, K_3 \ll K_1, K_3$

and $I \approx F\chi a_{V_M^{x-}} K_1$

The presence of $a_{V_M^{x-}}$ makes the elaboration of diagnostic criteria difficult, since no independent means have been devised to determine $a_{V_M^{x-}}$. Certainly $a_{V_M^{x-}}$ can be dependent on the applied voltage.

2/8/99

Important references

G. Lorang, N. Jallerat, K. Vu Quang and J.-P. Langeron.
Surface and Interface Analysis. Vol 16, 325-330 (1990)

There is evidence that C-4 alloy forms a bilayer film with an inner layer of chromium oxide and an outer layer of nickel oxide. C-4 is similar to C-22

N. E. Hakiki, M. Da Cunha Belo, A. M. P. Simões, M. G. S. Ferreira
J Electrochem. Soc., Vol 145, No 11 (1998)

This paper gives evidence that in stainless steels, an inner layer forms of Cr oxide, and an outer layer of Fe oxide. The Cr oxide behaves as a P-semiconductor (V_M^{x-}, metal cation conductor), and the Fe oxide as an n-semiconductor ($V_O^{\cdot\cdot}$, oxygen anion conductor).

Interesting references given in the above paper:

8. R. De Gryse, W. P. Gomes, F. Cardon, and J. Vennik,
J. Electrochem. Soc., 122, 711 (1975)
Talks about the correction to the surface charge capacitance (C_{sc}) by putting it in series with the Helmholtz capacitance (C_H).

Dielectric constant of chromium oxide and Fe oxide: 12

Sources:

18. B. Lovrecek and J. Sepaja, Electrochim. Acta, Vol 17, 1151 (1972)
19. E. Mahla and N. Nielsen, J. Electrochem. Soc., Vol 93, 1 (1948)
11. M. H. Dean and U. Stimming, J. Electroanal. Chem., Vol 228, 135 (1987)

7. N. E. Hakiki, S. Boudin, B. Rondot, and M. Da Cunha Belo
Corros. Sci, 37, 1809 (1995) → about Cr layer formation

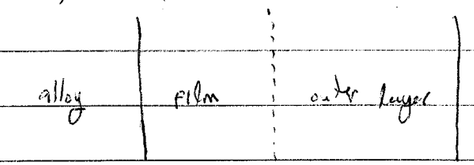
2/11/99

Reviewing the literature for stainless steels I found agreement in the following:

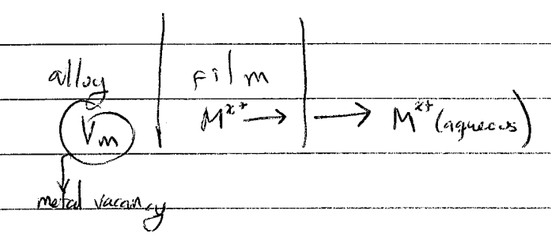
1) The film on stainless steel is of a bilayer nature, with an inner layer of Cr oxide (oxidation state III) and Fe oxide (III).
2) Mo helps in improving the corrosion resistance, but the mechanism is not clear, since Mo is barely found in the film.
3) Cr oxide is an ionic conductor, with negative majority carriers (n-type semiconductor). Macdonald believes that an n-type semiconductor is a V_O^{2+} conductor. I believe this view is wrong, since the classification must be made according to who is the main charge carrier (its sign), and not by regarding V_O^{2+} as a donor.
4) Mo can be present in several oxidation states (+4 or +6) depending on the applied voltage.

Even though these views are valid for stainless steels, there must be some similitude with Cr-Mo-Ni alloys.

Possibilities



According to the Point defect model, a film that is V_M^{x-} conductor just dissolves



The film does not "move" with respect to a fixed reference frame. However, plenty of vacancies are accumulated in the metal phase. According to Macdonald, these vacancies "merge" into the metal and "disapear".

There is, however, another possibility:

$$n V_m \longleftrightarrow \frac{x}{2} V_O^{\cdot\cdot} + V_M^{x-}$$

Thus, metal vacancies in the metal phase give rise to oxygen and metal vacancies in the film phase.

$$a_{V_O^{2+}}^{x/2}\, a_{V_M^{x-}} = K_{sp}\, a_{V_m}^{n} \quad ?$$

This is an interesting idea. For example, we may think that at the metal/film interface the following reactions happen:

(1) $m + V_M^{x-} \xrightarrow{K_1} M_M + V_m + xe^-$

(2) $n V_m \xrightarrow{K_2} \frac{x}{2} V_O^{2+} + V_M^{x-}$

In order for the V_m not to be accumulated at the metal/film interface, necessarily $a_{V_M^{x-}}\, n K_1 = K_2^{\circ}\, a_{V_m}^{n} \Rightarrow a_{V_M^{x-}} = \frac{K_2^{\circ} a_{V_m}^{n}}{n K_1}$

If the condition $a_{V_M^{x-}}\, n K_1 = K_2^{\circ} a_{V_m}^{n}$ is not achieved, there is accumulation of metal vacancies in the bulk metal, V_m, which causes detachment of the film from the metal. This may be the reason of pit initiation.

Note that K_1 depends on the local potential drop, which must equal a constant, in order for steady-state to be achieved. Let $\phi_{m/f}$ be the potential drop at the metal/film interface. $\phi_{m/f}$ is a constant; i.e., it is independent of the applied voltage.

Note the following. At the film/solution interface, the following reaction is expected to happen:

(3) $M_M \xrightarrow{K_3} M^{s+} + V_M^{x-} + (s-x)e^-$

V_M^{x-} generation: $J_{V_M^{x-}} = a_{V_m}^{n} K_2 - a_{V_M^{x-}} K_1$ at metal/film interface

V_M^{x-} generation at f/s interface: $J_{V_M^{x-}} = -K_3 \Theta$

At steady-state: $K_3 \Theta = \underbrace{a_{V_M^{x-}} K_1}_{= K_2^{\circ} a_{V_m}^{n} \frac{1}{n}} - a_{V_m}^{n} K_2 = \left(\frac{1}{n} - 1\right) K_2^{\circ} a_{V_m}^{n}$

If $n=1$, then $K_3 = 0$. If $n>1$, then we have some inconsistency.

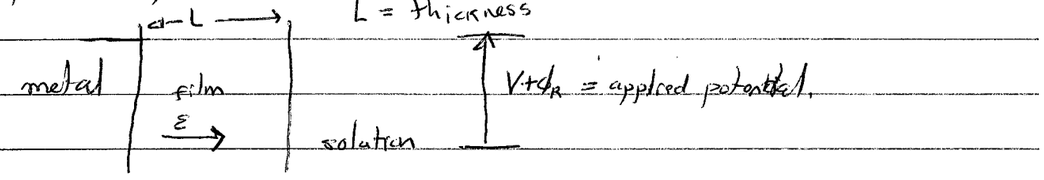
$K_3 < 0$!!

Would it be possible that $n<1$?

The way around this, is that the reaction happens in the following direction:

(3) $M^{s+} + V_M^{x-} + (s-x)e^- \xrightarrow{K_3} M_M$

The advantage of this approach is that it explains what happens to V_m, but it is not very consistent with the idea of the motion of the vacancies to be assisted by the electric field. Let us try to explain this further



If $V+\phi_R > 0$, then we expect the electric field, $\mathcal{E} \approx \frac{V+\phi_R}{L}$, to be also positive. $V_O^{\cdot\cdot}$ and V_M^{x-} seem to be created (according to equations (1) and (2)) at the metal/film interface, and are consumed at the film/solution interface (according to equation (3) and (4): $V_O^{2+} + H_2O \xrightarrow{K_4} O_O + 2H^+$).

Then both vacancies move from the metal phase to the solution phase

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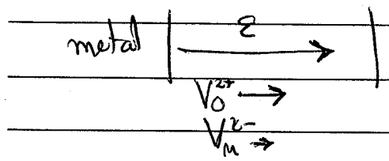


This may be a feasible situation, only if the mobility of V_M^{x-} >> mobility of V_O^{2+}. V_O^{2+} moves from left to the right, and "drags" behind V_M^{x-}.

V_M^{x-} can only move in the correct direction only if assisted by V_O^{2+}!

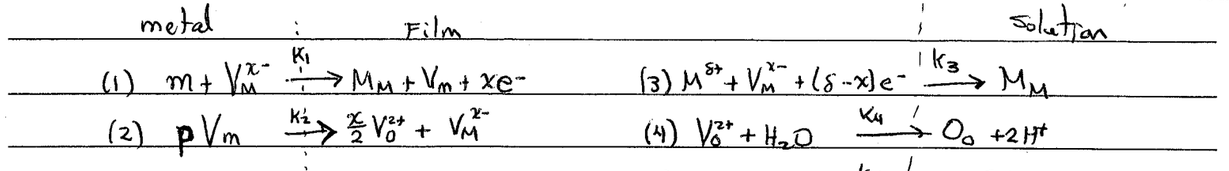
Is that true?

Can we build a PDM based on these ideas, and make it consistent with what has been published?

Let me explain why I consider necessary to review the basic ideas of the PDM. The PDM postulates that metal vacancies in the metal bulk, V_m, are created continuously (unless the film is not a V_M^{x-} conductor). If this is the case, then what happens to these V_m vacancies? The PDM does not provide an answer. It says that V_m merge into the metal and disappear ... just that, they disappear!

Macdonald explains that accumulation of these vacancies at the metal/film interface causes the film to detach, which will cause a pit to appear. From my point of view, these metal vacancies, V_m, should always accumulate, unless they are ~~annihilated~~ by some mechanism, which is not explained by the PDM.

So to avoid this "predicted accumulation of V_m at the m/f interface," I propose the following mechanism for the growth of a passive film:



metal/film interface:

$$J_{V_M^{x-}} = K_2 a_{V_m}^{p} - K_1 a_{V_M^{x-}}^{m/f}$$

$$J_{V_O^{2+}} = \frac{x}{2} K_2 a_{V_m}^{p}$$

Film formation $\propto a_{V_m}^{p} K_2$

Film/solution interface

$$J_{V_M^{x-}} = a_{M^{\delta+}} a_{V_M^{x-}}^{f/s} \theta K_3$$

$$J_{V_O^{2+}} = \theta a_{V_O^{2+}}^{f/s} a_W K_4$$

Film dissolution $\propto \theta K_5 a_{H^+}^{n}$

At steady state I expect no creation of V_m; then

$$p K_1 a_{V_M^{x-}}^{m/f} = K_2 a_{V_m}^{p}$$

Then $J_{V_M^{x-}} = (p-1) K_1 a_{V_M^{x-}}^{m/f}$ (I am assuming $p \geq 1$)

Total current:

$$I = F\left(x a_{V_M^{x-}}^{m/f} K_1 - (\delta-x)\theta a_{M^{\delta+}} a_{V_M^{x-}}^{f/s} K_3 + (\delta-x)\theta K_5 a_{H^+}^{n}\right)$$

For the case $\delta = x$, the total current becomes

$$I = F x a_{V_M^{x-}}^{m/f} K_1$$

$$a_{V_M^{x-}}^{m/f} = \frac{K_2 a_{V_m}^{p}}{p K_1} \Rightarrow I = Fx\left(\frac{K_2 a_{V_m}^{p}}{p K_1}\right) K_1 = Fx \frac{K_2 a_{V_m}^{p}}{p}$$

I found only one equation, which should be always valid if the model is correct. It is not possible to state two different equations for the case of anion vacancy or cation vacancy conduction. Therefore there is something wrong with the above idea, since cation conduction has a different behavior than anion conduction (based on I vs V plots).

I will try a different idea:

2/15/99 OPJ

metal | film | solution

(1) $m + V_M^{x-} \xrightarrow{k_1} M_M + V_m + xe^-$

(2) $p\,V_m \xrightarrow{k_2} \frac{x}{2} V_O^{2+} + V_M^{x-}$

(3) $m \xrightarrow{k_3} M_M + \frac{x}{2} V_O^{2+} + xe^-$

(4) $M_M \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} M^{\delta+} + V_M^{x-} + (\delta - x)e^-$

(5) $V_O^{2+} + H_2O \xrightarrow{k_5} O_O + 2H^+$

(6) $MO_{\delta/2}^{+x/2\,H^+} \xrightarrow{k_6} M^{\delta+} + \frac{\delta}{2} H_2O + (\delta - x)e^-$

$J_{V_M^{x-}}^{m/f} = a_{V_m}^{p} k_2 - a_{V_M^{x-}}^{m/f} k_1$

$J_{V_O^{2+}} = \frac{x}{2} a_{V_m}^{p} k_2 + \frac{x}{2} k_3$

Film formation $\propto a_{V_m}^{p} k_2 + k_3$

$J_{V_m}^{m/f} = \frac{k_2 a_{V_m}^{p}}{p} - k_1 a_{V_M^{x-}} = 0$ at steady-state

$J_{V_M^{x-}}^{m/f} = \theta k_{-4} a_{M^{\delta+}} a_{V_M^{x-}}^{f/s} - \theta k_4$

$J_{V_O^{2+}} = a_{V_O^{2+}} a_W \theta k_5$

Film dissolution is $a_{H^+}^{n} \theta k_6$

$I = F[x k_1 a_{V_M^{x-}} + x k_3 + (\delta - x) k_4 \theta - (\delta - x) k_{-4} a_{M^{\delta+}} a_{V_M^{x-}}^{m/f} + (\delta - x) a_{H^+}^{n} \theta k_6]$

For the case $\delta = x$ the above becomes

$I = F[x k_1 a_{V_M^{x-}} + x k_3]$

One of the implications under the above scheme is that V_O^{2+} and V_M^{x-} are transported simultaneously. It is not possible the conduction of one and only one of these species. Both must be always present.

At steady-state

$k_2 a_{V_m}^{p} = p a_{V_M^{x-}} k_1$ $\quad a_{V_m}^{p} k_2 + k_3 = \theta a_{H^+}^{n} k_6 = p a_{V_M^{x-}} k_1 + k_3$

$p a_{V_M^{x-}} k_1 = \theta a_{H^+}^{n} k_6 - k_3$

$I = F\left[\frac{1}{p}(\theta a_{H^+}^{n} k_6 - k_3) + k_3\right] x$

If $p = 1$, $I = Fx\,\theta a_{H^+}^{n} k_6 =$ constant if $\delta = x$

If $p \geq 1$ and $k_6 = 0$ $\quad I = F(1 - \frac{1}{p}) x k_3$

Note that $p a_{V_M^{x-}} k_1 = \theta a_{H^+}^{n} k_6 - k_3$, then if $k_6 \to 0$, $k_3 \to 0$

$\therefore$ k_6 cannot equal 0.

This makes sense, if $k_6 = 0$, then $I = 0$

If $\delta = x$, $a_{V_m}^{p} k_2 + k_3 = a_{H^+}^{n} \theta k_6$

$k_2 = k_2^\circ e^{\alpha_2 \gamma \phi_{m/f}}$ $\quad k_3 = k_3^\circ e^{\alpha_3 \gamma \phi_{m/f}}$

$\phi_{m/f}$ can be found as the root of the first equation $\Rightarrow \phi_{m/f}$ is a constant. Consequently k_3 is a constant.

$a_{V_m}^{p} k_2 - a_{V_M^{x-}}^{m/f} k_1 = \theta k_{-4} a_{M^{\delta+}} a_{V_M^{x-}}^{f/s} - \theta k_4$

I have seen that $\phi_{m/f}$ is a constant. Consequently the left-hand side of the above equation is a constant. The equation can only be valid if the potential drop at the film/solution interface is a constant! $\quad \phi_{f/s} = \phi_{f/s}^\circ =$ constant!

This contradicts the PDM which states $\phi_{f/s} = \alpha V + \beta\,pH + \phi_{f/s}^\circ$

$\varepsilon L = V + \phi_R - \phi_{m/f}^\circ - \phi_{f/s}^\circ$

The equation $\varepsilon L = V + \phi_R - \phi_{m/f}^\circ - \phi_{f/s}^\circ$ still predicts a linear relationship between the film thickness and the applied voltage, provided that ε is constant.

I think the postulate $\phi_{f/s} = \alpha V + \beta\,pH + \phi_{f/s}^\circ$ can be modified by $\phi_{f/s} = \beta\,pH + \phi_{f/s}^\circ$ and the same results will be obtained. I am not sure. This is just a guess.

4/19/1999 OPJ

One of the drawbacks of the prior approach is that both vacancies, V_O^{2+} and V_M^{x-}, move in the same direction. This possibility is feasible, but unlikely since the electric field inside the film must favor the motion along a given direction. $\overset{+}{\longrightarrow}$ $\overset{-}{\longleftarrow}$ The PDM, original version, is consistent with this requirement.

2/17/1999 OPR

Another idea

Metal/film interface

$M \xrightarrow{k_1} M_i^{x+} + V_m + xe$

$M + V_M^{x-} \xrightarrow{k_2} M_M + V_m + xe$

$n\,V_m \xrightarrow{k_3} \frac{x}{2} V_O^{2+} + V_M^{x-}$

$\frac{x}{2} V_O^{2+} + V_M^{x-} \xrightarrow{k_4} n\,V_m$

$J_{V_m} = -k_1 - k_2 a_{V_M^{x-}} + n k_3 a_{V_m}^n - n k_4 a_{V_m} a_{V_O^{2+}}^{x/2}$

$J_{V_M^{x-}} = -k_2 a_{V_M^{x-}} + k_3 a_{V_m}^n - k_4 a_{V_M^{x-}} a_{V_O^{2+}}^{x/2}$

$J_{V_O^{2+}} = \frac{x}{2} a_{V_m}^n k_3 - \frac{x}{2} k_4 a_{V_M^{x-}} a_{V_O^{2+}}^{x/2}$

In order to ensure that V_m and V_M^{x-} will not accumulate at the film solution interface $J_{V_m} = J_{V_M^{x-}} = 0$

$n\left[k_3 a_{V_m}^n - k_4 a_{V_M^{x-}} a_{V_O^{2+}}^{x/2}\right] = k_1 + k_2 a_{V_M^{x-}} \Rightarrow \frac{k_1 + k_2 a_{V_M^{x-}}}{n} = k_3 a_{V_m}^n - k_4 a_{V_M^{x-}} a_{V_O^{2+}}^{x/2}$

$k_3 a_{V_m}^n - k_4 a_{V_M^{x-}} a_{V_O^{2+}}^{x/2} = k_2 a_{V_M^{x-}}$

$k_4 = (n-1) k_2 a_{V_M^{x-}}$

$k_1 = (n-1) k_2 a_{V_M^{x-}}$ Necessarily $n \geq 1$

$J_{V_O^{2+}} = \frac{x}{2}\left(a_{V_m}^n k_3 - k_4 a_{V_M^{x-}} a_{V_O^{2+}}^{x/2}\right) = \frac{x}{2} k_2 a_{V_M^{x-}}$

$I_{ox} = Fx\left[k_1 + k_2 a_{V_M^{x-}}\right]$

Film/solution interface

$M_i^{x+} \xrightarrow{k_5} M_{(aq)}^{\delta+} + (\delta - x)e$

$MO_{x/2} + xH^+ \xrightarrow{k_6} M^{\delta+} + \frac{x}{2} H_2O + (\delta - x)e$

$V_O^{2+} + H_2O \xrightarrow{k_7} O_O + 2H^+$

$J_{M_i^{x+}} = k_5 a_{M_i^{x+}}$

$J_{V_O^{2+}} = k_7 a_{V_O^{2+}} a_w$

Film dissolution $\propto k_6 a_{H^+}^p$ OPR/4/19/99

Assume $k_4 = 0$, film formation/dissolution $\propto k_3 a_{V_m}^n$

Assuming $\delta = x$, the conclusion is that the voltage dependence of I_{ox} upon Voltage is due to $a_{V_M^{x-}}$

2/22/99 OPR

Apparently we can get a quite consistent description with

metal	Film	Solution
$M \xrightarrow{k_1} M_i^{x+} + V_m + xe$		$M_i^{x+} \xrightarrow{k_4} M_{(aq)}^{\delta+} + (\delta - x)e$
$M + V_M^{x-} \xrightarrow{k_2} M_M + V_m + xe$		$V_O^{2+} + H_2O \xrightarrow{k_5} O_O + 2H^+$
$n\,V_m \xrightarrow{k_3} \frac{x}{2} V_O^{2+} + V_M^{x-}$		$MO_{x/2} + xH^+ \xrightarrow{k_6} M^{\delta+} + \frac{x}{2} H_2O + (\delta - x)e^-$
$J_{V_m} = -k_1 - k_2 a_{V_M^{x-}} + n k_3 a_{V_m}^n$		$M_m \xrightarrow{k_7} M_{(aq)}^{\delta+} + V_m^{x-} + (\delta - x)e$
$J_{V_M^{x-}} = -k_2 a_{V_M^{x-}} + k_3 a_{V_m}^n$		
$J_{V_O^{2+}} = \frac{x}{2} a_{V_m}^n k_3$		

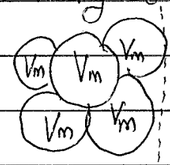
In order for true steady-state to be possible $J_{V_m} = J_{V_M^{x-}} = 0$?

$J_{V_m} = 0$ because there is no clear mechanism for the metal vacancies to "disappear" in the bulk metal, as the PDM proposes. I believe this is an inconsistency of the PDM, that will be avoided by requesting $J_{V_m} = 0$.

$J_{V_M^{x-}} = 0$ only if $k_7 = 0$. In general I expect $J_{V_M^{x-}} \leq 0$

Therefore $k_2 a_{V_M^{x-}} \geq k_3 a_{V_m}^n$

What about a moving boundary?



$a(t)$ = position of metal/film interface measured with respect to a fixed-in-the-laboratory reference frame

$\frac{da(t)}{dt} = -\frac{1}{\Omega} k_3 a_{V_m}^n$ (Ω → molar density of $MO_{x/2}$)

$V_{m/f}(t) = -\Omega k_3 a_{V_m}^n$ Ω = molar volume $\left(\frac{cm^3}{mol}\right)$ of $MO_{x/2}$

OPR 5/14/99

~~The PDM never takes into account the moving boundary!!~~

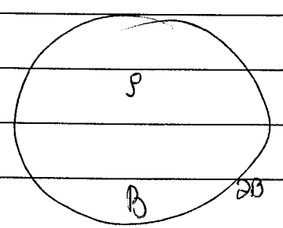
2/22/99 OPP

Chromium oxides (Cr_2O_3) have been studied but there is not complete agreement on who is the main charge carrier. There is evidence that cation vacancies and Cr interstitials (Cr_i^{3+}) are responsible for charge conduction in Cr_2O_3 films. These references discuss this issue in further detail:

E.A. Polman, T. Fransen and P.J. Gellings (Review Article)
J. Phys: Condens. Matter. Vol 1 (1989) 4497-4510

P. Kofstad and K.P. Lillerud
J. Electrochem. Soc.: Solid-State Science and Technology
Vol. 127, No 11 (1980) 2410-2414

It is necessary to clarify that in the above studies, the chromium oxide was grown at high temperatures (1000°C) and was not placed in an electrochemical environment. For example, it is argued (second reference) that chromium oxide is an intrinsic semiconductor at high oxygen pressures. This situation cannot be true in an oxide placed in contact with a solution, since intrinsic conduction requires a continuous supply of electrons and/or holes from the solution to the film. Thinking more deeply about it, it may hold true, if electrochemical reactions (electron participating) ~~2/22/99 OPP~~ contain happen at the film/solution interface.



ρ = charge density $[\rho] = coul/m^3$
$B \sim$ space region
$\partial B \sim$ boundary of B

2/22/99 OPP

Total charge $= Q = \int_B \rho(\vec{x})\, dV$

Conservation of charge: $0 = \frac{dQ}{dt} = \int_B \frac{\partial \rho}{\partial t} dV + \int_{\partial B} \rho \dot{\vec{x}} \cdot \hat{n}\, ds$

$$0 = \int_B \left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \dot{\vec{x}}) \right) dV$$

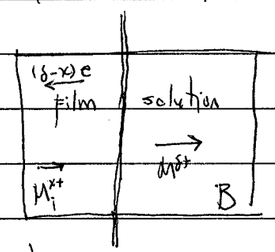
$\dot{\vec{x}}$ is the material velocity of the charged particles.
$[\rho \dot{\vec{x}}] = \frac{coul}{m^3} \cdot \frac{m}{s} = \frac{A}{m^2}$ $\rho \dot{\vec{x}} = \vec{i}$ is a current density.
At steady-state $\partial_t \rho = 0$, therefore $\int_B \nabla \cdot \vec{i}\, dV = 0$

$\nabla \cdot \vec{i} = 0$

Equivalently: $\int_{\partial B} \vec{i} \cdot \hat{n}\, ds = 0$

Reaction at the film/solution interface:

$M_i^{x+} \xrightarrow{K_4} M^{3+} + (\delta - x)e$



Evidently $F(\delta - x) K_4 a_{M_i^{x+}} + F x K_4 a_{M_i^{x+}} = F \delta K_4 a_{M_i^{3+}}$

$\int_{\partial B} \vec{i} \cdot \hat{n}\, ds = 0$ holds for this reaction.

$i_4 = F \delta K_4 a_{M_i^{3+}}$

Analogously

$V_O^{2\cdot} + H_2O \xrightarrow{K_5} O_O + 2H^+$

film	solution
$V_O^{2\cdot}$ →	$2H^+$ →

$2F K_5 a_{V_O^{2\cdot}} a_{H_2O} = i_5$

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$MO_{x_2} + xH^+ \xrightarrow{K_6} M^{\delta+} + \frac{x}{2} H_2O + (\delta - x)e$

Film	Solution
$(\delta-x)e \leftarrow$	$M^{\delta+} \rightarrow$
	$\leftarrow xH^+$

$I_6 = F(\delta - x) K_6 a_{H^+}^p$

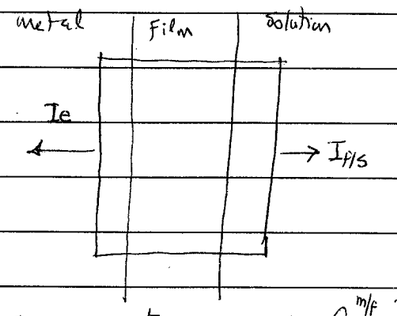
$M_M \xrightarrow{K_7} M^{\delta+}_{(aq)} + V_M^{x-} + (\delta - x)e$

Film	Solution
$\leftarrow V_M^{x-}$	$M^{\delta+}_{(aq)}$
$\leftarrow (\delta-x)e$	$\rightarrow$

$I_7 = F\delta K_7$

$I_{f/s} = I_4 + I_5 + I_6 + I_7 = F\left[\delta K_4 a_{M_i^{x+}} + 2K_5 a_{V_O^{2\cdot}} a_W + (\delta - x) K_6 a_{H^+}^p + \delta K_7\right]\theta$

(θ: coverage factor)



Assuming that no current flows through the lower and upper face

$I_{f/s} = I_e$

$I_e = F\left[xK_1 + xK_2 a_{V_m^{x-}}^{m/f}\right] = Fx\left[K_1 + K_2 a_{V_M^{x-}}^{m/e}\right]$

$J_{V_m}^{m/f} = -K_1 - K_2 a_{V_m^{x-}} + nK_3 a_{V_m}^n$

$J_{V_m^{x-}}^{m/f} = -K_2 a_{V_m^{x-}} + K_3 a_{V_m}^n$

$J_{V_O^{2\cdot}}^{m/f} = \frac{x}{2} a_{V_m}^n K_3$

$J_{M_i^{x+}}^{m/f} = K_1$

OPR 2/22/99

$J_{V_m^{x-}}^{f/s} = \cancel{K_4 a_{M_i^{x+}}^{f/s}} - K_7\theta$

$J_{V_O^{2\cdot}}^{f/s} = a_W a_{V_O^{2\cdot}} K_5 \theta$

$J_{M_i^{x+}}^{f/s} = K_4 a_{M_i^{x+}}^{f/s} \theta$

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Let's write down the reactions to have them handy

(1) $M \xrightarrow{K_1} M_i^{x+} + V_m + xe^-$

(2) $M + V_M^{x-} \xrightarrow{K_2} M_M + V_m + xe^-$

(3) $nV_m \xrightarrow{K_3} \frac{x}{2} V_O^{2\cdot} + V_M^{x-}$

(4) $M_i^{x+} \xrightarrow{K_4} M^{\delta+}(aq) + (\delta - x)e^-$

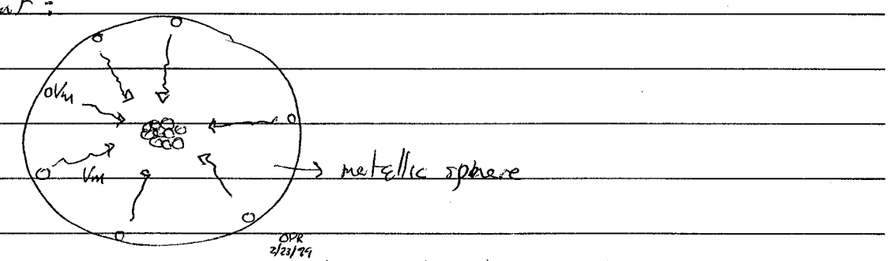
(5) $V_O^{2\cdot} + H_2O \xrightarrow{K_5} O_O + 2H^+$

(6) $MO_{x_2} + xH^+ \xrightarrow{K_6} M^{\delta+} + \frac{x}{2} H_2O + (\delta - x)e^-$

(7) $M_M \xrightarrow{K_7} M^{\delta+}(aq) + V_M^{x-} + (\delta - x)e$

According to the PDM, V_m are created continuously at the metal film interface. The PDM argues that accumulation of these vacancies leads to film detachment and pit initiation. I agree with that idea, but do not agree with the notion that the vacancies just "disapear" when steady-state is achieved.

Experiment:



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If the PDM is right, then it predicts the creation of a void in the geometrical center of the sphere, when the metal dissolves under steady-state conditions. Such void may be easily observed under the microscope. I will talk with Darrell about this.

If these voids indeed exist and grow with time, then the features and properties of the dissolving metal change with time. A metal that produces such voids is not reliable for a long term (10 000 years) applications.

2/23/99 QQ

I believe that a more appropriate description is to request that no voids are created at the metal/film interface. Therefore $J_{V_m}^{m/f} = 0$, and then $k_1 + k_2 a_{V_M}^{m/f\,x-} = n k_3 a_{V_m}^{n}$

a_{V_m} is very likely a constant of the material, that may depend on the temperature and the fabrication process.

Assume that $\phi_{m/f}$ is the potential drop at the metal/film interface, and that the rate constants follow a Tafel dependence on the local potential drop. Thus

$$k_i = k_i^{\circ}\, e^{z_i \frac{F}{RT} \alpha_i \phi_{M/f}}$$

$$a_{V_M}^{m/f\,x-} = \frac{n k_3 a_{V_m}^{n} - k_1}{k_2} \qquad \text{Necessarily } n k_3 a_{V_m}^{n} > k_1$$

$$J_{V_M}^{m/f\,x-} = -k_2 a_{V_m}^{x-} + \tfrac{1}{n} k_1 + \tfrac{1}{n} k_2 a_{V_m}^{m/f\,x-} = \left(\tfrac{1}{n} - 1\right) k_2 a_{V_m}^{m/f\,x-} + \tfrac{1}{n} k_1$$

I expect $J_{V_m}^{m/f\,x-} \le 0$

$$J_{V_m}^{m/f\,x-} = -k_2 a_{V_m}^{x-} + a_{V_m}^{n} k_3 \le 0 \iff a_{V_m}^{n} k_3 \le k_2 a_{V_m}^{x-}$$

$$\frac{k_1}{n} < a_{V_m}^{n} k_3 \le k_2 a_{V_m}^{x-} = n k_3 a_{V_m}^{n} - k_1$$

$$a_{V_m}^{n} k_3 \le n k_3 a_{V_m}^{n} - k_1 \iff (n-1) k_3 a_{V_m}^{n} \ge k_1$$

If $n = 1$, necessarily $k_1 = 0$, which means that interstitial conduction does not happen.

NECESSARILY $n \ge 1$.

The creation of $\frac{x}{2} V_O^{2\cdot}$ and V_M^{x-} vacancies requires of more than (at least) one V_m vacancy. This is a necessary condition.

An implicit assumption by Macdonald in the PDM is that $n = 1$.

$$\frac{k_1}{n} < n k_3 a_{V_m}^{n} - k_1 = k_2 a_{V_M}^{x-}$$

$$k_1 < n k_2 a_{V_M}^{x-}$$

Assume that $n > 1$, but $n \approx 1$, then $k_1 < n k_2 a_{V_M}^{x-}$ which means that most of the charge transport is due to the motion of V_M^{x-}, which is obvious since we would expect $k_1 \approx 0$.

$$J_{V_m}^{m/f\,x-} = \left(\tfrac{1}{n} - 1\right) k_2 a_{V_M}^{m/f\,x-} + \tfrac{1}{n} k_1 \qquad J_{V_M}^{f/s\,x-} = -k_7 \theta$$

$$J_{V_O^{2\cdot}}^{m/f} = \frac{x}{2} a_{V_m}^{n} k_3 = \frac{x}{2n}\left(k_1 + k_2 a_{V_M}^{m/f\,x-}\right) \qquad J_{V_O^{2\cdot}}^{f/s} = a_W a_{V_O^{2\cdot}}^{f/s} k_5 \theta$$

$$J_{M_i^{x+}}^{m/f} = k_1 \qquad J_{M_i^{x+}}^{f/s} = k_4 a_{M_i^{x+}}^{f/s} \theta$$

$$\dot{X}_{m/f} = -\Omega k_3 a_{V_m}^{n} = -\Omega \tfrac{1}{n}\left(k_1 + k_2 a_{V_M}^{m/f\,x-}\right) \qquad \dot{X}_{f/s} = -\Omega k_6 a_{H^+}^{p} \theta$$

$[\Omega] = m^3/mol$ = volume per unit of mole of M ions in the $MO_{x/2}$ oxide.

In order for steady-state to hold:

(1) $\left(\tfrac{1}{n} - 1\right) k_2 a_{V_M}^{m/f\,x-} + \tfrac{1}{n} k_1 = -k_7 \theta$ or $\left(1 - \tfrac{1}{n}\right) k_2 a_{V_M}^{m/f\,x-} - \tfrac{1}{n} k_1 = k_7 \theta$

(2) $\frac{x}{2n}\left(k_1 + k_2 a_{V_M}^{m/f\,x-}\right) = a_W a_{V_O^{2\cdot}}^{f/s} k_5 \theta$

(3) $k_1 = k_4 a_{M_i^{x+}}^{f/s} \theta$

(4) $\tfrac{1}{n}\left(k_1 + k_2 a_{V_M}^{m/f\,x-}\right) = k_6 a_{H^+}^{p} \theta = \frac{2}{x} a_W a_{V_O^{2\cdot}}^{f/s} k_5 \theta$

$$I_{f/s} = F\left[\delta k_4 a_{M_i^{x+}}^{f/s} + 2 k_5 a_{V_O^{2\cdot}}^{f/s} a_W + (\delta - x) k_6 a_{H^+}^{p} + \delta k_7\right]\theta$$

$$= F\left[\delta k_1 + \left[\tfrac{x}{n} k_1 + \tfrac{x}{n} k_2 a_{V_M}^{m/f\,x-}\right] + \left[(\delta - x)\tfrac{1}{n} k_1 + (\delta - x)\tfrac{1}{n} k_2 a_{V_M}^{m/f\,x-}\right] + \delta\left(1 - \tfrac{1}{n}\right) k_2 a_{V_M}^{m/f\,x-} - \tfrac{\delta}{n} k_1\right]$$

$$= F\left\{\left[\delta + \tfrac{x}{n} + \tfrac{\delta}{n} - \tfrac{x}{n} - \tfrac{\delta}{n}\right] k_1 + \left[\tfrac{x}{n} + \tfrac{\delta}{n} - \tfrac{x}{n} + \delta - \tfrac{\delta}{n}\right] k_2 a_{V_M}^{m/f\,x-}\right\}$$

$$= F\delta\left\{k_1 + k_2 a_{V_M}^{m/f\,x-}\right\}$$

On the other hand

$$I_e^{m/f} = Fx\left\{k_1 + k_2 a_{V_M}^{m/f\,x-}\right\}$$

Since $I_e^{m/f} = I_{f/s}$, necessarily $\delta = x$!!

Otherwise, steady-state cannot occur.

2/23/99

$$I_{f/s} = F\left[\chi K_4 a_{M_i^{x+}}^{f/s} + 2K_5 a_{V_O^{2\cdot}}^{f/s} a_W + \chi K_7\right]\theta$$

$$I_{f/s} = I_e^{m/f} = F\chi\left[K_1 + K_2 a_{V_m^{x-}}^{m/f}\right]$$

Assume that interstitial conduction does not occur, then $K_1 = 0 = K_4$

Since $\delta = \chi$, $K_6 = K_6^\circ$; i.e., the rate of dissolution of $MO_{x/2}$ is independent of the applied potential. In such a case

$$\frac{1}{n} K_2 a_{V_m^{x-}}^{m/f} = K_6^\circ a_{H^+}^p \theta = \frac{2}{\chi} a_W a_{V_O^{2\cdot}}^{f/s} K_5 \theta$$

$$I_{f/s} = F\chi n K_6^\circ a_{H^+}^p \theta$$

If $p = 0$ and θ = constant, then $I_{f/s}$ = constant!

a_{H^+} and θ can be potential dependent.

Observations:

1) $I_{f/s}$ = constant for the case $K_1 = 0$, regardless of the voltage dependence of the potential drop at the film/solution interface.

$$I_{f/s} = F\chi\left[K_1 + K_2 a_{V_m^{x-}}^{m/f}\right] = 2nF a_W K_5 a_{V_O^{2\cdot}}^{f/s} = \chi K_6^\circ n a_{H^+}^p \theta \quad \text{always!}$$

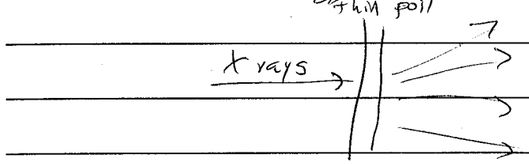
$$I_{f/s} = \chi K_6^\circ n a_{H^+}^p \theta \quad \text{always!}$$

This model predicts that the total current density depends only on the local pH and θ to define the potential dependence.

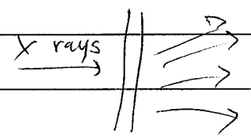
There is no freedom here. These ideas are too limited in what they can describe!!

I talked to Shridhar (Sridhar) about the idea of finding the voids, and he said that it would take too long for the voids to be formed. The dissolution rate of the metal is too low for appreciable accumulation of voids to happen.

He suggested another idea:



After exposure of the thin foil to the electrolyte



If accumulation of voids indeed occurs, then the DP2 must be different than DP1. If this is not the case, then nothing can be concluded.

2/24/99 OPR

I just realized that the Point Defect Model, as was originally published has another mistake. It is claimed that the reactions giving rise to the formation and dissolution of the film are

(1) $m + V_M^{x-} \xrightarrow{k_1} M_M + V_m + xe^-$ (3) $M_M \xrightarrow{k_3} M^{\delta+} + V_M^{x-} + (\delta-x)e^-$

(2) $m \xrightarrow{k_2} M_M + (\frac{x}{2})V_O^{2-} + xe^-$ (4) $V_O^{2-} + H_2O \xrightarrow{k_4} O_O + 2H^+$

(5) $MO_{x_2} + xH^+ \xrightarrow{k_5} M^{\delta+} + \frac{x}{2}H_2O + (\delta-x)e^-$

$I^{m/f} = F[x k_1 a_{V_M^{x-}} + x k_2]$

$I^{f/s} = F[\delta k_3 + 2k_4 a_w a_{V_O^{2-}} + (\delta-x) k_5 a_{H^+}^p]$

Because of steady-state requirements:

$k_1 a_{V_M^{x-}} = k_3$

$\frac{x}{2} k_2 = k_4 a_w a_{V_O^{2-}}$ $\quad k_2 = k_5 a_{H^+}^p$

$I^{f/s} = F[\delta k_1 a_{V_M^{x-}} + x k_2 + (\delta-x) k_2] = F\delta[k_1 a_{V_M^{x-}} + k_2]$

Since $I^{m/f} = I^{f/s}$ necessarily $\delta = x$

Consequently the oxidation state of dissolved species coincides always with the oxidation state of the metal in the oxide. If this is not the case, then the change in oxidation state happens only after the cation is in solution, and only after that.

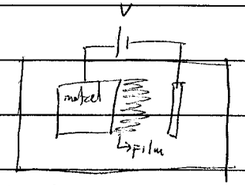
The PDM has two advantages over my model, it states a difference between V_O^{2-} and V_M^{x-} conduction, it helps to describe other behavior than constant current densities. The disadvantage is that it is not clear what happens to V_M.

All of the cases that Macdonald has analyzed $\delta = x$.

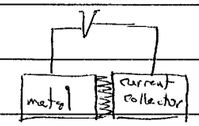
2/25/99 OPR

We may do the following experiment. Let grow an oxide at given conditions (applied voltage + environment conditions). Take the sample out of the solution and measure its capacitance. → That is not what we want. We want to have some C vs V mapping, so that we may infer the nature of the predominant defects. If we find this, then we can assert something about the nature of the film and how it changes with time.

Idea:



1st. step: grow film



2nd. step: measure capacitance as function of voltage.

If after the 2nd. step we find that the oxide is p-conductor, then the main lattice defect is V_M^{x-}. Conductivity is due to the motion of V_M^{x-}. If, on the other hand, the oxide turns out to be a n-conductor, then V_O^{2-} and M_i^{x+} are the majority carriers. If the last case holds, the PDM predicts that I vs V is a horizontal line; i.e., I (steady-state current density) is independent of the applied voltage.

OPR 2/25/99

The same experiment may be repeated for oxides grown ~~at~~ under different conditions.

I consider this way of measuring the capacitance to be more adequate. Spottky plots make sense, since $\frac{1}{C^2} \propto V$ only for an abrupt ($N_{ACC} >> N_{DON}$ or $N_{DON} >> N_{ACC}$, N = concentration) semiconductor junction. By taking the sample out of the solution, we simulate an abrupt junction. The only issue to determine is to find whether or not electronic (or hole) conduction occurs through the oxide film.

2/25/99 (QP)

Reference: G. T. Burstein and A. J. Davenport p.936-941
J. Electrochem. Soc. Vol. 136, No. 4, April 1989

The current-time relationship during anodic oxide film growth under high electric field.

A method is developed based on the analysis of current transients to compute parameters of the high-field model

Some equations in the paper:

Information potentially subject to copyright protection was redacted from this location. The redacted material is from the reference information listed at the top of this scientific notebook page.

Statement: If oxide growth is governed by a logarithmic growth law, then $\frac{\partial \log i}{\partial \log t} = -1$, exactly.

If not, $\frac{\partial \log i}{\partial \log t} \neq -1$, but close to -1.

Eq. [11]: $-\frac{X_1}{X} = \ln\left(\frac{X_1 ut}{X_1^2}\right) \Rightarrow X = -\frac{X_1}{\ln\left(\frac{X_1 ut}{X_1^2}\right)}$ $X^2 = \frac{X_1^2}{\ln^2\left(\frac{X_1 ut}{X_1^2}\right)}$

$\frac{X_1}{X^2}\frac{dx}{dt} = \frac{X_1^2}{X_1 ut}\frac{X_1 u}{X_1^2} = \frac{1}{t} \Rightarrow \frac{dx}{dt} = \frac{X^2}{X_1 t} = \frac{Mi}{2F\rho}$

$i = \frac{2F\rho}{M}\frac{dx}{dt} = \frac{2F\rho}{M}\frac{X^2}{X_1 t}$ $\frac{ui}{2F\rho} = \frac{X^2}{X_1 t} = \frac{1}{X_1 t}\frac{X_1^2}{\ln^2\left(\frac{X_1 ut}{X_1^2}\right)}$

$i = \frac{2F\rho}{M X_1 t}\frac{X_1^2}{\ln^2\left(\frac{X_1 ut}{X_1^2}\right)} = \frac{2F\rho X_1}{M t}\frac{1}{\ln^2\left(\frac{X_1 ut}{X_1^2}\right)}$

$\ln i = \ln\left(\frac{2F\rho X_1}{M}\right) - 2\ln\left[\ln\left(\frac{X_1 ut}{X_1^2}\right)\right] - \ln t \rightarrow$ Equation [16]

It means that $\frac{\partial \ln i}{\partial \ln t} = f(t)$

Cont. p 37

2/26/99 (QP)

Equation [22] states that

$$-\frac{\partial \log i}{\partial \log t} = \frac{\ln(i/\bar{A})}{2 + \ln(i/\bar{A})}$$

From a least-squares curve fitting, $\bar{A}$ can be computed.

Eq. [24]

Information potentially subject to copyright protection was redacted from this location. The redacted material is from the reference listed at the top of the previous page of this scientific notebook.

The authors claim that if it = constant, then a plot of $\log i$ vs $(it)^{-1/2}$ is a vertical line parallel to the $\log i$ axis. This statement is not quite correct. $i^2 \geq \xi_1 \Rightarrow i \geq \sqrt{\xi_1}$. I do not see why $it = \xi_1$ implies a vertical, parallel to $\log i$ axis, line.

Claim by the authors:

$i - t = \text{constant} = \xi_0 \Rightarrow -\frac{\partial \log i}{\partial \log t} = 1$

This is obviously wrong: $i = \xi_0 + t \Rightarrow \log i = \log(\xi_0 + t)$

$\frac{\partial \log i}{\partial \log t} = \frac{1}{\xi_0 + t}\frac{\partial t}{\partial \log t}$ $\frac{\partial \log t}{\partial t} = \frac{1}{t}$

$= \frac{1}{\xi_0 + t} t = \frac{t}{\xi_0 + t}$ which obviously is not -1.

In all of the figures reported in the paper, what is plotted is $\log i$ vs $(it)^{-1/2}$, which has nothing to do with Equation [24]

Another problem that I see is the scale. What is the scale

2/26/99 [illegible]

to be used?

Some problems observed.

$$\frac{dX}{dt} = u \exp\left(\frac{X_1}{X}\right)$$

Let us say $\frac{dX}{dt} > 0$, then X is an increasing function of t. In the limit $X \to \infty$, $\frac{dX}{dt} = u$, which indicates that the film thickness continues growing forever, without achieving a steady-state. Yet we know that steady-state is achieved.

When $t \to \infty$, $i \to 0$, which is consistent with the notion of the film always growing.

Eq. [21]

Information potentially subject to copyright protection was redacted from this location. The redacted material is from the reference listed at the top of page 36 ot this scientific notebook.

Equation [24] in the paper is incorrect.

From Eq. [21], if $t \to \infty$, $i \to 0$ very fast.

A possible solution to this problem may be to substitute i by $i - i_{ss}$ where $i_{ss} = \lim_{t \to \infty} i$

3/2/99 [illegible]

I used the ideas by Burstein and Davenport and tried to determine if a logarithmic growth law applies to the C22 alloy.

I used data (current density vs time) gathered by D Dunn.

The data is stored in C:/osvaldo/C-22/

I do not know details such as electrolyte composition, temperature and so forth. D. Dunn has such information. The data files are C22pc3.xls, C22pc4.xls, C22pc6.xls and C22pc7.xls. The names of these files were assigned by D. Dunn.

I found that the current density as function of time can be described approximately by

$$I(t) = I_{ss} + a_1 e^{-a_2 t} + \frac{a_3}{t}$$

I_{ss} is the steady-state current density. The parameters a_1, a_2 and a_3 were found via a least-squares technique available in Matlab. The values are listed

	I_{ss}	a_1	a_2	a_3
c22pc3.xls	1.75×10^{-7}	6.85×10^{-7}	9.86×10^{-4}	1.4×10^{-4}
c22pc4.xls	2.745×10^{-7}	7.21×10^{-17}	1.9775	3.33×10^{-4}
c22pc6.xls	5.038×10^{-9}	3.1176×10^{-13}	0.0388	2.0723×10^{-4}
c22pc7.xls	6.231×10^{-8}	8.15×10^{-12}	0.1507	0.0134

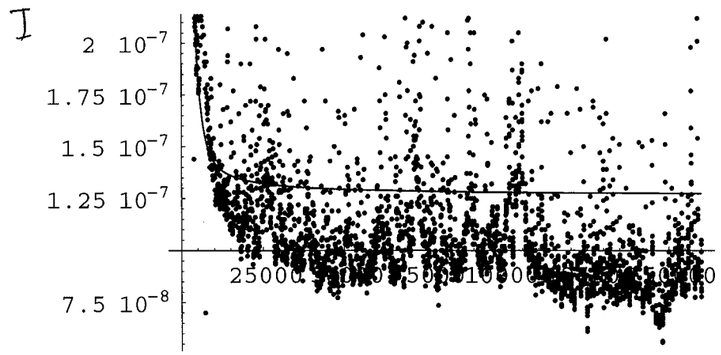
I ploted

Information potentially subject to copyright protection was redacted from this location. The redacted material is from the reference listed below.

This last equation is suggested by Lei Zhang et. al. in L. Zhang, D.D. Macdonald, E. Sikora and J. Sikora, J. Electrochem. Soc., Vol. 145, No. 3, March 1998.

The plots are attached next.

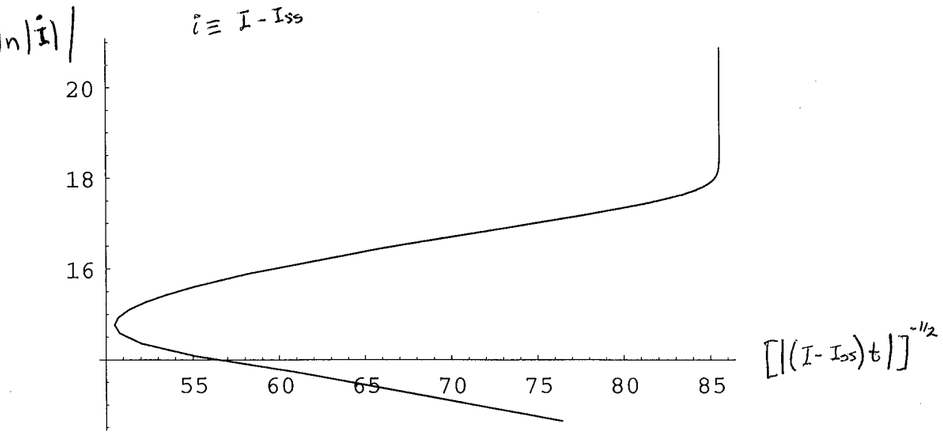
3/2/99 OPJ

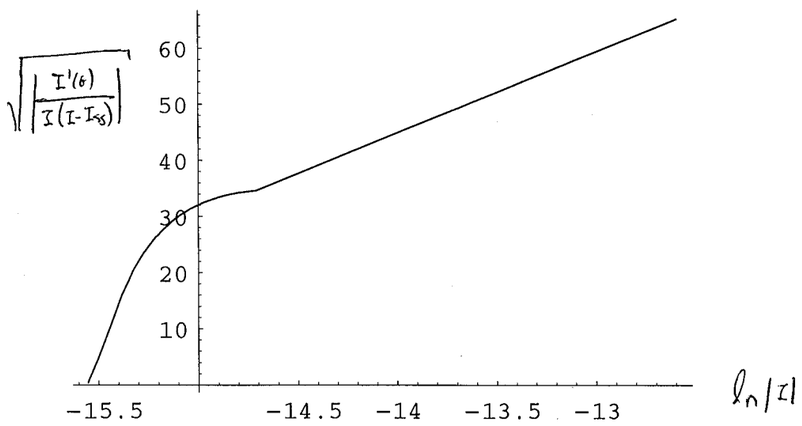


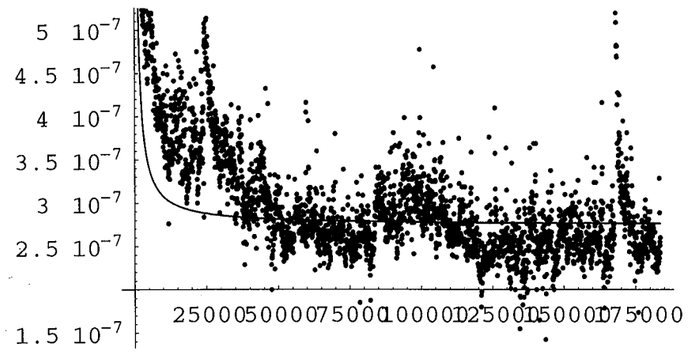
$V = 0.4\ V_{SCE}$

c22pc3.xls

$i \equiv I - I_{ss}$

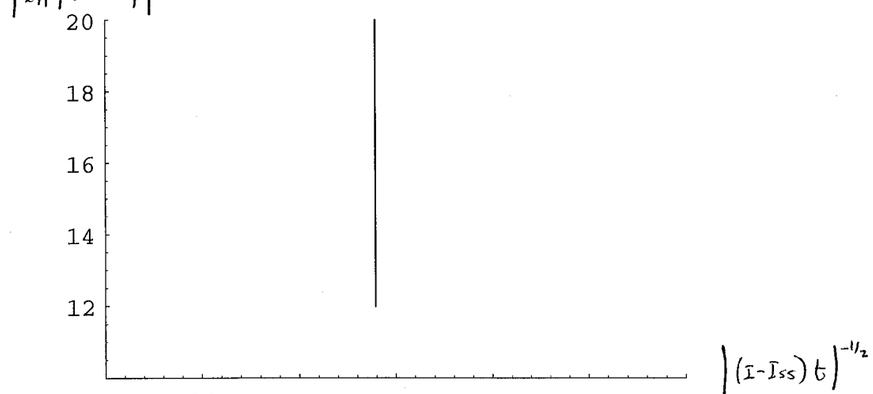


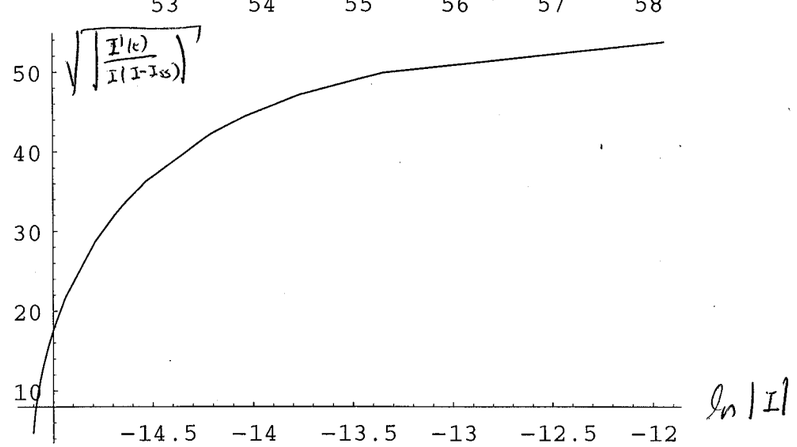




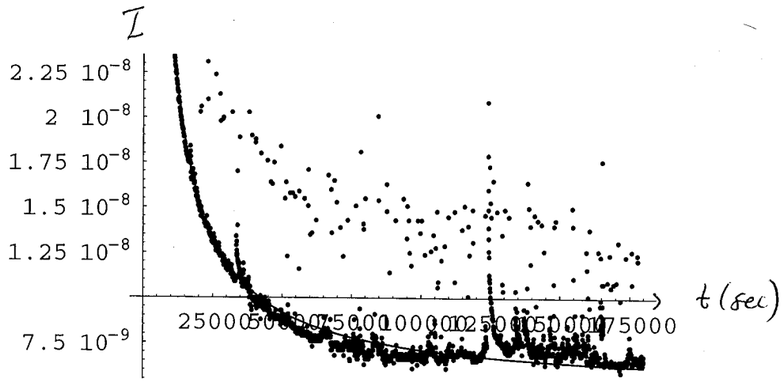
$V = 0.6\ V_{SCE}$

c22pc4.xls



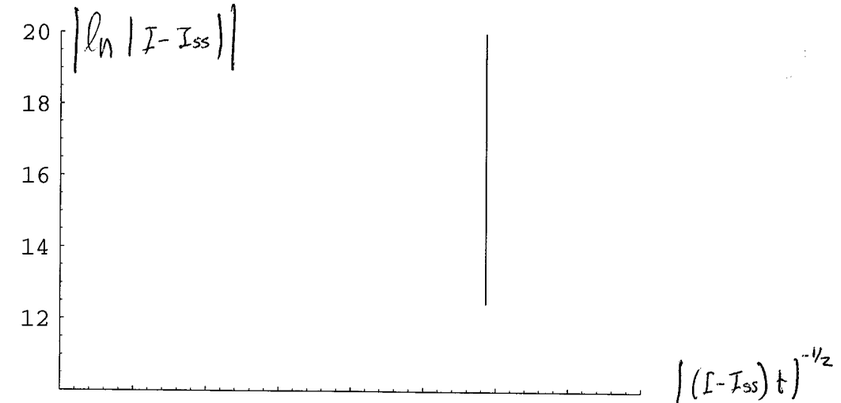


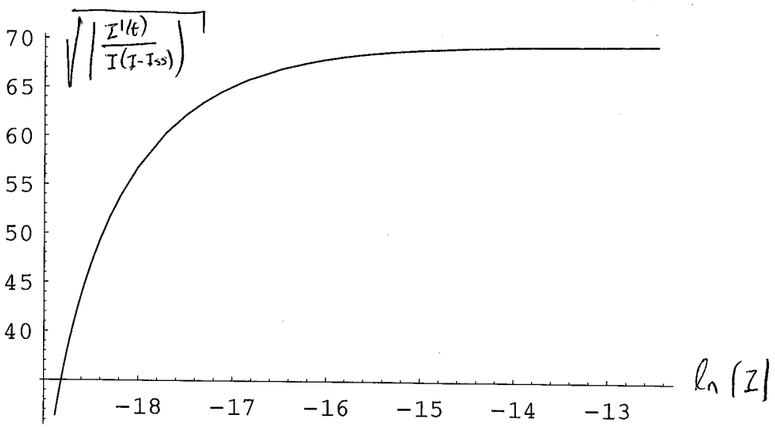
3/2/99

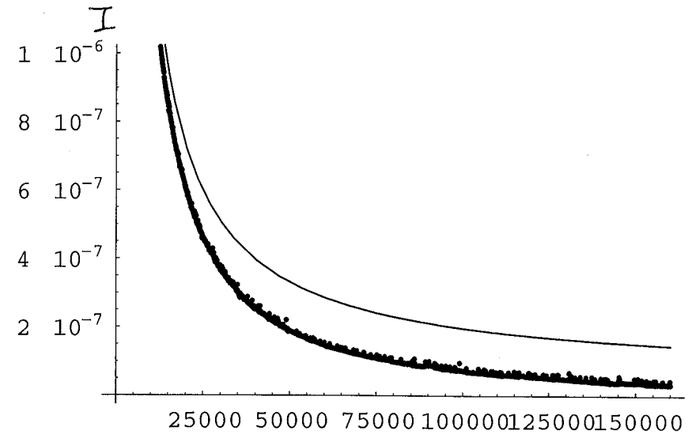


$V = 0.2\ V_{SCE}$

c22pc6.xls

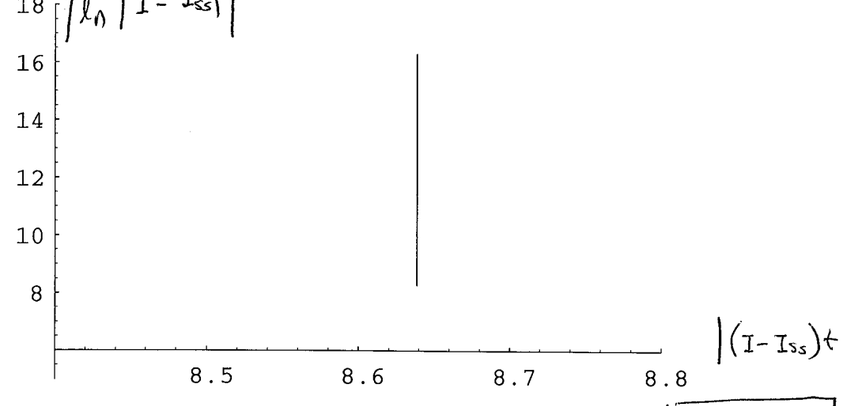


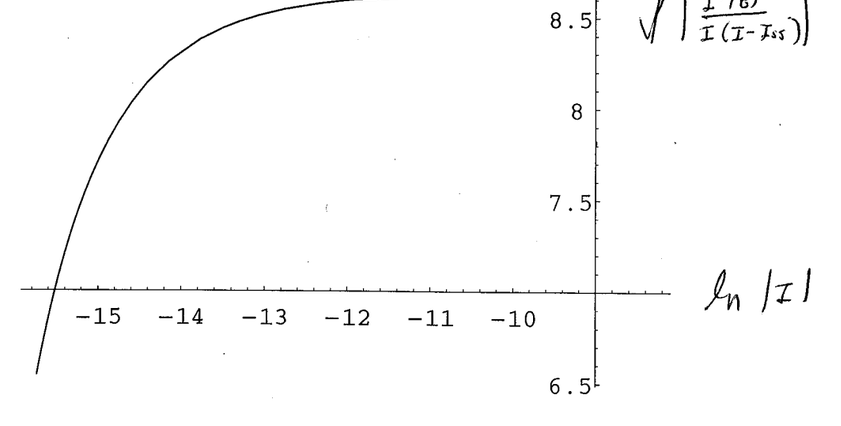




$V = 0.4\ V_{SCE}$

c22pc7.xls





$I(t) \simeq I_{ss} + a_1 e^{-a_2 t} + \frac{a_3}{t}$ reasonable description

$\ln|I - I_{ss}| = \ln|a_1 e^{-a_2 t} + \frac{a_3}{t}|$

$|(I - I_{ss})t| = |a_1 t e^{-a_2 t} + a_3|$

Evidently $|\ln(I - I_{ss})| \xrightarrow{t \to 0} +\infty$

$|(I - I_{ss})t| \xrightarrow{t \to 0} a_3$

A plot of $|\ln(I - I_{ss})|$ vs $|(I - I_{ss})t|^{-1/2}$ must be a vertical straight line, for t large enough. The vertical line is due to the function that I chose to describe $I(t)$. It would be interesting to find alternative descriptions (functions) of $I(t)$ not producing this vertical straight line.

Assuming that the vertical straight line is real, Burstein and Davenport argue that $(I - I_{ss})t$ = constant implies a direct logarithm growth rate; i.e., ~~$\ln|I - I_{ss}| =$~~ $I = A \ln t + B$, A,B constants.

On the other hand, L. Zhang et al. argue that $\sqrt{\left|\frac{I'(t)}{I(I - I_{ss})}\right|}$ vs $\ln I$ is a constant; i.e. $\sqrt{\left|\frac{I'(t)}{I(I - I_{ss})}\right|}$ is not function of $\ln I$. If that is the case, then conduction happens via the transport of oxygen vacancies. We can see that $\sqrt{\left|\frac{I'(t)}{I(I - I_{ss})}\right|}$ is nearly independent of the $\ln I$ in certain range, at least for the plots in pages 42 and 43.

$I'(t) = -a_1 a_2 e^{-a_2 t} - \frac{a_3}{t^2}$

$\left|\frac{I'(t)}{I(I - I_{ss})}\right| = \frac{a_1 a_2 e^{-a_2 t} + \frac{a_3}{t^2}}{\left(I_{ss} + a_1 e^{-a_2 t} + \frac{a_3}{t}\right)\left(a_1 e^{-a_2 t} + \frac{a_3}{t}\right)}$

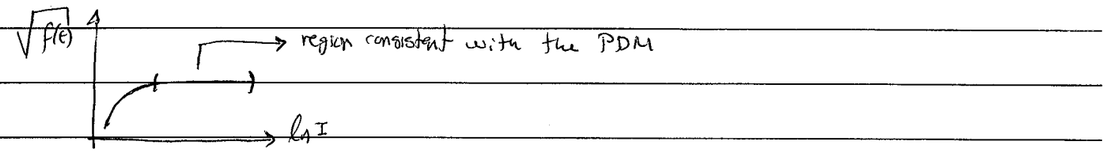
$t \to \infty \longrightarrow 0$

$t \to 0 \longrightarrow \frac{1}{a_3}$

Let $f(t) = \frac{I'(t)}{I(I - I_{ss})}$

$f(t) \xrightarrow{t \to \infty} 0$ is a mathematical limit, it is due to the proposed form for $I(t)$

$f(t) \xrightarrow{t \to 0} \frac{1}{a_3}$, depends on a_3, which depends on the curvature of $I(t)$ vs t plots. The curvature is well defined at $t \to 0$, and ill defined at $t \to \infty$.



I do believe that we indeed have some evidence that conduction is occurring via the transport of $V_O^{2\cdot}$ vacancies.

The oxide must be an n-type semiconductor.

I will try to find an alternative function $I(t)$ to discard the possibility of our conclusions to be due to the mathematical form assigned to $I(t)$.

Apparently $I(t) * t$ = constant. I will try to plot $\ln I$ vs $\ln t$ to see if a linear relationship is appropriate.

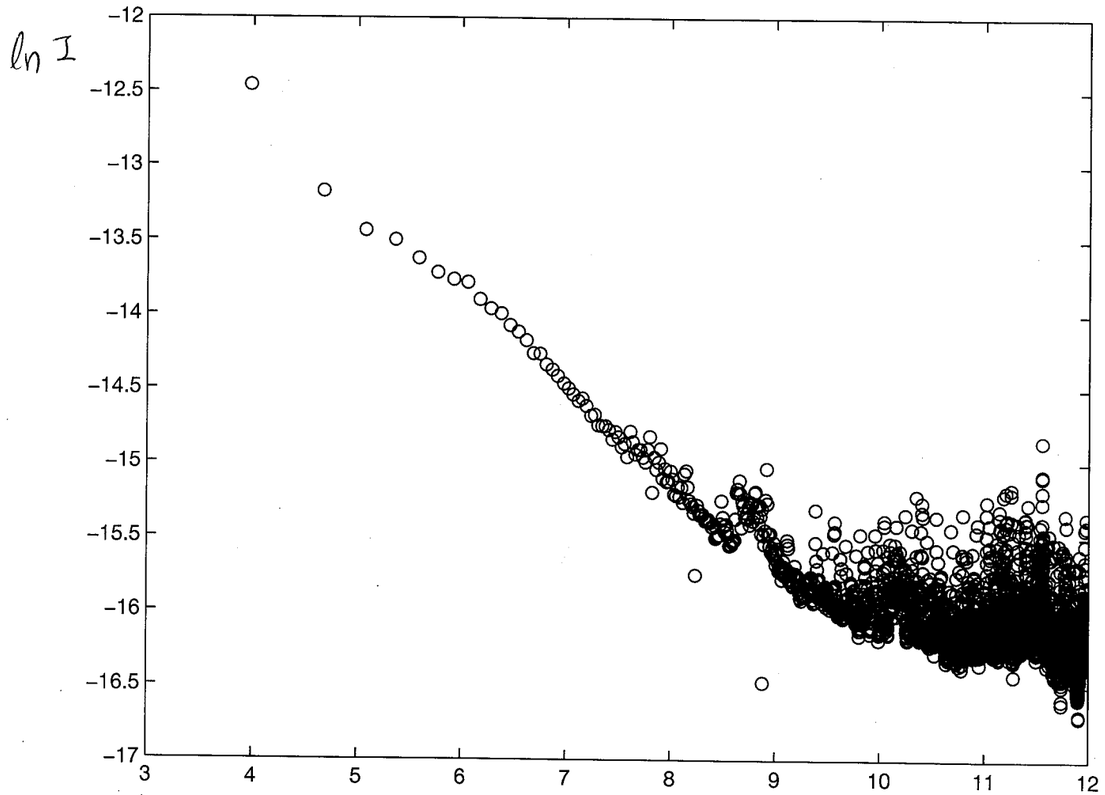
I found that $\ln I = a_0 \ln^3 t + a_1 \ln^2 t + a_2 \ln t + a_3$ describes quite well the data, except for data 4 (x22 pc7.xls). In that case, a polynomial in $\ln t$ of degree 7 works better.

$\frac{1}{I} I'(t) = \left(3 a_0 \ln^2 t + 2 a_1 \ln t + a_2\right)\frac{1}{t}$

$I'(t) = \left(a_0 \ln^3 t + a_1 \ln^2 t + a_2 \ln t + a_3\right)\left(3 a_0 \ln^2 t + 2 a_1 \ln t + a_2\right)\frac{1}{t}$

3/2/99 OPR

C22PC3.xls



OPR

Instruction for printing from vulcan:

** From matlab >> print -dps filename -f<figure number>

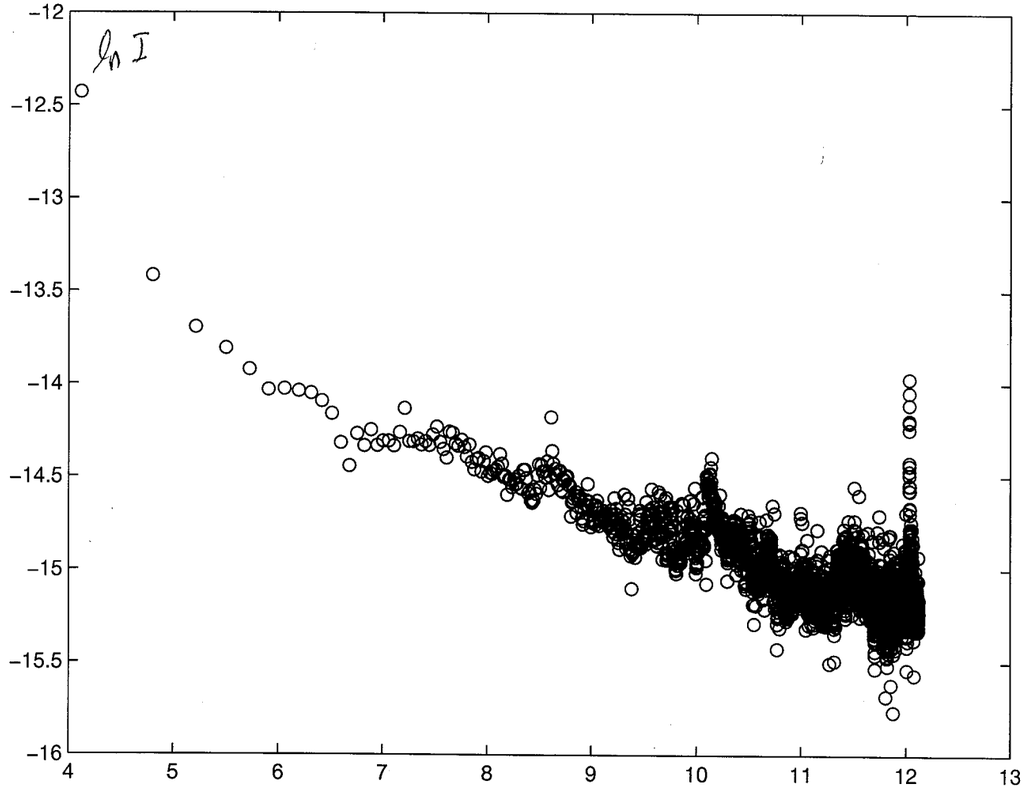
** From terminal: vulcan% lpr -P ps1725 ~/c-22/filename.ps

(capital P)

The objective of plots in ~~figures~~ 3/2/99 OPR pages 46-49 is to show that ln I vs ln t is reasonably smooth, and that a polynomial can be fitted.

3/2/99 OPR

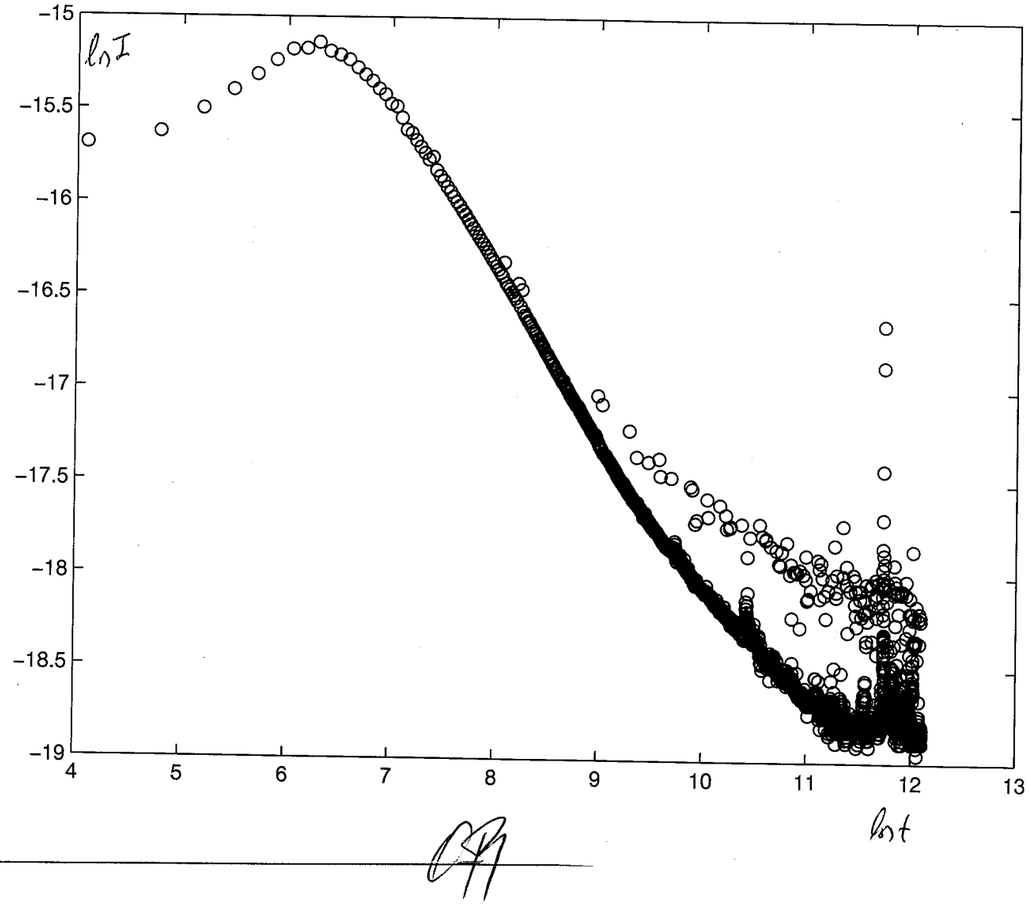
C22PC4.xls



OPR

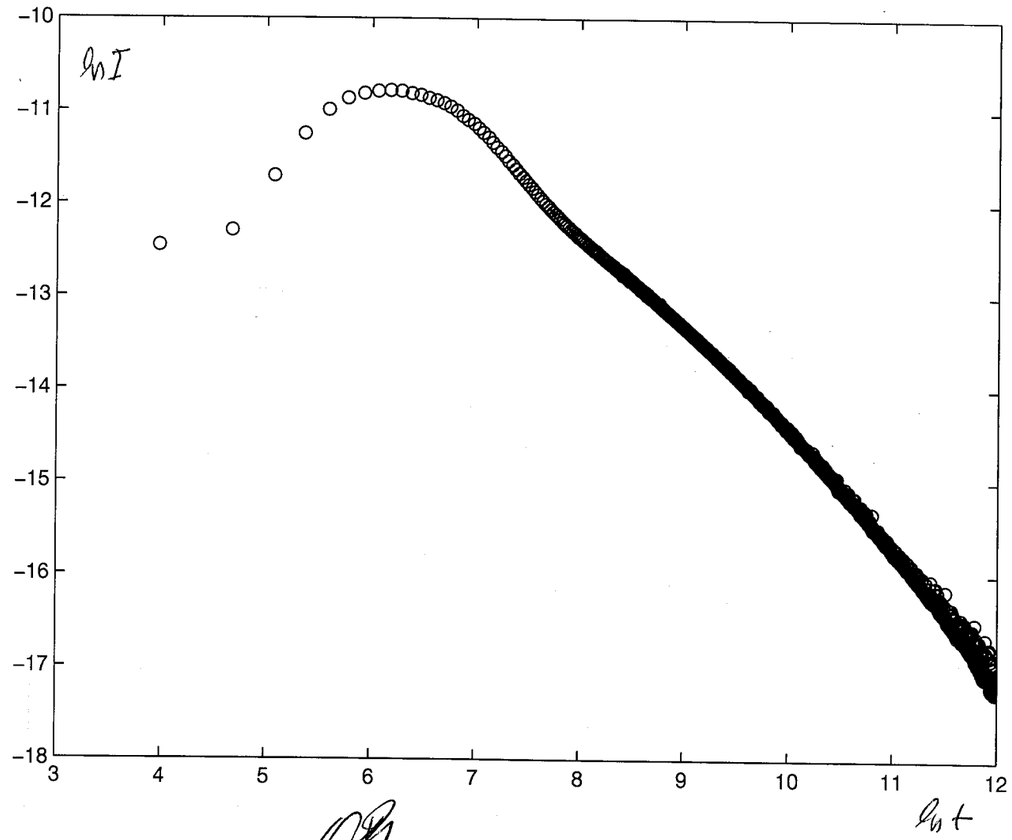
3/2/99

c22pc6.xls



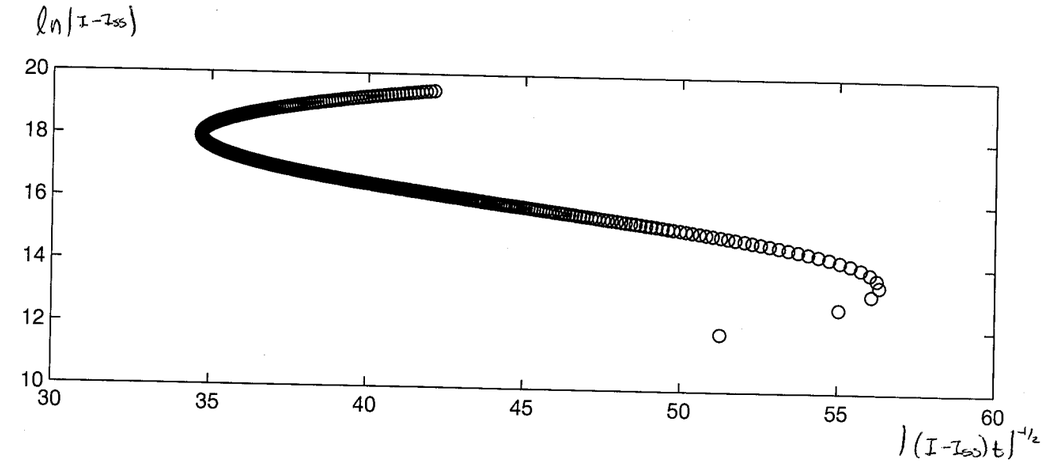
3/2/99

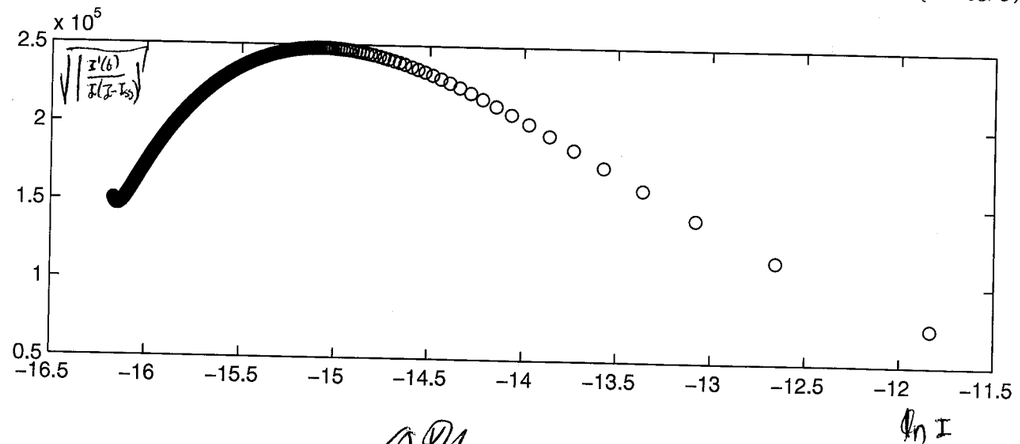
c22pc7.xls



3/2/99 OPY

C22pC3.xls

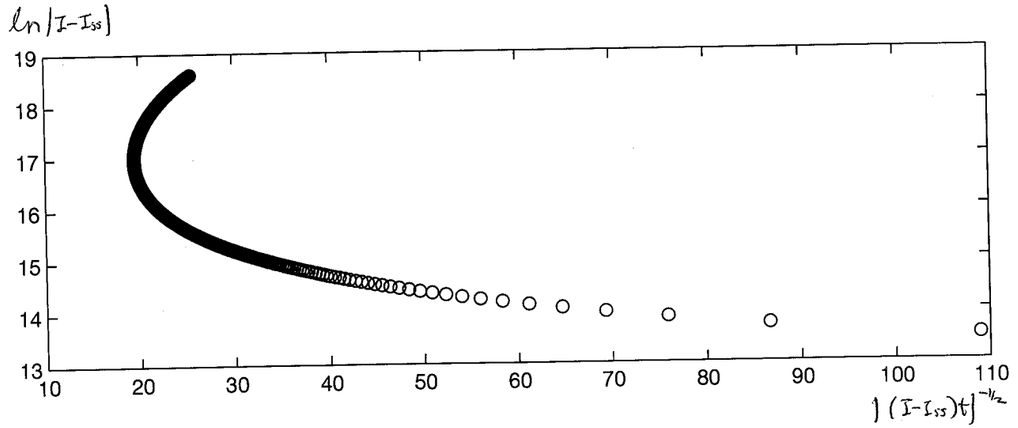


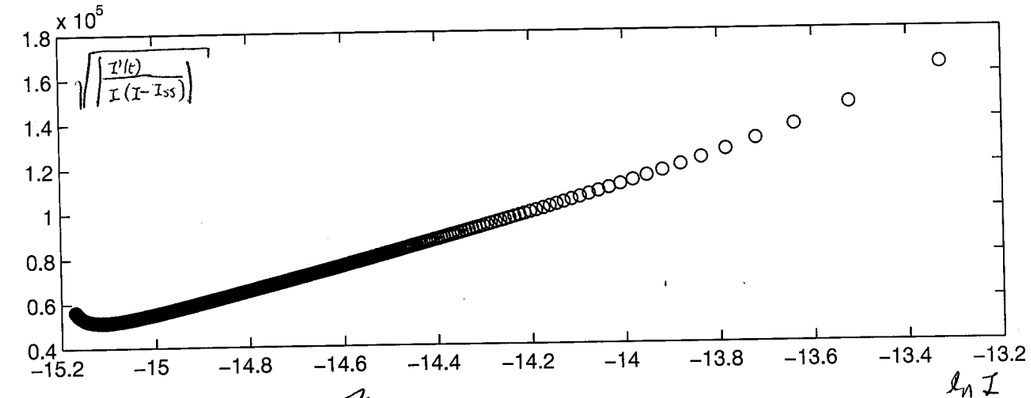


OPY

3/2/99 OPY

C22pC4.xls

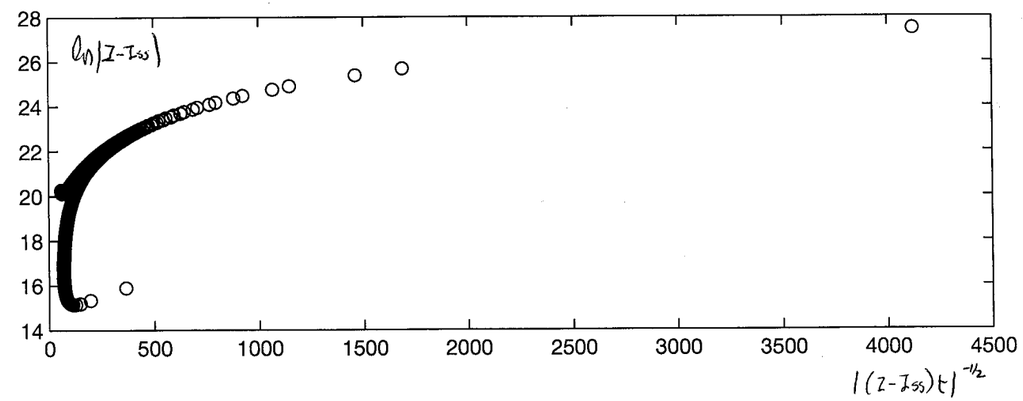


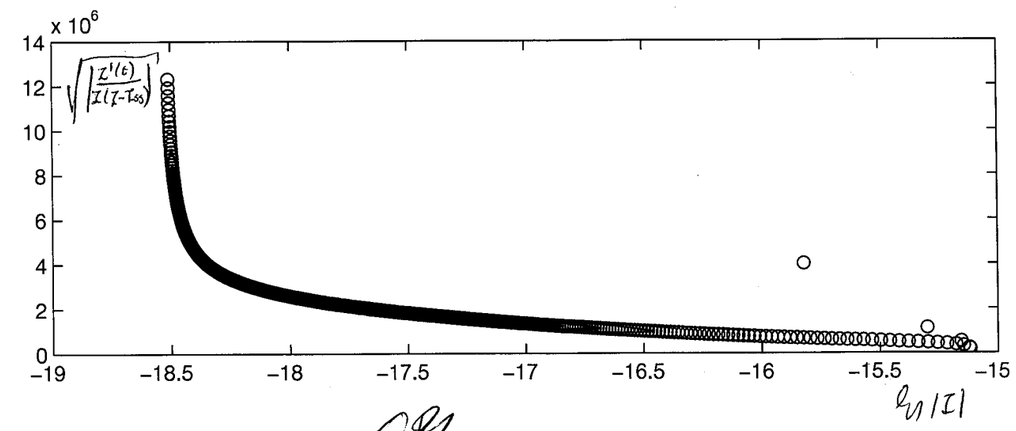


OPY

3/2/99 OFL

C22 PC6.xls (a)

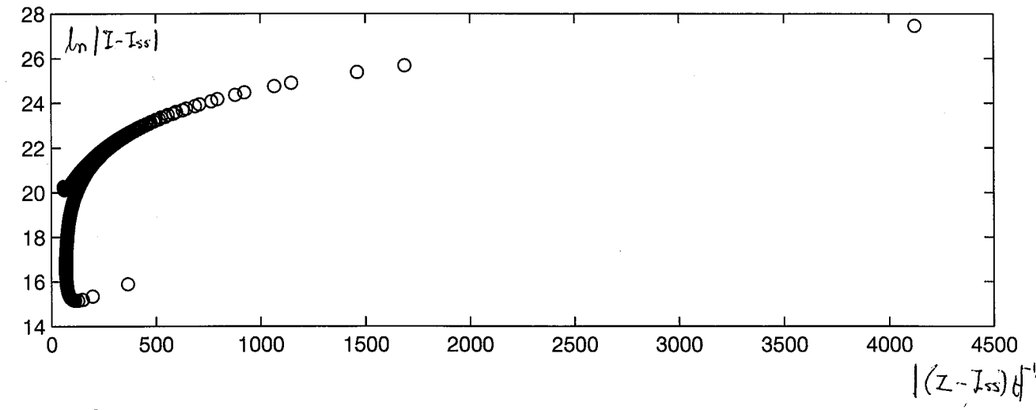


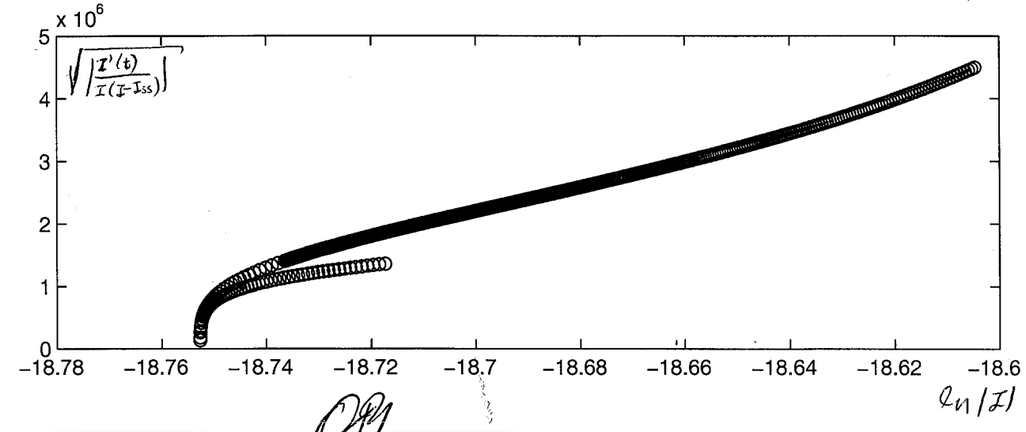


OFL

3/2/99 OFL

c22pc6.xls (b)

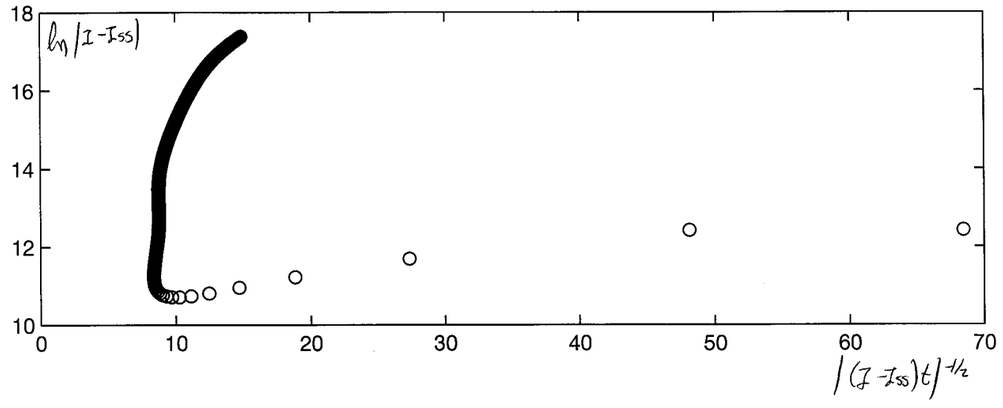


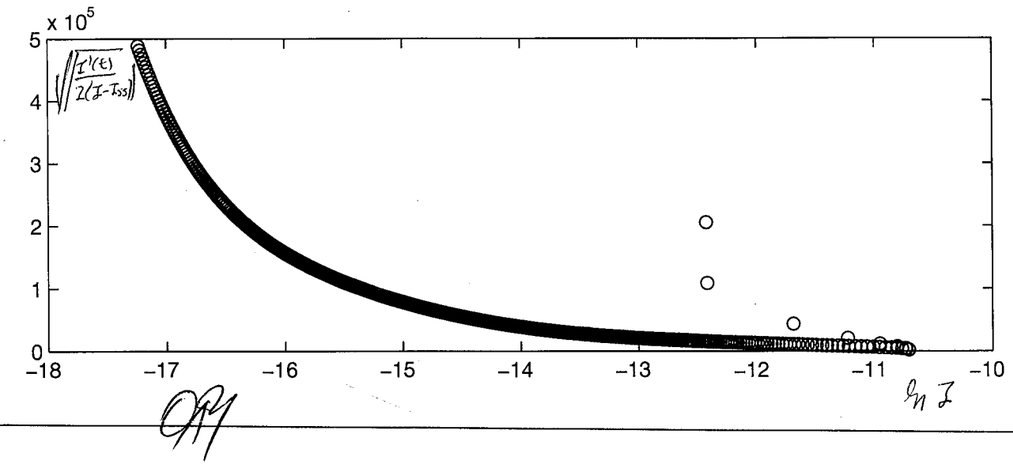


OFL

3/2/99 OFA

c22pc7.xls





OFA

3/3/99 OFA

The plots in pages 50-54 were generated fitting a polynomial to the $\ln I$ vs $\ln t$ data. Therefore, $\ln I$ is reasonably described by

$$\ln I = a_0 \ln^p t + a_1 \ln^{p-1} t + a_2 \ln^{p-2} t + \cdots + a_{p-1} \ln t + a_p$$

$p=3$ worked for data c22pc3.xls, c22pc4.xls and c22pc6.xls

$p=7$ worked for data c22pc7.xls

OFA

	a_0	a_1	a_2	a_3
c22pc3.xls	-3.9978107837789654e-03	1.6989910083959067e-01	-2.4246178362795598e+00	-4.6315293418379566e+00
c22pc4.xls	1.5766750973061246e-03	-2.6356026465490547e-02	-1.3898559074248251e-01	-1.2421493287204564e+01
c22pc6.xls	3.0583147230683911e-02	-7.9427317383292728e-01	5.9955681600081903e+00	-2.9154264672764242e+01
c22pc7.xls	-4.0634751627730491e-04	2.4437793559767725e-02	-6.1909297700173460e-01	8.5433075623527994e+00
	-6.9147196605128158e+01	3.2689959758211336e+02	-8.3187396865271353e+02	8.6345419683110367e+02
	a_4	a_5	a_6	a_7

The values of the coefficients a_0, a_1, a_2, a_3 are given above. In the case of c22pc7.xls, a_4, a_5, a_6 and a_7 have been also included.

In pages 50-54 we observe that $\sqrt{\left|\frac{I'(t)}{I(I-I_{ss})}\right|}$ vs $\ln I$ is not linear. In the paper by Lei Zhang et. al. it is included that $\sqrt{\left|\frac{I'(t)}{I(I-I_{ss})}\right|}$ is either linear on $\ln I$ or independant of $\ln I$. Here we observe that none of these possibilities hold.

In the paper by Burstein and Davenport it is argued that $\ln|I-I_{ss}|$ depends linearly on $|(I-I_{ss})t|^{-1/2}$. Here we observe that this is not the case.

The third relevant observation is that the way $I(t)$ is defined has a strong impact on the shape of $\ln|I(t)-I_{ss}|$ vs $|(I(t)-I_{ss})t|^{-1/2}$, and $\sqrt{\left|\frac{I'(t)}{I(I-I_{ss})}\right|}$ vs $\ln I(t)$. Note that the plots in pages 40-43 are very dissimilar to the plots in pages 50-54, even though they "represent" plots of the "same" data. The way the data is smoothened has a strong impact on the representation

of data ~~3/3/99~~ suggested by Burstein and Davenport, and Zhang and Macdonald. One wonders if these authors added some "make up" to their data, so that they produced the wanted results.

Is it worth collecting more data?

Note the following, the ratio $\frac{I'(t)}{I-I_{ss}}$ is ill defined in the limit when $t \to \infty$. $I(t) \xrightarrow[t\to\infty]{} I_{ss}$ and $I'(t) \xrightarrow[t\to\infty]{} 0$

$$\frac{I'(t)}{I-I_{ss}} \xrightarrow[t\to\infty]{} \frac{I''(t)}{I'(t)} \sim \text{not well defined.}$$

My claim is that $\frac{I'(t)}{I-I_{ss}}$ can be anything in the limit $t \to \infty$

$I'(t)/(I-I_{ss})$ only makes sense at $t << \infty$

The criterion by Macdonald and Chao may be used for $I \neq I_{ss}$, or $I >> I_{ss}$.

The criterion is quite bad since it is too sensitive of the way the data is smoothened.

Note that $I(t) \xrightarrow[t\to\infty]{} \begin{matrix} +\infty & a_0 > 0 \\ 0 & a_0 < 0 \end{matrix}$ as defined $\left(\ln I(t) = \sum_{j=0}^{n} a_j \ln^{n-j} t \right)$

It is not true that $I(t) \xrightarrow[t\to\infty]{} I_{ss}$. This may be causing some of the problems.

I tried another curve fitting function: $I(t) = I_{ss} + e^{-a_1 t} + \frac{a_2}{t^2} + \frac{a_3}{t}$

I obtained a good simulation of the data. I found comparable plots for the diagnostic criteria by L. Zhang and Macdonald and by Davenport et. al. as those displayed in pages 50-54. For the sake of brevity, the plots are not shown here, but are recorded electronically in the Mathematica file

osvaldo\C-22\computations.nb → see enclosed disks OPR 1/28/2000

We have found that the diagnostic criteria by Burstein and Davenport, and by Zhang-Macdonald are not helpful to discern the dissolution mechanism. It must be born in mind that these criteria were developed for non-alloying systems. I do think worth to apply the criteria on more extensive data.

Let me summarize some ideas mentioned in the literature about Cr_2O_3

Cr_2O_3 can be a cation interstitial conductor, specially at low O_2 pressures.

REFERENCES

[1] E.A. Polman, T. Fransen and P.J. Sellings.
J. Phys.: Condens. Matter. Vol 1 (1989) 4497-4510

[2] K.P. Lillerud and P. Kofstad
J. Electrochem. Soc: Vol. 127 (1980) 2397-2410

[3] P. Kofstad and K.P. Lillerud
J. Electrochem. Soc. Vol. 127 (1980) 2410-2419

[4] H. Hindam and D.P. Whittle
J. Electrochem. Soc. Vol 130 (1983) 1519-1523

Cr_2O_3 is a p-type intrinsic semiconductor. Reperences [1-4]
Authors in [2] and [3] suggest that conduction also occurs via the motion of cation vacancies. The authors in [4] prefer the idea of conduction occurring via the motion of interstitials.

IF vacancies predominate, they do so at high O_2 pressures ([1]-[3])

$\rho_{Cr_2O_3} = 5.21 \frac{gr}{cm^3}$ Reperence [4]

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[5] S. Hong, E. Kim, D-W Kim, J-H Sung, K. No
Journal of Non-Crystalline Solids Vol 221 (1997) 245-254
Refractive index of Cr_2O_3 $n = 2.5$
Band gap 4.7 - 5 eV

[6] M. O. Figueiredo, A. Correia dos Santos, M.J. Carmezim, M. Abbate, E.M.F. de Groot, H. Petersen, N. Braun
Analyst Vol. 119 (1994) 609-611
There is no conclusive evidence that Cr in Cr_2O_3 exists in other oxidation states than +3.

It must be noted that the studies in references [1] - [6] have been done with the sample exposed to controlled gas environments, usually with good control of the O_2 pressure. That is to say, none of the above studies has considered an aqueous electrolyte.

[7] N.S. McIntyre, T.C. Chan, and C. Chen
Oxidation of Metals, Vol. 33 (1990) 457-479
It is studied Cr-Ni alloys and the film formed at 500-600°C. The film is enriched in Cr, even though situations are analyzed such that Ni is the major film component.

[8] C. Brunner, H. Hutter, P. Wilhartitz, M. Grasserbauer
Mikrochim. Acta 125, 69-72 (1997)
The authors did an interesting experiment described as follows:

3/10/99

Cr_2O_3 is grown on pure Cr immersed in an environment of ^{16}O. After the oxide is present, the system is taken to an environment of ^{18}O. The authors found the following array:

Cr	mainly ^{16}O	mainly ^{18}O	environment
	Cr_2O_3		

The authors do not report Cr_2O_3, nor any stoichiometry at all. Because of the ~~doble~~ (OR 3/10/99) above finding, they concluded that Cr had to diffuse to the film/environment interface, and then react with O_2.

I do not think that this is a necessary condition. For example $V_O^{2\cdot}$ may move from the metal toward the environment and there "collect" a O atom. This also explains the accumulation of ^{18}O in the most external layers.

The only study on a similar alloy than C-22 that we have found so far is

[9] G. Lorang, N. Jallerat, K. Vu Quang and J.-P. Langeron
Surface and Interface Analysis, Vol 16, 325-330 (1990)
These authors studied Inconel 600 and Hastelloy C4 in NaCl media. C4 is similar to C22. They found that the film is essentially a chromium oxide, with some content of nickel oxide. The authors do not conclude anything concerning the oxidation states.

It is also found that Cl segregates on the external part of the film. Higher NaCl concentrations correlate quite well with thicker films.

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The findings in [8] and [9] are consistent. It must be born in mind that experiments in [9] utilized aqueous solutions, while those on [8] analyzed gaseous environments. However, the results are consistent.

Approximately, the composition of the film is (Reference [8])

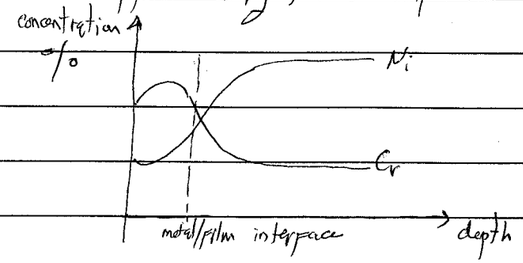
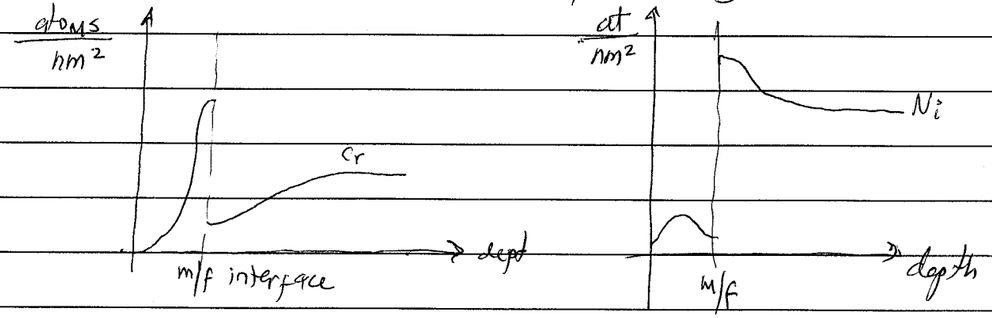


Figure 2 in reference [9] looks approximately



The authors did not find a significant presence of M_o in the passive film, but they acknowledge that this may be due to limitations in their experimental techniques.

3/10/99 OPR

[10] L. Zhang and D. D. Macdonald
Electrochimica Acta, Vol. 43, No. 18, pp. 2673-2685 (1998)

In this paper, Zhang does some numerical simulation and is able to describe profiles quite similar to those in Figure 2, Reference [9]. They studied a binary system $N_i - W$.

The model that they used is

Information potentially subject to copyright protection was redacted from this location. The redacted material is from the reference listed at the top of this of this scientific notebook.

I guess $\xi = \chi$ and $\lambda = \delta$ even though Macdonald has not shown this, but I have done it.

There are several points to outline. The concentration profile is described in terms of the motion of the m and A atoms in the metal bulk. In the barrier layer, the motion of M_M and $A_M^{(\delta-x)}$ cause the observed concentration profile. m and A, in the metal, can "jump" only into an existing vacancy, V_m. Analogously, M_M and $A_M^{(\delta-x)}$ can only "jump" into an existing vacancy, $V_M^{x'}$.

OPR 3/10/99 ~~Metal vacancies, $V_m^{x'}$, are considered fixed in space.~~

$V_O^{\cdot\cdot}$ vacancies are not considered in the description.

3/10/99 OPR

Even though Reaction (5) is taken into account, it is not taken into account when doing the numerical analysis. Note in Table 1 that $K_5 = 0$. Therefore, the film thickens continuously and consistent steady-state is never achieved. Indeed Figure 16 shows a continuous thickening of the film with time. Mi guess is that the rate of film formation is so slow that it can be neglected in the numerical analysis. Lei Zhang included a diagram to explain the algorithm followed to deal with the moving boundary. My guess is that he did not considered a moving boundary in his computations. He just corrected at the end, computing what would be the final thickness. I may be wrong in this supposition, but certainly the algorithm explained by Zhang is quite confusing, that I think it is not meant to be followed.

Another treatment of the moving boundary can be accomplished with an appropriate change of variables.

Note also that there is not any attempt to describe polarization curves.

The V_M vacancies are supposed to "disappear" at a given distance inside the bulk metal. The mechanism by which these vacancies disappear is never discussed.

3/16/99 OPR

Another reason why L. Zhang considered $K_5 = 0$ is because if not the treatment becomes quite complicated. Note that reaction (5) depends on the composition of the film. The quantity "y" is ill defined. It seems that it corresponds to an average stoichiometric composition. Therefore, if $K_5 \neq 0$, it is necessary to continuously compute the average composition. Another possibility is to consider the value of "y" at the film/solution interface. The y-value is given by the concentration of $A_M^{(\delta-x)+}$ at the film/solution interface. In any event, making $K_5 = 0$ simplifies the computations, and I consider this to be the main reason why L. Zhang chose $K_5 = 0$

In summary, a first approximation model for C-22 is

OPR 3/16/99

(1) $m \xrightarrow{K_1^0} M_i^{x+} + V_m + xe$

(2) ~~$m + V_M^{x'} \xrightarrow{K_2^m} M_M + V_m + xe$~~

(3) $A + V_M^{x'} \xrightarrow{K_3} A_M^{(\delta-x)} + V_m + \delta e$

(4) $m \xrightarrow{K_4} M_M + \frac{x}{2} V_O^{\cdot\cdot} + xe$

(5) $A \xrightarrow{K_5} A_M^{(\delta-x)} + \frac{x}{2} V_O^{\cdot\cdot} + \delta e$

(6) $M_i^{x+} \xrightarrow{K_6} M_{(aq)}^{3+} + V_M^{x'} + (3-x)e'$

(7) $M_M \xrightarrow{K_7} M_{(aq)}^{3+} + V_M^{x'} + (3-x)e'$

(8) $A_M^{(\delta-x)} \xrightarrow{K_8} A^{\lambda+} + V_M^{x'} + (\lambda-\delta)e'$

(9) $V_O^{\cdot\cdot} + H_2O \xrightarrow{K_9} O_O + 2H^+$

(10) $(M_{1-y}A_y)O_{x/2} + xH^+ \xrightarrow{K_{10}} (1-y)M^{3+} + yA^{\lambda+} + \frac{x}{2}H_2O + [3+(x-3)y-x]e'$

(11) $A_i^{\delta+} \xrightarrow{K_{11}} A^{\lambda+} + (\lambda-\delta)e'$

metal | film | solution

MAIN ASSUMPTIONS

(i) Conduction is mainly due to $A_i^{\delta+}$ and M_i^{x+} interstitials

The reason I believe to be this the case is that the flux of $V_M^{x'}$ is of the order of the flux of $A_M^{(\delta-x)}$ and M_M (see reactions 7-8). The motion of $A_M^{(\delta-x)}$ and M_M is quite slow, since this elements belong to the

oxide matrix. Therefore, the flux of $V_M^{x'}$ is quite small. The flux of $V_O^{2\cdot}$ is of the order of the rate of dissolution of the film, believed to be negligible. Consequently, the main contribution to the transport of charge comes from the motion of the interstitials.

(ii) The interstitial concentration is always kept low. This is why Zhang and Macdonald were able to compute concentration profiles without considering the presence of interstitial species. Consequently, to describe passive current densities, interstitials are relevant. On the other hand, when computing concentration profiles, interstitials can be neglected.

(iii) Since the interstitial concentration is low, classical mass transport equations hold (e.g. Ficks law).

I will rewrite the equations to define better labels. Besides, Equation (10) as defined by Zhang and Macdonald is incorrect.

(1a) $m \xrightarrow{k_1^m} M_i^{x+} + xe + V_m$ (4a) $M_i^{x+} \xrightarrow{k_4^m} M_{(aq)}^{\xi+} + (\xi - x)e'$

(1b) $A \xrightarrow{k_1^A} A_i^{\delta+} + \delta e + V_m$ (4b) $A_i^{\delta+} \xrightarrow{k_4^A} A_{(aq)}^{\lambda+} + (\lambda - \delta)e'$

(2a) $m + V_M^{x'} \xrightarrow{k_2^m} M_M + V_m + xe$ (5a) $M_M \xrightarrow{k_5^m} M^{\xi+} + V_M^{x'} + (\xi - x)e'$

(2b) $A + V_M^{x'} \xrightarrow{k_2^A} A_M^{(\delta-x)} + V_m + \delta e$ (5b) $A_M^{(\delta-x)} \xrightarrow{k_5^A} A_{(aq)}^{\lambda+} + V_M^{x'} + (\lambda - \xi)e'$

(3a) $m \xrightarrow{k_3^m} M_M + \frac{x}{2}V_O^{2\cdot} + xe'$ (6) $V_O^{\cdot\cdot} + H_2O \xrightarrow{k_6} O_O + 2H^+$

(3b) $A \xrightarrow{k_3^A} A_M^{(\delta-x)} + \frac{x}{2}V_O^{2\cdot} + \delta e'$ (7) $[M_{1-y}A_yO_{\frac{x}{2}}]^{y(\delta-x)} + xH^+ \xrightarrow{k_7} (1-y)M^{\xi+} + yA^{\lambda+} + \frac{x}{2}H_2O + [\xi - x + y(\lambda - \delta + x - \xi)]e'$

metal | film | solution

Note that Eq. (7) is different by the defined by Zhang and Macdonald, since they failed to consider that the oxide lattice $[M_{1-y}A_yO_{\frac{x}{2}}]^{y(\delta-x)}$ should have an associated charge of $y(\delta-x)$.

(1) Definitions 3/16/99

In order to shorten the next discussion let us define.

$\overline{K_1^m} \equiv k_1^m a_m^{m/f}$ m/f → metal film interface

$\overline{K_1^A} \equiv k_1^A a_A^{m/f}$ a → activity

$\overline{K_2^m} = k_2^m a_m^{m/f} a_{V_M^{x'}}^{m/f}$

$\overline{K_2^A} = k_2^A a_A^{m/f} a_{V_M^{x'}}^{m/f}$

$\overline{K_3^m} = k_3^m a_m^{m/f}$

$\overline{K_3^A} = k_3^A a_A^{m/f}$

$\overline{K_4^A} = k_4^A a_{A_i^{\delta+}}^{f/s}$ ~~m/f~~ f/s OPR 3/16/99 f/s → film-solution interface

$\overline{K_4^m} = k_4^m a_{M_i^{x+}}^{f/s}$ ~~m/f~~ f/s OPR 3/16/99

$\overline{K_5^m} = k_5^m a_{M_M}$

$\overline{K_5^A} = k_5^A a_{A_M}^{(\delta-x)}$

$\overline{K_6} = k_6 a_{V_O^{2\cdot}}^{f/s} a_{V_M}^{f/s}$

$\overline{K_7} = k_7 a_M^{1-y} a_{A_M^{\delta-x}}^{y} a_O^{x/2} a_{H^+}^{n}$

$a_M = \frac{C_M}{C_M^\circ}$ ~~(in a pure $MO_{\frac{x}{2}}$ film)~~

$C_M^\circ \rightarrow$ M concentration in a pure $MO_{x/2}$ film

$a_{A_M^{(\delta-x)}} = \frac{C_{A_M}}{C_M^\circ}$ → probably $a_{A_M^{(\delta-x)}} = \frac{C_{A_M}}{C_B^\circ}$? I do not know.

$a_o = \frac{C_o}{C_o^\circ} = 1$ by definition

$C_o^\circ \rightarrow$ O concentration in a pure $MO_{x/2}$ film.

We are implicitly assuming that $C_o = C_o^\circ$ always

$y = \frac{C_{A_M}}{C_M + C_{A_M}}$

Under that definition

$a_{A_M}^{y} \xrightarrow[C_{A_M} \to 0]{} 1$

and $a_M^{1-y} \xrightarrow[C_{A_M} \to 0]{} 1$

It is easy to show these limits. Then our definition is consistent.

$C_{A_M}^{C_{A_M}/(C_M + C_{A_M})} \sim \frac{C_{A_M}}{C_M + C_{A_M}} \ln C_{A_M} = \frac{\ln C_{A_M}}{\left(\frac{C_M}{C_{A_M}} + 1\right)} \xrightarrow{C_{A_M} \to 0} \frac{1}{-\frac{C_M}{C_{A_M}^2}} = -\frac{C_{A_M}}{C_M} \xrightarrow{C_{A_M} \to 0} 0$

$\therefore C_{A_M}^{\frac{C_{A_M}}{C_M + C_{A_M}}} \xrightarrow{C_{A_M} \to 0} 1$

3/17/99

The total current density is

$\frac{I^{m/f}}{F} = x\bar{K}_1^m + \delta\bar{K}_1^n + x\bar{K}_2^m + \delta\bar{K}_2^n + x\bar{K}_3^m + \delta\bar{K}_3^n$ → current density at metal/film interface

On the other hand, at the film/solution interface

$\frac{I^{f/s}}{F} = \xi\bar{K}_4^m + \lambda\bar{K}_4^n + \xi\bar{K}_5^m + \lambda\bar{K}_5^n + 2\bar{K}_6 + (\xi - x + y(\lambda-\xi))\bar{K}_7$

At steady-state $I^{m/f} = I^{f/s}$

Steady-state requirements:

Interstitials: $\begin{cases} \bar{K}_1^m = \bar{K}_4^m \\ \bar{K}_1^n = \bar{K}_4^n \end{cases}$

$V_M^{x'}$: $\bar{K}_2^m + \bar{K}_2^n = \bar{K}_5^m + \bar{K}_5^n$

$V_O^{2\cdot}$: $\frac{x}{2}(\bar{K}_3^m + \bar{K}_3^n) = \bar{K}_6 \Rightarrow x(\bar{K}_3^m + \bar{K}_3^n) = 2\bar{K}_6$

M_M : $\bar{K}_2^m + \bar{K}_3^m = \bar{K}_5^m + (1-y)\bar{K}_7$

$A_m^{(\delta-x)}$: $\bar{K}_2^n + \bar{K}_3^n = \bar{K}_5^n + y\bar{K}_7$

Film formation equals film dissolution: $\bar{K}_3^m + \bar{K}_3^n = \bar{K}_7$

The idea now is to express $\bar{K}_i^{f/s}$ at the f/s interface in terms of $\bar{K}_j^{'s}$ at the m/f interface.

(1) $\bar{K}_7 = \bar{K}_3^m + \bar{K}_3^n$

(2) $\bar{K}_5^n = \bar{K}_2^n + \bar{K}_3^n - y(\bar{K}_3^m + \bar{K}_3^n) = \bar{K}_2^n - y\bar{K}_3^m + (1-y)\bar{K}_3^n$

(3) $\bar{K}_5^m = \bar{K}_2^m + \bar{K}_3^m + (y-1)(\bar{K}_3^m + \bar{K}_3^n) = \bar{K}_2^m + (y-1)\bar{K}_3^n + y\bar{K}_3^m$

Evidently $\bar{K}_5^m + \bar{K}_5^n = \bar{K}_2^m + \bar{K}_2^n$ which means that these definitions are consistent with conservation in $V_O^{2\cdot}$.

Finally (4) $2\bar{K}_6 = x(\bar{K}_3^m + \bar{K}_3^n)$ $\quad \simeq \bar{K}_6 = \bar{K}_3^m + \bar{K}_3^n = \bar{K}_7$

$\bar{K}_6 = \frac{x}{2}\bar{K}_7$ ↔ it is obvious that this has to be the case.

We now compute the current density at the film/solution interface based on (1) − (4)

$\frac{1}{F}I^{f/s} = \xi\bar{K}_1^m + \lambda\bar{K}_1^n + \xi(\bar{K}_2^m + [y-1]\bar{K}_3^n + y\bar{K}_3^m) + \lambda(\bar{K}_2^n - y\bar{K}_3^m + (1-y)\bar{K}_3^n)$
$+ x(\bar{K}_3^m + \bar{K}_3^n) + (\xi - x + y[\lambda-\xi])(\bar{K}_3^m + \bar{K}_3^n)$

3/17/99

$\frac{1}{F}I^{f/s} = \xi\bar{K}_1^m + \lambda\bar{K}_1^n + \xi\bar{K}_2^m + \lambda\bar{K}_2^n + \bar{K}_3^n[\xi(y-1) + \lambda(1-y) + x + \xi - x + y(\lambda-\xi)]$
$+ \bar{K}_3^m[\xi y - \lambda y + x + \xi - x + y(\lambda-\xi)]$

$\frac{1}{F}I^{f/s} = \xi\bar{K}_1^m + \lambda\bar{K}_1^n + \xi\bar{K}_2^m + \lambda\bar{K}_2^n + \xi\bar{K}_3^m + \lambda\bar{K}_3^n$

On the other hand, at the m/f interface

$\frac{1}{F}I^{m/f} = x\bar{K}_1^m + \delta\bar{K}_1^n + x\bar{K}_2^m + \delta\bar{K}_2^n + x\bar{K}_3^m + \delta\bar{K}_3^n$

Clearly $I^{f/s} = I^{m/f}$ if and only if $\xi = x$ and $\lambda = \delta$

The implication is that dissolved species exist only in the same oxidation state as they exist in the oxide lattice.

If that is not the case, then there are two possibilities:

(i) Species in solution are reduced or oxidized by a mechanism that has nothing to do with the oxide dynamics, but that has some influence in the total current density.

(ii) Steady-state cannot be achieved. Either the film grows or dissolves continuously, without the achievement of steady-state. The current density decreases, increases or oscillates in time.

For chromium oxides, no oxygen transport has been reported. That leads us to believe that $J_O = \frac{x}{2}(\bar{K}_3^m + \bar{K}_3^n)$ is negligible. $\bar{K}_3^m, \bar{K}_3^n \simeq 0$

Consequently, $\bar{K}_7, \bar{K}_6 \simeq 0$

For chromium oxides, two main cases have been reported in the literature, that it is an interstitial conductor, or that it is a vacancy, $V_M^{x'}$, conductor.

Let us carry out the following associations

$M \sim Cr$ $\quad x = \xi = 3$

$A \sim N$: $\quad \lambda = \delta = 2$

3/17/99 QFY

$A_M^{(\delta-x)} = N_{i_{Cr}}^{-1}$

$V_M^{x\prime} = V_{Cr}^{3\prime}$

The formation of $V_{Cr}^{3\prime}$ in the presence of $N_{i_{Cr}}^{-1}$ is not energetically favorable: The system $[Cr_{Cr} - V_{Cr}^{3\prime}]$ has less electrostatic energy than the system $[N_{i_{Cr}}^{-1} - V_{Cr}^{3\prime}]$. As a consequence, I believe that the concentration of $V_{Cr}^{3\prime}$ is reduced. The vacancy flux, in the presence of Ni in the oxide lattice, must be negligible.

The best candidates responsible for the transport of charge are interstitials.

Given the above argument, let us assume that

$I^{m/f} \simeq \chi \bar{K}_i^m + \delta \bar{K}_i^A$

$\bar{K}_i^m = K_i^m a_m^{m/f}$

$\bar{K}_i^A = K_i^A a_A^{m/f}$

$a_m = \frac{C_M}{C_M + C_A}$ $\quad C_{M,A} \rightarrow$ M(A) concentration in the alloy

$a_A = \frac{C_A}{C_M + C_A}$

A better symbol instead of a is $X \rightarrow$ fraction concentration

$\frac{1}{F} I^{m/f} \simeq \chi K_i^m X_m^{m/f} + \delta K_i^A X_A^{m/f}$

$\frac{1}{F} I^{m/f} = \frac{1}{(C_M + C_A)^{n/A}} [\chi K_i^m C_m^{m/f} + \delta K_i^A C_A^{m/f}]$

On the other hand, at the film/solution interface:

$\frac{1}{F} I^{f/s} = \chi \bar{K}_4^m + \delta \bar{K}_4^A$

$\bar{K}_4^m = K_4^m a_{M_i^{x+}}^{f/s}$ $\quad \bar{K}_4^A = K_4^A a_{A_i^{\delta+}}^{f/s}$

$a_{M_i^{x+}} = \frac{C_{M_i^{x+}}}{C_0}$ $\quad C_0 = 1 M$

$a_{A_i^{\delta+}} = \frac{C_{A_i^{\delta+}}}{C_0}$

It is not evident that the passive current density can be affected by the environmental variables.

3/18/99 QFY

What about the production of metal vacancies in the metal bulk

$J_{V_m} = \bar{K}_1^m + \bar{K}_1^A + \bar{K}_2^m + \bar{K}_2^A$

Assuming that $\bar{K}_2^m, \bar{K}_2^A << \bar{K}_1^m, \bar{K}_1^A$

$J_{V_m} \simeq \frac{1}{F} I^{m/f}$

Let us say that $I^{m/f} \approx 10^{-8}$ A/cm²

$J_{V_m} \simeq \frac{1}{F} I^{m/f} \approx 10^{-13} \frac{mol}{cm^2 \cdot s}$

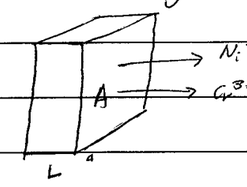
$\rho_{Cr} = 7.19 \frac{gr}{cm^3}$ $\quad M_{Cr} = 52 gr/mol$

$\rho_{Ni} = 8.9 gr/cm^3$ $\quad M_{Ni} = 58.7 gr/mol$

Assume an alloy of 60% Ni and 40% Cr.

$\rho_{alloy} \sim 8 gr/cm^3$ $\quad M_{alloy} \sim 56 gr/mol$ of $Cr + Ni$

Molar density $\sim \frac{8}{56} = 0.143 \frac{mol}{cm^3}$



Say that we have a slab of alloy of thickness L and cross-section A, as indicated above.

Atoms in the material $= 0.143 A L$ moles

Rate of dissolution $= 10^{-13} A \frac{mol}{s}$

Time to dissolve 1% of the atoms in the slab $= \frac{0.01 (0.143) A L}{10^{-13} A}$ seconds

Time (1%) $\sim 14 \times 10^9 L$ seconds $\quad L$ in cm

time (1%) $\sim 14 \times 10^{-9} (cm^{-1} L)$ seconds

time (1%) $\sim 165284 (cm^{-1} L)$ days

If $L \sim 10^{-6} m = 10^{-4} cm \Rightarrow$ time (1%) ~ 16.3 days

1% vacancies will accumulate in 17 days in a slab of thickness 10^{-4} m

3/18/99

Some observations.

Taking into account that $x = \xi$ and $\delta = \lambda$

Current producing reactions:

(1a) $M \xrightarrow{k_1^m} M_i^{x+} + V_m + xe'$ (4a) $M_i^{x+} \xrightarrow{k_4^m} M_{(aq)}^{x+}$

(1b) $A \xrightarrow{k_1^A} A_i^{\delta+} + V_m + \delta e'$ (4b) $A_i^{\delta+} \xrightarrow{k_4^A} A_{(aq)}^{\delta+}$

Concentration determining reactions:

(2a) $m + V_m^{x'} \xrightarrow{k_2^m} M_M + V_m + xe$ (5a) $M_M \xrightarrow{k_5^m} M_{(aq)}^{x+} + V_M^{x'}$

(2b) $A + V_m^{x'} \xrightarrow{k_2^A} A_M^{\delta-x} + V_m + \delta e$ (5b) $A_M^{\delta-x} \xrightarrow{k_5^A} A^{\delta+}_{(aq)} + V_M^{x'}$

(3a) $m \xrightarrow{k_3^m} M_M + \frac{x}{2} V_O^{2\cdot} + xe$ (6) $V_O^{2\cdot} + H_2O \xrightarrow{k_6} O_O + 2H^+$

(3b) $A \xrightarrow{k_3^A} A_M^{\delta-x} + \frac{x}{2} V_O^{2\cdot} + \delta e$ (7) $[M_{1-y} A_y O_{\frac{x}{2}}]^{y(\delta-x)} + xH^+ \xrightarrow{k_7}$

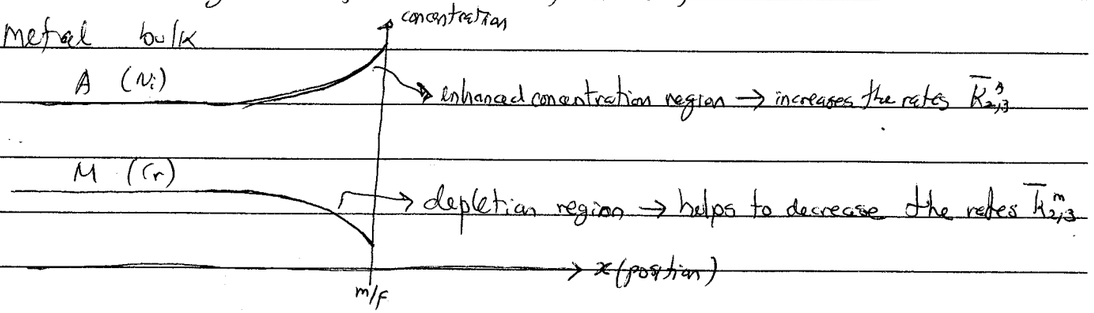
$(1-y) M^{x+} + y A^{\delta+} + \frac{x}{2} H_2O$

Metal/film interface

Assume that preferential oxidation of M (i.e. Cr) occurs; i.e.,

$K_2^m, K_3^m \gg K_2^A, K_3^A$

In this case, we expect the following concentration profile at the (in the neighborhood of) the metal-film interface:

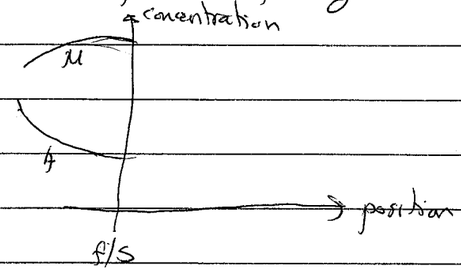


Film/solution interface

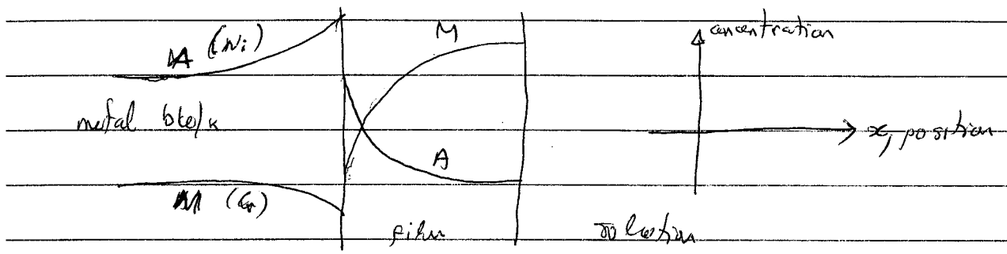
Assume in this case that preferential dissolution of A (i.e., Ni) occurs. That is to say

$K_5^A \gg K_5^m$

At the film/solution interface we expect the following situation



The whole panorama may look like



The concentration profiles can be rationalized in terms of these arguments.

Reaction (7) is needed to guarantee that the film will achieve a given thickness in time. If $K_7 \approx 0$, the film thickness grows until the system achieves equilibrium. In this case no current is produced. The question to answer here is, do our data indeed reflect steady-state information? Are we waiting long enough?

Assume that Ni in the oxide lattice exists substitutionally. If the oxide lattice is Cr_2O_3 ($CrO_{3/2}$), then Ni_{Cr}^{-1} has a -1 charge. We 3/19/99 would expect these negative sites to form complexes with the moving positive interstitials. Therefore $Ni_{i\cdot\cdot\cdot}^{+}$ will form complexes with Cr_i^{3+} and Ni_i^{2+}. The final effect is that the conductivity is decreased and the alloy results more corrosion resistant than the pure metal.

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Assume the following complexation reaction:

$$Cr_i^{3+} + N_{i_{cr}}^{-1} \overset{K_{cr}}{=} Cr N_{i_{cr}}^{+2}$$

Let C_{cr} be the "total" Chromium concentration; i.e.,

$$C_{cr} = [Cr_i^{3+}] + [Cr\,N_{i_{cr}}^{+2}]$$

$$C_i \equiv [Cr_i^{3+}]$$

$$K_{cr} = \frac{[Cr_i^{3+}][N_{i_{cr}}^{-1}]}{[Cr\,N_{i_{cr}}^{+2}]} \Rightarrow \frac{[Cr_i^{3+}][N_{i_{cr}}^{-1}]}{K_{cr}} = [Cr\,N_{i_{cr}}^{+2}]$$

$$C_{cr} = [Cr_i^{3+}]\left\{1 + \frac{[N_{i_{cr}}^{-1}]}{K_{cr}}\right\}$$

$$[Cr_i^{3+}] = C_i = \frac{C_{cr}}{1 + \frac{[N_{i_{cr}}^{-1}]}{K_{cr}}}$$

$$J_i = J_{cr_i^{3+}} = -D_{cr_i}\nabla C_i + \frac{D_{cr_i} z_i F}{RT} C_i \mathcal{E}$$

$$J_{cr_i^{3+}} = -\frac{D_{cr_i}}{1 + \frac{[N_{i_{cr}}^{-1}]}{K_{cr}}}\nabla C_{cr} + \frac{D_{cr_i}}{1 + \frac{[N_{i_{cr}}^{-1}]}{K_{cr}}} \frac{F}{RT} z_i C_i \mathcal{E}$$

Assuming $\frac{\partial}{\partial x}\left\{\frac{[N_{i_{cr}}^{-1}]}{K_{cr}}\right\} = 0$

D_{eff} = effective diffusion coefficient = $\frac{D_{cr_i}}{1 + \frac{[N_{i_{cr}}^{-1}]}{K_{cr}}}$

If $[N_{i_{cr}}^{1-}]$ increases, D_{eff} decreases. The meaning is that the presence of Ni in a chromium oxide helps to enhance the corrosion resistance of the film.

$[N_i]$ cannot increase indefinitely within the oxide. NiO on Ni is not a very protective layer. Besides, the conduction mechanism in NiO is mainly due to $V_{Ni}^{2\prime}$, which is different to what was assumed here (that conduction is due to interstitials). That is to say, our description is only "valid" only if the Ni concentration in the Cr oxide is below certain threshold (that we do not know).

3/24/99

Reference: Passivity of Metals, Edited by Robert P. Frankenthal and Jerome Kruger

Paper → Passivity and Breakdown of Passivity of Nickel, Cobalt, and Chromium. K. E. Heusler. p. 771 – 801

Gustavo has a copy of this book

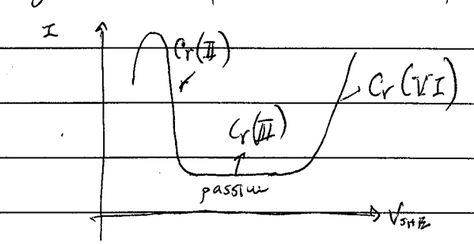
The paper is a good exposition of passivation theory. It makes reference to a model developed by Vetter:

[K. J. Vetter, Z. Elektrochem., Vol 66, 577 (1962); J. Electrochem. Soc., Vol 110, 597 (1963); Electrochim. Acta, Vol. 16, 1923 (1971)]

It shows evidence that the passive current density in Ni is function of the applied potential, and the solution pH. Figure 3 shows evidence that the film thickness is function of the applied potential, and that it is a decreasing function of the applied potential, for potentials less than 1 V_{SHE}, and an increasing function of the potential for potentials above 1.2 V_{SHE}. It is not true that the film thickness is always an increasing function of the applied voltage, as has been claimed somewhere else.

The case of cobalt is interesting. Figure 5 shows polarization curves. It is evident that these polarization curves cannot be explained in terms of a simple model. It is important to say that the author found a bilayer structure for the film on Co. The complex behavior can only be explained in terms of the secondary layer.

Figure 7 is a polarization curve of Cr in 0.5 M sulfuric acid.



3/24/99 CRP

Picture → passive: Dissolution product: Cr(II)

Passive: " " Cr(III)

Transpassive: " " Cr(VI)

In the Cr Pourbaix-diagram it is seen that the passive - transpassive potential transition occurs at the equilibrium potential for the reaction $Cr(VI) \rightarrow Cr(III) + 3e$ Reaction (1).

At potentials above the equilibrium potential for $Cr(VI) = Cr(III) + 3e$, Cr(III) oxidizes, releasing extra electrons that form the excess current in the transpassive region.

$Cr(III) \rightarrow Cr(VI) + 3e \qquad K = K^\circ e^{\frac{\alpha 3F}{RT}\phi_{f/s}}$

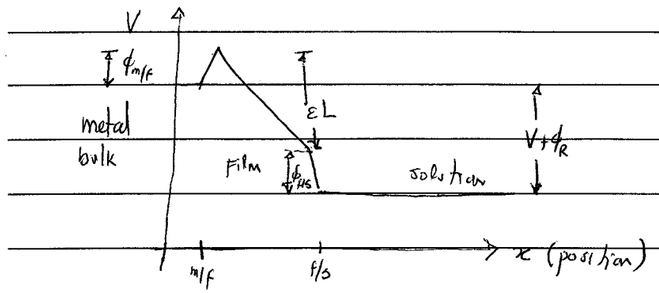
K is an increasing function of $\phi_{f/s}$

This may be an explanation for the transpassive dissolution.

Note that the passive current density is independent of the applied potential. If the main ionic conductor is the film are interstitials, then the passive current density can be explained by assuming that the potential drop at the metal/film interface is a constant (i.e; independent of the applied voltage).

This paper is consistent with the notion that the main charge carriers are interstitials.

3/24/99 CRP



$V + \phi_R - \phi_{m/f} = \phi_{f/s} + \varepsilon L$

$\phi_{f/s}$ → potential drop at the film/solution interface

$\phi_{m/f}$ → potential drop at the metal/film interface

$V+\phi_R$ → applied potential, ϕ_R accounts for the liquid junction potential

ε → average electric field

L → film thickness.

$$L = \frac{V + \phi_R - \phi_{m/f} - \phi_{f/s}}{\varepsilon}$$

Experimentally is usually found that $\frac{\partial L}{\partial V} = \text{constant} = L_V$

Let $\alpha_m \equiv \frac{\partial \phi_{m/f}}{\partial V}$ and $\alpha_s \equiv \frac{\partial \phi_{f/s}}{\partial V}$

Let us assume that α_m and α_s are quasi-constant. Then

$\phi_{m/f} = \alpha_m V + f_{m/f}$ and $\phi_{f/s} = \alpha_s V + f_{f/s}$

where $f_{m/f}$ and $f_{f/s}$ are not functions of the applied potential.

$$L_V = \frac{\partial L}{\partial V} = \frac{\varepsilon(1 - \alpha_m - \alpha_s) - (V + \phi_R - \phi_{m/f} - \phi_{f/s})\frac{\partial \varepsilon}{\partial V}}{\varepsilon^2}$$

$$\varepsilon^2 L_V = \varepsilon(1 - \alpha_m - \alpha_s) - (V + \phi_R - \phi_{m/f} - \phi_{f/s})\frac{\partial \varepsilon}{\partial V}$$

$$(V + \phi_R - \phi_{m/f} - \phi_{f/s})\frac{\partial \varepsilon}{\partial V} = \varepsilon(1 - \alpha_m - \alpha_s) - \varepsilon^2 L_V$$

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$$\frac{d\mathcal{E}}{-L_V\mathcal{E}^2+(1-\alpha_m-\alpha_s)\mathcal{E}} = \frac{dV}{(V+\phi_R-\phi_{m/c}-\phi_{f/s})}$$

$$\int_{V_0}^{V}\frac{dV}{(1-\alpha_m-\alpha_s)V+\phi_R-f_{m/c}-f_{f/s}} = \frac{1}{(1-\alpha_m-\alpha_s)}\int_{V_0}^{V}\frac{dV}{V+\frac{\phi_R-f_{m/c}-f_{f/s}}{1-\alpha_m-\alpha_s}}$$

$$= \frac{1}{1-\alpha_m-\alpha_s}\ln\frac{V+\frac{\phi_R-f_{m/c}-f_{f/s}}{1-\alpha_m-\alpha_s}}{V_0+\frac{\phi_R-f_{m/c}-f_{f/s}}{1-\alpha_m-\alpha_s}} \qquad (1)$$

$$-L_V\mathcal{E}^2+(1-\alpha_m-\alpha_s)\mathcal{E} = -L_V\left[\mathcal{E}^2+\frac{1-\alpha_m-\alpha_s}{-L_V}\mathcal{E}+\frac{1}{4L_V^2}(1-\alpha_m-\alpha_s)^2-\frac{1}{4L_V^2}(1-\alpha_m-\alpha_s)^2\right]$$

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$$= -L_V\left\{\left[\mathcal{E}^2-\frac{1}{2L_V}(1-\alpha_m-\alpha_s)\right]^2-\frac{1}{4L_V^2}(1-\alpha_m-\alpha_s)^2\right\}$$

$$= \frac{1}{4L_V}(1-\alpha_m-\alpha_s)^2-L_V\left[\mathcal{E}-\frac{1}{2L_V}(1-\alpha_m-\alpha_s)\right]^2$$

$$= \frac{1}{4L_V}(1-\alpha_m-\alpha_s)^2\left\{1-\frac{4L_V^2}{(1-\alpha_m-\alpha_s)^2}\left[\mathcal{E}-\frac{1}{2L_V}(1-\alpha_m-\alpha_s)\right]^2\right\}$$

let $x = \frac{2L_V}{1-\alpha_m-\alpha_s}\left[\mathcal{E}-\frac{1}{2L_V}(1-\alpha_m-\alpha_s)\right] = \frac{2L_V\mathcal{E}}{1-\alpha_m-\alpha_s}-1$

$$dx = \frac{2L_V}{1-\alpha_m-\alpha_s}d\mathcal{E} \Rightarrow d\mathcal{E} = \frac{1-\alpha_m-\alpha_s}{2L_V}dx$$

$$\int_{\mathcal{E}_0}^{\mathcal{E}}\frac{d\mathcal{E}}{-L_V\mathcal{E}^2+(1-\alpha_m-\alpha_s)\mathcal{E}} = \frac{1-\alpha_m-\alpha_s}{2L_V}\frac{4L_V}{(1-\alpha_m-\alpha_s)^2}\int_{x_0}^{x}\frac{dx}{1-x^2}$$

$$= \frac{2}{(1-\alpha_m-\alpha_s)}\ln\frac{1+2L_V\mathcal{E}\frac{1}{1-\alpha_m-\alpha_s}-1}{2-\frac{2L_V\mathcal{E}}{1-\alpha_m-\alpha_s}}\cdot\frac{2-\frac{2L_V\mathcal{E}_0}{1-\alpha_m-\alpha_s}}{\frac{2L_V\mathcal{E}_0}{1-\alpha_m-\alpha_s}}$$

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$$= \frac{2}{1-\alpha_m-\alpha_s}\ln\frac{\mathcal{E}}{\mathcal{E}_0}\cdot\frac{1-\frac{L_V\mathcal{E}_0}{1-\alpha_m-\alpha_s}}{1-\frac{L_V\mathcal{E}}{1-\alpha_m-\alpha_s}} \qquad (2)$$

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(1) and (2) must be equal, then

$$2\ln\frac{\mathcal{E}}{\mathcal{E}_0}\frac{1-\frac{L_V\mathcal{E}_0}{1-\alpha_m-\alpha_s}}{1-\frac{L_V\mathcal{E}}{1-\alpha_m-\alpha_s}} = \ln\frac{V+\frac{\phi_R-f_{m/c}-f_{f/s}}{1-\alpha_m-\alpha_s}}{V_0+\frac{\phi_R-f_{m/c}-f_{f/s}}{1-\alpha_m-\alpha_s}}$$

$$\left[\frac{\mathcal{E}}{1-\frac{L_V\mathcal{E}}{1-\alpha_m-\alpha_s}}\right]^2 = \left[\frac{\mathcal{E}_0}{1-\frac{L_V\mathcal{E}_0}{1-\alpha_m-\alpha_s}}\right]^2\frac{V(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}}{V_0(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}}$$

$$\left[\frac{\mathcal{E}}{1-\alpha_m-\alpha_s-L_V\mathcal{E}}\right]^2 = \left[\frac{\mathcal{E}_0}{1-\alpha_m-\alpha_s-L_V\mathcal{E}_0}\right]^2\frac{V(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}}{V_0(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}}$$

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3/25/99 OPR

I did a mistake somewhere. Checking with the Mathematica tables, I found the following value of the integral:

$$\int\frac{d\mathcal{E}}{-L_V\mathcal{E}^2+(1-\alpha_n-\alpha_s)\mathcal{E}} = \frac{1}{1-\alpha_n-\alpha_s}\left\{\ln\mathcal{E}-\ln(-1+L_V\mathcal{E}+\alpha_m+\alpha_s)\right\}$$

Then $$\int_{\mathcal{E}_0}^{\mathcal{E}}\frac{d\mathcal{E}}{-L_V\mathcal{E}^2+(1-\alpha_n-\alpha_s)\mathcal{E}} = \frac{1}{1-\alpha_m-\alpha_s}\ln\left[\frac{\mathcal{E}}{L_V\mathcal{E}+\alpha_m+\alpha_s-1}\cdot\frac{L_V\mathcal{E}_0+\alpha_m+\alpha_s-1}{\mathcal{E}_0}\right] \qquad (2)$$

Equating (1) and (2)

$$\frac{\mathcal{E}}{L_V\mathcal{E}+\alpha_m+\alpha_s-1} = \frac{\mathcal{E}_0}{L_V\mathcal{E}_0+\alpha_m+\alpha_s-1}\frac{V(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}}{V_0(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}}$$

$$\mathcal{E} = \frac{\mathcal{E}_0\left[V-V(\alpha_m+\alpha_s)+\phi_R-f_{m/c}-f_{f/s}\right]}{\mathcal{E}_0L_VV+V_0-\mathcal{E}_0L_VV_0-V_0(\alpha_m+\alpha_s)+\phi_R-f_{m/c}-f_{f/s}}$$

$$\mathcal{E} = \frac{V(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}}{L_VV+\frac{V_0}{\mathcal{E}_0}-L_VV_0-\frac{V_0}{\mathcal{E}_0}(\alpha_m+\alpha_s)+\frac{\phi_R-f_{m/c}-f_{f/s}}{\mathcal{E}_0}}$$

By definition $L = \frac{V(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}}{\mathcal{E}} = L_VV+\frac{V_0}{\mathcal{E}_0}(1-\alpha_m-\alpha_s)-L_VV_0+\frac{\phi_R-f_{m/c}-f_{f/s}}{\mathcal{E}_0}$

$\mathcal{E}_0 \equiv \mathcal{E}(V_0)$

$L_0 \equiv L(V_0) = \frac{1}{\mathcal{E}_0}\left[V_0(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}\right] \rightarrow$ constant.

$L(V) = L_V(V-V_0)+\frac{1}{\mathcal{E}_0}\left[V_0(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}\right]$

(3) $\mathcal{E}(V) = \frac{V(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}}{L_V(V-V_0)+\frac{1}{\mathcal{E}_0}\left[V_0(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}\right]}$ → this result can be obtained without computing any integral at all.

Macdonald always assumes $\mathcal{E}=\mathcal{E}_0=$ constant. Then

$\mathcal{E}_0L_VV-\mathcal{E}_0L_VV_0+V_0(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s} = V(1-\alpha_m-\alpha_s)+\phi_R-f_{m/c}-f_{f/s}$

$\Leftrightarrow L_V = \frac{1-\alpha_m-\alpha_s}{\mathcal{E}_0} = \frac{\partial L}{\partial V}$, which is what Macdonald always gets.

Equation (3) is of more general validity than the specific case $\mathcal{E}(V)=\mathcal{E}_0$

Macdonald's assumptions: $\alpha_m=0$, $f_{f/s} = \beta pH + \phi^\circ_{f/s}$, $f_{m/c} = \phi^\circ_{m/c}$

04/05/1999 OPR

Preparer: M B Brodsky, C.H. Sowers and N.J. Zaluzec

In-situ HVEM studies of the early stages of oxidation of Nickel and Nickel-Chromium alloys.

Ultramicroscopy Vol 25 (1989) 247-256

It is a good discussion of the early formation of NiO and Cr_2O_3 on Ni-Cr alloys. It supports the statement that the Ni and Cr oxidation states are 2 and 3 respectively.

It is said that addition of Cr to Ni enhances the dissolution (oxidation rates) compared to that of pure Ni, due to increased cation vacancy concentration in the scale. However additions of 20-30 at% Cr results in reduced oxidation rates.

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Reference: D.L. Douglass, The Oxidation Mechanism of Dilute Ni-Cr Alloys, Corrosion-Science, 1968, Vol 8, pp. 665 to 678

It is supported the statement that the addition of little Cr to Ni enhances the oxidation rate, but that after or above a given Cr concentration threshold the opposite holds.

It mentions that the film is made of a bilayer structure, with Cr_2O_3 in contact with the metal, and NiO, with the solution. It is reported the presence of voids at the Cr_2O_3/NiO interface. It is suggested that these voids MAY ALSO EXIST IN THE METAL. References are given to support this suggestion.

The voids at the Cr_2O_3/NiO can be rationalized in terms of the PDM as follows. NiO is believed to be a $V_{Ni}^{2'}$ conductor. On the other hand, Cr_2O_3 is likely to be a $V_O^{2\cdot}$ or $Cr_{i\,\text{interstitial}}^{3\cdot}$ conductor. At the Cr_2O_3/NiO interface $V_{Ni}^{2'}$ are not annihilated at the same rate at which they are created at the NiO/solution interface, thus the voids are created. $V_{Ni}^{2'}$ are not annihilated at a fast enough rate because Cr_2O_3 IS NOT a cation vacancy conductor. Recall in the model that I analyzed, that had the configuration,

$$|\text{Alloy}\,|\,Cr_2O_3\,|\,NiO\,|\,\text{solution} \qquad (1)$$

that steady-state can be achieved only if Cr_2O_3 and NiO conduct the same kind of defects. The voids ~~noted~~ OPR 5/14/99 experimentally observed tell me that steady-state is not achieved. The portrait that I have presented is consistent with experimental data, but it is not the only one.

The configuration noted in (1) was studied from page 2 to page 9.

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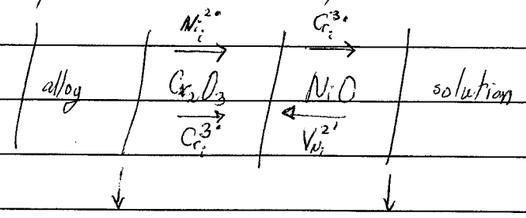
I did not explain some of the implications of such scheme. These implications indicated me that the idea was not worth-while to be further pursued. Let me explain some of the implications.



$I_{Ni} = \text{constant}$ $\quad I_{Ni} = f(V)$

In order for steady-state to happen $f(V) = \text{constant}$ which is a situation that I considered quite restrictive. However, if $f(V) \neq \text{constant}$, more vacancies are produced at the outer layer/solution interface, than those consumed at the Cr_2O_3/NiO interface, and the voids are created.

In the analysis up to page 9 it is easily seen that, if steady-state holds, a cation vacancy-conductor (anion-vacancy conductor) inner layer must be covered by a cation-vacancy conductor (anion-vacancy conductor) outer layer. There is not much freedom in the available possibilities. Note that interstitials are not considered. That lack of freedom suggested me that the idea may be wrong.

Now I believe that this possibility must be kept open, since experimental data reported in the paper by Douglass can be explained nicely on the basis of the double-layer scheme.

I just talked to Sridhar and he reminded me that the objective of this study is the computation of the steady-state current density on the basis of independently measurable quantities. The problem is defining the most appropriate mechanism resembling the actual phenomena.

From page 66:

$$\frac{1}{F} I^{fls} = \chi \bar{K}_4^m + \delta \bar{K}_4^n + \chi \bar{K}_5^m + \delta \bar{K}_5^n + 2\bar{K}_6 + y(\delta - \chi)\bar{K}_7$$

$$= \chi \bar{K}_1^m + \delta \bar{K}_1^n + \chi \bar{K}_3^m + \delta \bar{K}_3^n + \chi\left(\bar{K}_3^m + \bar{K}_3^n\right) + y(\delta - \chi)\left(\bar{K}_3^m + \bar{K}_3^n\right)$$

$$= \chi \bar{K}_1^m + \delta \bar{K}_1^n + [(1-y)\chi + y\delta]\left(\bar{K}_3^m + \bar{K}_3^n\right) + \chi \bar{K}_5^m + \delta \bar{K}_5^n$$

let ~~$m = N_i$, $n = Cr$~~

~~$\chi = 2$, $\delta = 3$~~ → highly likely

let $m = Cr$ and $n = N_i$

$\bar{K}_1^m = a_{Cr}^{m/f} K_1^{Cr} = \text{constant}$ $\qquad \bar{K}_5^m = a_{Cr_{Cr}}^{fls} K_5^{Cro} e^{\chi \alpha_5^{Cr} \frac{F}{RT} \phi_{fls}}$

$\bar{K}_1^n = a_{Ni}^{m/f} K_1^{Ni} = \text{constant}$ $\qquad \bar{K}_5^n = a_{Ni_{Cr}}^{} K_5^{Ni:o} e^{\delta \alpha_5^{Ni} \frac{F}{RT} \phi_{fls}}$

$\bar{K}_3^n = a_{Ni}^{m/f} K_3^{Ni}$

$\bar{K}_3^m = a_{Cr}^{m/f} K_3^{Cr}$

$\chi = 3$, $\delta = 2$ } very likely

If $\phi_{fls} = \alpha V + \beta\, pH + \phi_{fls}^{\circ}$, then

$$\bar{K}_5^m = a_{Cr_{Cr}}^{fls} K_5^{\circ Cr} e^{\chi \alpha_5^{Cr} \frac{F}{RT} \phi_{fls}^{\circ}} e^{\chi \alpha_5^{Cr} \frac{F}{RT} \beta\, pH} e^{\chi \alpha_5^{Cr} \frac{F}{RT} \alpha V}$$

$$\bar{K}_5^n = a_{Ni_{Cr}}^{fls} K_5^{\circ Ni} \exp\left(\delta \alpha_5^{Ni} \frac{F}{RT} \phi_{fls}^{\circ}\right) \exp\left(\delta \alpha_5^{Ni} \frac{F}{RT} \beta\, pH\right) \exp\left(\delta \alpha_5^{Ni} \frac{F}{RT} \alpha V\right)$$

Because of the fact that Cr_2O_3 seems to be either $V_O^{2\cdot}$ and/or interstitial conductor I believe that $\bar{K}_5^m << \bar{K}_1^m, \bar{K}_3^m$

Because Darrell is measuring a constant current density, I expect

$\bar{K}_5^m, \bar{K}_5^n << \bar{K}_1^m, \bar{K}_1^n, \bar{K}_3^n, \bar{K}_3^m$

First approximation: $\bar{K}_5^m, \bar{K}_5^n << \bar{K}_{1,3}^{m/n}$

$$\frac{i}{F} I^{fls} = \chi k_1^{Cr} a_{Cr}^{m/f} + \delta K_1^{Ni:} a_{Ni}^{m/f} + \left(a_{Ni}^{m/f} K_3^{Ni:} + a_{Cr}^{m/f} k_3^{Cr}\right)[(1-y)\chi + y\delta]$$

$$i \overset{?}{=} \frac{A_{rea}^{fls}(Ni_{Cr})}{\text{Total area}}$$

5/17/99 QPR

Reference: F. G. Hodge and B. E. Wilde, Corrosion-NACE, Vol. 26, No 6, June 1970 p.p. 146 – 150

This paper studies the effect of Cl^- on the anodic dissolution of Ni–Cr alloys. It contains the following statement:

Information potentially subject to copyright protection was redacted from this location. The redacted material, a statement about dissolution of heterogeneous alloys is fromthe reference listed below.

24. M. Stern. Corrosion, 14, 329t (1958).

I interpret the above statement as follows:

Let I_{Ni} and I_{Cr} be the current densities of the pure phases under the environmental conditions of interest. Then the current density of a Ni–Cr alloy can be computed as

(1) $$I(\text{alloy}) = \frac{\text{surface}(Ni)}{\text{Total surface}} I_{Ni} + \frac{\text{surface}(Cr)}{\text{Total surface}} I_{Cr}$$

where surface(Ni, Cr) is the surface at the metal/solution interface.

Note that our last equation in page 81 is consistent with the above equation in the limit when $K_3^{Ni,Cr} \to 0$.

Hodge reports a case (Figure 3) where equation (1) predicts a reasonably close answer, ~~but he admits~~ GPR 5/17/99

Hodge reports another procedure (Steigerwald–Greene[25]) to describe the dissolution of singhe phase nickel alloys, which was not successful.

25. R. F. Steigerwald and N. D. Greene. J. Electrochem. Soc. Vol 109, p. 1026 (1962).

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$$\frac{1}{F} I = a_{Cr}^{m/f}\{\chi K_1^{Cr} + [(1-y)\chi + y\delta]K_3^{Cr}\} + a_{Ni}^{m/f}\{\delta K_1^{Ni} + [(1-y)\chi + y\delta]K_3^{Ni}\}$$

$a_{Cr,Ni}^{m/f} = ?$

Assume we define $a_{Cr}^{m/f} = \frac{\text{Surface (Cr) at m/f}}{\text{Total surface}}$

Other possibility is $a_{Cr}^{m/f} = [Cr]^{m/f} / \text{Total concentration}$

In both cases, for a binary alloy, $a_{Ni}^{m/f} = 1 - a_{Cr}^{m/f}$, then

$$\frac{1}{F} I \approx \delta K_1^{Ni} + [(1-y)\chi + y\delta]K_3^{Ni} + \{\chi K_1^{Cr} - \delta K_1^{Ni} + [(1-y)\chi + y\delta](K_3^{Cr} - K_3^{Ni})\} a_{Cr}^{m/f}$$

We expect $K_3^{Cr} > K_3^{Ni}$; since otherwise the assumption for the film to be enforced of mainly Cr_2O_3 is not valid.

Let us assume $y \approx 1$, then

$$\frac{1}{F}\frac{\partial I}{\partial a_{Cr}^{m/f}} = \chi K_1^{Cr} - \delta K_1^{Ni} + [(1-y)\chi + y\delta](K_3^{Cr} - K_3^{Ni})$$

Let $[Cr]$ represent the bulk concentration in the alloy. It is reasonable to expect that $\frac{\partial a_{Cr}^{m/f}}{\partial [Cr]} > 0$

We know that $\frac{1}{F}\frac{\partial I}{\partial [Cr]} = \frac{1}{F}\frac{\partial I}{\partial a_{Cr}^{m/f}}\frac{\partial a_{Cr}^{m/f}}{\partial [Cr]}$ → i.e., the current density increases when $[Cr]$ decreases.

$$= \left(\frac{\partial a_{Cr}^{m/f}}{\partial [Cr]}\right)\left(\chi K_1^{Cr} - \delta K_1^{Ni} + [(1-y)\chi + y\delta][K_3^{Cr} - K_3^{Ni}]\right)$$

Consequently $\chi K_1^{Cr} - \delta K_1^{Ni} + [(1-y)\chi + y\delta](K_3^{Cr} - K_3^{Ni}) < 0$

which implies $K_1^{Ni} > K_1^{Cr}$

A less clear implication is that interstitial conduction is more important than V_O^{2+} conduction. Therefore, in this model, interstitial conduction is STRICTLY NECESSARY. ~~I will never be able to prove that V_O^{2+} conduction is more important, on the basis of this model.~~ GPR 5/17/99

5/20/99 OPR

I would like to find some means of relating the amount of dissolved material to the rate of dissolution.

We repeat the reactions in page 70 to have them handy:

(1a) $Cr \xrightarrow{K_1^{Cr}} Cr_i^{x+} + Vm + xe'$ (4a) $Cr_i^{x+} \xrightarrow{K_4^{Cr}} Cr^{x+}(aq)$

(1b) $Ni \xrightarrow{K_1^{Ni}} Ni_i^{\delta+} + Vm + \delta e'$ (4b) $Ni_i^{\delta+} \xrightarrow{K_4^{Ni}} Ni^{\delta+}(aq)$

(2a) $Cr + V_{Cr}^{x'} \xrightarrow{K_2^{Cr}} Cr_{Cr} + Vm + xe'$ (5a) $Cr_{Cr} \xrightarrow{K_5^{Cr}} Cr^{x+}(aq) + V_{Cr}^{x'}$

(2b) $Ni + V_{Cr}^{x'} \xrightarrow{K_2^{Ni}} Ni_{Cr}^{\delta-x} + Vm + \delta e'$ (5b) $Ni_{Cr}^{\delta-x} \xrightarrow{K_5^{Ni}} Ni_i^{\delta+}(aq) + V_{Cr}^{x'}$

(3a) $Cr \xrightarrow{K_3^{Cr}} Cr_{Cr} + \frac{x}{2} V_O^{2\cdot} + xe'$ (6) $V_O^{2\cdot} + H_2O \xrightarrow{K_6} O_O + 2H^+$

(3b) $Ni \xrightarrow{K_3^{Ni}} Ni_{Cr}^{\delta-x} + \frac{x}{2} V_O^{2\cdot} + \delta e'$ (7) $[Cr_{1-y}Ni_y O_{\frac{x}{2}}]^{y(\delta-x)+} + x H^+ \xrightarrow{K_7} (1-y) Cr^{x+}(aq) + y Ni^{\delta+}(aq) + \frac{x}{2} H_2O$

alloy | film | solution

Very likely $x=3$, $\delta=2$

OPR, 5/20/99

$\frac{1}{F} I_{Ni} = \bar{K}_1^{Ni} + \bar{K}_2^{Ni} + \bar{K}_3^{Ni}$ → From page 66

$\frac{1}{F} I_{Ni} = \bar{K}_1^{Ni} + (\bar{K}_5^{Ni} + y\bar{K}_7 - \bar{K}_3^{Ni}) + \bar{K}_3^{Ni}$

From page 66 $\bar{K}_7 = \bar{K}_3^{Ni} + \bar{K}_3^{Cr}$

Then $\frac{1}{F} I_{Ni} = \bar{K}_1^{Ni} + \bar{K}_5^{Ni} + y(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

$\bar{K}_5^{Ni}$ is a term that is voltage-dependent. I believe it can be neglected, compared to the other terms, since the steady-state current measured is not voltage dependent. Then,

$J_{Ni} = \frac{1}{F} I_{Ni} \approx \bar{K}_1^{Ni} + y(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$ → Flux of Ni-ions into the solution, mol/m²

Analogously

$\frac{1}{F} I_{Cr} = \bar{K}_1^{Cr} + \bar{K}_2^{Cr} + \bar{K}_3^{Cr}$

From page 66: $\bar{K}_2^{Cr} = \bar{K}_5^{Cr} + (1-y)\bar{K}_7 - \bar{K}_3^{Cr}$, $\bar{K}_7 = \bar{K}_3^{Ni} + \bar{K}_3^{Cr}$

Then $J_{Cr} = \bar{K}_5^{Cr} + \bar{K}_1^{Cr} + (1-y)\bar{K}_7 - \bar{K}_3^{Cr} + \bar{K}_3^{Cr} = \bar{K}_5^{Cr} + \bar{K}_1^{Cr} + (1-y)(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

Neglecting $\bar{K}_5^{Cr}$: $J_{Cr} = \bar{K}_5^{Cr} + \bar{K}_1^{Cr} + (1-y)(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

5/20/99 OPR

I did a mistake in not considering that current densities and fluxes are scaled by the oxidation state.

OPR, 5/20/99

$J_{Ni} = \frac{1}{\delta F} I_{Ni} = \frac{1}{\delta}[\bar{K}_1^{Ni} + \bar{K}_2^{Ni} + \bar{K}_3^{Ni}]$

From page 66: $\bar{K}_2^{Ni} = \bar{K}_5^{Ni} + y\bar{K}_7 - \bar{K}_3^{Ni}$, $\bar{K}_7 = \bar{K}_3^{Ni} + \bar{K}_3^{Cr}$

$J_{Ni} = \frac{1}{\delta}[\bar{K}_1^{Ni} + \bar{K}_5^{Ni} + y\bar{K}_7 - \bar{K}_3^{Ni} + \bar{K}_3^{Ni}] = \frac{1}{\delta}[\bar{K}_1^{Ni} + \bar{K}_5^{Ni} + y(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})]$

$J_{Ni} = \frac{1}{\delta}[\bar{K}_5^{Ni} + \bar{K}_1^{Ni} + y(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})]$

$\bar{K}_5^{Ni}$ is a term that is voltage-dependent. I believe it can be neglected, compared to other terms, since the steady-state current measured is not voltage dependent. Then $J_{Ni} \approx \frac{1}{\delta}[\bar{K}_1^{Ni} + y(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})]$

$J_{Ni} \approx \frac{1}{\delta}[x\,\delta\, a_{Ni}^{m/f} K_1^{Ni} + y(\delta a_{Ni}^{m/f} K_3^{Ni} + x a_{Cr}^{m/f} K_3^{Cr})]$

$J_{Ni} \approx a_{Ni}^{m/f}(K_1^{Ni} + yK_3^{Ni}) + y\frac{x}{\delta} a_{Cr}^{m/f} K_3^{Cr}$

On the other hand

$J_{Cr} = \frac{1}{xF} I_{Cr} = \frac{1}{x}[\bar{K}_1^{Cr} + \bar{K}_2^{Cr} + \bar{K}_3^{Cr}]$

From page 66: $\bar{K}_2^{Cr} = \bar{K}_5^{Cr} + (1-y)\bar{K}_7 - \bar{K}_3^{Cr}$, $\bar{K}_7 = \bar{K}_3^{Ni} + \bar{K}_3^{Cr}$

$J_{Cr} = \frac{1}{x}[\bar{K}_1^{Cr} + \bar{K}_5^{Cr} + (1-y)(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})]$

$J_{Cr} \approx \frac{1}{x}[\bar{K}_1^{Cr} + (1-y)(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})]$ → neglecting $\bar{K}_5^{Cr}$, by the same reasons given above.

$J_{Cr} \approx \frac{1}{x}[x\, a_{Cr}^{m/f} K_1^{Cr} + (1-y)(x a_{Cr}^{m/f} K_3^{Cr} + \delta a_{Ni}^{m/f} K_3^{Ni})]$

$J_{Cr} \approx a_{Cr}^{m/f}(K_1^{Cr} + [1-y]K_3^{Cr}) + \frac{\delta}{x}(1-y) a_{Ni}^{m/f} K_3^{Ni}$

I did another mistake, in this page I defined $\bar{K}_i = z_i a_i K_i$, which is inconsistent with the definitions in page 66. There I defined $\bar{K}_i = a_i k_i$. I will start all over again.

5/20/99 CPJ

$J_{Ni} = \frac{1}{F} I_{Ni} = \bar{K}_1^{Ni} + \bar{K}_2^{Ni} + \bar{K}_3^{Ni}$

From page 66: $\bar{K}_2^{Ni} = \bar{K}_5^{Ni} + y\bar{K}_7 - \bar{K}_3^{Ni}$ and $\bar{K}_7 = (\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

$\bar{K}_2^{Ni} = \bar{K}_5^{Ni} - \bar{K}_3^{Ni} + y(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

$J_{Ni} = \bar{K}_1^{Ni} + [\bar{K}_5^{Ni} - \bar{K}_3^{Ni} + y(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})] + \bar{K}_3^{Ni} = \bar{K}_1^{Ni} + \bar{K}_5^{Ni} + y(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

Analogously for Cr

$J_{Cr} = \frac{1}{xF} I_{Cr} = \bar{K}_1^{Cr} + \bar{K}_2^{Cr} + \bar{K}_3^{Cr}$

From page 66: $\bar{K}_2^{Cr} = \bar{K}_5^{Cr} + (1-y)\bar{K}_7 - \bar{K}_3^{Cr}$, and $\bar{K}_7 = \bar{K}_3^{Ni} + \bar{K}_3^{Cr}$

$\bar{K}_2^{Cr} = \bar{K}_5^{Cr} - \bar{K}_3^{Cr} + (1-y)(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

$J_{Cr} = \bar{K}_1^{Cr} + \bar{K}_5^{Cr} + (1-y)(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

$\frac{1}{F} I_{m/f} = \delta J_{Ni} + x J_{Cr} = x\bar{K}_1^{Cr} + \delta\bar{K}_1^{Ni} + x\bar{K}_5^{Cr} + \delta\bar{K}_5^{Ni} + [\delta y + (1-y)x](\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

which is equivalent to the first equation in page 81.

We have previously argued that $\bar{K}_5^{Ni,Cr}$ is a term that is dependent on the applied potential. Since Darrell is not measuring any potential dependence, I believe such terms to be negligible

$J_{Cr} \cong \bar{K}_1^{Cr} + (1-y)(\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

$\left.\begin{aligned} \bar{K}_1^{Cr} &= a_{Cr}^{m/f} K_1^{Cr}, & \bar{K}_1^{Ni} &= a_{Ni}^{m/f} K_1^{Ni} \\ \bar{K}_3^{Cr} &= a_{Cr}^{m/f} K_3^{Cr}, & \bar{K}_3^{Ni} &= a_{Ni}^{m/f} K_3^{Ni} \end{aligned}\right\}$ consistent with definitions in page 65

$J_{Cr} \approx a_{Cr}^{m/f} K_1^{Cr} + (1-y)(a_{Ni}^{m/f} K_3^{Ni} + a_{Cr}^{m/f} K_3^{Cr}) = a_{Cr}^{m/f}[K_1^{Cr} + (1-y)K_3^{Cr}] + (1-y)a_{Ni}^{m/f} K_3^{Ni}$

$J_{Ni} \approx \bar{K}_1^{Ni} + y(\bar{K}_3^{Ni} + \bar{K}_3^{Cr}) = a_{Ni}^{m/f} K_1^{Ni} + y(a_{Ni}^{m/f} K_3^{Ni} + a_{Cr}^{m/f} K_3^{Cr}) = a_{Ni}^{m/f}[K_1^{Ni} + yK_3^{Ni}] + y a_{Cr}^{m/f} K_3^{Cr}$

We need now to define a relationship between the flux and the concentration. I will assume that the concentration ~~at~~ near the solution, at the film/solution interface is proportional to the flux at the f/s interface.

5/21/99 CPJ

This relationship can be justified as follows. Assume that the electric field is negligible, and that the effective diffusion thickness is Δx, then $J_i \approx \frac{D_i C_i^{f/s}}{\Delta x}$, $J_i \propto C_i^{f/s}$

Another possibility is to assume that the concentration gradient is negligible, and that the flux in the neighborhood of film is mainly due to migration. Thus $J_i \approx D_i C_i^{f/s} \frac{z_i F \varepsilon}{RT}$, $J_i \propto C_i^{f/s}$

I cannot guarantee that $J_i \propto C_i^{f/s}$ will always hold. However, under the above circumstances, the assumption $J_i \propto C_i^{f/s}$ is valid.

Let us assume $J_i = \xi_i C_i^{f/s}$ where $\xi_i = \frac{D_i}{\Delta x}$ or $\xi_i = D_i \frac{z_i F \varepsilon}{RT}$

Let M_{Cr} and M_{Ni} be the molar weight of chromium and Ni, respectively

$\frac{W_{Cr}}{W_{Ni}} = \frac{M_{Cr} C_{Cr}^{f/s}}{M_{Ni} C_{Ni}^{f/s}} \approx \frac{M_{Cr}\xi_{Ni} J_{Cr}^{f/s}}{M_{Ni}\xi_{Cr} J_{Ni}^{f/s}} = \frac{M_{Cr}\xi_{Ni}}{M_{Ni}\xi_{Cr}} \frac{J_{Cr}^{f/s}}{J_{Ni}^{f/s}}$

$\frac{W_{Cr}}{W_{Ni}} = \frac{M_{Cr}\xi_{Ni}}{M_{Ni}\xi_{Cr}} \frac{a_{Cr}^{m/f}[K_1^{Cr} + (1-y)K_3^{Cr}] + (1-y)a_{Ni}^{m/f} K_3^{Ni}}{a_{Ni}^{m/f}[K_1^{Ni} + yK_3^{Ni}] + y a_{Cr}^{m/f} K_3^{Cr}}$

Let us assume that $a_{Ni}^{m/f} = 1 - a_{Cr}^{m/f}$

$\frac{W_{Cr}}{W_{Ni}} = \frac{M_{Cr}\xi_{Ni}}{M_{Ni}\xi_{Cr}} \frac{a_{Cr}^{m/f}[K_1^{Cr} + (1-y)(K_3^{Cr} - K_3^{Ni})] + (1-y)K_3^{Ni}}{a_{Cr}^{m/f}[y(K_3^{Cr} - K_3^{Ni}) - K_1^{Ni}] + K_1^{Ni} + yK_3^{Ni}}$

$\frac{1}{F} I_{m/f} \simeq x\bar{K}_1^{Cr} + \delta\bar{K}_1^{Ni} + [\delta y + (1-y)x](\bar{K}_3^{Ni} + \bar{K}_3^{Cr})$

$= x\bar{K}_1^{Cr} + [\delta y + (1-y)x]\bar{K}_3^{Cr} + \delta\bar{K}_1^{Ni} + [\delta y + (1-y)x]\bar{K}_3^{Ni}$

$= a_{Cr}^{m/f}[xK_1^{Cr} + [\delta y + (1-y)x]K_3^{Cr}] + a_{Ni}^{m/f}[\delta K_1^{Ni} + [\delta y + (1-y)x]K_3^{Ni}]$

$= \delta K_1^{Ni} + [\delta y + (1-y)x]K_3^{Ni} + \{xK_1^{Cr} - \delta K_1^{Ni} + [(1-y)x + \delta y](K_3^{Cr} - K_3^{Ni})\} a_{Cr}^{m/f}$

$W_{Cr} = \frac{M_{Cr}}{\xi_{Cr}}\{a_{Cr}^{m/f}[K_1^{Cr} + (1-y)(K_3^{Cr} - K_3^{Ni})] + (1-y)K_3^{Ni}\}$

$W_{Ni} = \frac{M_{Ni}}{\xi_{Ni}}\{a_{Cr}^{m/f}[y(K_3^{Cr} - K_3^{Ni}) - K_1^{Ni}] + K_1^{Ni} + yK_3^{Ni}\}$

5/21/99 OPR

Assume that we can determine $I_{M/F} = I_{M/F}(a_{cr}^{M/F})$

$W_{cr}^{sol} = W_{cr}^{sol}(a_{cr}^{M/F})$

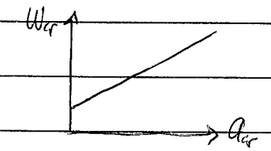
$W_{Ni}^{sol} = W_{Ni}^{sol}(a_{cr}^{M/F})$

and $\left.\begin{aligned} I_{M/F} &= b_I + m_I a_{cr}^{M/F} \\ W_{cr} &= b_{cr} + m_{cr} a_{cr}^{M/F} \\ W_{Ni} &= b_{Ni} + m_{Ni} a_{cr}^{M/F} \end{aligned}\right\}$ just linear relationships

then

(1) $b_I = \delta K_1^{Ni} + [(1-y)\chi + y\delta] K_3^{Ni} > 0$

(2) $m_I = \chi K_1^{cr} - \delta K_1^{Ni} + [(1-y)\chi + \delta y](K_3^{cr} - K_3^{Ni})$



(3) $b_{cr} = \frac{M_{cr}}{\xi_{cr}}(1-y) K_3^{Ni} > 0$

(4) $m_{cr} = \frac{M_{cr}}{\xi_{cr}}\left[K_1^{cr} + (1-y)(K_3^{cr} - K_3^{Ni})\right] > 0$

(5) $b_{Ni} = \frac{M_{Ni}}{\xi_{Ni}}\left(K_1^{Ni} + y K_3^{Ni}\right) > 0$

(6) $m_{Ni} = \frac{M_{Ni}}{\xi_{Ni}}\left[y(K_3^{cr} - K_3^{Ni}) - K_1^{Ni}\right] \Rightarrow K_3^{cr} - K_3^{Ni} = \left(\frac{m_{Ni}\xi_{Ni}}{M_{Ni}} + K_1^{Ni}\right)\frac{1}{y} > 0$ OPR, 5/21/99

~~OPR 5/21/99 $\therefore K_3^{cr} > K_3^{Ni}$, which is obvious~~

~~if the film is supposed to be mainly composed of Cr_2O_3.~~

In principle, m_{Ni} can be either positive or negative.

We expect $K_3^{cr} - K_3^{Ni} > 0$, then $K_1^{Ni} > -\frac{m_{Ni}\xi_{Ni}}{M_{Ni}}$

From b_{Ni}: $K_3^{Ni} = \frac{1}{y}\left(\frac{\xi_{Ni} b_{Ni}}{M_{Ni}} - K_1^{Ni}\right)$

(7) From b_{cr}: $K_3^{Ni} = \frac{1}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}}$

$\frac{1}{y}\left(\frac{\xi_{Ni} b_{Ni}}{M_{Ni}} - K_1^{Ni}\right) = \frac{1}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}}$

(8) $K_1^{Ni} = \frac{\xi_{Ni} b_{Ni}}{M_{Ni}} - \frac{y}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}} > 0$ $\qquad K_1^{Ni} = \frac{\xi_{Ni} b_{Ni}}{M_{Ni}} - \frac{y}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}}$

From (6), and (7), and (8)

~~$K_3^{cr} = \frac{1}{y}\left(\frac{\xi_{Ni} b_{Ni}}{M_{Ni}} - K_1^{Ni}\right)$~~ OPR, 5/21/99

$K_3^{cr} = \frac{1}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}} + \frac{1}{y}\left[\frac{\xi_{Ni} b_{Ni}}{M_{Ni}} - \frac{y}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}} + \frac{m_{Ni}\xi_{Ni}}{M_{Ni}}\right]$

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(9) $K_3^{cr} = \frac{1}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}} + \frac{1}{y}\left[\frac{\xi_{Ni}}{M_{Ni}}(b_{Ni} + m_{Ni}) - \frac{y}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}}\right] = \frac{1}{y}\frac{\xi_{Ni}}{M_{Ni}}(b_{Ni} + m_{Ni}) > 0$

Consequently $b_{Ni} > -m_{Ni}$

(7) $K_3^{Ni} = \frac{1}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}}$

(8) $K_1^{Ni} = \frac{\xi_{Ni} b_{Ni}}{M_{Ni}} - \frac{y}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}}$

$K_3^{cr} - K_3^{Ni} = \frac{1}{y}\frac{\xi_{Ni}}{M_{Ni}}(b_{Ni} + m_{Ni}) - \frac{1}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}} > 0$ $\rightarrow$ expected

From (4): $K_1^{cr} = \frac{\xi_{cr} m_{cr}}{M_{cr}} - (1-y)\left\{\frac{1}{y}\frac{\xi_{Ni}}{M_{Ni}}(b_{Ni} + m_{Ni}) - \frac{1}{1-y}\frac{\xi_{cr} b_{cr}}{M_{cr}}\right\}$

$K_1^{cr} = \frac{\xi_{cr} m_{cr}}{M_{cr}} + \frac{\xi_{cr} b_{cr}}{M_{cr}} - \frac{1-y}{y}\frac{\xi_{Ni}}{M_{Ni}}(b_{Ni} + m_{Ni})$

(10) $K_1^{cr} = \frac{\xi_{cr}}{M_{cr}}(m_{cr} + b_{cr}) - \frac{1-y}{y}\frac{\xi_{Ni}}{M_{Ni}}(b_{Ni} + m_{Ni})$

SUMMARY:

$K_1^{cr} = \frac{\xi_{cr}}{M_{cr}}(b_{cr} + m_{cr}) - \frac{1-y}{y}\frac{\xi_{Ni}}{M_{Ni}}(b_{Ni} + m_{Ni})$

$K_1^{Ni} = \frac{\xi_{Ni}}{M_{Ni}} b_{Ni} - \frac{y}{1-y}\frac{\xi_{cr}}{M_{cr}} b_{cr}$

$K_3^{cr} = \frac{1}{y}\frac{\xi_{Ni}}{M_{Ni}}(b_{Ni} + m_{Ni})$

$K_3^{Ni} = \frac{1}{1-y}\frac{\xi_{cr}}{M_{cr}} b_{cr}$

} determined on the basis of mass measurements

Note that the above rate constants depend on ξ_{cr}, ξ_{Ni}, and y. These three parameters are not really well defined. I treated y as a constant, but y should be function of the $a_{cr}^{M/F}$. So to avoid complications, y is set as constant.

It is going to be quite difficult to fulfill the restrictions: $K_3^{cr} > K_3^{Ni}$, $K_1^{cr} < K_1^{Ni}$, and $K_i > 0$. Some of these restrictions appear to contradict each other.

For example, $K_3^{cr} > 0$ implies $b_{Ni} + m_{Ni} > 0 \Rightarrow b_{Ni} > -m_{Ni}$

$K_1^{Ni} > 0$ implies $b_{Ni} > \frac{y}{1-y}\frac{M_{Ni}}{M_{cr}}\frac{\xi_{cr}}{\xi_{Ni}} b_{cr}$ (11)

$K_1^{Ner} > 0$ implies $0 < b_{Ni} + m_{Ni} < \frac{y}{1-y}\frac{M_{Ni}}{\xi_{Ni}} \cdot \frac{\xi_{cr}}{M_{cr}}(b_{cr} + m_{cr})$ (12)

In virtue of the above inequality, necessarily $m_{Ni} < \frac{y}{1-y}\frac{M_{Ni}}{M_{cr}}\frac{\xi_{cr}}{\xi_{Ni}} m_{cr}$, but it does not guarantee that (12) will hold. That can be guaranteed only if $\frac{y}{1-y}\frac{M_{Ni}}{M_{cr}}\frac{\xi_{cr}}{\xi_{Ni}} m_{cr} \gg m_{Ni} \Rightarrow$ doable $\therefore y \approx 1$, or $\xi_{cr} \gg \xi_{Ni}$

5/21/99 QPJ

From $K_3^{Cr} > K_3^{Ni} \Rightarrow \frac{1}{y}\frac{\xi_{Ni}}{M_{Ni}}(b_{Ni} + m_{Ni}) > \frac{1}{1-y}\frac{\xi_{Cr}}{M_{Cr}} b_{Cr}$

$$b_{Ni} + m_{Ni} > \frac{y}{1-y}\frac{M_{Ni}}{M_{Cr}}\frac{\xi_{Cr}}{\xi_{Ni}} b_{Cr} \qquad (13)$$

before we requested $b_{Ni} > \frac{y}{1-y}\frac{M_{Ni}}{M_{Cr}}\frac{\xi_{Cr}}{\xi_{Ni}} b_{Cr}$ (12)

If (12) holds and $m_{Ni} > 0$, then (13) holds.

If $m_{Ni} < 0$, then it is enough to request $b_{Ni} >> \frac{y}{1-y}\frac{M_{Ni}}{M_{Cr}}\frac{\xi_{Cr}}{\xi_{Ni}} b_{Cr}$ (14)

Note that if $y \approx 1$ and/or $\xi_{Cr} >> \xi_{Ni}$, very likely (14) will not hold. If y and/or ξ_{Cr}, ξ_{Ni} are adjusted to make (12) to hold, (14) will fail to be valid.

(12) and (14) can be guaranteed without contradiction if

$b_{Ni} >> b_{Cr}$ and $m_{Cr} >> m_{Ni}$

$$0 < K_1^{Ni} - K_1^{Cr} = \frac{\xi_{Ni}}{M_{Ni}}\Big[b_{Ni}\underbrace{\Big(1+\frac{1-y}{y}\Big)}_{\frac{1}{y}} + m_{Ni}\Big] - \frac{\xi_{Cr}}{M_{Cr}}\Big[b_{Cr}\underbrace{\Big(1+\frac{y}{1-y}\Big)}_{\frac{1}{1-y}} + m_{Cr}\Big]$$

Thus $\frac{\xi_{Ni}}{M_{Ni}}\Big[b_{Ni}\Big(1+\frac{1-y}{y}\Big) + m_{Ni}\Big] > \frac{\xi_{Cr}}{M_{Cr}}\Big[b_{Cr}(1/1-y) + m_{Cr}\Big]$

$$b_{Ni}\Big(\frac{1}{y}\Big) + m_{Ni} > \frac{M_{Ni}}{M_{Cr}}\frac{\xi_{Cr}}{\xi_{Ni}}\Big[\frac{b_{Cr}}{1-y} + m_{Cr}\Big]$$

$b_{Ni} >> b_{Cr}$ is consistant with the above, but not $m_{Cr} >> m_{Ni}$. Probably $m_{Cr} > 0 > m_{Ni}$, m_{Ni} just slightly less than zero, and $b_{Ni} >> b_{Cr}$. It is doable.

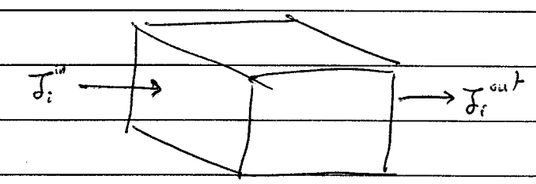
There are many restrictions on $m_{Cr}, m_{Ni}, b_{Cr}, b_{Ni}$ difficult to accomplish. These parameters are intended to be obtained experimentally, and it seems difficult that they will satisfy the restrictions.

6/1/99 QPJ

The problem with the approach in prior pages is that

- measurement of the instantaneous concentration of the ions in the solution next to the alloy surface is needed. This concentration is not well defined. For example we may use a rotating disk electrode at such velocity that the ion concentration in the alloy neighborhood is practically zero. The passive current density will probably be unafected by the disk velocity. Therefore, a correlation between fluxes and concentrations is not evident.
- ξ_{Cr} and ξ_{Ni} are treated as fitting parameters, thus introducing more uncertainties into our analysis.

Rather than measuring a local concentration, we may try to measure the total concentration, and relate that to the rate of dissolution.



, assume $J_i^{out} = 0$

$$\frac{dm_i}{dt} = M_i J_i A \qquad [M_i] = mol^{-1}gr = gr/mol$$

$[J_i] = mol\ m^{-2}\ s^{-1}$

$[A] = m^2 \rightarrow$ alloy surface, for example

$m_i = m_i^\circ + M_i J_i A t$, assuming J_i to be constant.

$$J_i = \frac{m_i - m_i^\circ}{M_i A t}$$

In prior pages I denoted mass with W. In order to make the notation consistant: $\frac{dw_i}{dt} = M_i J_i A \Rightarrow w_i = w_i^\circ + M_i J_i A t$

$$J_i = \frac{\overset{\text{QPR, 6/1/99}}{\cancel{m}}\ w_i - w_i^\circ}{M_i A t}$$

Milton Stern, (Corrosion, Vol 14(7) 1958 pp. 329t-332t

The author studied the variation of surface electrodes. To mimic galvanic couples he chose materials with comparable equilibrium potentials (open circuit potential, corrosion potential?). He found excellent results by applying the formula $i_T = f_1 i_1 + f_2 i_2$, where f_i is the surface fraction, and i_i is the stand-alone current density. Stern also computed the effect on the corrosion potential.

R.F. Steigerwald and N.D. Greene. The Anodic Dissolution of Binary Alloys. J. Electrochem. Soc. Vol 109 (1962) p. 1026-34 (1962)

Steigerwald used Stern's ideas to predict the current density of alloys. If Stern's ideas worked for isolated and mechanically attached electrodes, then they should work too for heterogeneous alloys. A heterogeneous alloy is defined as a metal mixture, without the formation of mixed compounds. Therefore, a heterogeneous alloy resembles the original forming metals by patches. Thus the formula for the current density is

$$i_T = i_A f_A + i_B f_B \qquad (1)$$

i_A and i_B are the current densities of the stand-alone metals, and f_A, f_B is the surface fraction of the metal. The surface fraction equals the volume fraction, which can be computed from the weight composition and the specific gravity of the components.

Formula (1) does not assume any preferential (nor congruential) dissolution.

Steigerwald and Greene found that their formula did not always work. They propose the following algorithm to compute the dissolution current.

i) Determine the corrosion potential of the alloy

ii) Shift the pure metal current densities so that their corrosion potential coincides with the alloy corrosion potential.

iii) $$i_T = \frac{i_A i_B (Z_A N_A + Z_B N_B)}{Z_A N_B i_B + Z_B N_B i_A} \qquad (2)$$

The above formula was computed by assuming congruent dissolution. $N_{A,B}$ are the mole fractions in the alloy, $Z_{A,B}$ are the oxidation numbers of the ions.

It is argued that formula (2) applies to homogeneous allays. It cannot be used to explain preferential dissolution.

The authors assumed:

$i_A f_A = Z_A N_A K$ ← same K to guarantee congruential dissolution.

$i_B f_B = Z_B N_B K$ ←

The results in the paper in using Eq. (2) are qualitatively good, but the quantitative prediction is poor. Comparisons are made on log scaled plots, diminishing the extent of the variation.

Eq. (2) is not quite useful to assess changes in the current density, since it assumes congruential dissolution.

R. Kirchheim, B. Heine, H. Fischmeister, S. Hofmann, H. Knote and U. Stolz
The Passivity of Iron-Chromium Alloys
Corrosion Science, Vol. 29, No 7, pp. 899-917 (1989)

The authors again assume congruent dissolution, and carry out an approach comparable to their predecessors. ajpr 6/16/99

Because of congruent dissolution } $i_{Cr} = i^{\circ}_{Cr} X^{alloy}_{Cr}$ $i_{Fe} = i^{\circ}_{Fe} X^{alloy}_{Fe}$

Thus $i^{\circ} = i^{\circ}_{Cr} + i^{\circ}_{Fe}$. X_j is the molar fraction.

On the other hand, at the film/electrolyte interface

$i_{Cr} = i^{\circ}_{Cr} X^{f/e}_{Cr}$ $i_{Fe} = i^{\circ}_{Fe} X^{f/e}_{Fe}$

Where i°_{i} are the stationary current densities for pure Fe and Cr; $X^{f/e}_{i,Cr}$ is

the molar fraction at the film/electrolyte interface.

By equating the current densities at the alloy/film interface to the current densities at the film/solution interface, the authors found

$$X_{Cr}^{f/e} = \frac{\sigma X_{Cr}^{a}}{1 - X_{Cr}^{a} + \sigma X_{Cr}^{a}} \qquad \sigma = \frac{i_{Co}^{Fe}}{i_{Co}^{Cr}}$$

By assuming that, inside the film

$$i_{Cr} = X_{Cr}^{f} D_{Cr} K \exp\left(\frac{\alpha S F E Z_{Cr}}{RT}\right)$$

$$i_{Fe} = X_{Fe}^{f} D_{Fe} K \exp\left(\frac{\alpha S Z_{Fe} F E}{RT}\right)$$

Thus $$\frac{i_{Cr,f}}{i_{Fe,f}} = \frac{X_{Cr}^{f} D_{Cr}}{X_{Fe}^{f} D_{Fe}}$$

and by equating the current densities to the current densities inside the film, one gets

$$X_{Cr}^{f} = \frac{\beta X_{Cr}^{a}}{1 - X_{Cr}^{a} + \beta X_{Cr}^{a}} \qquad \beta = \frac{D_{Fe}}{D_{Cr}}$$

The formulas were fitted to experimental data and a fairly good description was achieved. It is predicted that more Fe than Cr must be present in the electrolyte, but it was not verified.

Formulas for the passivation potential are provided, but they have to be corrected via a fitting factor.

This approach is a little better than prior ones in the sense that Chromium enrichment and depletion is explained. The formulas rely on the hypothesis of congruent dissolution.

In the papers reviewed in pages 92-94 there has never been any attempt to validate the conclusions with actual measurements of the electrolyte concentration.

I have not found any paper where mass fluxes are measured, and from them current densities are determined. Mass concentrations have been measured, but as functions of ~~the electrolyte concentration, and not of~~ the applied voltage (not of the alloy composition). Preferential dissolution has been measured as function of the applied voltage.

OPR 6/16/99

We need to measure the preferential dissolution as function of the alloy composition. From these measurements, we should be able to draw the passive current density as function of the alloy composition. To the best of my knowledge, this has not been done before. It would also be beneficial to determine the composition profile of the film, and of the alloy as function of the location.

I believe that I can determine the rate constants of the relevant reactions by the mass measurements and passive current measurements. Two major unknowns are $a_i^{m/f}$ and $a_i^{f/s}$, which are the molar fractions at the metal/film and film/solution interface respectively. The challenge is to define $a_i^{m/f}(X_i)$ and $a_i^{f/s}(X_i)$, where X_i is the bulk molar fraction. The simplest approach will be to propose empirical functions, with adjustable parameters.

How do we define $a_i^{m/f}(X_i)$ and $a_i^{f/s}(X_i)$?

8/5/99

From page 66:

$$\bar{K}_2^{Cr} + \bar{K}_2^{Ni} = \bar{K}_5^{Cr} + \bar{K}_5^{Ni}$$

Since $\bar{K}_5^{Cr,Ni}$ are small terms (otherwise the current density would be potential dependent), then it follows that $\bar{K}_2^{Cr,Ni}$ are also small terms compared to the other reaction rates.

$$\bar{K}_2^{Cr} + \bar{K}_3^{Cr} = \bar{K}_5^{Cr} + (1-y)\left(\bar{K}_3^{Cr} + \bar{K}_3^{Ni}\right)$$

$$\bar{K}_2^{Ni} + \bar{K}_3^{Ni} = \bar{K}_5^{Ni} + y\left(\bar{K}_3^{Cr} + \bar{K}_3^{Ni}\right)$$

If we approximate $\bar{K}_2^{Ni,Cr} \approx 0$ and $\bar{K}_5^{Cr,Ni} \approx 0$

from the above expressions we obtain

$$y\,\bar{K}_3^{Cr} = (1-y)\,\bar{K}_3^{Ni} \qquad y\left(\bar{K}_3^{Cr} + \bar{K}_3^{Ni}\right) = \bar{K}_3^{Ni}$$

$$y = \frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}} = \frac{a_{Ni}^{m/f} K_3^{Ni}}{a_{Cr}^{m/f} K_3^{Cr} + a_{Ni}^{m/f} K_3^{Ni}}$$

Certainly "y" cannot be approximated by a constant as previously discussed.

$y \to 0$ if $\left\{ \begin{array}{l} K_3^{Ni} \to 0 \\ K_3^{Cr} \to \infty \\ a_{Ni}^{m/f} \to 0 \end{array} \right\}$ predominant dissolution of Cr

$y \to 1$ if $\left\{ \begin{array}{l} K_3^{Cr} \to 0 \\ a_{Cr}^{m/f} \to 0 \end{array} \right.$ $\to$ Slow Cr dissolution $\to$ No Cr present in alloy

I do not expect $y \to 1$ since by hypothesis the film is mainly made of Cr_2O_3. $y \approx 1$ breaks our hypothesis and corresponds to a different case.

It is expected to have $K_3^{Cr} > K_3^{Ni}$

$$y = f\left(a_{Cr}^{m/f}, a_{Ni}^{m/f}\right)$$ ↑ activity, → molar fraction, concentration

The problem is still defining $a = f(X)$

We may carry the crude approximation $a = X$

8/6/99

Reference: J. B. Lumsden and R. W. Staehle, Composition of Protective Films on Iron and Stainless Steels, Surface Analysis Techniques for Metallurgical Applications, ASTM STP 596, American Society for Testing and Materials, 1976, pp. 39-51

The authors found that neither Mo nor S enrich the film, which is opposed to the hypothesis that the higher resistance of Mo-containing alloys is due to the Mo enrichment of the film. This paper shows evidence that that hypothesis may be false.

The role of Mo is not conclusive. Some authors speculate that the resistance to pitting is due to the beneficial effect of molybdates, and others to the incorporation of Mo on the passive film, and others to a combination of both. None of these hypotheses has been fully substantiated.

There is a fourth hypothesis, that is the participation of Mo on the activation-controlled processes. Probably the presence of a highly charged (positively) center (+6) in the bulk alloy structure may decrease the dissolution or kinetic rate constants of the oxidation reactions.

COMMENT ON THE STEADY-STATE HYPOTHESIS

The PDM assumes that the rate of vacancy production equals the rate of vacancy consumption. This condition is not the most general condition. Steady-state can be granted if

Rate (vacancy production) ≤ Rate (vacancy consumption).

~~Thus, if Rate (vacancy production) < Rate (vacancy consumption) the vacancy concentration in the film equals zero. The vacancy concentration differs from zero only if Rate(VP) = Rate(VC).~~ OPR 8/6/99

8/6/99 [illegible]

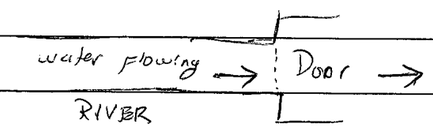
In general Rate($VP^{\text{vacancy production}}$) <= Rate($VC^{\text{consumption}}$)

The approach that we have taken is not incorrect, since ~~an~~ OPR 8/6/99 statement like

Rate(VP) < Rate(VC)

means that the mechanism for vacancy consumption has all of the potential to "get rid of" the vacancies produced. The following analogy helps in the understanding of this subtle observation.

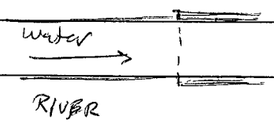
Case 1: Rate(VP) < Rate(VC)



All of the incoming water makes is through the door

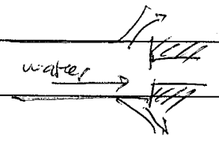
Case R(VP) < Rate(VC)

Case 2: Rate(VP) = Rate(VC)



The door is of exactly the right size to allow for the flux of water.

Case 3: Rate(VP) > Rate(VC)



The door does not allow for the flow of all of the water, an the water finds different paths.

In cases 1 and 2 the rate of vacancy consumption equalizes the rate of vacancy production. Thus our approach is adequate. Equalizing is not appropriate for the analysis of transients.

Case 3 is associated with the rupture of steady-state. Pitting corrosion may be produced in this case.

8/6/99 [illegible]

Problem I: The model seems appropriate if the film is mainly Cr_2O_3. However, it will not be able to account for the transition to a NiO film. ¿How do I describe a more general case?

Problem II: The model does not account for the dissolution of Mo.

I will begin by analyzing problem II.

Assumption: Mo is not incorporated into the passive film, as some studies indicate.

Composition of C-22 Source: Darell's paper

Ni - 57.8	W - 3.0
Cr - 21.4	C - 0.004
Mo - 13.6	
Fe - 3.8	
Co - 0.09	

I will neglect the presence of Fe, Co, W, and C. The presence of Mo cannot be neglected.

The paper by M.A. Cavanaugh, J.A. Kargol, J. Nickerson, and N.F. Fiore, (The Anodic Dissolution of a Ni-Base Superalloy, Vol. 39 (1983) Corrosion-NACE p. 144-150) provides some evidence that in Hastelloy Alloy C-276 Mo dissolves almost congruently with respect to Ni.

Cavanaugh et al. used polarization diagrams to predict preferential dissolution of the cations. They postulate that ~~those~~ OPR 8/6/99 preferential dissolution is controlled solely by the corrosion potential and the polarization scan of the pure substance.

8/9/99

Some authors have found Mo enrichment in the film. However, there is not a universal agreement on this, and I believe it is safer to assume that it does not happen.

A possible mechanism for the dissolution of Ni-Cr-Mo alloys, consistent with the idea of the non-incorporation of Mo in the passive film is:

(1a) $Cr \xrightarrow{K_1^{Cr}} Cr_i^{x+} + V_m + xe'$ (4a) $Cr_i^{x+} \xrightarrow{K_4^{Cr}} Cr^{x+}(aq)$

(1b) $Ni \xrightarrow{K_1^{Ni}} Ni_i^{\delta+} + V_m + \delta e'$ (4b) $Ni_i^{\delta+} \xrightarrow{K_4^{Ni}} Ni^{\delta+}(aq)$

(1c) $Mo \xrightarrow{K_1^{Mo}} Mo_i^{3+} + V_m + 3e'$ (4c) $Mo_i^{3+} \xrightarrow{K_4^{Mo}} Mo^{3+}(aq)$

(2a) $Cr + V_{Cr}^{x'} \xrightarrow{K_2^{Cr}} Cr_{Cr} + V_m + xe'$ (5a) $Cr_{Cr} \xrightarrow{K_5^{Cr}} Cr^{x+} + V_{Cr}^{x'}$

(2b) $Ni + V_{Cr}^{x'} \xrightarrow{K_2^{Ni}} Ni_{Cr}^{\delta-x} + V_m + \delta e'$ (5b) $Ni_{Cr}^{\delta-x} \xrightarrow{K_5^{Ni}} Ni^{\delta+} + V_{Cr}^{x'}$

(3a) $Cr \xrightarrow{K_3^{Cr}} Cr_{Cr} + \frac{x}{2} V_O^{2\cdot} + xe'$ (6) $V_O^{2\cdot} + H_2O \xrightarrow{K_6} O_O + 2H^+$

(3b) $Ni \xrightarrow{K_3^{Ni}} Ni_{Cr}^{\delta-x} + \frac{x}{2} V_O^{2\cdot} + \delta e'$ (7) $[Cr_{1-y} Ni_y O_{\frac{x}{2}}]^{y(\delta-x)} + xH^+ \xrightarrow{K_7} (1-y) Cr^{x+} + y Ni^{\delta+} + \frac{x}{2} H_2O$

$y = \frac{[Ni]}{[Ni]+[Cr]}$ at the film $[X]$ = Molar concentration of substance X.

This scheme does not affect conceptually the ideas developed so far. The current density is modified by the addition of $I_{Mo} = 3F A_{Mo} K_1^{Mo}$ which is a constant.

8/11/99

I found the following interesting fact.

In p. 96 we found $y = \frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}}$

On the other hand $y = \left. \frac{[Ni]}{[Ni]+[Cr]} \right|_{\text{film/solution interface}}$

Assume that rather than working with a local concentration, we interpret y as an average concentration fraction. Then y is a quantity that can be directly measured. From y we may get an estimate of the ratio $\frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr}}$

$\bar{K}_3^{Ni} = y(\bar{K}_3^{Cr} + \bar{K}_3^{Ni})$ $(1-y)\bar{K}_3^{Ni} = y\bar{K}_3^{Cr}$

$$\boxed{\frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr}} = \frac{y}{1-y}}$$

We obtained the equation $y = \frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}}$ by assuming that $\bar{K}_5^{Cr}, \bar{K}_5^{Ni} << \bar{K}_3^{Ni}, \bar{K}_3^{Cr}$

From this assumption it also follows that $\bar{K}_2^{Cr}, \bar{K}_2^{Ni} << \bar{K}_3^{Ni}, \bar{K}_3^{Cr}$ (since $\bar{K}_2^{Cr} + \bar{K}_2^{Ni} = \bar{K}_5^{Cr} + \bar{K}_5^{Ni}$)

What if we assume $y = \frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}}$ but not $\bar{K}_5^{Cr}, \bar{K}_5^{Ni} << \bar{K}_3^{Ni}, \bar{K}_3^{Cr}$?

In other words what are the necessary and sufficient conditions that guarantee $y = \frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}}$?

PROPOSITION: $y = \frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}}$ if and only if $\bar{K}_2^{Cr} = \bar{K}_5^{Cr}$ and $\bar{K}_2^{Ni} = \bar{K}_5^{Ni}$

Proof: From page 66 $\bar{K}_5^{Cr} = \bar{K}_2^{Cr} + (y-1)\bar{K}_3^{Ni} + y\bar{K}_3^{Cr}$

$\bar{K}_5^{Ni} = \bar{K}_2^{Ni} - y\bar{K}_3^{Cr} + (1-y)\bar{K}_3^{Ni}$

IF $y = \frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}}$ then $\bar{K}_5^{Cr} = \bar{K}_2^{Cr}$ and $\bar{K}_5^{Ni} = \bar{K}_2^{Ni}$

Also, if $\bar{K}_5^{Cr} = \bar{K}_2^{Cr}$ then $y = \frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}}$ and $\bar{K}_5^{Ni} = \bar{K}_2^{Ni}$

In other words, Assuming $y = \frac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}}$ is equivalent to assume $\bar{K}_2^{Cr} = \bar{K}_5^{Cr}$ and $\bar{K}_2^{Ni} = \bar{K}_5^{Ni}$

8/11/99

$$\frac{1}{F} I^{F/S} = x\bar{K}_4^{Cr} + \delta \bar{K}_4^{Ni} + x\bar{K}_5^{Cr} + \delta \bar{K}_5^{Ni} + 2\bar{K}_6 + y(\delta - x)\bar{K}_7$$

$$\frac{1}{F} I^{M/F} = x\bar{K}_1^{Cr} + \delta \bar{K}_1^{Ni} + x\bar{K}_2^{Cr} + \delta \bar{K}_2^{Ni} + x\bar{K}_3^{Cr} + \delta \bar{K}_3^{Ni}$$

In order for the two expressions to be equivalent necessarily

$$2\bar{K}_6 + y(\delta - x)\bar{K}_7 = x\bar{K}_3^{Cr} + \delta \bar{K}_3^{Ni}$$

From page 66: $\bar{K}_7 = \bar{K}_3^{Cr} + \bar{K}_3^{Ni}$ and

$$2\bar{K}_6 = x(\bar{K}_3^{Cr} + \bar{K}_3^{Ni})$$

We know (or assume) that $y = \dfrac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}}$

$$2\bar{K}_6 + y(\delta - x)\bar{K}_7 = x(\bar{K}_3^{Cr} + \bar{K}_3^{Ni}) + y(\delta - x)(\bar{K}_3^{Cr} + \bar{K}_3^{Ni})$$

$$= x\bar{K}_3^{Cr} + x\bar{K}_3^{Ni} + (\delta - x)\bar{K}_3^{Ni} = x\bar{K}_3^{Cr} + \delta \bar{K}_3^{Ni}$$ ✓

Consequently, neglecting $\bar{K}_2^{Cr}$, $\bar{K}_2^{Ni}$, the current density can be approximated as $\frac{1}{F} I^{M/F} = x\bar{K}_1^{Cr} + \delta \bar{K}_1^{Ni} + x\bar{K}_3^{Cr} + \delta \bar{K}_3^{Ni}$

or if we include the presence of Mo:

$$\frac{1}{F} I^{M/F} = x\bar{K}_1^{Cr} + \delta \bar{K}_1^{Ni} + 3\bar{K}_1^{Mo} + x\bar{K}_3^{Cr} + \delta \bar{K}_3^{Ni}$$

Under this circumstance, the passive current density is a linear combination of a_{Cr}, a_{Ni}, a_{Mo}. Deviation from linearity may be attributed to several reasons:

- $a_x^{M/F} \neq$ component concentration in the bulk of the alloy
- K_j^x may be also a function of the alloy composition
- The model is certainly wrong! I hope this last choice is not the case.

The choice $y = \bar{K}_3^{Ni} / \bar{K}_3^{Cr} + \bar{K}_3^{Ni}$ simplifies all of the equations. For example:

$$J_{Cr} = \bar{K}_1^{Cr} + \bar{K}_2^{Cr} + \bar{K}_3^{Cr}$$

$$J_{Ni} = \bar{K}_1^{Ni} + \bar{K}_2^{Ni} + \bar{K}_3^{Ni}$$

$$J_{Mo} = \bar{K}_1^{Mo}$$

8/12/99

Evidently $\frac{1}{F} I^{F/S} = \frac{1}{F} I = x J_{Cr} + \delta J_{Ni} + 3 J_{Mo}$

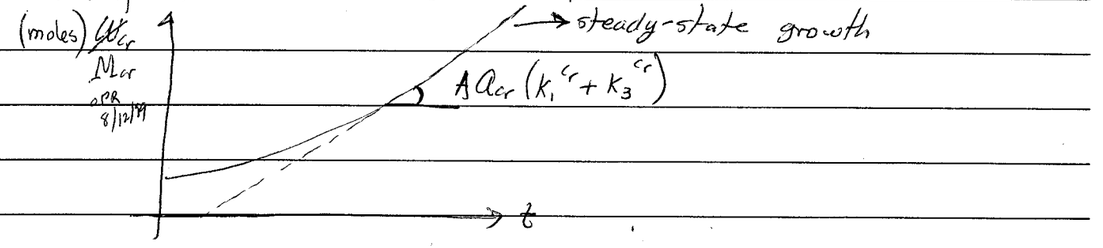
It is a quite straight-forward relationship.

Keep in mind that what simplifies the equations is the equation $y = \dfrac{\bar{K}_3^{Ni}}{\bar{K}_3^{Cr} + \bar{K}_3^{Ni}}$

We have discussed that such equation seems to be valid under the hypothesis that the passive current density is independent of the applied voltage, and also that the potential drop at the film/solution interface is function of the applied voltage (not necessarily a linear function), and that the potential drop at the metal/film interface is constant.

Darrell Dunn has found that the passive current density is quite independent of environmental factors. Effectively, it is not evident, in the expression for the current density, how the environmental elements affect the passive current density.

$$J_{Cr}(\text{Surface}) = \frac{d\,{}^{OPR\ 8/12/99}M_{Cr}}{dt} = \frac{d\,{}^{OPR\ 8/12/99}M_{Cr}}{dt} = (\text{Surface})\, a_{Cr}\left(K_1^{Cr} + K_3^{Cr}\right)$$



The slope is function of the alloy composition

$$y\,a_{cr}\,K_3^{cr} \cong (1-y)\left(K_5^{cr} + a_{Ni}K_3^{Ni}\right) \approx (1-y)\,a_{Ni}K_3^{Ni}$$

$K_3^{cr} = 0 \Rightarrow (y=1,\ \text{or}\ a_{Ni}=0,\ \text{or}\ K_3^{Ni}=0)$

Since $y=1$ or $a_{Ni}=0$ are not possible,

$K_3^{cr}=0 \Rightarrow K_3^{Ni}=0$

$K_3^{Ni}=0 \Rightarrow (y=0,\ a_{cr}=0\ \text{or}\ K_3^{cr}=0)$

$a_{cr}=0$ is not possible, then

$K_3^{Ni}=0 \Rightarrow y=0$ or $K_3^{cr}=0$

It is feasible to have $K_3^{Ni}=0$, $y=0$, and $K_3^{cr}\neq 0$

The worst-case scenario is $K_3^{cr}=K_3^{Ni}=0$. In this case, dissolution is due to the transport of interstitials, which creates vacancies in the metal. The film is always the same, and it can "get old."

We know:

$$K^{Ni} \equiv K_1^{Ni} + K_3^{Ni}$$

$$K^{cr} \equiv K_1^{cr} + K_3^{cr}$$

$$K^{cr} < K^{Ni}$$

$$\frac{y}{1-y}\,\frac{a_{cr}}{a_{Ni}} = \frac{K_3^{Ni}}{K_3^{cr}} \quad \text{assuming } K_3^{cr}\neq 0$$

$$y = \frac{a_{Ni}K_3^{Ni}}{a_{cr}K_3^{cr} + a_{Ni}K_3^{Ni}}$$

$$K_{Ni} = K_1^{Ni} + \frac{y}{1-y}\,\frac{a_{cr}}{a_{Ni}}\,K_3^{cr}$$

$$K_{cr} = K_1^{cr} + K_3^{cr}$$

We have an incomplete system!! Three unknowns (K_1^{Ni}, K_3^{cr}, K_1^{Ni}) and just two equations.

We need to make further assumptions to arrive at numerical data.

There is a subtle step that needs some attention:

From page 66:

$$a_{cr}\,a_{V_{cr}^{x'}}\,K_2^{cr} = \bar{K}_2^{cr} = (1-y)\left(K_5^{cr} + \bar{K}_3^{Ni}\right) - y\,\bar{K}_3^{cr}$$

$$a_{Ni}\,a_{V_{cr}^{x'}}\,K_2^{Ni} = \bar{K}_2^{Ni} = y\left(K_5^{Ni} + \bar{K}_3^{cr}\right) - (1-y)\,a_{Ni}K_3^{Ni}$$

$\bar{K}_2^{cr}$ and $\bar{K}_2^{Ni}$ are potential dependent, unless $K_5^{cr} \ll \bar{K}_3^{Ni}$ and $K_5^{Ni} \ll \bar{K}_3^{cr}$, if so

$$\bar{K}_2^{cr} \approx (1-y)\,\bar{K}_3^{Ni} - y\,\bar{K}_3^{cr} \geq 0$$

$$\bar{K}_2^{Ni} \approx y\,\bar{K}_3^{cr} - (1-y)\,\bar{K}_3^{Ni} \geq 0$$

consequently $(1-y)\,\bar{K}_3^{Ni} - y\,\bar{K}_3^{cr} \approx 0$

Rather than setting $\bar{K}_2^{cr}\approx 0$ and $\bar{K}_2^{Ni}\approx 0$, we can say $\bar{K}_2^{cr} \ll \bar{K}_3^{cr}$ and $\bar{K}_2^{Ni} \ll \bar{K}_3^{Ni}$

I have proved that if $\bar{K}_5^{cr} \ll \bar{K}_3^{Ni}$ and $\bar{K}_5^{Ni} \ll \bar{K}_3^{cr}$, then ($\bar{K}_2^{cr} \ll \bar{K}_3^{cr}$ and $\bar{K}_2^{Ni} \ll \bar{K}_3^{Ni}$)

Since $I = F\left[\chi\left(\bar{K}_1^{cr} + \bar{K}_3^{cr} + \bar{K}_2^{cr}\right) + \delta\left(\bar{K}_1^{Ni} + \bar{K}_3^{Ni} + \bar{K}_2^{Ni}\right) + 3\,\bar{K}_1^{M_0}\right]$

then

$$I \approx F\left[\chi\left(\bar{K}_1^{cr} + \bar{K}_3^{cr}\right) + \delta\left(\bar{K}_1^{Ni} + \bar{K}_3^{Ni}\right) + 3\,\bar{K}_1^{M_0}\right]$$

10/4/99 CPM

The advantage of assuming $\bar{K}_5^{Cr} << \bar{K}_3^{Ni}$ and $\bar{K}_5^{Ni} << \bar{K}_3^{Cr}$ is that we get an expression for y: $y \cong \frac{a_{Ni} k_3^{Ni}}{a_{Cr} k_3^{Cr} + a_{Ni} k_3^{Ni}}$

The description is quite consistant

Note that the same conclusion can be achieved if we assume $\bar{K}_2^{Cr} = (1-y) K_5^{Cr}$, which implies $\bar{K}_2^{Ni} = y K_5^{Ni}$

There is not any reason of why this equation should hold.

Just for curiosity:

$$y = \frac{K_5^{Ni}}{\bar{K}_2^{Ni}} \Rightarrow \bar{K}_2^{Cr} = \left(1 - \frac{K_5^{Ni}}{\bar{K}_2^{Ni}}\right) K_5^{Cr}$$

$$\bar{K}_2^{Cr} = \frac{1}{\bar{K}_2^{Ni}} \left(\bar{K}_2^{Ni} - K_5^{Ni}\right) K_5^{Cr}$$

$$\bar{K}_2^{Cr} \bar{K}_2^{Ni} = \left(\bar{K}_2^{Ni} - K_5^{Ni}\right) K_5^{Cr}$$

$$a_{Cr} a_{Ni} \left(a_{V_{Cr}^{x'}}\right)^2 K_2^{Ni} K_2^{Cr} = \left(a_{Ni} a_{V_{Cr}^{x'}} K_2^{Ni} - K_5^{Ni}\right) K_5^{Cr}$$

It is a quadratic expression on $a_{V_{Cr}^{x'}}$, which can be solved to define $a_{V_{Cr}^{x'}}$ as function of the voltage and a_{Cr}, a_{Ni}. My guess is that such an expression will be inconsistent with other steady-state relationships.

The conclusion here is that there is a point where I need to assume interstitial or oxygen vacancy conduction, or a mixture of both. It is not feasible so far, at least for Cr, to decide who is the main responsible for charge conduction.

10/5/99 CPM

Darrell has reported passive dissolution rates in the range

$\underbrace{5 \times 10^{-9} \frac{A}{cm^2}}_{[Cl^-] = 1\,M}$ to $\underbrace{1.3 \times 10^{-7} \frac{A}{cm^2}}_{[Cl^-] = 0.028\,M}$

pH = 8 pH = 0.7

T = 95°C T = 95°C

Reference: The Passivity of Iron-Chromium Alloys

R. Kirchheim, B. Heine, H. Fischmeister, S. Hofmann, H. Knote and U. Stolz

Corrosion Science, Vol. 29, No 7 pp. 899-917, 1989

Passive current density for Cr: 1.4×10^{-8} A/cm², [0, 1 V_{SHE}]

1N H_2SO_4 at 25°C

Reference: R.F. Steigerwald and N.D. Greene

The anodic dissolution of binary alloys, J. Electrochem. Soc. Vol. 109, No. 11, p. 1026-1034 (1962)

Passive current density for Cr: $\sim 10^{-6}$ A/cm², [-0.4, 0.8 V_{SCE}]

1N H_2SO_4 T=?

Ko Okamoto, Passive Film of 18-8 stainless steel structure and its function

Corrosion Science, 1973, Vol. 13, p.p. 471-489

Passive current density for Cr: $\sim 10^{-7}$ A/cm², [0, 0.8 V_{SCE}]

no environment nor temperature given.

10/5/99 QFY

Effect of Chloride Ion on the Anodic Dissolution Kinetics of Chromium-Nickel Binary Alloys in Dilute Sulfuric Acid
F. G. Hodge and B. E. Wilde
Corrosion - Nace, Vol. 26, No. 6, June 1970 p. 146-150

Passive current density for Cr: 6×10^{-6} A/cm² [-0.2, 0.8 V_{SCE}]
1 N H_2SO_4 at 25°C

NOTE: The applied potential was varied in 65mV increments in the noble direction every three minutes. → not true steady-state.

Diffusion of Chromium in nickel-base Ni-Cr-Fe alloys
Two volume diffusion coefficients are reported for two different steels

$D_V = 4 \times 10^{-4} \exp(-283\ kJ\ mol^{-1}/RT)\ m^2 s^{-1}$

$D_V = 6.5 \times 10^{-4} \exp(-296\ kJ\ mol^{-1}/RT)\ m^2 s^{-1}$

$T \approx 1000$ K → high T experiments. Is it valid to extrapolate the result at lower T?

At least D_V gives us idea of how fast are the processes.

The passive current density for Cr in 1N H_2SO_4 at 25°C has been reported to range from 1.4×10^{-8} A/cm² to 6×10^{-6} A/cm². Almost three orders of magnitude of difference!

Based on this information, we may argue

$I_{Cr} \overset{?}{=} 3F(K_1^{Cr} + K_3^{Cr})$
$\overset{?}{}$

10/5/99 QFY

There is an on-going discussion of who is the main charge carrier in a Cr_2O_3 film. The three opinions are found in the literature: interstitials, oxygen vacancies, and cation vacancies.

If $K_3^{Ni} = 0$, then there would not be any incorporation of Ni_i into the Cr_2O_3 lattice. Since we believe that such incorporation occurs, $K_3^{Ni} \neq 0$.

$K_3^{Ni} \neq 0$, $0 < y < 1$, $a_{Ni} \neq 0 \Rightarrow K_3^{Cr} \neq 0$, according to the results in page 104. Furthermore,

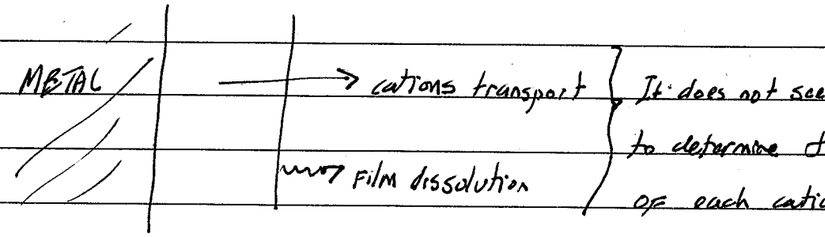
$K_3^{Cr} > K_3^{Ni}$, otherwise, Cr would not be the matrix element in Cr_2O_3, which is clearly a contradiction.

This is a very important conclusion, because of the following reason:

$$\underbrace{a_{Cr} K_3^{Cr} + a_{Ni} K_3^{Ni}}_{\text{rate of film formation}} = \underbrace{K_8 (1-y)^{1-y} y^y (a_{H^+})^n}_{\text{rate of film dissolution}}$$

Therefore, the rate of film dissolution is different from zero. This is the third equation that is missing. Unfortunately, it is practically impossible to measure this rate directly.

10/6/99 QRJ



It does not seem easy to determine the origin of each cation.

Assume L represents the thickness of the film. (cm)

ρ is the film density $\left(\frac{gr}{cm^3}\right)$

r rate of film dissolution $\left(\frac{mol}{s \cdot cm^2}\right)$

M is the molecular weight of the film $\left(\frac{gr}{mol}\right)$

A is the surface (cm^2)

$$\text{mass} = \rho L A$$

$$\text{moles} = \frac{\rho L A}{M}$$

$$\text{time to dissolve the film} = \frac{\frac{\rho L A}{M}}{rA} = \frac{\rho L}{Mr}$$

$$\text{time to dissolve} = \left(\frac{\rho}{M}\right)\frac{L}{r}$$

$\rho_{Cr_2O_3} = 5.21 \frac{gr}{cm^3}$

H. Hindam and D.P. Whittle, J. Electrochem. Soc., Vol 130, (1983) 1519-1523

$$M = 2 \times 51.9961 + 3 \times 15.9996 = 151.991 \frac{gr}{mol}$$

$$\frac{\rho}{M} = 3.43 \times 10^{-2} \frac{mol}{cm^3}$$

10/6/99 QRJ

$L \rightarrow 10-20$ Å, $1-2$ nm

Source: AES Depth profiling of passive overlayers formed on Nickel Alloys
G. Lorang, N. Jallerat, K. Vu Quang and J.-P. Langeron
Surface and Interface Analysis, Vol. 16, 325-330 (1990)

I will assume $L = 1\,nm = 10^{-9}\,m = 10^{-7}\,cm$

$I = 1.3 \times 10^{-7} \frac{A}{cm^2}$ → Darell's data. I will take $I = 10^{-7} \frac{A}{cm^2}$

$F = 9.64867 \times 10^4\ C\,mol^{-1} = 9.64 \times 10^4\ A \cdot s\,Mol^{-1}$

$$\frac{I}{F} = \frac{10^{-7}\ A/cm^2}{F} \simeq 10^{-12} \frac{mol}{cm^2 \cdot s}$$

$$\frac{I}{F} = 3 a_{Cr} (K_1^{Cr} + K_3^{Cr}) + 2 a_{Ni} (K_1^{Ni} + K_3^{Ni}) + 6 a_{Mo} K_1^{Mo}$$

ALLOY 22

$[a_{Cr}] \simeq 21.4\ \%$ Weight percent $\quad f_{Cr} = 21.4 \times 10^{-2}$

$[Mo] = 13.6\ \%$ weight percent $\quad f_{Mo} = 0.136$

$[Ni] =$ balance $\sim 58.2\ \%$ $\quad F_{Ni} = 0.582$

$[Fe] = 3.8\ \%$ $\quad F_{Fe} = 0.038$

$[W] = 3\ \%$ $\quad F_W = 0.03$

ρ (alloy 22) $= 8.69 \frac{gr}{cm^3}$

$$\text{moles}(Cr) = f_{Cr} \rho_{22} V / M_{Cr} \qquad \text{moles}(W) = \frac{f_W \rho_{22} V}{M_W}$$

$$\text{moles}(Mo) = \frac{f_{Mo} \rho_{22} V}{M_{Mo}}$$

$$\text{moles}(Ni) = \frac{f_{Ni} \rho_{22} V}{M_{Ni}} \qquad \text{moles(total)} = \rho_{22} V \sum_i \frac{f_i}{M_i}$$

$$\text{moles}(Fe) = \frac{f_{Fe} \rho_{22} V}{M_{Fe}}$$

$$a_j = \frac{\rho_{22} V \frac{f_j}{M_j}}{\rho_{22} V \sum_i \frac{f_i}{M_i}} = \frac{\frac{f_j}{M_j}}{\sum_i \frac{f_i}{M_i}}$$

10/6/99 OFY

$\frac{f_{Cr}}{M_{Cr}} = \frac{0.214}{51.996} = 4.116 \times 10^{-3}$ mol/gr

$\frac{f_{Mo}}{M_{Mo}} = \frac{0.136}{95.94} = 1.42 \times 10^{-3}$ mol/gr

$\frac{f_{Ni}}{M_{Ni}} = \frac{0.582}{58.69} = 9.9 \times 10^{-3}$ mol/gr

$\frac{f_{Fe}}{M_{Fe}} = \frac{0.038}{55.847} = 6.8 \times 10^{-4}$ mol/gr

$\frac{f_W}{M_W} = \frac{0.03}{183.84} = 1.63 \times 10^{-4}$ mol/gr

$\sum_i \frac{f_i}{M_i} = 1.63 \times 10^{-2}$

$a_{Cr} = \frac{\frac{f_{Cr}}{M_{Cr}}}{\sum_i \frac{f_i}{M_i}} = \frac{4.116 \times 10^{-3}}{1.63 \times 10^{-2}} = 0.2526$

$a_{Mo} = \frac{1.42 \times 10^{-3}}{1.63 \times 10^{-2}} = 0.087$

$a_{Ni} = \frac{9.9 \times 10^{-3}}{1.63 \times 10^{-2}} = 0.6086$

$a_{Fe} = \frac{6.8 \times 10^{-4}}{55.847} = \frac{6.8 \times 10^{-4}}{1.63 \times 10^{-2}} = 0.04176$ (OPR 10/6/99)

$a_W = \frac{1.63 \times 10^{-4}}{1.63 \times 10^{-2}} = 0.01$

Mo went from 13.6 weight % to 8.7 molar %. This is due to the high molecular weight of Mo

10/6/99 OFY

For Alloy 22

$a_{Cr} \approx 0.2526$

$a_{Mo} \approx 0.087$

$a_{Ni} \approx 0.6086$

$\frac{I}{F} = \chi a_{Cr}(K_1^{Cr} + K_2^{Cr}) + \delta a_{Ni}(K_1^{Ni} + K_3^{Ni}) + \xi a_{Mo} K_1^{Mo}$

Assume Mo dissolves congruently with respect to Ni, then

$K_1^{Mo} = K_1^{Ni} + K_3^{Ni}$

Some evidence for this assumption can be found in M. A. Cavanaugh, J. A. Kargol, J. Nickerson, and N. F. Fiore, The Anodic Dissolution of a Ni-Base Superalloy Corrosion-NACE, Vol. 39, No. 4, 1983, p. 144-150

let $K^{Cr} = K_1^{Cr} + K_3^{Cr}$

$K^{Ni} = K_1^{Ni} + K_3^{Ni}$

Assume we use data reported by Kirchheim et. al (page 107) on the passive current density of Cr and postulate

$3FK^{Cr} = 1.4 \times 10^{-8}$ A cm^{-2}

↳ error OPR 1/31/00 ⇒ this error is propagated to comp. in next pages.

$I - 3F K^{Cr} a_{Cr} = 10^{-7} \frac{A}{cm^2} - 3(0.2526)\left(1.4 \times 10^{-8} \frac{A}{cm^2}\right) = 8.939 \times 10^{-8} \frac{A}{cm^2}$

$I - 3F a_{Cr} K^{Cr} = (2a_{Ni} + 6a_{Mo}) K^{Ni} F$

$FK^{Ni} = \frac{8.939 \times 10^{-8} \frac{A}{cm^2}}{(2 \times \underbrace{0.2526}_{0.6086} + 6 \times 0.087)} = \underbrace{8.7 \times 10^{-8} \text{ A cm}^{-2}}_{5.1396 \times 10^{-8} \text{ A cm}^{-2}}$

OPR 10/6/99

10/6/99 CPM

In principle it is possible to determine K^{Cr} and K^{Ni} from electrolyte concentration measurements. Such measurements must be entirely consistent with electrochemical measurements.

There is nothing that forbids interstitial conduction to be zero. However, the only mechanism that I envision for the transport of Mo, without being incorporated into the passive film, is interstitial transport. If Mo can be transported interstitially, I do not see any reason of why Cr and Ni couldn't be transported interstitially.

I will assume $K_1^{Cr} = K_3^{Cr}$ and

$K_1^{Ni} = K_3^{Ni}$

Then $K_1^{Cr} = \frac{1}{2}K^{Cr}$, $K_3^{Cr} = \frac{1}{2}K^{Cr}$

$K_1^{Ni} = \frac{1}{2}K^{Ni}$, $K_3^{Ni} = \frac{1}{2}K^{Ni}$

I do not have any strong justification for the above choice. I will proceed with it to continue with my back of the envelope computations.

$F K_1^{Cr} = F K_3^{Cr} = \frac{1}{2} F K^{Cr} = 7 \times 10^{-9}\ A/cm^2$

$F K_1^{Ni} = F K_3^{Ni} = \frac{1}{2} F K^{Ni} = 43.5 \times 10^{-9}\ A/cm^2$

It is clear that the above numbers are on the verge of electrochemical resolution.

r = rate of film formation and dissolution.

$Fr = F(a_{Cr} K_3^{Cr} + a_{Ni} K_3^{Ni})$

$= (0.2526)(7 \times 10^{-9}\ A\,cm^{-2}) + 0.6086\,(43.5 \times 10^{-9}\ A\,cm^{-2})$

$= 28.2 \times 10^{-9}\ A\,cm^{-2}$

$r = 2.927 \times 10^{-13} \frac{mol}{cm^2 \cdot s}$

time for the film to reform $= \left(\frac{\delta}{M}\right)\frac{L}{r}$

$\frac{\delta}{M} = 3.43 \times 10^{-2} \frac{mol}{cm^3}$, page 110

$L = 10^{-7}$ cm, page 111

$r = 2.927 \times 10^{-13}\ mol\ cm^{-2}\ s^{-1}$

time $= 11,718.21\ s = 3.255$ hr !!

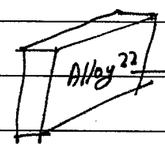
The meaning of this short time, is that anything in the bulk metal will have an immediate impact on the film behavior.

- What is the rate of metal dissolution?
- What is the rate of void volume formation?
- What is the consequence of preferential dissolution?

10/8/99 OPR

Rate of metal dissolution?

Time to deplete the Alloy of N_i?



$V = SL$ $\quad mass = \frac{V \rho}{\rho_{OPR\ 10/8/99}}$ $\quad mass\ N_i = \frac{f_{N_i} V \rho}{\rho_{OPR\ 10/8/99}}$

$moles\ N_i = \frac{mass\ N_i}{M_{N_i}} = \frac{f_{N_i} V \rho}{M_{N_i} \rho_{OPR\ 10/8/99}} = \frac{f_{N_i} S L \rho}{M_{N_i} \rho_{OPR\ 10/8/99}}$

$r_{N_i} = a_{N_i} K^{N_i} = (0.6086) \frac{8.7 \times 10^{-8}\ A\ cm^{-2}}{F}$

$r_{N_i} = 5.4876 \times 10^{-13} \frac{mol}{cm^2 \cdot s}$

$time = \frac{moles\ N_i}{r_{N_i} \cdot S} = \frac{\frac{f_{N_i} S L \rho}{M_{N_i} \rho_{OPR\ 10/8/99}}}{r_{N_i} S} = \frac{f_{N_i} L \rho}{M_{N_i} \rho_{OPR\ 10/8/99} r_{N_i}}$

$f_{N_i} = 0.582$

$time = \frac{0.582\ (2cm)\ 8.69 \frac{gr}{cm^3}}{(58.69 \frac{gr}{mol})(5.49 \times 10^{-13} \frac{mol}{cm^2 \cdot s})} = 314.07 \times 10^7\ s$

$= 87.241 \times 10^6\ hr = 3.635 \times 10^6\ days = 9952.24\ years$

This computation is not accurate. If N_i dissolves preferentially, then the alloy composition changes, and the dissolution rate changes too.

How the prior number compares to our "classical" computations?

$CR = \frac{K\ i_{corr}\ EW}{\rho}$

$EW = 26.04 \frac{gr}{mol}$, $\rho = 8.69 \frac{gr}{cm^3}$, $K = 3,270\ mm\ gr\ A^{-1}\ cm^{-1}\ yr^{-1}$

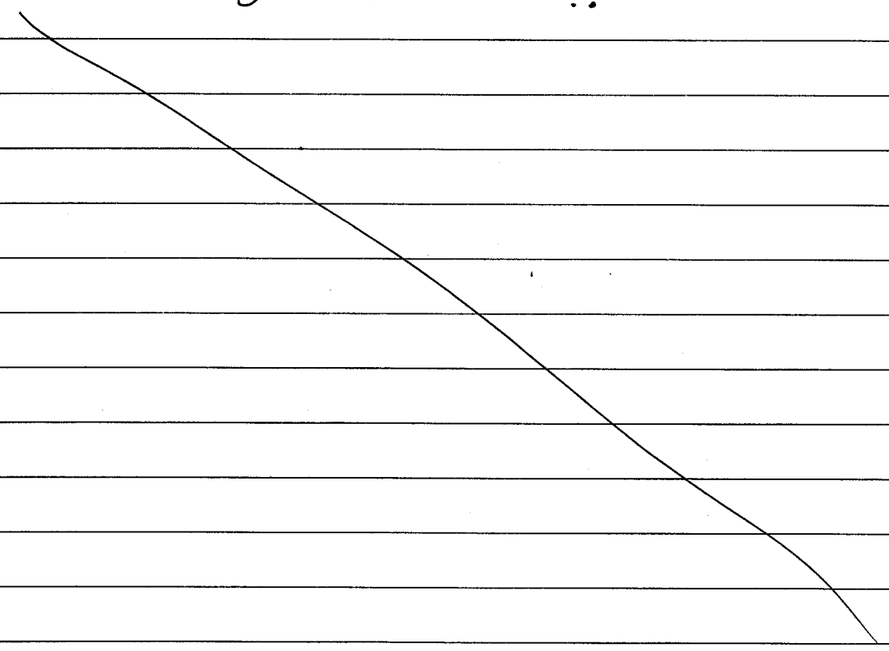
$I = 10^{-7}\ A\ cm^{-2}$ → for this example.

$\frac{(3270\ mm\ gr\ A^{-1}\ cm^{-1}\ yr^{-1})(26.04)}{8.69 \frac{gr}{cm^3}} = 9798.7\ mm\ A^{-1}\ cm^2\ yr^{-1}$

$CR = 10^{-7}\ A\ cm^{-2}\ (9798.7\ mm\ A^{-1}\ cm^2\ yr^{-1}) = 9.7987 \frac{mm}{yr}$

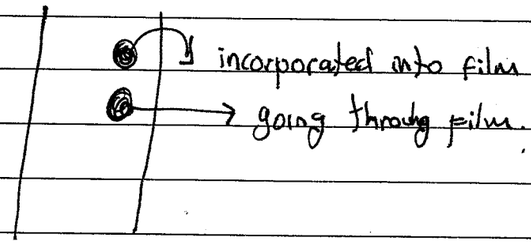
$time = \frac{20\ mm}{CR} = 20,410.84\ yr$

We are overestimating the failure time!!



10/8/99 QFY

Rate of void generation?



Rate of film formation $= a_{Cr} K_3^{Cr} + a_{Ni} K_3^{Ni}$

$= 2.727 \times 10^{-13}$ mol cm^{-2} s^{-1}

Rate of void formation $= a_{Cr} K_1^{Cr} + a_{Ni} K_1^{Ni} + a_{Mo} K_1^{Mo}$

$F K_1^{Mo} = 8.7 \times 10^{-8}$ A cm^{-2}

$F K_1^{Cr} = F K_3^{Cr} = 7 \times 10^{-9}$ A cm^{-2}

$F K_1^{Ni} = F K_3^{Ni} = 43.5 \times 10^{-9}$ A cm^{-2}

$F \times$(Rate of film formation) $= F(0.2526) K_3^{Cr} + 0.6086 F K_3^{Ni}$

$= 1.7682 \times 10^{-9}$ A cm^{-2} $+ 2.6474 \times 10^{-8}$ A cm^{-2}

$= 2.82 \times 10^{-8}$ A cm^{-2}

Rate of film formation $= 2.927 \times 10^{-13} \frac{mol}{cm^2 \cdot s}$

$F \times$(rate of void formation) $= (0.2526) F K_1^{Cr} + (0.6086) F K_1^{Ni}$

$+ (0.087) F K_1^{Mo}$

$= 1.768 \times 10^{-9}$ A cm^{-2} $+ 2.6474 \times 10^{-8}$ A cm^{-2} $+ 7.56 \times 10^{-9}$ A cm^{-2}

$= 3.58 \times 10^{-8}$ A cm^{-2}

rate of void formation $= 3.7 \times 10^{-13} \frac{mol}{cm^2 \cdot s}$

rate of void formation + rate of film dissolution $= 6.64 \times 10^{-13} \frac{mol}{cm^2 \cdot s}$

10/8/99 QFY

Time that takes the film to dissolve:

moles (total) $= \rho_{22} V \sum_i \frac{f_i}{m_i} = \rho_{22} V (1.63 \times 10^{-2}) \frac{mol}{gr}$

$V = 5$ L

$\frac{\text{moles (total)}}{\text{rate}} = \frac{\rho_{22} \cancel{5} L (1.63 \times 10^{-2} \frac{mol}{gr})}{6.64 \times 10^{-13} \frac{mol}{cm^2 \cdot s} \cancel{5}} = 24.54 \times 10^9 \frac{cm^2 s}{g} \rho_{22} L$

$= 213.32 \frac{s}{cm} L = 426.65 \times 10^9$ s $= 118.5 \times 10^6$ hr

$= 4.93 \times 10^6$ d $= 13519.64$ yr ✗

This time should be comparable to the time estimated on page 117, but it is not. It is surprising that these computations do not match.

Note that this should be the dissolution time independently of the occurrence of interstitial or oxygen vacancy conduction. QFR 10/8/99

Average volume of each cation in the alloy:

m = mass

$\frac{m}{\rho_{22}} = Vol$

moles $= m \sum_i \frac{f_i}{M_i}$

average volume $= \frac{Vol}{\#\text{moles}} = \frac{\frac{m}{\rho}}{m \sum_i \frac{f_i}{M_i}} = \frac{1}{\rho_{22} \sum_i \frac{f_i}{M_i}}$

average volume $= \frac{1}{8.69 \frac{gr}{cm^3} (1.63 \times 10^{-2} \frac{mol}{gr})} = (0.141)^{-1} \frac{cm^3}{mol} = 7.0598 \frac{cm^3}{mol}$

10/8/99 AFY

Velocity of the interface?

Rate film formation = rate film dissolution

$= 2.927 \times 10^{-13}$ mol / cm^{-2} s^{-1}

$\rho_{22} \times S$ = Total mass

moles total $= \rho_{22} V \sum_i \frac{f_i}{m_i} = \rho_{22} S \Delta x \sum_i \frac{f_i}{M_i}$

time to dissolve moles in Δx?

time for the interface to move Δx?

$$\text{time} = \frac{\rho_{22} S \Delta x \sum_i \frac{f_i}{m_i}}{\text{rate } S} = \frac{\rho_{22} \Delta x \sum_i \frac{f_i}{M_i}}{\text{rate}}$$

$$\text{velocity of interface} = \frac{\Delta x}{\text{time}} = \frac{\Delta x}{\frac{\rho_{22} \Delta x \sum_i \frac{f_i}{M_i}}{\text{rate}}} = \frac{\text{rate}}{\rho_{22} \sum_i \frac{f_i}{M_i}}$$

Velocity of interface $= \frac{2.927 \times 10^{-13} \text{ mol cm}^{-2} \text{s}^{-1}}{869 \frac{\text{gr}}{\text{cm}^3} \left(1.63 \times 10^{-2} \frac{\text{mol}}{\text{gr}}\right)} =$

$= 2.0664 \times 10^{-12} \frac{\text{cm}}{\text{s}}$

$= 7.4 \times 10^{-9} \frac{\text{cm}}{\text{hr}} = 1.785 \times 10^{-7} \frac{\text{cm}}{\text{d}} = 6.52 \times 10^{-5} \frac{\text{cm}}{\text{yr}}$

Velocity $= 6.52 \times 10^{-4} \frac{\text{mm}}{\text{yr}} = 6.52 \times 10^{-4} \frac{\text{mm}}{\text{yr}}$

The time that it takes the interface to run 20 mm is $\frac{20 \text{ mm}}{6.52 \times 10^{-4} \frac{\text{mm}}{\text{yr}}} = 30,674.84$ yr

This number is greater than the number reported on page 119, as expected.

10/11/99 AFY

These computations are intended to verify that the formula on page 117 is accurate.

On page 112:

$a_{cc} = 0.2526$

$a_{MO} = 0.087$

$a_{Ni} = 0.6086$

$a_{Fe} = 0.04176$

$a_W = 0.01$

Assuming congruent dissolution:

$I = F(5 a_{cc} + 6 a_{MO} + 2 a_{Ni} + 3 a_{Fe} + 6 a_W) K$

$$K = \frac{I}{F(3 a_{cc} + 2 a_{Ni} + 6 a_{MO} + 6 a_W + 3 a_{Fe})} \qquad [K] = \frac{\text{mol}}{\text{cm}^2 \cdot \text{sec}}$$

$$\text{rate}\left(\frac{\text{cm}}{\text{s}}\right) = K \frac{1}{\rho_{22} \sum_i \frac{f_i}{M_i}}$$

$$K = \frac{I}{F(2.68228)} \frac{1}{\rho_{22} \sum_i \frac{f_i}{M_i}} = 7.0598 \frac{\text{cm}^3}{\text{mol}}$$

$$\text{rate}(\text{cm s}^{-1}) = \frac{I}{F}(2.632 \text{ cm}^3 \text{ mol}^{-1}) = I\left(2.72785 \times 10^{-5} \frac{\text{cm}^3}{\text{A} \cdot \text{s}}\right)$$

$I = 10^{-7}$ A cm^{-2}

rate (cm s^{-1}) $= 2.73 \times 10^{-12} \frac{\text{cm}}{\text{s}}$

time ($L = 2$ cm) $= 733.2 \times 10^9$ s $= 203.7 \times 10^6$ hr

$= 8.48 \times 10^6$ d $= 23232.99$ yr → similar to result on page 117.

10/11/99 QFY

If I repeat the computations, but neglect the presence of W and F, the time that I obtain is

$$\text{time}(L = 2\,\text{cm}) = 21\,628.16\ \text{yr}$$

This time is much closer to the time on page 117.

The concern is that by that time, N_i has dissolved completely. I believe that failure can be achieved at a much shorter time.

Evolution in time of alloy composition?

Notation: m = total # of moles

m_i = total # of moles of i

$$a_{Cr} = \frac{m_{Cr}}{m}, \quad a_{Ni} = \frac{m_{Ni}}{m}, \quad a_{Mo} = \frac{m_{Mo}}{m}$$

K^i = rate of dissolution of i, mol cm^{-2} s^{-1}

$$K^{Cr} = K_1^{Cr} + K_3^{Cr}$$

$$K^{Ni} = K_1^{Ni} + K_3^{Ni}$$

$$K^{Mo} = K_1^{Mo}$$

I will neglect, for the moment, the voids generated inside the metal alloy.

$$dm_i = -a_i K^i S\, dt \qquad S = S = \text{surface area}$$

$$dm_i = -\frac{m_i}{m} K^i S\, dt$$

10/11/99 QFY

$$m\, dm_i = -m_i K^i S\, dt$$

$$m = \sum_i m_i$$

$$m \sum_i dm_i = m\, d \sum_i m_i = m\, dm = -\sum_i m_i K^i S\, dt$$

$$m\, dm = -\left(\sum_i m_i K^i\right) S\, dt$$

$$m \frac{dm}{dt} = -\left(\sum_i m_i K^i\right) S$$

$$\frac{dm_i}{dt} = -\frac{m_i}{m} K^i S$$

$$\frac{d^2 m_i}{dt^2} = -\frac{1}{m} S \frac{dm_i}{dt} K^i + \frac{m_i}{m^2} K^i S \frac{dm}{dt}$$

$$m^2 \frac{d^2 m_i}{dt^2} = -m S \frac{dm_i}{dt} K^i + \frac{dm}{dt} S\, m_i K^i$$

$$m \frac{dm_i}{dt} = -m_i K^i S$$

$$m^2 \frac{d^2 m_i}{dt^2} = (K^i S)^2 m_i + S \frac{dm}{dt} m_i K^i$$

adding: $\sum_i$:

$$m^2 \frac{d^2 m}{dt^2} = \sum_i (K^i S)^2 m_i + \frac{dm}{dt}\left(-m \frac{dm}{dt}\right)$$

$$\boxed{m^2 \frac{d^2 m}{dt^2} + m\left(\frac{dm}{dt}\right)^2 = S^2 \sum_i K^{i\,2} m_i}$$

10/11/99

$$m\frac{dm_i}{dt} = -m_i k^i S \qquad \frac{dm_i}{dt} = -\frac{m_i}{m} k^i S$$

$$m\frac{d^2 m_i}{dt^2} + \frac{dm}{dt}\frac{dm_i}{dt} = -k^i S\frac{dm_i}{dt} = S^2 k^{i2}\frac{m_i}{m}$$

$$m^2\frac{d^2 m_i}{dt^2} + m\frac{dm}{dt}\frac{dm_i}{dt} = S^2 k^{i2} m_i$$

Adding $\sum_i$:

$$m^2\frac{d^2 m}{dt^2} + m\left(\frac{dm}{dt}\right)^2 = S^2\sum_i k^{i2} m_i$$

Which is exactly the same equation as the obtained on page 123.

Probably this equation cannot be decoupled. I have reasons to believe that decoupling is impossible.

$$m\frac{dm_i}{dt} = -m_i k^i S \qquad \frac{dm_i}{dt} = -\frac{m_i}{m} k^i S$$

$$m_i(t_{n+1}) = m_i(t_n) + \frac{dm_i}{dt}\Delta t = m_i(t_n) - \frac{m_i(t_n)}{m(t_n)} k^i S\,\Delta t$$

$$m(t_{n+1}) = \sum_i m_i(t_{n+1}) = m(t_n) + -\frac{S}{m(t_n)}\sum_i k^i m_i(t_n)\,\Delta t$$

It should be straightforward to solve the above problem.

$$\text{moles}_i = m_i = \frac{f_i \rho_{22} V}{M_i} = \frac{f_i \rho_{22} L S}{M_i}$$

$\rho_{22} = 8.69\ \frac{gr}{cm^3}$

$\frac{f_{Cr}}{M_{Cr}} = 4.116\times10^{-3}\ mol\,gr^{-1}$

$\frac{f_{Mo}}{M_{Mo}} = 1.42\times10^{-3}\ mol\,gr^{-1}$

$\frac{f_{Ni}}{M_{Ni}} = 9.9\times10^{-3}\ mol\,gr^{-1}$

I will ignore the presence of Fe and W

$$m_o = \sum_i m_i = L S \rho_{22}\sum_i \frac{f_i}{M_i} = L S \rho_{22}\,(0.0154436\ mol\,gr^{-1})$$

ignoring Fe and W

$$m_o = L S (0.13414\ mol\,cm^{-3})$$

In order to avoid the extensive quantities, I will consider

$$\frac{m_o}{S} = (0.13414\ mol\,cm^{-3})\,L = 0.2683\ mol\,cm^{-2} \qquad L = 2\ cm$$

$$\frac{m(t_{n+1})}{S} = \frac{m(t_n)}{S} - \frac{1}{m(t_n)}\sum_i k^i m_i(t_n)\,\Delta t$$

$$\frac{m_i(t_{n+1})}{S} = \frac{m_i(t_n)}{S} - \frac{m_i(t_n)}{m(t_n)} k^i\,\Delta t$$

$$\frac{m_{Cr}(t_0)}{S} = L\rho_{22}\,(4.116\times10^{-3}\ gr\,cm^{-3}) = 0.07153608\ mol\,cm^{-2}$$

$$\frac{m_{Mo}(t_0)}{S} = 0.0246796\ mol\,cm^{-2}$$

$$\frac{m_{Ni}(t_0)}{S} = 0.172062\ mol\,cm^{-2}$$

10/11/99 QAJ

On page 113: $FK^{Cr} = 1.4 \times 10^{-8}$ A cm^{-2}

$FK^{Ni} = 8.7 \times 10^{-8}$ A cm^{-2}

$FK^{Mo} = 8.7 \times 10^{-8}$ A cm^{-2}

10/16/99 QAJ

I did a mistake on page 113:

$FK^{Cr} = 1.4 \times 10^{-8}$ A cm^{-2}

$FK^{Ni} = 5.1356 \times 10^{-8}$ A cm^{-2}

$FK^{Mo} = 5.1356 \times 10^{-8}$ A cm^{-2}

12/7/99 QAJ

Paper QQ1.5, Fall 99 MRS meeting

Analysis of dry storage temperature limits for zircalloy-clad spent nuclear fuel.

Troy A. Hayes, Univ. of Califoria, San Diego, Dept of Mechanical and Aerospace Engineering tahayes@ucsd.edu

Hayes mentioned the presence of vacancies (voids) in the cladding. The voids age generated by creep, and change the mechanical properties of the materials. The author reported an equation to compute the time to fracture. Certainly the materials were subjected to stress. The parameters to be plugged in the equation are ill defined and the time to fracture is quite sensitive of minor variations in the parameters.

Reference:

Cavity formation and metallurgical changes induced by growth of oxide scale. H. E. Evans, Materials Science and Technology, Vol. 4, 1089 (1988)

This is an excellent paper. It proposes that the oxide forms into the metal by annihilation of vacancies at the metal/oxide interface. This is completely consistent with Macdonald's model:

$$A \longrightarrow A^{x+} + xe' + V_m$$

$$V_m \longrightarrow V_A^{x'} + \frac{x}{2} V_O^{2\cdot} \quad \rightarrow \text{annihilation of the vacancy}$$

$$V_A^{x'} + A^{x+} \longrightarrow A_A$$

$$A \longrightarrow A_A + \frac{x}{2} V_O^{2\cdot} + xe' \quad \rightarrow \text{oxide formation}$$

The mechanism is consistent with Evans' ideas

1/28/2000

Reference MRS Fall 99,
Analysis of Dry Storage Temperature Limits for Zircaloy-Clad Spent Nuclear Fuel.
T.A. Hayes, R.S. Rosen, M.E. Kassner, and K.S. Vecchio.

$$\delta D_{gb} = 4.2^{+5.9}_{-2.5} \times 10^{-13} e^{\frac{-167 \pm 7 \text{ KJ mol}^{-1}}{RT}} \quad m^2 s^{-1}$$

Cavity spacing = 0.1 - 0.2 μm
These parameters seem to be valid for zircaloy.

Reference:
Intergranular fracture at elevated temperature
Rishi Raj and M.F. Ashby
Acta Metallurgica, Vol. 23, June 1975

Time to rupture

Information potentially subject to copyright protection was redacted from this location. The redacted material, equations, is from the reference listed directly above this statement.

γ — surface free energy per unit area of the matrix material
r → radius of curvature of the void surface.
ρ → number of voids per cm^2

Parameters needed for Alloy 22
$r, \gamma, \rho, \sigma_{ys}$
We may choose σ_{ys} as the yield strength.

Before proceeding further, I will try to compute the vacancy concentration in the alloy, and its evolution in time

1/31/00

Estimate of the rate constants for two extreme values of the passive current density for alloy 22.

Dakath: d:\osvaldo\CLSTic-22\rate constants.xls			
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide
rho_c22	8.69	gr/cm^3	Density of Alloy 22
F	9.65E+04	C/mol	Faraday's constant
I_22	5.00E-09	A/cm^2	Passive current density for Alloy 22, from 5x10^{-9} A/cm^2 to 1.3x10-7 A/cm^2
ICr	1.40E-08	A/cm^2	Passive current density for Cr, page 113 of Scientific Notebook 304: 1.4x10^{-8} A/cm^2
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22
ESTIMATED RATE CONSTANTS			
kCr	4.83659E-14	mol/(s cm^2)	**k1Cr**
kNi	8.72157E-15	mol/(s cm^2)	**k3Cr**
kMo	8.72157E-15	mol/(s cm^2)	k1Ni
			k3Ni

Dakath: d:\osvaldo\CLSTic-22\rate constants.xls			
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide
rho_c22	8.69	gr/cm^3	Density of Alloy 22
F	9.65E+04	C/mol	Faraday's constant
I_22	1.30E-07	A/cm^2	Passive current density for Alloy 22, from 5x10^{-9} A/cm^2 to 1.3x10-7 A/cm^2
ICr	1.40E-08	A/cm^2	Passive current density for Cr, page 113 of Scientific Notebook 304: 1.4x10^{-8} A/cm^2
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22
ESTIMATED RATE CONSTANTS			
kCr	4.83659E-14	mol/(s cm^2)	Assuming k1Cr = k3Cr and kMo=kNi
kNi	7.53589E-13	mol/(s cm^2)	**k1Cr**
kMo	7.53589E-13	mol/(s cm^2)	**k3Cr**
			k1Ni
			k3Ni

2.42E-14	mol/(s cm^2)	Assuming k1Cr = k3Cr and kMo=kNi
2.42E-14	mol/(s cm^2)	
7.52E-13	mol/(s cm^2)	Necessarily k3Cr > k3Ni
1.12E-15	mol/(s cm^2)	

These tables have a mistake. See page 133

opk 2/1/00

1/31/00

The main assumptions in the computation of the numbers on page 130 is that M_o dissolves congruently with respect to N_i; i.e., $K_1^{M_o} = K_1^{N_i} + K_2^{N_i}$.

The assumption $y = 0.1$ is needed to guarantee that $K_3^{Cr} > K_3^{N_i}$

I have implemented a set of equations on page 125 for the computation of the number of particles in the alloy. From the number of particles, the molar fraction follows.

Moles in the system = moles = $\rho_{22} V \sum_i \frac{f_i}{M_i}$

$V = LS$ $L = 2$ cm $S \rightarrow$ surface area

$\frac{V}{\text{moles}}$ = volume per mol = $\frac{1}{\rho_{22} \sum_i \frac{f_i}{M_i}} = \hat{v}$, specific volume.

$\frac{L}{\text{moles}} = \hat{l}$ = specific length = $\frac{1}{S \rho_{22} \sum_i \frac{f_i}{M_i}}$

On page 125 we had

$$\frac{m_j(t_{n+1})}{S} = \frac{m_j(t_n)}{S} - \frac{m_j(t_n)}{m(t_n)} \left(K_j^{Inst} + K_j^{film}\right) \Delta t$$

$$\frac{m(t_{n+1})}{S} = \frac{m(t_n)}{S} - \frac{1}{m(t_n)} \sum_j K_j\, m_j(t_n)\, \Delta t$$

$K_j^{inst} = K_j^1$ (K_1^{Cr} or $K_1^{N_i}$) or $K_1^{M_o}$)

$K_j^{film} = K_3^j$ (K_3^{Cr} or $K_3^{N_i}$)

1/31/00 QPY

The method on page 131 is a first order method.
let us improve the integration order

γ $f(x+h) = f(x) + h'f'(x) + \frac{1}{2}f'' h^2 + \frac{1}{6}f''' h^3 + O(h^3)$

β $f(x-h) = f(x) - h'f'(x) + \frac{1}{2}f'' h^2 - \frac{1}{6}f''' h^3 + O(h^3)$

α $f(x-2h) = f(x) - 2hf' + 2f'' h^2 - \frac{2^3}{2\cdot 3}f''' h^3 + O(h^3)$

$2\alpha + \frac{1}{2}\beta + \frac{1}{2}\gamma = 0 \rightarrow 4\alpha + \beta + \gamma = 0$

$-\frac{4}{3}\alpha - \frac{1}{6}\beta + \frac{1}{6}\gamma = 0 \rightarrow -8\alpha - \beta + \gamma = 0$

let $\beta = 1 \Rightarrow \begin{cases} 4\alpha + \gamma = -1 \\ -8\alpha + \gamma = 1 \end{cases} \Rightarrow 12\alpha = -2$

$\alpha = -\frac{1}{6}$

$\gamma = -1 - 4\alpha = -1 + \frac{4}{6} = -\frac{2}{6} = -\frac{1}{3}$

$\beta = 1, \quad \alpha = -\frac{1}{6} \quad \gamma = -\frac{1}{3}$

$\beta = 6, \quad \alpha = -1 \quad \gamma = -2 \qquad -2, 6, -1$

$-2f(x+h) + 6f(x-h) - f(x-2h)$

$= -2f(x) + (5)f(x) + (-2 - 6 + 2)f'h + O(h^3)$

$-2f(x+h) + 6f(x-h) - f(x-2h) = 3f(x) - 6f'(x)h + O(h^3)$

Thus $f(x+h) = \frac{1}{2}\left[-3f(x) + 6f(x-h) - f(x-2h) + 6f'(x)h\right]$

$f(x+h) = \frac{1}{2}\left[-3f(x) + 6f(x-h) - f(x-2h)\right] + 3f'(x)h + O(h^3)$

I found that this method is highly unstable, and it is not worthwhile to implement it numerically. The reason is that given $f'(x)$, the above formula does not guarantee that $f(x+h) < f(x)$

If $f'(x) = 0$, it is not necessarily true that $f(x+h) = f(x)$

The first order method is much better in this sense.

2/1/00 QPY

I found an error on both tables on page 130. I had concluded before that Ni dissolves preferentially over Cr. However, on both tables on page 130

$K_{Cr} > K_{Ni}$

which implies that Cr dissolves preferentially. This is an inconsistency.

Assume I_L is the lowest possible current density for Alloy 22 in the system.

$I_L = a_{Cr} I_{Cr} + F\left[\delta a_{Ni} K^{Ni} + 3 a_{Mo} K^{Mo}\right]$

$I_L = a_{Cr} F x K^{Cr} + F\left[\delta a_{Ni} K^{Ni} + 3 a_{Mo} K^{Mo}\right]$

Assume $K^{Ni} = K^{Mo}$

$I_L = a_{Cr} F x K^{Cr} + F K^{Ni}\left[\delta a_{Ni} + 3 a_{Mo}\right]$

$K^{Ni} = \dfrac{I_L - a_{Cr} I_{Cr}}{F(\delta a_{Ni} + 3 a_{Mo})} > K^{Cr}$

$I_L > F(\delta a_{Ni} + 3 a_{Mo}) K^{Cr} + a_{Cr} F x K^{Cr}$

$K^{Cr} < \dfrac{I_L}{F(\delta a_{Ni} + 3 a_{Mo} + x a_{Cr})}$

Substituting $I_L = 5\times10^{-9}$ A/cm² and the molar fractions for Alloy 22 (assuming that only Ni, Cr, and Mo are present in the system) yields

$I_{Cr} = x F K^{Cr} \leq 6.00708\times10^{-9}$ A/cm²

I will set $I_{Cr} = 6\times10^{-9}$ A/cm²

2/1/00 AFY

I have shown that $K_3^{Cr} > 0$. Otherwise, it is not possible the formation of a Cr_2O_3 film. On the other hand, nothing forbids $K_1^{Cr} = 0$. This will imply that conduction in Cr_2O_3 on Cr is due to oxygen vacancies. I do not have a strong argument to depend this situation, but it is worthwhile to explore this possibility.

$$\hat{v} = \frac{1}{\rho_{22} \sum_j \frac{f_j}{M_j}} = 7.448 \ \frac{cm^3}{mol}$$ } assuming only Ni, Cr, Mo in the system

Dakath: d:\osvaldo\CLSTic-22\rate constants.xls

rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide			
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide			
rho_c22	8.69	gr/cm^3	Density of Alloy 22			
F	9.65E+04	C/mol	Faraday's constant			
I_22	5.00E-09	A/cm^2	Passive current density for Alloy 22, from 5x10^{-9} A/cm^2 to 1.3x10-7 A/cm^2			
ICr	6.00E-09	A/cm^2	Passive current density for Cr, page 113 of ~~Scientific Notebook 304: 1.4x10^{-8} A/cm^2~~ Assumed			
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22			
ESTIMATED RATE CONSTANTS						
kCr	2.07282E-14	mol/(s cm^2)		**k1Cr**	1.04E-14	mol/(s cm^2)
kNi	2.07634E-14	mol/(s cm^2)		**k3Cr**	1.04E-14	mol/(s cm^2)
kMo	2.07634E-14	mol/(s cm^2)		k1Ni	2.03E-14	mol/(s cm^2)
				k3Ni	4.78E-16	mol/(s cm^2)
					1	

LOWER

Assumed

Dakath: d:\osvaldo\CLSTic-22\rate constants.xls

rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide			
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide			
rho_c22	8.69	gr/cm^3	Density of Alloy 22			
F	9.65E+04	C/mol	Faraday's constant			
I_22	5.00E-09	A/cm^2	Passive current density for Alloy 22, from 5x10^{-9} A/cm^2 to 1.3x10-7 A/cm^2			
ICr	6.00E-09	A/cm^2	Passive current density for Cr, page 113 of ~~Scientific Notebook 304: 1.4x10^{-8} A/cm^2~~ Assumed			
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22			
ESTIMATED RATE CONSTANTS						
kCr	2.07282E-14	mol/(s cm^2)		**k1Cr**	1.04E-14	mol/(s cm^2)
kNi	7.65631E-13	mol/(s cm^2)		**k3Cr**	1.04E-14	mol/(s cm^2)
kMo	7.65631E-13	mol/(s cm^2)		k1Ni	7.65E-13	mol/(s cm^2)
				k3Ni	4.78E-16	mol/(s cm^2)
					1	

Upper

Dakath: d:\osvaldo\CLST\c-22\rate constants.xls							1.56184E-07	U3
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide					
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide					
rho_c22	8.69	gr/cm^3	Density of Alloy 22					
F	9.65E+04	C/mol	Faraday's constant					
I_22	1.30E-07	A/cm^2	Passive current density for Alloy 22, from 5×10^{-9} A/cm^2 to 1.3×10-7 A/cm^2					
ICr	1.40E-08	A/cm^2	Passive current density for Cr, page 113 of Scientific Notebook 304: 1.4×10^{-8} A/cm^2					
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22					
ESTIMATED RATE CONSTANTS			kCr=k1Cr+k3Cr					
kCr	4.83659E-14	mol/(s cm^2)	**k1Cr**	0	mol/(s cm^2)	Assuming k1Cr = 0 and kMo=kNi		
kNi	7.53589E-13	mol/(s cm^2)	**k3Cr**	4.83659E-14	mol/(s cm^2)			
kMo	7.53589E-13	mol/(s cm^2)	k1Ni	7.51359E-13	mol/(s cm^2)	Necessarily k3Cr > k3Ni, but kCr<k1Ni+k3Ni		
			k3Ni	2.23039E-15	mol/(s cm^2)	1		

Dakath: d:\osvaldo\CLST\c-22\rate constants.xls							1.56184E-07	U4
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide					
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide					
rho_c22	8.69	gr/cm^3	Density of Alloy 22					
F	9.65E+04	C/mol	Faraday's constant					
I_22	1.30E-07	A/cm^2	Passive current density for Alloy 22, from 5×10^{-9} A/cm^2 to 1.3×10-7 A/cm^2					
ICr	1.40E-08	A/cm^2	Passive current density for Cr, page 113 of Scientific Notebook 304: 1.4×10^{-8} A/cm^2					
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22					
ESTIMATED RATE CONSTANTS			kCr=k1Cr+k3Cr					
kCr	4.83659E-14	mol/(s cm^2)	**k1Cr**	2.4183E-14	mol/(s cm^2)	Assuming k1Cr = 0 and kMo=kNi		
kNi	7.53589E-13	mol/(s cm^2)	**k3Cr**	2.4183E-14	mol/(s cm^2)			
kMo	7.53589E-13	mol/(s cm^2)	k1Ni	7.52474E-13	mol/(s cm^2)	Necessarily k3Cr > k3Ni, but kCr<k1Ni+k3Ni		
			k3Ni	1.1152E-15	mol/(s cm^2)	1		

Turned to QA records on 5/1/00

2/1/00

Dakath: d:\osvaldo\CLST\c-22\rate constants.xls							6.00708E-09	L2
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide					
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide					
rho_c22	8.69	gr/cm^3	Density of Alloy 22					
F	9.65E+04	C/mol	Faraday's constant					
I_22	5.00E-09	A/cm^2	Passive current density for Alloy 22, from 5×10^{-9} A/cm^2 to 1.3×10-7 A/cm^2					
ICr	6.00E-09	A/cm^2	~~Passive current density for Cr, page 113 of Scientific Notebook 304: 1.4×10^{-8} A/cm^2~~ Assumed					
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22					
ESTIMATED RATE CONSTANTS								
kCr	2.07282E-14	mol/(s cm^2)	**k1Cr**	0	mol/(s cm^2)	Assuming k1Cr = 0 and kMo=kNi		
kNi	2.07634E-14	mol/(s cm^2)	**k3Cr**	2.07282E-14	mol/(s cm^2)			
kMo	2.07634E-14	mol/(s cm^2)	k1Ni	1.98075E-14	mol/(s cm^2)	Necessarily k3Cr > k3Ni, but kCr<k1Ni+k3Ni		
			k3Ni	9.55882E-16	mol/(s cm^2)	1		

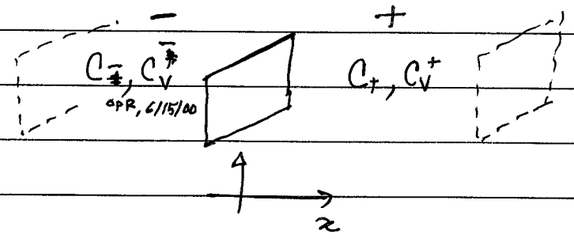
2/1/00

Dakath: d:\osvaldo\CLST\c-22\rate constants.xls							1.56184E-07	U2
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide					
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide					
rho_c22	8.69	gr/cm^3	Density of Alloy 22					
F	9.65E+04	C/mol	Faraday's constant					
I_22	1.30E-07	A/cm^2	Passive current density for Alloy 22, from 5×10^{-9} A/cm^2 to 1.3×10-7 A/cm^2					
ICr	6.00E-09	A/cm^2	~~Passive current density for Cr, page 113 of Scientific Notebook 304: 1.4×10^{-8} A/cm^2~~ Assumed					
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22					
ESTIMATED RATE CONSTANTS								
kCr	2.07282E-14	mol/(s cm^2)	**k1Cr**	0	mol/(s cm^2)	Assuming k1Cr = 0 and kMo=kNi		
kNi	7.65631E-13	mol/(s cm^2)	**k3Cr**	2.07282E-14	mol/(s cm^2)			
kMo	7.65631E-13	mol/(s cm^2)	k1Ni	7.64675E-13	mol/(s cm^2)	Necessarily k3Cr > k3Ni, but kCr<k1Ni+k3Ni		
			k3Ni	9.55882E-16	mol/(s cm^2)	1		

6/15/00 QPR

I presented my work at the MRS conference in the last week in April. One of the criticisms is that my model does not account for the finite time that it takes for the vacancies to diffuse into the bulk metal.

I will try to correct this limitation, without spending a lot of time. The first question to answer is what is it the constitutive equation for the diffusion of vacancies?



$C_{-,+}$ represents the concentration of components in the $-,+$ region.
$C_V^{-,+}$ " " " " vacancies " " " "
The regions are infinitesimal regions.

The flux is then

$$J = \Xi\left(C_- C_V^+ - C_+ C_V^-\right)$$

jump forward is proportional to C_-, and the vacancies in $+$, C_V^+. 6/15/00 QPR

Analogously, jump backward: proportional to C_+, and the vacancies in $-$, C_V^-.

$$C_- C_V^+ - C_+ C_V^- = C_- C_V^+ - C_- C_V^- + C_V^- C_- - C_+ C_V^-$$
$$= C_-\left(C_V^+ - C_V^-\right) + C_V^-\left(C_- - C_+\right)$$
$$= -C_V^- \nabla C\, \Delta x + C_- \nabla C_V\, \Delta x$$

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This suggests that the constitutive equation for component transport is of the form

$$J = \left(\Xi'\left(-C_V \nabla C + C \nabla C_V\right)\right.$$

In the limit when $C_V = C_V^\circ$ = constant, we have

$$J = -\Xi' C_V^\circ \nabla C$$

which must be equivalent to

$$J = -D \nabla C$$ QPR 6/16/00, consequently

$$\Xi' C_V^\circ = D \Rightarrow \Xi' = \frac{D}{C_V^\circ}$$

The constitutive equation for the transport of solid state components under the presence of vacancies is

$$J = -\frac{D}{C_V^\circ}\left(C_V \nabla C - C \nabla C_V\right) \qquad (1)$$

The above equation is perfectly symmetrical. It differs from the equation by L. Zhang in

Electrochimica Acta, Vol 43, No. 18, pp. 2673-2685, 1998 QPR 6/16/00

There he proposes

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In this last equation, when $C_V \to \infty$, $J \to -D \nabla C_V$, which is pure solid-state diffusion. This approach or conclusion is incorrect. If C_V is large, then the solid state components have more room to move around, and diffusion must be enhanced.

From the mathematical point of view, vacancies and solid-state particles are equivalent. This equivalence is captured by the symmetry of Equation (1). On the other hand, Equation (2) is non-symmetric, which suggests that the transport of vacancies is mathematically different to the transport of particles.

6/16/00 QAJ

I cannot see what is that difference.

I expect the transport equation to be symmetrical. It is a situation similar to the transport of electrons and holes in semiconductors. Once an electron is promoted from the valence band into the conduction band, a hole is left in the conduction band. Mathematically speaking, electrons and holes are equivalent, and thus the transport laws are similar. 6/16/00 QAJ
In the same line of reasoning, particles and vacancies are mathematically equivalent, and thus the transport constitutive equations must be equivalent.

Constitutive equation

$$J = -\frac{D}{C_V^\circ}\left(C_V \nabla C - C \nabla C_V\right)$$

$$J_{Cr} = -\frac{D^{Cr}}{C_V^\circ}\left(C_V \nabla C_{Cr} - C_{Cr} \nabla C_V\right)$$

$$J_{Ni} = -\frac{D^{Ni}}{C_V^\circ}\left(C_V \nabla C_{Ni} - C_{Ni} \nabla C_V\right)$$

$$J_{Mo} = -\frac{D^{Mo}}{C_V^\circ}\left(C_V \nabla C_{Mo} - C_{Mo} \nabla C_V\right)$$

$$J_V = -\frac{D^{Ni}}{C_V^\circ}\left(C_{Ni} \nabla C_V - C_V \nabla C_{Ni}\right) - \frac{D^{Cr}}{C_V^\circ}\left(C_{Cr} \nabla C_V - C_V \nabla C_{Cr}\right) - \frac{D^{Mo}}{C_V^\circ}\left(C_{Mo} \nabla C_V - C_V \nabla C_{Mo}\right)$$

$$J_V = -\frac{1}{C_V^\circ}\left(D^{Ni} C_{Ni} + D^{Cr} C_{Cr} + D^{Mo} C_{Mo}\right)\nabla C_V + \frac{C_V}{C_V^\circ}\left(D^{Ni} \nabla C_{Ni} + D^{Cr} \nabla C_{Cr} + D^{Mo} \nabla C_{Mo}\right)$$

→ Vacancy flux

As boundary condition we have

$$J_V = -\left(K_i^{Cr} a_{Cr} + K_i^{Ni} a_{Ni} + K_i^{Mo} a_{Mo}\right)$$

$$a_{Cr} = \frac{C_{Cr}}{\sum C_i} \qquad a_{Ni} = \frac{a_{Ni}}{\sum C_i} \qquad a_{Mo} = \frac{a_{Mo}}{\sum C_i}$$

$$\frac{\partial C_V}{\partial t} = -\nabla \cdot J_V$$

$$\sum C_i + C_V = C_T = \text{constant} \rightarrow \text{assumption.}$$

It seems that solving the whole diffusion problem at once is going to be quite complicated. I need to make some simplifying assumptions to latter see if a better approach can be accomplished.

Assumption: $D^{Ni} \simeq D^{Cr} \simeq D^{Mo} = D$

Then $J_V = -\frac{D}{C_V^\circ}\left(\sum C_i\right)\nabla C_V + \frac{C_V}{C_V^\circ} D \nabla \sum C_i$

$\sum_i C_i + C_V = C_T = \text{constant} \rightarrow$ assumption

$\Rightarrow \sum_i C_i = C_T - C_V$

$\nabla \sum_i C_i + \nabla C_V = 0 \Rightarrow \nabla \sum_i C_i = -\nabla C_V$

$$J_V = -\frac{D}{C_V^\circ}\left(C_T - C_V\right)\nabla C_V - \frac{C_V}{C_V^\circ} D \nabla C_V = -\frac{D}{C_V^\circ} C_T \nabla C_V$$

So complex for this!

$$J_V = -\left(\frac{D}{C_V^\circ} C_T\right)\nabla C_V = -D^{eff} \nabla C_V$$

This limit makes sense, and can only be guaranteed with my symmetric equation (1) on page 139.

$$\frac{dC_V}{dt} = -\nabla \cdot J_V = D^{eff} \nabla^2 C_V$$

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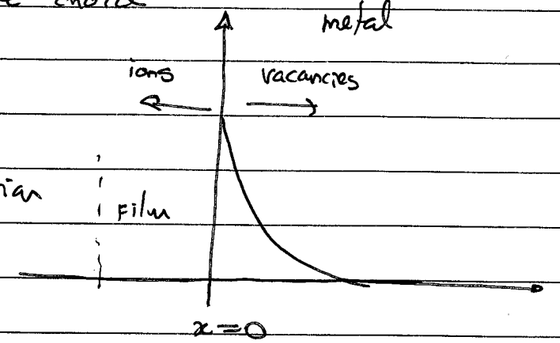
Coordinate choice



$J_v(x=0)$ is given, as function of a_i and constants

$C_v = C_v(x, t)$

$t=0 \quad J_v^\circ = J_v(x=0)$ is known

$-D^{eff} \nabla C_v = J_v^\circ \qquad \nabla C_v = \frac{-C_v(0,0) + C_v(1,0)}{\Delta x}$

$+\frac{D^{eff}}{\Delta x}\left(C_v(0,0) - C_v(1,0)\right) = J_v^\circ$ (6/16/00 OPR)

$\Rightarrow C_v(1,0) = -J_v^\circ \frac{\Delta x}{D} + C_v(0,0) \rightarrow C_v(1,0) < 0$! (could be; conceptual)

At time 0, there is no gradient!

I see that this boundary condition is not adequate.

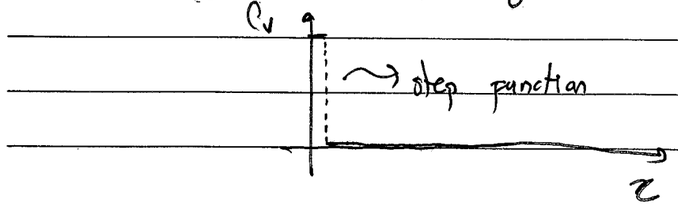
After Δt, C_v° vacancies are injected to the metal.

$J_v^\circ \frac{\Delta t}{L} = C_v^\circ$ (6/16/00 OPR)

$L \rightarrow$ one or two monolayers $= \Delta x$

$C_v^\circ = J_v^\circ \frac{\Delta t}{\Delta x}$

We have the following situation, at $t = \Delta t$



6/16/00

Notation

$C_{k,\ell} = C_v(x = x_k, t = t_\ell)$

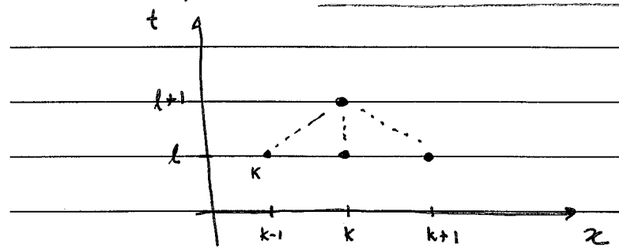
$\left.\frac{\partial C}{\partial t}\right|_{k,\ell} \approx \frac{C_{k,\ell+1} - C_{k,\ell}}{\Delta t}$ (6/16/00 OPR)

$\left.\frac{\partial^2 C}{\partial x^2}\right|_{k,\ell} \approx \frac{C_{k-1,\ell} - 2C_{k,\ell} + C_{k+1,\ell}}{(\Delta x)^2}$

If we define $\lambda = \Delta t / \Delta x^2$, then ; Caution!! λ must be dimensionless

$C_{k,\ell+1} = \lambda C_{k-1,\ell} + (1-2\lambda) C_{k,\ell} + \lambda C_{k+1,\ell}$

↳ dimensionless λ



At time $\ell+1$, the vacancy concentration at $x=0$ can be computed as

$C_{0,\ell+1} = C_{0,\ell} - \sum_{i=1}^{N} C_{i,\ell+1} + J_v^\circ \frac{\Delta t}{\Delta x}$ ⇒ only valid for $\ell = 0$

the sum is going to underestimate ⇒ an integral is needed!

Vacancies that have moved:

$\eta(x=1,\infty) = A \int_{x=x_1}^{\infty} C_v(x)\, dx$

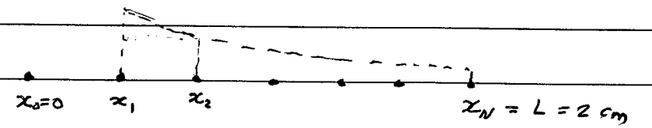
At any time, the number of vacancies at $x = x_0 = 0$ can be computed as

$\text{vacancies}(x=0,\ t=t_{\ell+1}) = \text{total vacancies injected from } t=0 \text{ to } t=t_{\ell+1}$ (6/16/00 OPR)

$- A \int_{x=x_1}^{\infty} C_v(\eta, t=t_\ell)\, d\eta$

6/16/00

Integration algorithm:



$$\int_{x_1}^{L} C_v(\eta,t)\,d\eta \overset{OPR}{\simeq} \cancel{\tfrac{1}{2}(x_1+x_2)} \tfrac{1}{2}(C_{1,t}+C_{2,t})\Delta x + \tfrac{1}{2}(C_{2,t}+C_{3,0})\Delta x + \cdots + \tfrac{1}{2}(C_{N-1}+C_N)\Delta x$$

$$\simeq \tfrac{1}{2}\Delta x\,(C_{1,t} + 2C_{2,t} + 2C_{3,t} + \cdots + 2C_{N-1,t} + C_{N,t})$$

I do not think that it will be necessary to use a higher order integration formula, but we'll see.

What about the boundary condition?

Note that $A\int_{x_1}^{L} C_v(\eta,t)\,d\eta \leq$ # vacancies injected from $t=0$ to $t=t$

It is important for the above condition to be fulfilled.

It would not make sense otherwise.

It should not be very difficult to incorporate the case where the oxide grows into the film. THIS IS IN ESCENCE VACANCY DESTRUCTION. We can incorporate the concept of vacancy destruction, but I will do that at a later stage.

$$J_v(0,t) = \frac{1}{m(0,t)}\left(K_i^{Cr} m_{Cr} + K_i^{N_i} m_{N_i} + K_i^{M_o} m_{M_o}\right)$$

m_i represents moles of i

$$m = \sum_j m_j$$

6/16/00

$$C_v(0,t) = J_v(0,0)\,\Delta t/\Delta x$$

$$C_v + \sum_i C_i = C_T = \text{constant}$$

$$\sum C_i = C_T - C_v$$

$$\cancel{C_{N_i}(0,\Delta t) = C_{N_i}(0,0) - K_i^{N_i}\frac{m_{O_i}}{m}(0,0)\,\Delta t/\Delta x}$$ OPR 6/16/00

$$J_{o,t} = \frac{1}{m_{O,t}}\left(K_i^{Cr} m_{O,t}^{Cr} + K_i^{N_i} m_{O,t}^{N_i} + K_i^{M_o} m_{O,t}^{M_o}\right)$$

$$J_{o,t} = \frac{1}{m_{O,t}}\sum_i K_i^i m_{O,t}^i$$

$$m_{O,t} = \sum_i m_{O,t}^i = (C_T - C_v)S\Delta x = (C_T - C_{O,t})S\Delta x$$

$$J_{o,t} = \frac{1}{(C_T - C_{O,t})S\Delta x}\sum_i K_i^i m_{O,t}^i$$

$m_{O,0}^i$ are known $\Rightarrow$ these are the number of moles of i in the volume $S\Delta x$

$$m_{O,t}^i = C_{O,t}^i\,S\Delta x$$

$$\therefore\quad J_{O,t} = \frac{1}{(C_T - C_{O,t})}\sum_i K_i^i C_{O,t}^i$$

Assume we know $J_{O,0}; J_{O,1}; \cdots; J_{O,t}$

How do we compute $J_{O,t+1}$?

I have a problem with the indexes. I need to work out this problem step by step. I wanted to do induction, but it is not going to work.

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$k=0$
$t=0$, $C^v_{0,l} = 0$ for $k = 0, \dots, N$

$k=1$;

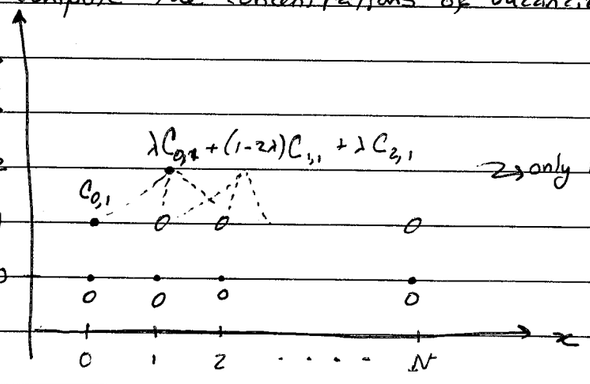
$$C^v_{0,1} = \frac{\sum_i K_1^i C^i_{0,0}}{C_T} \frac{\Delta t}{\Delta x} \qquad C_{0,1} = \frac{\sum_i K_1^i C^i_{0,0}}{C_T} \frac{\Delta t}{\Delta x}$$

$$C_{0,1} = \frac{\sum_i K_1^i C^i_{0,0}}{C_T} \frac{\Delta t}{\Delta x} \quad , \quad C_{0,l} = 0 \quad \text{for } l = 1, 2, \dots, N$$

$C_{0,1}$ is computed on the basis of quantities at $t=0$

$l=2$ using $C_{K,l+1} = \lambda C_{K-1,l} + (1-2\lambda) C_{K,l} + \lambda C_{K+1,l}$ ← CARE! λ is dimensionless!!!

we can compute the concentrations of vacancies at $t=$



For $l=2$ $\quad C_{1,2} = \lambda C_{0,1}$ and $C_{K,2} = 0 \quad K = 2, 3, \dots, N$

OPR 6/16/00

$$C_{0,2} = \frac{\sum_i K_1^i C^i_{0,0}}{C_T} \frac{\Delta t}{\Delta x} + \frac{\sum_i K_1^i C^i_{0,1}}{C_T} \frac{\Delta t}{\Delta x} - \lambda C_{0,1}$$

OPR 6/16/00 ~~$\lambda = \frac{\Delta t}{\Delta x^2}$~~

Dimensionless representation

$$\frac{\partial C_v}{\partial t} = D^{eff} \frac{\partial^2 C_v}{\partial x^2} \Rightarrow$$

Define $\bar{C} = \frac{C_v}{C_T} \Rightarrow \frac{\partial \bar{C}}{\partial t} = D^{eff} \frac{\partial^2 \bar{C}}{\partial x^2}$

$D^{eff} \sim \frac{m^2}{s}$ $\qquad \bar{t} = \frac{D^{eff} t}{L^2}$

6/16/00 OPR

$$\bar{x} = \frac{x}{L} \; ; \quad \bar{t} = \frac{D^{eff} t}{L^2} \; ; \quad \bar{C} = \frac{C_v}{C_T}$$

Dimensionless equation

$$\frac{\partial \bar{C}}{\partial \bar{t}} = \frac{\partial^2 \bar{C}}{\partial \bar{x}^2}$$

[1] $\bar{C}_{K,l+1} = \lambda \bar{C}_{K-1,l} + (1-2\lambda) \bar{C}_{K,l} + \lambda \bar{C}_{K+1,l}$

$$\lambda = \Delta\bar{t}/\Delta\bar{x}^2 = \frac{D^{eff} \Delta t}{L^2} \frac{L^2}{\Delta x^2} = \frac{D^{eff} \Delta t}{\Delta x^2}$$

multiplying by C_T

Equivalently $C_{K,l+1} = \lambda C_{K-1,l} + (1-2\lambda) C_{K,l} + \lambda C_{K+1,l}$

For $l=2$

$$C_{0,2} = \frac{\sum_i K_1^i C^i_{0,0}}{C_T} \frac{\Delta t}{\Delta x} + \frac{\sum_i K_1^i C^i_{0,1}}{C_T} \frac{\Delta t}{\Delta x} - \underbrace{\lambda C_{0,1}}_{\frac{1}{2}\lambda C_{0,1} \rightarrow \text{integral}}$$

$C_{1,2}$ * 0

Integral $= \frac{1}{2} C_{1,2} \Delta x S$

$= \frac{1}{2} \lambda C_{0,1} \Delta x S$

$C^{N_i, K_1, M_0}_{0,1} = ?$

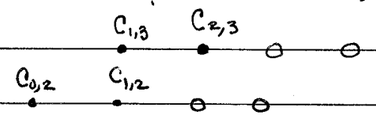
$$C^{N_i}_{0,1} = C^{N_i}_{0,0} - \frac{K_1^{N_i}}{C_T} C^{N_i}_{0,0} \frac{\Delta t}{\Delta x} = \left(1 - \frac{K_1^{N_i}}{C_T} \frac{\Delta t}{\Delta x}\right) C^{N_i}_{0,0}$$

and similarly for C_r and M_0 :

$$C^i_{0,1} = C^i_{0,0} - \frac{K_1^i}{C_T} (C^{N_i}_{0,0}) \frac{\Delta t}{\Delta x} = \left(1 - \frac{K_1^i}{C_T} \frac{\Delta t}{\Delta x}\right) C^i_{0,0} \quad *$$

Note that $\sum_i C^i_{0,1} + C_{0,1} = \sum_i C^i_{0,0} = C_T$, which is quite consistant

For $l=3$



$C_{1,3}$ & $C_{2,3}$ are easily obtained with equation [1]

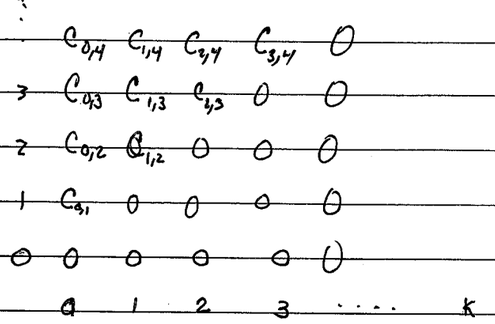
$$C_{K,l+1} = \lambda C_{K-1,l} + (1-2\lambda) C_{K,l} + \lambda C_{K+1,l} + \sum_i K_1^i C^i_{0,2}$$

$$C_{0,3} = \frac{\Delta t}{\Delta x} \frac{1}{C_T} \left\{ \sum_i K_1^i C^i_{0,0} + \sum_i K_1^i C^i_{0,1} \right\} - \frac{1}{2} (C_{1,3} + 2 C_{2,3} + 0)$$

what about $C^i_{0,2}$?

We need to make sure that $\sum_i C^i_{0,2} + C_{0,2} = C_T$ or $\sum_i C^i_{0,2} = C_T - C_{0,2}$

6/19/00 OR



How do we determine $C^i_{k,l}$? $i = N_i, C_r, M_o$

The assumption is that these elements have the same diffusion coefficient; therefore, they are equivalent in transport terms.

$l = 1$

$\Delta_1 C = C_{0,1} - C_{0,0} = C_{0,1}$ → useless

$C^i_{0,1} = \left(1 - \frac{K_i}{C_T}\frac{\Delta C}{\Delta x}\right) C^i_{0,0}$ → known

$l = 2 \quad C_{0,2} = C_{0,1} + \underbrace{\frac{1}{C_T}\sum K_i C^i_{0,1}\frac{\Delta t}{\Delta x}}_{\text{~~this term is not correct~~}} - C_{1,2}$ OR 6/19/00

$C^T_{0,1} = \sum_i C^i_{0,1}$

$C_{0,2} = C_{0,1} + \underbrace{\frac{1}{C^T_{0,1}}\sum_i K_i C^i_{0,1}\frac{\Delta t}{\Delta x}}_{\text{vacancies diffusing away}} - C_{1,2}$

→ this term is not correct

is expect it to go to zero as $C^i_{0,1} \to 0$

which does not happen.

Correct equation: $C_{0,2} = C_{0,1} + \frac{1}{C_T}\sum K_i C^i_{0,1}\frac{\Delta t}{\Delta x} - C_{1,2}$

Restriction: $C_{0,2} \leq C_T$ *

6/19/00 OR

At $K=1$, $l=2$

$\Delta C^T_{1,2} = C_T - C_{1,2} = C^T_{1,2} = C^T_{1,2}$

$C^i_{1,2} = C^i_{1,1} - \frac{C^i_{1,1}}{C^T_{1,2}} C_{1,2}$

$\sum C^i_{1,2} = \sum_i C^i_{1,1} - \frac{C_{1,2}}{C^T_{1,2}} \sum_i C^i_{1,1} = C_T - C_{1,2}\frac{C_T}{C^T_{1,2}} = C_T - C_{1,2}$

$\sum C^i_{1,2} + C_{1,2} = C_T$ ✓ makes sense.

$C^i_{1,2} = C^i_{1,1} - \frac{C^i_{1,1}}{C_T} C_{1,2}$

$l = 3$

$C^i_{1,3} = C^i_{1,2} - \frac{C^i_{1,2}}{C^T_{1,2}}\left(C_{1,3} - C_{1,2}\right)$

$\sum C^i_{1,3} = C^T_{1,2} - (C_{1,3} - C_{1,2}) = C^T_{1,2} - C_{1,3} + C_{1,2}$

$= C_T - C_{1,2} - C_{1,3} + C_{1,2} = C_T - C_{1,3}$ ✓

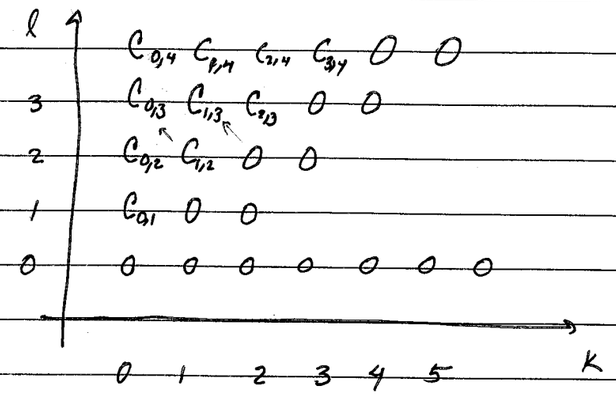
$C^i_{2,3} = C^i_{2,2} - \frac{C^i_{2,2}}{C^T_{2,2}}\left(C_{2,3} - C_{2,2}\right)$

$C^T_{2,2} = C_T$

$\sum C^i_{2,3} = C_T - (C_{2,3}) \Rightarrow \sum_i C^i_{2,3} + C_{2,3} = C_T$ ✓

I have a complete set of rules that can be put in the form of an algorithm.

6/19/00



$l = 0$ $\begin{cases} C_{K,0} = 0 \\ C^i_{K,0} = \text{constants} \\ \sum_i C^i_{K,0} = C_T = \text{constant} \end{cases}$

$l = 1$ $\quad C_{0,1} = \frac{\Delta t}{C_T \Delta x} \sum_i k_i^i C^i_{0,0}$

$C^i_{0,1} = \left(1 - \frac{k_i^i \Delta t}{C_T \Delta x}\right) C^i_{0,0} \Rightarrow \sum_i C^i_{0,1} = C_T - C_{0,1}$ ✓

$l = 2$ $\quad C_{0,2} = C_{0,1} + \frac{\Delta t}{C_T \Delta x} \sum_i k_i^i C^i_{0,1} - C_{1,2}$

$C_{1,2} = \lambda C_{0,1} + (1-2\lambda) C_{1,1} + \lambda C_{2,1} = \lambda C_{0,1}$

$C^i_{0,2} = C^i_{0,1} - \frac{k_i^i \Delta t}{C_T \Delta x} C^i_{0,1} + \frac{C^i_{1,1}}{C^T_{1,1}} C_{1,2}$

(gain)

$\sum C^i_{0,2} = (C_T - C_{0,1}) + C_{1,2} - (C_{0,2} - C_{0,1} + C_{1,2})$

$= C_T - C_{0,2} \Rightarrow \sum_i C^i_{0,2} + C_{0,2} = C_T$ ✓

$C^i_{1,2} = C^i_{1,1} - \frac{C^i_{1,1}}{C^T_{1,1}} C_{1,2}$

(loss)

$\sum_i C^i_{1,2} = C^T_{1,1} - C_{1,2} \Rightarrow \sum_i C^i_{1,2} + C_{1,2} = C_T$ ✓

6/19/00

$l = 3$

$C_{0,3} = C_{0,2} + \frac{\Delta t}{C_T \Delta x} \sum_i k_i^i C^i_{0,2} - (C_{1,3} - C_{1,2})$

↳ this equation makes physical sense; however, it is not entirely consistent with the physical restriction that

$C_{0,3} + C_{1,3} + C_{2,3} =$ total vacancies injected at $t = 3$

I need to account for this.

$C_{0,3} = \frac{\Delta t}{C_T \Delta x} \left(\sum_i k_i^i C^i_{0,0} + \sum_i k_i^i C^i_{0,1} + \sum_i k_i^i C^i_{0,2} \right) - (C_{1,3} + C_{2,3})$

$C_{1,3}$ & $C_{2,3}$ are easily computed with

$C_{K,l+1} = \lambda C_{K-1,l} + (1-2\lambda) C_{K,l} + \lambda C_{K+1,l}$

$C^i_{0,3} = ?$

$C_{0,3} - C_{0,2} =$ vacancies in $-$ vacancies out $= \frac{\Delta t}{C_T \Delta x} \sum_i k_i^i C^i_{0,2} -$ vacancies out

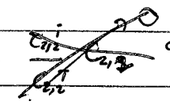
vacancies out $= \frac{\Delta t}{C_T \Delta x} \sum_i k_i^i C^i_{0,2} - C_{0,3} + C_{0,2}$

$C^i_{0,3} = C^i_{0,2} - \frac{\Delta t}{C_T \Delta x} k_i^i C^i_{0,2} + (\text{vacancies out}) \frac{C^i_{1,2}}{C^T_{1,2}} \qquad C^T_{1,2} = \sum_i C^i_{1,2}$

Note that $\sum_i C^i_{0,3} = \underbrace{C^T_{0,2}}_{C_T - C_{0,2}} - \frac{\Delta t}{C_T \Delta x} \sum_i k_i^i C^i_{0,2} + \frac{\Delta t}{C_T \Delta x} \sum_i k_i^i C^i_{0,2} - C_{0,3} + C_{0,2}$

$= -C_{0,3} + C_T$

Consequently $\sum_i C^i_{0,3} + C_{0,3} = C_T$ ✓

$C^i_{1,3} = C^i_{1,3} - \frac{C^i_{1,2}}{C^T_{1,2}} (C_{1,3} - C_{1,2}) +$  OPR 6/19/00

$\sum_i C^i_{1,3} = C^T_{1,2} - C_{1,3} + C_{1,2} = (C_T - C_{1,2}) - C_{1,3} + C_{1,2} = C_T - C_{1,3}$

$\therefore C^T_{1,3} + C_{1,3} = C_T$ ✓

$C^i_{2,3} = C^i_{2,2} - \frac{C^i_{1,2}}{C^T_{2,2}} (C_{2,3} - 0) \qquad \sum C^i_{2,3} = C^T_{2,3} = C_T - C_{2,3}$

6/19/00 QPy

$l = 4$

$C_{1,4}$; $C_{2,4}$; $C_{3,4}$ easily obtained

$$C_{0,4} = \left(\sum_{l=0}^{3} \sum_{i} K_i^i C_{0,l}^i \right) - \left(\sum_{K=1}^{3} C_{K,4} \right)$$

vacancies injected to the lattice

vacancies from $K=1$ to $K=3$

$$C_{0,4}^i = C_{0,3}^i - \frac{C_{0,3}^i}{C_T} K_i^i \frac{\Delta t}{\Delta x} + \text{atoms coming from } l-1$$

prior concentration

injected vacancies

$$\text{atoms from } l=1 = \left(C_{0,3} - C_{0,4} + \frac{\Delta t}{C_T \Delta x} \sum_i K_i^i C_{0,3}^i \right) \frac{C_{1,3}^i}{C_{1,3}^T}$$

Rationale for last term

$C_{0,4} - C_{0,3}$ = vacancies in − vacancies out

$$C_{0,4} - C_{0,3} = \frac{\Delta t}{C_T \Delta x} \sum_i K_i^i C_{0,3}^i - \text{vacancies out}$$

$$\text{vacancies out} = C_{0,3} - C_{0,4} + \frac{\Delta t}{C_T \Delta x} \sum_i K_i^i C_{0,3}^i$$

$$\text{atoms } i \text{ from } l=1 = \frac{C_{1,3}^i}{C_{1,3}^T} (\text{vacancies out})$$

Therefore, it follows that

$$C_{0,4}^i = C_{0,3}^i - \frac{C_{0,3}^i}{C_T} K_i^i \frac{\Delta t}{\Delta x} + \left[C_{0,3} - C_{0,4} + \frac{\Delta t}{C_T \Delta x} \sum_j K_i^j C_{0,3}^j \right] \frac{C_{1,3}^i}{C_{1,3}^T}$$

Verification

$$\sum_i C_{0,4}^i = C_{0,3}^T + C_{0,3} - C_{0,4} = C_T - C_{0,4}$$

$$\therefore \sum_i C_{0,4}^i + C_{0,4} = C_T \quad \checkmark$$

$$C_{1,4}^i = C_{1,3}^i - (C_{1,4} - C_{1,3}) \frac{C_{1,3}^i}{C_{1,3}^T}$$

6/19/00 OPy

Verification: $\sum_i C_{1,4}^i = C_{1,3}^T - C_{1,4} + C_{1,3} = C_{1,4}^T - C_{1,4}$ ✓

Rationale: $C_{1,4}^i = C_{1,3}^i$ − atoms injected to $K=0$

$$C_{2,4}^i = C_{2,3}^i - (C_{2,4} - C_{2,3}) \frac{C_{2,3}^i}{C_{2,3}^T}$$

6/19/00 QPy

$$C_{3,4}^i = C_{3,3}^i - (C_{3,4} - C_{3,3}) \frac{C_{3,3}^i}{C_{3,3}^T}$$

$l = 5$

for ~~$l=1$ to $l=5$~~ (OPy 6/19/00) $K = 1$, to $l-1$

$$C_{K,l+1} = \lambda C_{K-1,l} + (1-2\lambda) C_{K,l} + \lambda C_{K+1,l} \qquad (1)$$

$$C_{0,l} = \frac{\Delta t}{C_T \Delta x} \left(\sum_{r=0}^{l-1} \sum_i K_i^i C_{0,r}^i \right) - \sum_{K=1}^{l-1} C_{K,l} \qquad (2)$$

$$(3) \quad C_{0,l}^i = C_{0,l-1}^i - \frac{C_{0,l-1}^i}{C_T} K_i^i \frac{\Delta t}{\Delta x} + \left[C_{0,l-1} - C_{0,l} + \frac{\Delta t}{C_T \Delta x} \sum_j K_i^j C_{0,3}^j \right] \frac{C_{1,l-1}^i}{C_{1,l-1}^T}$$

For $r = 1, l-1$

$$C_{r,l}^i = C_{r,l-1}^i - (C_{r,l} - C_{r,l-1}) \frac{C_{r,l-1}^i}{C_{r,l-1}^T} \qquad (4)$$

Equations (1) to (4) suffice to find all of the concentrations

By induction, it is possible to prove that

$$C_{K,l}^T + C_{K,l} = C_T = \text{constant}$$

Restriction

$$C_{0,l} \leq C_T$$

$$C_{K,l}^i \geq 0$$

What if $C_{0,l} = C_T$?

What if $l = 2$ cm (total length)?

6/19/00 QPQ

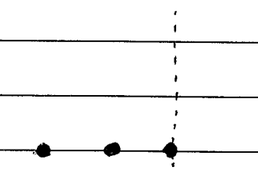
What if $C_{o,\ell} = C_T$?

The equations are selected so that if $C_{o,\ell} = C_T$, then dissolution is stopped until new components are again available in the lattice. In this case, dissolution will be limited by solid state diffusion.

Another possibility is that whenever $C_{o,\ell} = C_T$ we could consider the thickness of the slab to degrease. This may be a more conservative approach, but it will require some extra thinking.

The decreasing step would be fixed, Δx. This is a good solution that must be further investigated.

What if $k = 2$ cm



Extrapolation formula:

$$f(x+h) = f(x) + f'(x)h + \frac{1}{2}h^2 f''(x) + \frac{1}{3!}h^3 f'''(x) + O(h^3)$$

A $f(x-h) = f(x) - f'(x)h + \frac{1}{2}h^2 f''(x) - \frac{1}{6}h^3 f'''(x) + O(h^3)$

B $f(x-2h) = f(x) - 2h f'(x) + 2h^2 f''(x) - \frac{4}{3}h^3 f'''(x) + O(h^3)$

C $f(x-3h) = f(x) - 3h f'(x) + \frac{9}{2}h^2 f''(x) - \frac{9}{2}h^3 f'''(x) + O(h^3)$

I want to get rid of the therms f', f'', f'''

$$\frac{1}{6} - \frac{1}{6}A - \frac{4}{3}B - \frac{9}{2}C = 0$$

$$\frac{1}{2} + \frac{1}{2}A + 2B + \frac{9}{2}C = 0$$

$$1 - A - 2B - 3C = 0$$

(1) $A + 8B + 27C = 1$

$A + 4B + 9C = -1$

$A + 2B + 3C = 1$

$A = 6$, $b = -4$, $C = 1$ ⇝ solution

$$f(x+h) + 6f(x-h) - 4f(x-2h) + f(x-3h) = (\overbrace{1+6-4+1}^{4})f(x) + O(h^3)$$

~~$C_{k+1,\ell} = -6C_{k,\ell} + 4C_{k-1,\ell} - C_{k-2,\ell} + O(\Delta x^3)$~~ QPQ 6/19/00

$C_{k+1,\ell} = 4C_{k,\ell} - 6C_{k-1,\ell} + 4C_{k-2,\ell} - C_{k-3,\ell}$

I will use the above formula if $x_{k+1} = 2$cm

QPQ 6/19/00

~~Two~~ second order formulas

$C_{k+1} = C_{k-2} - 3C_{k-1} + 3C_k = 3C_k - 3C_{k-1} + C_{k-2}$ ⇝ 2nd order extrapolation

~~$C_{k+1} = \frac{3}{2}C_k + 3C_{k-1} - \frac{1}{2}C_{k-2}$~~ QPQ 6/19/00

6/20/00 QPQ

I just discovered a problem. In the results that I presented at the Spring MRS 2000 meeting is solved numerically the equation

$$\frac{dm_i}{dt} = -S\frac{m_i}{m}K^i \qquad K^i = K_1^{Cr} + K_2^{Cr},\ K_1^{Ni} + K_2^{Ni},\ K_1^{Mo}$$

and $$\frac{dm_v}{dt} = \frac{S}{m}\left(K_1^{Cr} m_{Cr} + K_1^{Ni} m_{Ni} + K_1^{Mo} m_{Mo}\right)$$

with $m = \sum_{Ni,Cr,Mo} m_i$ = total number of moles.

The numerical solution is implemented on page 124 & 125.

The right approach is considering

$$m = \sum m_i + m_v$$

The results that I presented at the meeting are flawed! It should be straightforward to correct the problem.

6/20/00 OPR

I will correct at a later time the problem of the wrong computations presented at the MRS 2000 spring meeting. The reason I discovered my computations are wrong, is because the equation $\frac{dm_i}{dt} = -S\frac{m_i}{M}K^i$

predicts that $\frac{dm_i}{dt} = -SK^i$ in the limit when $M \to 0$

This limit does not make physical sense. The limit that makes sense is to have $\frac{dm_i}{dt} \to 0$ as $m_i \to 0$.

Recall that the current density is an average on a surface. In the limit when the amount of reactive elements on that surface go to zero, so does the current density.

If the area of determination (i.e. measurement) were corrected to account for this decrease in the amount of reactive elements, then $\frac{dm_i}{dt} \to$ constant as $m \to 0$ would make sense, but this is not the case. My computations on pages 124 & 125 are flawed, and they will be corrected later.

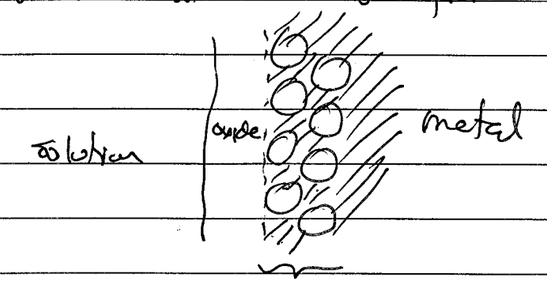
Dealing with another issue, I have performed some computations. I implemented Eqs. (1), (2), (3), (4) on page 153. I found that vacancies accumulate at the surface, decreasing the dissolution rate.

Recall that Eqs. (1), (2), (3), (4) do not take into account the rate of film dissolution provided by k_3^c $i = Ni, Cr$. This can be neglected based on preliminary computations.

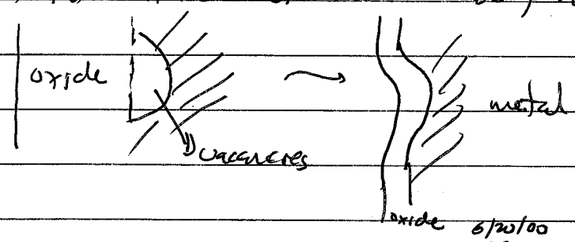
6/20/00 OPR

I will try to implement an improvement to the model.

Consider a situation as depicted as follows



When the concentration of vacancies exceeds a certain molar fraction, the material can be considered to be porous.



6/20/00 OPR

After a given porosity, say P_{max}, we cannot consider that the interface metal-film moves to a new position such that porosity $\leq P_{max}$.

What is the value of P_{max}?

I do not know, but I will consider $P_{max} = 50\%$

6/20/00 OFY

I am having problems in trying to implement the idea of the moving interface. Let's see again.

Because the way Mathematica handels indices, I will change my prior notation:

$$C_{t_\ell, x_k} = C_v(t=t_\ell, x=x_k)$$

↳ time ↳ position (before we had first time, and pos.

$\ell = 0$ 0 0 0 0 0 ... 0 → K

$\ell = 1$ C_{10} 0 0 ...

injected vacancies $= \left(\sum_i k_i^i C_{\ell 0}^i\right)\frac{\Delta t}{G\Delta x}$

$C_{\ell 0}$ = injected vacancies $\ell = 1$

$C_{\ell 0}^i = C_{\ell-1,0}^i\left(1 - \frac{k_i^i \Delta t}{G\Delta x}\right)$

$$\sum_i C_{\ell 0}^i + C_{\ell 0} = C_T = \sum_i C_{\ell-1,0}^i = C_T$$

$\ell = 2$ and so on ...

injected(ℓ) $= \left(\sum_i k_i^i C_{\ell 0}^i\right)\frac{\Delta t}{G\Delta x}$

Total vacancies injected = Tot Vac $= \sum_{j=0}^{\ell}$ injected(j)

Find $C_{\ell_K = C_{1K}}$ for $K = 2$ to $\min(\ell-1, N)$ $N = \max K$

OFY 6/20/00

We can find $C_{\ell K}$ easily with the finite difference diffusion.

$$C_{\ell,0} = \text{Tot Vac} - \sum_{K=2}^{N} C_{\ell K}$$

Note the following Tot Vac = total vacancies injected has to be changed in case the metal/film interface is redefined

$$\text{Tot Vac} = \text{Tot Vac} - \sum_{K=0}^{new} C_{\ell K}$$

where ℓ_{OFY} "new" is the new position of the metal/film interface.

6/20/00 OFY

I have selected some kinetic rates in the TPD 4.0 Mannual:

$I \sim 1.63\times10^3$ to 1.7×10^4 $\frac{C}{m^2 yr}$, 0.01 and 99.9 percentiles

Normal distribution.

$$I_L = 1.63\times10^3 \frac{C}{m^2(3600\times24\times365.25)} = 5.165 \frac{A}{m^2} \times10^{-5} = 5.165\times10^{-9}\frac{A}{cm^2}$$

$$I_H = 5.387\times10^{-4}\frac{A}{m^2} = 5.387\times10^{-8}\frac{A}{cm^2}$$

The current density for alloy 22 ranges from $5\times10^{-9}\frac{A}{cm^2}$ to $5.4\times10^{-8}\frac{A}{cm^2}$

In the paper presented at the MRS I assumed that Ni dissolves stoichiometrically with respect to Mo or viceversa

6/21/00 OFY

M.A. Cavanaugh, J.A. Kargol, J. Nickerson, and N.F. Fiore

The Anodic Dissolution of a Ni-Base Superalloy.

Corrosion-NACE, Vol. 39, N. 4, April, 1983

In this paper it is reported selectivity coefficients for alloy C-276 in chloride and sulfuric acid.

In chloride, the dissolution rate is in the order

$Fe \geq Ni > Mo > Cr$

This is consistent with my conclusion that $k_1^{Ni} + k_2^{Ni} > k_1^{Cr} + k_3^{Cr}$

The above conclusion is based on theoretical grounds.

At the MRS 2000 conference I assumed that

$$k_1^{Mo} = k_1^{Ni} + k_3^{Ni}$$

I think it is more adequate to assume

$$k_1^{Mo} = \frac{1}{2}\left(k_1^{Ni} + k_3^{Ni} + k_1^{Cr} + k_3^{Cr}\right)$$ ⇒ more consistent with Cavanaugh's paper.

6/21/00 QFY

Diffusion coefficients:

$D = 8 \times 10^{-17}\ m^2 s^{-1} = 8 \times 10^{-13}\ cm^2 s^{-1}$ ⇝ diffusion coefficient for Cr in 19Cr-25Ni steel at 800°C

Source: Figure 9, p. 1074 in

H.E. Evans, Cavity formation and metallurgical changes induced by growth of oxide scale,
Materials Science and Technology, Vol. 4, December 1988 p. 1089

T.-F. Chen, Y. IIJIMA, K.-I. Hirano, and K. Yamauchi,
Diffusion of chromium in nickel-base Ni-Cr-Fe Alloys,
Journal of Nuclear Materials, Vol. 169 (1989) 285-290

Volume and grain boundary diffusion of chromium in

Information potentially subject to copyright protection was redacted from this location. The redacted material, equations, is from the reference listed directly above this statement.

6/21/00 QFY

The activation energies reported by Chen et al indicate that solid state diffusion at room temperature is negligible. For practical purposes, it can be assumed that the metal remains the same at all times.

Note that the effective diffusion coefficient for vacancies is $D^{eff} = \frac{C_T}{C_V^0} D$

C_V^0 is the vacancy concentration at a reference temperature, say room temperature

6/21/00 QPR

Macdonald says that dopant levels in ~~zinc~~ passive films are of the order of $10^{20} - 10^{21}\ cm^{-3}$ → p. 959 in

D.D. Macdonald, Passivity - the key to our metals-based civilization
Pure Appl. Chem., Vol. 71, No. 6, pp. 951-978. 1999

Critical areal concentration of vacancies: $10^{16}\ cm^{-2}$, p. 3448 in
The Point defect model for the passive state
D.D Macdonald, J. Electrochem. Soc., Vol. 139, No. 12 (1992)
p. 3434 - 3447

M. Urquidi-Macdonald & D.D. Macdonald, Theoretical Analysis of the Effects of Alloying elements on distribution functions of passivity breakdown.
J. Electrochem. Soc., Vol. 136, No. 4, April 1989 pp. 961-967
The concentration of vacancies was taken as $5 \times 10^{20}\ cm^{-3}$

Vacancy concentration $\sim 10^{20}\ cm^{-3}$ → bout in the film.

6/21/00 QAJ

I do not seem to find any report on the concentration of the metal vacancies in the bulk of the alloy.

10^{15} cm^{-3}

seems to me a reasonable number.

$C_V^0 = \frac{10^{15}}{6\times10^{23}} \sim 2\times10^{-7}$ mol cm^{-3} → guess

$C_T \sim 0.1$ mol cm^{-3}

$\therefore \frac{C_T}{C_V^0} \sim 60\times10^6 = 6\times10^7 \sim 10^8$

At 100°C, $D \sim 10^{-39}$ cm^2 s^{-1}

$D\frac{C_T}{C_V^0} \sim 10^{-31}$ cm^2 s^{-1}

I will select $D\frac{C_T}{C_V^0} = 10^{-30}$ cm^{2}s^{-1} which seems to me a reasonable value.

With this diffusion coefficient, everything is going to concentrate on the surface of the alloy.

The last problem that remains to be worked out is that of the critical porosity.

Macdonald proposes 10^{16} cm^{-2} as the critical surface concentration. This has another meaning. I think it is better the selection of a critical local porosity, Pmax. After P > Pmax, the metal/film surface is redefined at a location such that P < Pmax.

The numbers are ready to do something!

7/9/00 QAJ

Case 1

$$\frac{Z_{Cr} I_{22}}{Z_{Ni} a_{Ni} + Z_{Cr} a_{Cr} + Z_{Mo} a_{Mo}} = 6.01\text{E-}09 \text{ A/cm}^2 \quad 1.201416153$$

rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide
rho_c22	8.69	gr/cm^3	Density of Alloy 22
F	96486.7	C/mol	Faraday's constant
I_22	5.00E-09	A/cm^2	Passive current density for Alloy 22, from 5x10^{-9} A/cm^2 to 5.4x10-8 A/cm^2
ICr	6.00E-09	A/cm^2	Kirchheim et al. [1989]: **1.4x10^{-8} A/cm^2**. Based on lowest data reported by D. Dunn (see above row **x10^{-9} A/cm^2**
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22, y=0.1

ESTIMATED RATE CONSTANTS			kCr=k1Cr+k3Cr; Case 1: k1Cr=k3Cr=0.5*kCr; Case 2: k1Cr=0 and k3Cr=kCr
kCr	2.07282E-14	mol/(s cm^2)	**Case:** 1 **Write 1 or 2, see above**
kNi	2.07634E-14	mol/(s cm^2)	
kMo	2.07458E-14	mol/(s cm^2)	Necessarily k3Cr > k3Ni, but kCr<k1Ni+k3Ni
kMo=0.5*(kCr+kNi), Assumption	4.77941E-16	mol/(s cm^2)	**0 if False that kCr<kNi; 1 if True:** 1

Case 2

$$\frac{Z_{Cr} I_{22}}{Z_{Ni} a_{Ni} + Z_{Cr} a_{Cr} + Z_{Mo} a_{Mo}} = 6.01\text{E-}09 \text{ A/cm}^2 \quad 1.201416153$$

rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide
rho_c22	8.69	gr/cm^3	Density of Alloy 22
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ICr	6.00E-09	A/cm^2	Kirchheim et al. [1989]: **1.4x10^{-8} A/cm^2**. Based on lowest data reported by D. Dunn (see above row **x10^{-9} A/cm^2**
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22, y=0.1

ESTIMATED RATE CONSTANTS			kCr=k1Cr+k3Cr; Case 1: k1Cr=k3Cr=0.5*kCr; Case 2: k1Cr=0 and k3Cr=kCr
kCr	2.07282E-14	mol/(s cm^2)	**Case:** 2 **Write 1 or 2, see above**
kNi	2.07634E-14	mol/(s cm^2)	
kMo	2.07458E-14	mol/(s cm^2)	Necessarily k3Cr > k3Ni, but kCr<k1Ni+k3Ni
kMo=0.5*(kCr+kNi), Assumption	9.55882E-16	mol/(s cm^2)	**0 if False that kCr<kNi; 1 if True:** 1

Case 3								
			$\frac{Z_{Cr} I_{22}}{Z_{Ni} a_{Ni} + Z_{Cr} a_{Cr} + Z_{Mo} a_{Mo}} =$		6.49E-08	A/cm^2	1.201416153
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide				
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide				
rho_c22	8.69	gr/cm^3	Density of Alloy 22				
F	96486.7	C/mol	Faraday's constant				
I_22	5.40E-08	A/cm^2	Passive current density for Alloy 22, from 5x10^{-9} A/cm^2 to 5.4x10-8 A/cm^2				
ICr	6.00E-09	A/cm^2	Kirchheim et al. [1989]: **1.4x10^{-8} A/cm^2**. Based on lowest data reported by D. Dunn (see above row) **6x10^{-9} A/cm^2.**				
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22, y=0.1				
ESTIMATED RATE CONSTANTS			**kCr=k1Cr+k3Cr**			Case 1: k1Cr=k3Cr=0.5*kCr; Case 2: k1Cr=0 and k3Cr=kCr	
kCr	2.07282E-14	mol/(s cm^2)	**k1Cr**	1.03641E-14	mol/(s cm^2)	**Case:**	1 **Write 1 or 2, see above**
kNi	3.12752E-13	mol/(s cm^2)	**k3Cr**	1.03641E-14	mol/(s cm^2)		
kMo	1.6674E-13	mol/(s cm^2)	k1Ni	3.12274E-13	mol/(s cm^2)	Necessarily k3Cr > k3Ni, but kCr<k1Ni+k3Ni	
kMo=0.5*(kCr+kNi), Assumption			k3Ni	4.77941E-16	mol/(s cm^2)	**0 if False that kCr<kNi; 1 if True:**	1

7/7/00 4 OPR

Case 4								
			$\frac{Z_{Cr} I_{22}}{Z_{Ni} a_{Ni} + Z_{Cr} a_{Cr} + Z_{Mo} a_{Mo}} =$		6.49E-08	A/cm^2	1.201416153
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide				
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide				
rho_c22	8.69	gr/cm^3	Density of Alloy 22				
F	96486.7	C/mol	Faraday's constant				
I_22	5.40E-08	A/cm^2	Passive current density for Alloy 22, from 5x10^{-9} A/cm^2 to 5.4x10-8 A/cm^2				
ICr	6.00E-09	A/cm^2	Kirchheim et al. [1989]: **1.4x10^{-8} A/cm^2**. Based on lowest data reported by D. Dunn (see above row) **6x10^{-9} A/cm^2.**				
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22, y=0.1				
ESTIMATED RATE CONSTANTS			**kCr=k1Cr+k3Cr**			Case 1: k1Cr=k3Cr=0.5*kCr; Case 2: k1Cr=0 and k3Cr=kCr	
kCr	2.07282E-14	mol/(s cm^2)	**k1Cr**	0	mol/(s cm^2)	**Case:**	2 **Write 1 or 2, see above**
kNi	3.12752E-13	mol/(s cm^2)	**k3Cr**	2.07282E-14	mol/(s cm^2)		
kMo	1.6674E-13	mol/(s cm^2)	k1Ni	3.11796E-13	mol/(s cm^2)	Necessarily k3Cr > k3Ni, but kCr<k1Ni+k3Ni	
kMo=0.5*(kCr+kNi), Assumption			k3Ni	9.55882E-16	mol/(s cm^2)	**0 if False that kCr<kNi; 1 if True:**	1

7/7/00

Case 5								
			$\frac{Z_{Cr} I_{22}}{Z_{Ni} a_{Ni} + Z_{Cr} a_{Cr} + Z_{Mo} a_{Mo}} =$		6.49E-08	A/cm^2	1.201416153
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide				
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide				
rho_c22	8.69	gr/cm^3	Density of Alloy 22				
F	96486.7	C/mol	Faraday's constant				
I_22	5.40E-08	A/cm^2	Passive current density for Alloy 22, from 5x10^{-9} A/cm^2 to 5.4x10-8 A/cm^2				
ICr	1.40E-08	A/cm^2	Kirchheim et al. [1989]: **1.4x10^{-8} A/cm^2**. Based on lowest data reported by D. Dunn (see above row) **6x10^{-9} A/cm^2.**				
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22, y=0.1				
ESTIMATED RATE CONSTANTS			**kCr=k1Cr+k3Cr**			Case 1: k1Cr=k3Cr=0.5*kCr; Case 2: k1Cr=0 and k3Cr=kCr	
kCr	4.83659E-14	mol/(s cm^2)	**k1Cr**	2.4183E-14	mol/(s cm^2)	**Case:**	1 **Write 1 or 2, see above**
kNi	3.0071E-13	mol/(s cm^2)	**k3Cr**	2.4183E-14	mol/(s cm^2)		
kMo	1.74538E-13	mol/(s cm^2)	k1Ni	2.99595E-13	mol/(s cm^2)	Necessarily k3Cr > k3Ni, but kCr<k1Ni+k3Ni	
kMo=0.5*(kCr+kNi), Assumption			k3Ni	1.1152E-15	mol/(s cm^2)	**0 if False that kCr<kNi; 1 if True:**	1

Case 6								
			$\frac{Z_{Cr} I_{22}}{Z_{Ni} a_{Ni} + Z_{Cr} a_{Cr} + Z_{Mo} a_{Mo}} =$		6.49E-08	A/cm^2	1.201416153
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide				
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide				
rho_c22	8.69	gr/cm^3	Density of Alloy 22				
F	96486.7	C/mol	Faraday's constant				
I_22	5.40E-08	A/cm^2	Passive current density for Alloy 22, from 5x10^{-9} A/cm^2 to 5.4x10-8 A/cm^2				
ICr	1.40E-08	A/cm^2	Kirchheim et al. [1989]: **1.4x10^{-8} A/cm^2**. Based on lowest data reported by D. Dunn (see above row) : **6x10^{-9} A/cm^2.**				
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22, y=0.1				
ESTIMATED RATE CONSTANTS			**kCr=k1Cr+k3Cr**			Case 1: k1Cr=k3Cr=0.5*kCr; Case 2: k1Cr=0 and k3Cr=kCr	
kCr	4.83659E-14	mol/(s cm^2)	**k1Cr**	0	mol/(s cm^2)	**Case:**	2 **Write 1 or 2, see above**
kNi	3.0071E-13	mol/(s cm^2)	**k3Cr**	4.83659E-14	mol/(s cm^2)		
kMo	1.74538E-13	mol/(s cm^2)	k1Ni	2.98479E-13	mol/(s cm^2)	Necessarily k3Cr > k3Ni, but kCr<k1Ni+k3Ni	
kMo=0.5*(kCr+kNi), Assumption			k3Ni	2.23039E-15	mol/(s cm^2)	**0 if False that kCr<kNi; 1 if True:**	1

8/9/00

$$\frac{Z_{Cr} I_{22}}{Z_{Ni} a_{Ni} + Z_{Cr} a_{Cr} + Z_{Mo} a_{Mo}} = 6.49E\text{-}08 \text{ A/cm}^2 \qquad 1.201416153$$

Case 7	d:\osvaldo\cl\tc-22\rate constants 3.xls		
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide
rho_c22	8.69	gr/cm^3	Density of Alloy 22
F	96486.7	C/mol	Faraday's constant
I_22	5.40E-08	A/cm^2	Passive current density for Alloy 22, from 5×10^{-9} A/cm^2 to 5.4×10-8 A/cm^2
ICr	1.40E-08	A/cm^2	Kirchheim et al. [1989]: 1.4×10^{-8} A/cm^2. Based on lowest data reported by D. Dunn (see above row) : 6×10^{-9} A/cm^2.
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22, y=0.1

Case 1: k1Cr=k3Cr=0.5*kCr; **Case 2**: k1Cr=0 and k3Cr=kCr; **Case 3**: k1Cr=kCr, k3Cr = 0, and k3Ni=0

ESTIMATED RATE CONSTANTS			kCr=k1Cr+k3Cr		
kCr	4.83659E-14	mol/(s cm^2)	**k1Cr**	4.83659E-14	mol/(s cm^2)
kNi	3.0071E-13	mol/(s cm^2)	**k3Cr**	0	mol/(s cm^2)
kMo	1.74538E-13	mol/(s cm^2)	k1Ni	3.00071E-13	mol/(s cm^2)
kMo=0.5*(kCr+kNi), Assumption			k3Ni	0	mol/(s cm^2)

Case:	3	Write 1, 2, or 3, see above
		Necessarily kCr<k1Ni+k3Ni; k3Cr>k3Ni if k3Ni>0.
		0 if False that kCr<kNi; 1 if True: 1

Estimates in this page were computed with the spreadsheet rate constants 3.xls

8/9/00

Proposition:

If $I = F\left[x a_{Cr} (K_1^{Cr} + K_3^{Cr}) + \delta a_{Ni} (K_1^{Ni} + K_3^{Ni}) + \tfrac{3}{2} a_{Mo} K_1^{Mo} \right]$

and $I_{Cr} = xF(K_1^{Cr} + K_3^{Cr}) \Rightarrow K_1^{Cr} + K_3^{Cr} = \frac{I_{Cr}}{xF}$

and $K_1^{Ni} + K_3^{Ni} > K_1^{Cr} + K_3^{Cr}$

then $$I_{Cr} < \frac{xI}{\delta a_{Ni} + x a_{Cr} + \tfrac{3}{2} a_{Mo}} \qquad (1)$$

Proof:

let $K_1^{Mo} = p(K_1^{Cr} + K_3^{Cr}) + (1-p)(K_1^{Ni} + K_3^{Ni})$

if $0 \le p \le 1$, then $K_1^{Cr} + K_3^{Cr} \le K_1^{Mo} \le K_1^{Ni} + K_3^{Ni}$

$$I = a_{Cr} I_{Cr} + F\delta a_{Ni} (K_1^{Ni} + K_3^{Ni}) + a_{Mo} P \tfrac{3}{x} I_{Cr} + a_{Mo} (1-p) F \tfrac{3}{2} (K_1^{Ni} + K_3^{Ni})$$

$$= I_{Cr} (a_{Cr} + P \tfrac{3}{x} a_{Mo}) + F(K_1^{Ni} + K_3^{Ni}) \left[\delta a_{Ni} + (1-p) \tfrac{3}{2} a_{Mo} \right]$$

$$F(K_1^{Ni} + K_3^{Ni}) = \frac{I - (a_{Cr} + P \tfrac{3}{x} a_{Mo}) I_{Cr}}{\delta a_{Ni} + (1-p) \tfrac{3}{2} a_{Mo}} \rightarrow F(K_1^{Cr} + K_3^{Cr}) = \frac{I_{Cr}}{x}$$

$$xI - (x a_{Cr} + p \tfrac{3}{2} a_{Mo}) I_{Cr} \ge (\delta a_{Ni} + (1-p) \tfrac{3}{2} a_{Mo}) I_{Cr}$$

$$xI > (\delta a_{Ni} + x a_{Cr} + \tfrac{3}{2} a_{Mo}) I_{Cr},$$

$$I_{Cr} < \frac{xI}{\delta a_{Ni} + x a_{Cr} + \tfrac{3}{2} a_{Mo}}$$

QED

The only restriction for the validity of the above conclusion is that

$K_1^{Mo} = p(K_1^{Cr} + K_3^{Cr} - K_1^{Ni} - K_3^{Ni}) + K_1^{Ni} + K_3^{Ni} > 0$

then $p(K_1^{Ni} + K_3^{Ni} - K_1^{Cr} - K_3^{Cr}) < K_1^{Ni} + K_3^{Ni}$

$$p < \frac{K_1^{Ni} + K_3^{Ni}}{K_1^{Ni} + K_3^{Ni} - K_1^{Cr} - K_3^{Cr}}$$

} this is the only restriction for the validity of (1)

$\delta a_{Ni} + (1-p) \tfrac{3}{2} a_{Mo} > 0 \Rightarrow \delta a_{Ni} > (p-1) \tfrac{3}{2} a_{Mo}$

$p \tfrac{3}{2} a_{Mo} < \delta a_{Ni} + \tfrac{3}{2} a_{Mo}$

$$p < \frac{\delta a_{Ni} + \tfrac{3}{2} a_{Mo}}{\tfrac{3}{2} a_{Mo}}$$

8/9/00

Case 7	d:\osvaldo\clst\c-22\rate constants 3.xls					
rho_Cr2O3	5.21	gr/cm^3	Density of chromium oxide	$\frac{Z_{Cr} I_{22}}{Z_{Ni} a_{Ni} + Z_{Cr} a_{Cr} + Z_{Mo} a_{Mo}}$ =	6.49E-08	A/cm^2	1.201416153
MCr2O3	151.991	gr/mol	Molecular weight of chromium oxide				
rho_c22	8.69	gr/cm^3	Density of Alloy 22				
F	96486.7	C/mol	Faraday's constant				
I_22	5.40E-08	A/cm^2	Passive current density for Alloy 22, from 5×10^{-9} A/cm^2 to 5.4×10-8 A/cm^2				
ICr	1.40E-08	A/cm^2	Kirchheim et al. [1989]: 1.4×10^{-8} A/cm^2. Based on lowest data reported by D. Dunn (see above row) : 6×10^{-9} A/cm^2.				
y	0.10		Assumed fraction of sites occupied by Ni in the Cr2O3 film on Alloy 22, y=0.1				
ESTIMATED RATE CONSTANTS			**kCr=k1Cr+k3Cr**	**Case 1**: k1Cr=k3Cr=0.5*kCr; **Case 2**: k1Cr=0 and k3Cr=kCr; **Case 3**: k1Cr=kCr, k3Cr = 0, and k3Ni=0			
kCr	4.83659E-14	mol/(s cm^2)	**k1Cr**	4.83659E-14	mol/(s cm^2)	**Case:**	3	Write 1, 2, or 3, see above
kNi	3.0071E-13	mol/(s cm^2)	**k3Cr**	0	mol/(s cm^2)			
kMo	1.74538E-13	mol/(s cm^2)	k1Ni	3.0071E-13	mol/(s cm^2)	Necessarily kCr<k1Ni+k3Ni. k3Cr>k3Ni if k3Ni>0.		
kMo=0.5*(kCr+kNi), Assumption			k3Ni	0	mol/(s cm^2)	0 if False that kCr<kNi; 1 if True:		1

Estimates in this page were computed with the spreadsheet rate constants 3.xls

8/9/00

Proposition:

If $I = F[x a_{Cr}(K_1^{Cr}+K_3^{Cr}) + \delta a_{Ni}(K_1^{Ni}+K_3^{Ni}) + \xi a_{Mo} K_1^{Mo}]$

and $I_{Cr} = xF(K_1^{Cr}+K_3^{Cr}) \Rightarrow K_1^{Cr}+K_3^{Cr} = \frac{I_{Cr}}{xF}$

and $K_1^{Ni}+K_3^{Ni} > K_1^{Cr}+K_3^{Cr}$

then $I_{Cr} < \frac{xI}{\delta a_{Ni} + x a_{Cr} + \xi a_{Mo}}$ (1)

Proof:

let $K_1^{Mo} = p(K_1^{Cr}+K_3^{Cr}) + (1-p)(K_1^{Ni}+K_3^{Ni})$

if $0 \le p \le 1$, then $K_1^{Cr}+K_3^{Cr} \le K_1^{Mo} \le K_1^{Ni}+K_3^{Ni}$

$$I = a_{Cr} I_{Cr} + F\delta a_{Ni}(K_1^{Ni}+K_3^{Ni}) + a_{Mo} P \frac{\xi}{x} I_{Cr} + a_{Mo}(1-p)F\xi(K_1^{Ni}+K_3^{Ni})$$

$$= I_{Cr}(a_{Cr} + P\frac{\xi}{x} a_{Mo}) + F(K_1^{Ni}+K_3^{Ni})[\delta a_{Ni} + (1-p)\xi a_{Mo}]$$

$$F(K_1^{Ni}+K_3^{Ni}) = \frac{I - (a_{Cr} + P\frac{\xi}{x} a_{Mo}) I_{Cr}}{\delta a_{Ni} + (1-p)\xi a_{Mo}} > F(K_1^{Cr}+K_3^{Cr}) = \frac{I_{Cr}}{x}$$

$$xI - (x a_{Cr} + p\xi a_{Mo}) I_{Cr} > (\delta a_{Ni} + (1-p)\xi a_{Mo}) I_{Cr}$$

$$xI > (\delta a_{Ni} + x a_{Cr} + \xi a_{Mo}) I_{Cr},$$

$$I_{Cr} < \frac{xI}{\delta a_{Ni} + x a_{Cr} + \xi a_{Mo}}$$

QED

The only restriction for the validity of the above conclusion is that

$$K_1^{Mo} = p(K_1^{Cr}+K_3^{Cr} - K_1^{Ni} - K_3^{Ni}) + K_1^{Ni} + K_3^{Ni} > 0$$

then $p(K_1^{Ni}+K_3^{Ni} - K_1^{Cr} - K_3^{Cr}) < K_1^{Ni}+K_3^{Ni}$

$$p < \frac{K_1^{Ni}+K_3^{Ni}}{K_1^{Ni}+K_3^{Ni} - K_1^{Cr} - K_3^{Cr}}$$ } this is the only restriction for the validity of (1)

$\Rightarrow \delta a_{Ni} + (1-p)\xi a_{Mo} > 0 \Rightarrow \delta a_{Ni} > (p-1)\xi a_{Mo}$

$$p\xi a_{Mo} < \delta a_{Ni} + \xi a_{Mo}$$

$$p < \frac{\delta a_{Ni} + \xi a_{Mo}}{\xi a_{Mo}}$$

8/9/00 OPR

$$K_1^{M_o} = p(K_1^{Cr} + K_3^{Cr}) + (1-p)(K_1^{Ni} + K_3^{Ni})$$

$$K_1^{M_o} = p(K^{Cr} - K^{Ni}) + K^{Ni}$$

$$p < \frac{\delta a_{Ni} + 3 a_{Mo}}{3 a_{Mo}}$$

$$K^{Cr} - K^{Ni} < 0 \Rightarrow p(K^{Cr} - K^{Ni}) > \frac{(\delta a_{Ni} + 3 a_{Mo})(K^{Cr} - K^{Ni})}{3 a_{Mo}}$$

$$K_1^{M_o} = p(K^{Cr} - K^{Ni}) + K^{Ni} > K^{Ni} + \frac{(\delta a_{Ni} + 3 a_{Mo})}{3 a_{Mo}}(K^{Cr} - K^{Ni})$$

Therefore, the result (1) in page 167 is valid provided that

$$K^{Ni} - \frac{\delta a_{Ni} + 3 a_{Mo}}{3 a_{Mo}}(K^{Ni} - K^{Cr}) < K_1^{M_o}$$

(1)

It seems that the result is almost valid for every $K_1^{M_o} > 0$

It can be proved that (1) is also valid if

$$0 \le K_1^{M_o} < K^{Ni} - \frac{\delta a_{Ni} + 3 a_{Mo}}{3 a_{Mo}}(K^{Ni} - K^{Cr})$$

I have the feeling that this term is < 0

If effectively the above term is < 0, then the inequality (1) is valid always, for every $K_1^{M_o} > 0$.

8/9/2000 OPR

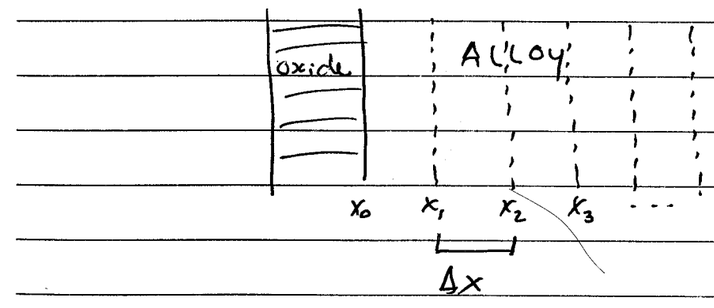
Turned to QA records on 9/13/2000 OPR

9/21/00 OPR

9/21/00 OPR

I have been documenting relevant computations at a ~~8/21/00 OPR~~ paper located at d:/asvaldo/dst/c-22/PassivityNiCrMo.wpd. Multiple comments are provided at that paper making reference to this scientific notebook. Comments are hidden in the text, and can be located on the left side of the word perfect document. They are labeled as [OPR]. Single clicking on the box will display the comment.

The latest version of the paper could have a number in the name; e.g. PassivityNiCrMo3.wpd. In the paper I discuss that the estimates of the alloy lifetime based on finite difference computations do not depend on the selection of the spatial step, Δx, nor the time step, Δt. In the computations that follow, I am trying to understand why this is the case.



Diffusion coefficients are very small, and the concentration of vacancies at all times for $x > x_1$ is always negligible. Therefore, the following equations can be used to describe the concentrations between x_0 and x_1:

$$\frac{d m_i}{dt} = -S \frac{m_i}{m_T} K_1^i \qquad i = Ni, Cr, Mo$$

9/21/00 OPB 9/21/00

m_i represents the number of atoms between x_0 and x_1.

$m_T = C_T S \Delta x$ → position step (cm)

S → reference surface (cm^2)

C_T → total concentration (mol/cm^3)

m_T → constant.

The solution to such equation is

$$m_i = m_i^0 \, e^{-\frac{S}{m_T} k_i^i t} \qquad \frac{S}{m_T} = \frac{1}{C_T \Delta x}$$

$$\hookrightarrow m_i^0 = C_i^0 S \Delta x$$

C_i^0 → initial concentration of i

Equivalently $C_i = C_i^0 \, e^{-\frac{1}{C_T \Delta x} k_i^i t}$

Since at all times $C_v + C_{N_i} + C_{C_r} + C_{M_o} = C_T$ = constant,

then $C_v(t) = C_T - C_{N_i}(t) - C_{C_r}(t) - C_{M_o}(t)$

The critical concentration fraction, P_{max}, is defined as the maximal vacancy fraction after which rupture of the film occurs.

In consistency with the Case 7 in the file

d:/osvaldo/clst/c-22/comp4.nb

we select $P_{max} = 0.5$.

I need to find the time, t_c, such that

$$C_v(t_c) = P_{max} \, C_T$$

If $t_c \propto \Delta x$ this would explain why the lifetime estimates are independent of the time step Δx.

9/21/2000

If $t_c \propto \Delta x$, the corrosion rate defined as

$$r = \frac{\Delta x}{t_c}$$

is constant, independent of the selection of Δx and of time. In the computations summarized at a spread sheet, we prove that indeed this is the case. Therefore, estimates of the lifetime do not depend on Δx!

d:\osvaldo\clst\c-22\ReslifeC22.xls\Case7Support

Δx Delx (cm)	Pmax = 0.1 Time to reach Pmax (yr) t_c	Δx Delx (cm)	Pmax = 0.2 Time to reach Pmax (yr) t_c	Δx Delx (cm)	Pmax = 0.5 Time to reach Pmax (yr) t_c	Δx Delx (cm)	Pmax = 0.7 Time to reach Pmax (yr) t_c	Δx Delx (cm)	Pmax = 0.9 Time to reach Pmax (yr) t_c
1.00E-07	0.000206	1.00E-07	0.000443	1.00E-07	0.001492	1.00E-07	0.002948	1.00E-07	0.009053
1.00E-06	0.002056	1.00E-06	0.004426	1.00E-06	0.014915	1.00E-06	0.029478	1.00E-06	0.090537
0.00001	0.020555	0.00001	0.044261	0.00001	0.149152	0.00001	0.29478	0.00001	0.905345
0.0001	0.205557	0.0001	0.442613	0.0001	1.491522	0.0001	2.947805	0.0001	9.053338
0.001	2.055572	0.001	4.426129	0.001	14.91522	0.001	29.47791	0.001	90.53685
0.01	20.55522	0.01	44.26132	0.01	149.1522	0.01	294.7799	0.01	905.3686

Osvaldo Pensado 9/21/2000

The reason of why the lifetime does not depend on the space time step is explored in this worksheet. Approximations are made to provide an analytical solution to surface concentrations (it is assumed that all of the vacancies accumulate on the surface, wich is almost right). It is proved that there is a linear dependence between the time to achieve the critical concentration, Pmax, and the position step Δx. Let us call this time tc. The corrosion rate can be computed as Δx/tc, which is a constant. Therefore, the failure time is independent of the selection of the spatial step Δx. Additional details in Scientific Notebook 304, page 169-171.

The above numbers have been generated with the Mathematica notebook comp4.nb, entries on 9/21/2000
d:\osvaldo\clst\c-22\comp4.nb
See the above notebook and Scientific Notebook 304, p. 169-171 for additional details.

The above computations show the linear dependence between Δx and t_c. Any reasonably small value of Δx can be selected for the finite difference computations.

9/21/2000

9/27/2000 Qfy

I did some additional research to verify that $\frac{\Delta x}{t_c}$ is constant, since this is not intuitive.

Let us define t' as $t' = \frac{K_1^{Ni}\, t}{C_T \Delta x}$

$C(t) = C_{Ni}(t) + C_{Cr}(t) + C_{Mo}(t)$ can be approximated, reasonably well by an exponential function.

$$C(t') = C_{Ni}^{\circ} e^{-t'} + C_{Mo}^{\circ} e^{-\frac{K_1^{Mo}}{K_1^{Ni}} t'} + C_{Cr}^{\circ} e^{-\frac{K_1^{Cr}}{K_1^{Ni}} t'}$$

Note that $\frac{dC}{dt'} < 0$ for every t'

Therefore $C(t')$ is a monotonic function and it has inverse. Let us call C^{-1} this inverse.

$$C_v(t') = C_T - C(t')$$

The time at which P_{max} is established can be computed as

$$C_v(t_o') = C_T - C(t_o') = P_{max} C_T$$

$$C(t_o') = (1 - P_{max}) C_T$$

$$t_o' = C^{-1}[(1-P_{max}) C_T) = \frac{K_1^{Ni}\, t_o}{C_T \Delta x}$$

Therefore $t_o = \frac{C_T \Delta x}{K_1^{Ni}} C^{-1}[(1-P_{max}) C_T]$

or $\frac{\Delta x}{t_o} = \frac{K_1^{Ni}}{C_T\, C^{-1}[(1-P_{max}) C_T]}$

The function C^{-1} must be defined numerically (it does not have a closed form), but in general is well defined.

The conclusion is that $\frac{\Delta x}{t_o}$ = corrosion rate is a constant, that depends only on P_{max}.

Under what conditions is the above conclusion valid?

$$C(t) = C_{Ni}^{\circ} e^{-\frac{K_1^{Ni} t}{C_T \Delta x}} + C_{Cr}^{\circ} e^{-\frac{K_1^{Cr} t}{C_T \Delta x}} + C_{Mo}^{\circ} e^{-\frac{K_1^{Mo} t}{C_T \Delta x}}$$

We can defined $C_2(\lambda) = C_{Ni}^{\circ} e^{-\frac{K_1^{Ni}}{C_T}\lambda} + C_{Cr}^{\circ} e^{-\frac{K_1^{Cr}}{C_T}\lambda} + C_{Mo}^{\circ} e^{\frac{K_1^{Mo}}{C_T}\lambda}$

then $C_2\left(\frac{t}{\Delta x}\right) = C(t)$

Note that $C_2'(\lambda) < 0 \Rightarrow C_2^{-1}(\bar{c})$ exists.

$$C_v = C_T - C_2(\lambda)$$

$$C_T - C_2(\lambda_o) = P_{max} C_T \Rightarrow C_2(\lambda_o) = (1 - P_{max}) C_T$$

$$\lambda_o = C_2^{-1}[(1-P_{max}) C_T]$$

$$t_o = \Delta x\, C_2^{-1}[(1-P_{max}) C_T]$$

$$\frac{\Delta x}{t_o} = \frac{1}{C_2^{-1}[(1-P_{max}) C_T]} = \text{constant!}$$

The only two requirements for the above conclusion are

1. C_2^{-1} exists
2. $C(t)$ can be written as $C(t) = C_2\left(\frac{t}{\Delta x}\right)$

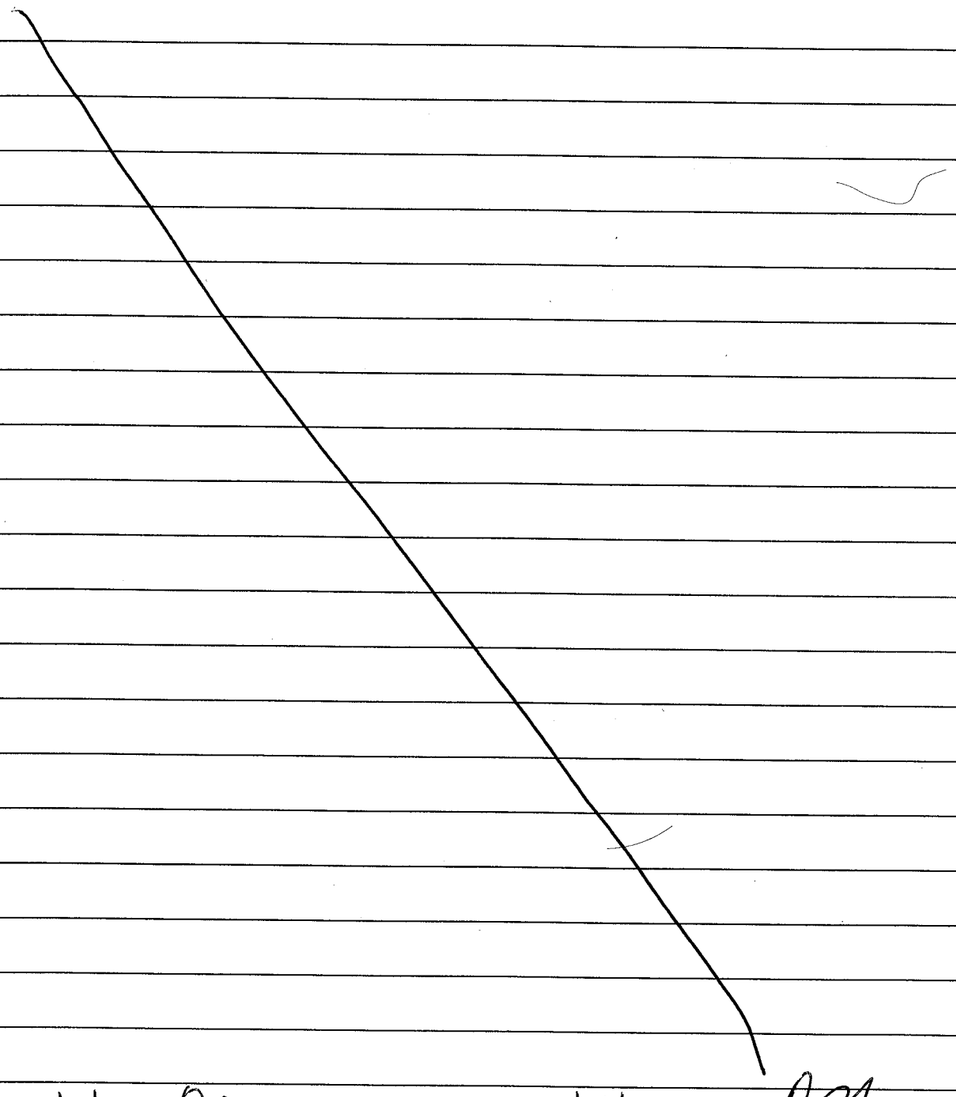
The point 2 is guaranteed because the diffusion coefficient is very small.

The point 1 is expected to have wide generality. However, other situations are envisioned where the surface concentration oscillates in time.

9/27/2000 QA

Under that circumstance, point 1 would be false. Therefore, if the diffusion coefficient is not small, it is necessary to apply some physical restrictions on the selection of the position step, Δx.

9/27/2000 QA



Turned to QA records on 4/4/2001 QA

6/26/2001 QA

It has been suggested, by Dr. Macdonald, that vacancies in the bulk of the metal are not an issue. My computations do not support such statement. I need to perform additional scoping calculations to convince myself that vacancies are an issue or not.

Constitutive equation

$$\frac{\partial C_v}{\partial t} = D \vec{\nabla}^2 C_v$$

At $x=0$ (metal/film interface)

$$\vec{J}_v = -D \vec{\nabla} C_v - \underbrace{\frac{K}{C_0}}_{\text{vacancies injected in the metal due to anodic dissolution of the film.}} (C_0 - C_v) \quad x=0$$

I am approximating the passive current density as

$I = F K \frac{C_0 - C_v}{C_0}$ ⇝ It is an oversimplification, but it is ok for scoping computations

Assuming interstitial dissolution, the passive current density is

$$I = F(\chi a_{Cr} K_i^{Cr} + \delta a_{Ni} K_i^{Ni} + \xi a_{Mo} K_i^{Mo})$$

If I arbitrarily assume $K = \chi K_i^{Cr} = \delta K_i^{Ni} = \xi K_i^{Mo}$, then

$$I = F k (a_{Cr} + a_{Ni} + a_{Mo}) = F K \frac{C_0 - C_v}{C_0}$$

The relationship $\chi K_i^{Cr} = \delta K_i^{Ni} = \xi K_i^{Mo}$ is not accurate. However, for the sake of scoping calculations it is OK to use it. That relationship is not a way off.

QA

6/26/01

at $X=0$ $\quad \vec{J}_v = -D\nabla C_v - \frac{K}{C_0}(C_0 - C_v)$

C_0 is the total number of sites per unit of volume.

$\nabla \cdot \vec{J}_v = -D\nabla^2 C_v + \frac{K}{C_0}\nabla C_v \quad X=0$

At $x=0$: $\quad \frac{\partial C_v}{\partial t} = -\nabla\cdot\vec{J}_v = D\nabla^2 C_v - \frac{K}{C_0}\nabla C_v$

$\partial_t C_v = D\partial_{xx}^2 C_v - \frac{K}{C_0}\partial_x C_v \quad X=0 \rightsquigarrow$ boundary condition

Initial condition $C_v = 0 \quad X>0$

Need to express constitutive equation in dimensionless form

$D \sim \frac{cm^2}{s} \qquad K \sim \frac{mol}{cm^2 \cdot s} \Rightarrow \frac{K}{C_0} \sim \frac{cm}{s}$

$\frac{D}{K} C_0 \sim cm \Longrightarrow$ reference length

$\mathcal{L} = \frac{DC_0}{K}$

$\tau = \frac{\mathcal{L}^2}{D} = \frac{D^2C_0^2}{K^2D} = \frac{DC_0^2}{K^2} \Rightarrow$ reference time

$\frac{\partial}{\partial t}\frac{C_v}{C_0} = D\frac{\partial^2}{\partial x^2}\frac{C_v}{C_0} \Rightarrow \tau\frac{\partial}{\partial t}\frac{C_v}{C_0} = \left(\frac{DC_0^2}{K^2}\right) D\frac{\partial^2 C_v}{\partial x^2 C_0}$

$t' = \frac{t}{\tau} \qquad C = \frac{C_v}{C_0} \rightarrow \frac{\partial}{\partial t'}C = \frac{D^2C_0^2}{K^2}\frac{\partial^2}{\partial x^2}C$

$x' = \frac{x}{\mathcal{L}} = \frac{x}{\frac{DC_0}{K}} \Rightarrow \frac{\partial C}{\partial t'} = \frac{\partial^2 C}{\partial x'^2}$

At $x=0$

$\tau\frac{\partial}{\partial t}C = \frac{D^2C_0^2}{K^2}\frac{\partial^2}{\partial x^2}C - \underbrace{\frac{DC_0^2}{K^2}\frac{K}{C_0}}_{\frac{DC_0}{K}}\frac{\partial}{\partial x}C$

$\Rightarrow \frac{\partial}{\partial t'}C = \frac{\partial^2}{\partial x'^2}C - \frac{\partial}{\partial x'}C$

6/26/01

$D \sim 10^{-30}\ cm^2/s$

$K_1^{Cr} \sim 4.84\times10^{-14}\ \frac{mol}{s\cdot cm^2}$, $K_1^{Ni} \sim 3\times10^{-13}\ \frac{mol}{s\cdot cm^2}$, $K_1^{Mo} \sim 1.74\times10^{-13}\ \frac{mol}{s\cdot cm^2}$

$K \sim \frac{1}{3}\left(3K_1^{Cr} + 2K_1^{Ni} + 6K_1^{Mo}\right) \sim 5.96\times10^{-13} \sim 6\times10^{-13}\ \frac{mol}{s\cdot cm^2}$

$C_0 \sim 0.134\ mol/cm^3$

$\mathcal{L} = \frac{DC_0}{K} \sim 2.23\times10^{-17}\ cm$

$\tau = \frac{\mathcal{L}^2}{D} = 4.988\times10^{-8}\ sec \sim 5\times10^{-8}\ sec$

$t' = \frac{t}{\tau} \qquad x' = \frac{x}{\mathcal{L}} \Rightarrow t = \tau t' \ \&\ x = \mathcal{L}x'$

t' and x' ranges have to be very large

$1_{yr} = 31557600\ sec$

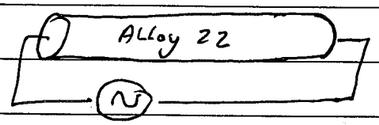
$t' \in [0, 6\times10^{14}] \rightsquigarrow$ 1yr simulation!

Forget it! It is not going to work!

8/27/01 QM

SKIN EFFECT

Idea by Sridhar:



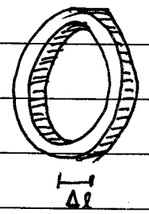
measure resistances at high frequencies
Current concentrates on surface at high frequencies.

$R = \rho \frac{l}{A}$ if $A \to 0$, $R \to \infty$.

Seems that the ~~ampmeter does~~ OPR 8/27/01 meter of resistance (ohmmeter) does not need to have small resolution.

$\rho \propto \frac{1}{\tau} \propto \Sigma v$ $\quad v \sim$ velocity at Fermi surface

↳ time to scatter $\quad \Sigma \sim$ scattering cross-section



let $n \sim$ density of defects.

$n \Delta l \sim$ surface density of defects.

Δl is fixed by physical dimensions of defect

$\Sigma = n \Delta l A \dot{\vartheta} \longrightarrow$ scattering cross-section of a single defect.

↳ surface area

$\rho \propto (\Delta l A \vartheta v) n$

The important conclusion is that the resistivity is proportional to the density of defects.

$$\frac{R_1}{R_0} = \frac{\rho_1}{\rho_0} = \frac{n_1}{n_0}$$

QM

8/27/01 QM

From page 177

$k \sim 6 \times 10^{-13}$ mol/s·cm²

OPR 8/27/01

~~$A \Delta l n_1 = n_0 A \Delta l +$~~

$S = 2\pi r L$

$n_d \to$ number of defects:

$$\frac{d}{dt}(n_d) = kS = k(2\pi r L)$$

$$n_d^0 = n_0 (2\pi r) \Delta r L$$

$$n_d = n_0 (2\pi r) \Delta r L + (2\pi r L) k t$$

$$n_1 = \frac{n_d}{2\pi r \Delta r L} = n_0 + \frac{2\pi r L}{2\pi r L \Delta r} k t = n_0 + \frac{1}{\Delta r} k t$$ ⇝ number of defects per unit of volume.

$$\frac{n_1}{n_0} = 1 + \frac{kt}{\Delta r n_0} = 1 + \left(\frac{k}{\Delta r n_0}\right) t$$

Assume $n_0 \sim 10^{-9}$ mol/cm³

$\Delta r = 10$ nm $= 10 \cdot 10^{-9}$ m $= 10^{-8}$ m $= 10^{-6}$ cm $= 10^{-6}$ cm

$n_0 \Delta r \sim 10^{-15}$ mol cm⁻²

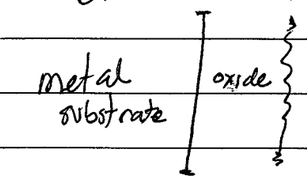
$\frac{k}{\Delta r n_0} \sim 6 \times 10^{-13} \times 10^{15}$ s⁻¹ $= 600$ s⁻¹ if $n_0 \sim 10^{-9}$ mol cm⁻³

In principle, there is good chance of detecting changes in resistivity. It is important to compare the resistivity of the as-received sample vs resistivity of oxidized sample.

QM Turned to QA on 10/9/2001

1/31/2002 OPR

Hypotheses of uniform dissolution:



1. Dissolution must proceed at a stoichiometric rate.

$$I = F\left[\chi a_{Cr}\left(K_1^{Cr}+K_3^{Cr}\right)+\delta a_{Ni}\left(K_1^{Ni}+K_3^{Ni}\right)+\xi a_{Mo} K_1^{Mo}\right]$$

$$J_{Cr} = a_{Cr}\left(K_1^{Cr}+K_3^{Cr}\right) = a_{Cr} K_{tot}^{Cr}$$ OPR, 1/31/02

$$J_{Ni} = a_{Ni}\left(K_1^{Ni}+K_3^{Ni}\right) = a_{Ni} K_{tot}^{Ni}$$ OPR 1/31/02

$$J_{Mo} = a_{Mo} K_1^{Mo}$$

$$I = F\left(\chi J_{Cr} + \delta J_{Ni} + \xi J_{Mo}\right)$$

Let x_{Cr}°, x_{Ni}°, x_{Mo}° represent the initial weight fraction. OPR, 1/31/02

$$1 = x_{Cr}^{\circ} + x_{Ni}^{\circ} + x_{Mo}^{\circ}$$

Let ρ_A be the alloy density, and V_T, the total volume.

$m_{alloy} = \rho_A V_T$ → total mass

$m_{Cr} = x_{Cr}^{\circ}\rho_A V_T$ → Cr mass

$m_{Ni} = x_{Ni}^{\circ}\rho_A V_T$ → Ni mass

$m_{Mo} = x_{Mo}^{\circ}\rho_A V_T$ → Mo mass

Let M_{Cr}, M_{Ni}, M_{Mo} be the equivalent weights (kg/mol)

$$\#\text{ moles of Cr} = \frac{x_{Cr}^{\circ}\rho_A V_T}{M_{Cr}}, \text{ and so on}$$

$$\#\text{ moles total} = \left(\frac{x_{Cr}^{\circ}\rho_A}{M_{Cr}} + \frac{x_{Ni}^{\circ}\rho_A}{M_{Ni}} + \frac{x_{Mo}^{\circ}}{M_{Mo}}\right)\rho_A V_T$$ OPR, 1/31/02 OPR, 1/31/02

$$a_{Cr}^{\circ} = \frac{x_{Cr}^{\circ}/M_{Cr}}{\frac{x_{Cr}^{\circ}}{m_{Cr}} + \frac{x_{Ni}^{\circ}}{M_{Ni}} + \frac{x_{Mo}^{\circ}}{M_{Mo}}}, \text{ and so on}$$

1/31/2002 OPR

Stoichiometric dissolution can occur if and only if

$$\frac{J_{Cr}}{J_{Ni}} = \frac{a_{Cr}^{\circ}}{a_{Ni}^{\circ}}, \quad \frac{J_{Cr}}{J_{Mo}} = \frac{a_{Cr}^{\circ}}{a_{Mo}^{\circ}}, \quad \frac{J_{Ni}}{J_{Mo}} = \frac{a_{Ni}^{\circ}}{a_{Mo}^{\circ}}$$

$$\frac{K_{tot}^{Cr}}{K_{Ni}} = \left(\frac{a_{Cr}^{\circ}}{a_{Cr}^{m/f}}\right)\left(\frac{a_{Ni}^{m/f}}{a_{Ni}^{\circ}}\right) \text{ and so on}$$

$$\frac{K^{Cr}}{K_{Mo}} = \left(\frac{a_{Cr}^{\circ}}{a_{Cr}^{m/f}}\right)\left(\frac{a_{Mo}^{m/f}}{a_{Mo}^{\circ}}\right), \quad \frac{K^{Ni}}{K^{Mo}} = \left(\frac{a_{Ni}^{\circ}}{a_{Ni}^{m/f}}\right)\left(\frac{a_{Mo}^{m/f}}{a_{Mo}^{\circ}}\right)$$

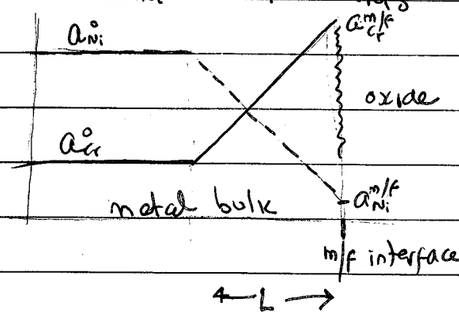
There is no reason whatsoever of why the above equations should hold.

The above equations, if valid, could be used to compute the kinetic rates if the concentration fractions are known.

The problem does not end there.

Assume $K_{Ni} > K_{Mo} > K_{Cr}$

$$a_{Ni}^{\circ} > a_{Cr}^{\circ} > a_{Mo}^{\circ}$$



$$\frac{\partial C_T}{\partial t} = 0 = \nabla_x\left(J_{Cr} + J_{Ni} + J_{Mo} + J_V\right)$$ 1/31/02 OPR

$$\Rightarrow J_{Cr} + J_{Ni} + J_{Mo} = J_T = \text{constant}$$

Assuming that Ni has higher mobility than Cr:

$$J_{Ni} \sim D_{Ni}\frac{C_{Ni}^{\circ} - C_{Ni}^{m/f}}{L}$$

The only solution for the concentration to be invariant with time is that $J_x^{diff} = J_x^{kinetic}$

I do not see any reason of why the above equation should hold.

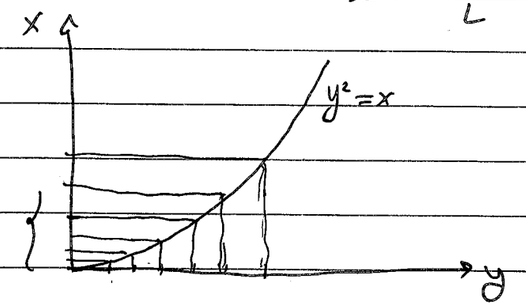
I do not see why steady-state happens!!

2/25/2002 DM

Objective, rewrite $\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2}$ with a change in variables, so that I have a description with greater density of points near the interface.

$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2}$ $\rightsquigarrow$ t and x are dimensionless

$x \sim \frac{x}{L}$ and $t \sim \frac{tP}{L^2}$



$y^2 = x \qquad 2y\,dy = dx \qquad \frac{\partial}{\partial x} = \frac{1}{2y}\frac{\partial}{\partial y}$

$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2}$ $\rightsquigarrow$ dimensionless diffusion equation.

$$\frac{\partial c}{\partial x} = \frac{1}{2y}\frac{\partial c}{\partial y} \Rightarrow \frac{\partial^2 c}{\partial x^2} = \frac{1}{2y}\frac{\partial}{\partial y}\left(\frac{1}{2y}\frac{\partial c}{\partial y}\right)$$

$$\frac{\partial^2 c}{\partial x^2} = \frac{1}{2y}\left\{\frac{1}{2y}\frac{\partial^2 c}{\partial y^2} - \frac{1}{2y^2}\frac{\partial c}{\partial y}\right\} = \frac{1}{4y^2}\left\{\frac{\partial^2 c}{\partial y^2} - \frac{1}{y}\frac{\partial c}{\partial y}\right\}$$

$$\left.\frac{\partial^2 c}{\partial y^2}\right|_{ij} = \frac{1}{2\Delta y^2}\left\{C_{ij-1} - 2C_{ij} + C_{ij+1}\right\}$$

$$\left.\frac{\partial c}{\partial y}\right|_{ij} = \frac{1}{2\Delta y}\left\{-C_{ij-1} + C_{ij+1}\right\}$$

2/25/2002 DM

$$\left(\frac{\partial^2 c}{\partial y^2} - \frac{1}{y}\frac{\partial c}{\partial y}\right)\Big|_{ij} = \left(\frac{1}{\Delta y^2} + \frac{1}{y_j}\frac{1}{2\Delta y}\right)C_{ij-1} - \frac{2}{\Delta y^2}C_{ij} + \left(\frac{1}{\Delta y^2} - \frac{1}{y_j}\frac{1}{2\Delta y}\right)C_{ij+1}$$

$$\frac{1}{4y^2}\left(\frac{\partial^2 c}{\partial y^2} - \frac{1}{y}\frac{\partial c}{\partial y}\right)\Big|_{ij} = \frac{1}{4y_j^2\Delta y}\left\{\left(\frac{1}{\Delta y} + \frac{1}{2y_j}\right)C_{ij-1} - \frac{2}{\Delta y}C_{ij} + \left(\frac{1}{\Delta y} - \frac{1}{2y_j}\right)C_{ij+1}\right\}$$

$$\frac{\partial c}{\partial t} = \frac{1}{\Delta t}\left(C_{i+1,j} - C_{ij}\right)$$

$$C_{i+1,j} = C_{ij} + \frac{\Delta t}{4y_j^2\Delta y}\left\{\left(\frac{1}{\Delta y} + \frac{1}{2y_j}\right)C_{ij-1} - \frac{2}{\Delta y}C_{ij} + \left(\frac{1}{\Delta y} - \frac{1}{2y_j}\right)C_{ij+1}\right\}$$

y_j is dimensionless, equally spaced, and ranges for 0 to 1

$\Delta t \sim \frac{D_{eff}\,t}{L^2}$; i.e., Δt is also dimensionless

Boundary condition $J(y=1) = 0$

$\frac{\partial c}{\partial t} = -\nabla \cdot \vec{J}$ (nodes: $i,j-1$; i,j; $i+1,j$)

$$(C_{i+1,j} - C_{ij})\Delta x = -(J_{ij} - J_{i,j-1})\Delta t = J_{i,j-1}\,\Delta t$$

$$J_{ij-1} = -D\frac{C_{ij} - C_{ij-1}}{\Delta x}$$

$$C_{i+1,j} = C_{ij} + J_{ij-1}\frac{\Delta t}{\Delta x} = C_{ij} - D\left(C_{ij} - C_{ij-1}\right)\Delta t/\Delta x^2$$

if $C_{ij} = 0 \Rightarrow C_{i+1,j} = D\,C_{i,j-1}\frac{\Delta t}{\Delta x^2} = C_{ij-1}\,D\left(\frac{\Delta t}{\Delta x^2}\right)$

Necessarily $D\frac{\Delta t}{\Delta x^2} < 1$, since otherwise $C_{i+1,j} > C_{ij-1}$ and that would imply vacancy creation.

DM

OM 2/25/2002

$y_n = (n-1)\,\Delta y \qquad n = 1, 2, 3, 4 \ldots$

$x_n = (n-1)^2 \Delta y^2 L$

$x_{n+1} = n^2 \Delta y^2 L$

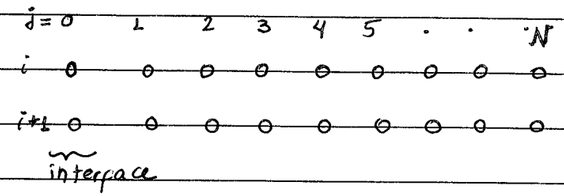
$\Delta x_n = x_{n+1} - x_n = \Delta y^2 L\,[n^2 - (n-1)^2] = \Delta y^2 L\,(2n-1)$

$\Delta x_1 = \Delta y^2 L$

OM

3/8/2002 I realized that it is not worth it pursuing the idea of the greater density of points near the interface. Due to computer memory constraints, it will not be possible to simulate complete alloy thicknesses. Simulations should concentrate on a fraction of the alloy thickness.

I need to summarize the equations that I have used in the finite difference computations.



Vacancy concentration

$C^V_{i+1,0}$ = Vacancies in the system $- \sum_{j=1}^{N} C^V_{i+1,j}$

Vacancies from $j=1$ to N

Vacancies in the system = C^{VT}_{i+1} = total number of vacancies at $t=i+1$

$C^{VT}_{i+1} = C^{VT}_i + \text{injected} - \text{ejected}$

injected → vacancies injected from $t=i$ to $t=i+1$ at $j=0$

ejected → " ejected " " at $j=N$

3/8/2002 OM

$\text{injected} = \dfrac{K_1^{Ni} C_{i,0}^{Ni} + K_1^{Cr} C_{i,0}^{Cr} + K_1^{Mo} C_{i,0}^{Mo}}{C_T} \dfrac{\Delta t}{\Delta x} = \dfrac{\Delta t}{C_T \Delta x}\left(K_1^{Ni} C_{i,0}^{Ni} + K_1^{Cr} C_{i,0}^{Cr} + K_1^{Mo} C_{i,0}^{Mo}\right)$

= Vacancies injected in the Δt interval

ejected = 0 for a closed system

ejected = $(C^V_{i,N-1} - C^V_{i,N})\, D \dfrac{\Delta t}{\Delta x^2}$ (vacancies in system)

Summary $C^V_{i+1,0} = C^{VT}_{i+1} - \sum_{j=1}^{N} C_{i+1,j}$ (vacancies from $j=1$ on)

$C^{VT}_{i+1} = C^{VT}_i + \text{injected} - \text{ejected}$

$\text{injected} = \dfrac{\Delta t}{C_T \Delta x}\left(K_1^{Ni} C_{i,0}^{Ni} + K_1^{Cr} C_{i,0}^{Cr} + K_1^{Mo} C_{i,0}^{Mo}\right)$

$\text{ejected} = \begin{cases} 0 & \text{for a closed system} \\ (C^V_{i,N-1} - C^V_{i,N})\, D \dfrac{\Delta t}{\Delta x^2} & \text{free boundary at } x=N \end{cases}$

Note that $C^{VT}_{i+1} = \sum_{j=0}^{N} C^V_{i,j} = C^V_{i+1,0} + \sum_{j=1}^{N} C^V_{i+1,j} = \left(C^{VT}_{i+1} - \sum_{j=1}^{N}\right) + \sum_{j=1}^{N}$

$= C^{VT}_{i+1}$

Thus, the definition of C^{VT}_{i+1} is consistent

$C^{VT}_{i+1} = \begin{cases} \sum_{j=0}^{N} C^V_{i+1,j} \\ C^{VT}_i + \text{injected} - \text{ejected} \rightarrow \text{more useful in an algorithm} \end{cases}$

1 FROM $j=1$ to $N-1$, vacancy concentrations are computed as

$C_{i+1,j} = \lambda C_{i,j-1} + (1-2\lambda) C_{i,j} + \lambda C_{i,j+1} \qquad \lambda = D \dfrac{\Delta t}{\Delta x^2}$

$j = N$

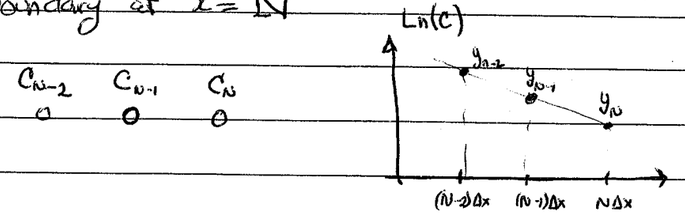
$C_{i+1,N} = \begin{cases} C_{i,N} + \left(C^V_{i,N-1} - C^V_{i,N}\right) D \dfrac{\Delta t}{\Delta x^2} & \text{for a closed system} \\ \dfrac{C^2_{i+1,N-1}}{C_{i+1,N-2}} & \text{for a free boundary at } X=N \end{cases}$

See next page for derivation of this formula

→ linear-logarithmic extrapolation

3/8/2002 OPY

Free boundary at $x = N$



$$y - y_{N-1} = \left(\frac{y_{N-1} - y_{N-2}}{\Delta x}\right)(x - (N-1)\Delta x)$$

$$y_N = y_{N-1} + \frac{y_{N-1} - y_{N-2}}{\Delta x}\Delta x = y_{N-1} + y_{N-1} - y_{N-2} = 2y_{N-1} - y_{N-2}$$

$y_{N-1} = \ln(C_{N-1}) \quad y_j = \ln(C_j)$

$$\ln C_N = 2\ln C_{N-1} - \ln C_{N-2} = \ln C_{N-1}^2 - \ln C_{N-2} = \ln\left(\frac{C_{N-1}^2}{C_{N-2}}\right)$$

$$\Rightarrow C_N = \frac{C_{N-1}^2}{C_{N-2}} \Rightarrow \text{derived from linear-logarithmic extrapolation}$$

Vacancy concentration has been worked out

1st step : Compute $C^V_{i+1,j} \quad j = 1 \cdots N$

2nd step : Compute $C^V_{i+1,0}$

3rd step $i \to i+1$

Atom concentration

$j = 0$, metal/film interface

$C_{i+1,0} = C_{i,0} - (\text{atoms ejected}) + (\text{atoms diffusing in from position } j=1)$

$$\text{atoms ejected} = \frac{C_{i,0}}{C_T} K_1 \frac{\Delta t}{\Delta x} \rightsquigarrow \text{atoms injected into the oxide film}$$

$$[\text{atoms diffusing in from } j=1] = \left(C^V_{i,0} + \text{vacancies injected} - C^V_{i+1,0}\right)\frac{C_{i,1}}{C^{Ni}_{i,1} + C^{Cr}_{i,1} + C^{Mo}_{i,1}}$$

Note that $\left[C^V_{i,0} + \text{vacancies injected} - C^V_{i+1,0}\right]$ is a measurement of the vacancies diffusing away from the interface. A fraction of the total number of vacancies moving away corresponds to the Ni atoms jumping in.

3/8/2002 OPY

$j = 0$

Two options, or in general

eq. valid if $J_A \sim \frac{D^A_{C_V}} C^A \nabla C_V$, $C_V \ll 1$

$$C^A_{i+1,0} = C^A_{i,0} - \underbrace{\frac{C^A_{i,0}}{C_T} K_1^A \frac{\Delta t}{\Delta x}}_{\text{atoms ejected}} + \underbrace{\left(C^V_{i,0} + \text{vacancies injected} - C^V_{i+1,0}\right)}_{\text{vacancies diffusing away from } j=0} \underbrace{\frac{D^A C^A_{i,1}}{D^A C^A_{i,1} + D^B C^B_{i,1} + D^C C^C_{i,1}}}_{\text{atoms A jumping to } j=0 \text{ from } j=1}$$

Note that if $D^A = D^B = D^C$ the above formula reduces to

$$C^A_{i+1,0} = C^A_{i,0} - \frac{C^A_{i,0}}{C_T} K_1^A \frac{\Delta t}{\Delta x} + \left(C^V_{i,0} + \text{vacancies injected} - C^V_{i+1,0}\right)\frac{C^A_{i,1}}{C^A_{i,1} + C^B_{i,1} + C^C_{i,1}}$$

which is the formula used in subroutines defined in Mathematica packages Fire2.m, vacancyDiffusion.m, and vacancyDiffusionC.m.

From page 140: $J = -\frac{D}{C_V}(C_V \nabla C - C \nabla C_V)$

$$J_V = -\frac{1}{C_V^0}\left(D^{Ni}C_{Ni} + D^{Cr}C_{Cr} + D^{Mo}C_{Mo}\right)\nabla C_V + \frac{C_V}{C_V^0}\left(D^{Ni}\nabla C_{Ni} + D^{Cr}\nabla C_{Cr} + D^{Mo}\nabla C_{Mo}\right)$$

I have shown that if $D^{Ni} = D^{Cr} = D^{Mo} \Rightarrow J_V = -\left(\frac{D}{C_V^0} C_T\right)\nabla C_V = -D^{eff}\nabla C_V$

In general $C_V \ll C_{Ni}, C_{Cr}, C_{Mo}$ $\Rightarrow J_V \sim -\frac{1}{C_V^0}\left(D^{Ni}C_{Ni} + D^{Cr}C_{Cr} + D^{Mo}C_{Mo}\right)\nabla C_V$

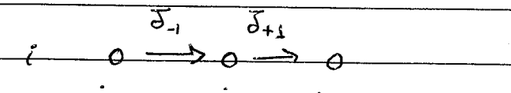
$\nabla C_{Mo,Ni,Cr} \ll \nabla C_V$

I am going to assume that $C_V \ll C_{Ni}, C_{Cr}, C_{Mo}$ } For assumption

If $D^{Ni} \neq D^{Cr} \neq D^{Mo}$, Equation 1 on page 185 must be modified as well

3/8/2002 CAY

$$J_V \sim \frac{1}{C_V^0}\left(D^{Ni}C^{Ni} + D^{Cr}C^{Cr} + D^{Mo}C^{Mo}\right)\nabla C_V$$



$$J_{-1} \sim \frac{1}{C_V^0}\left(D^{Ni}C^{Ni}_{ij} + D^{Cr}C^{Cr}_{ij} + D^{Mo}C^{Mo}_{ij}\right)\frac{1}{\Delta x}\left(C^V_{ij-1} - C^V_{ij}\right)$$

$$J_{+1} \sim \frac{1}{C_V^0}\left(D^{Ni}C^{Ni}_{ij} + D^{Cr}C^{Cr}_{ij} + D^{Mo}C^{Mo}_{ij}\right)\frac{1}{\Delta x}\left(C^V_{ij} - C^V_{ij+1}\right)$$

$$C^V_{i+1,j} = C^V_{ij} + J_{-1}\frac{\Delta t}{\Delta x} - J_{+1}\frac{\Delta t}{\Delta x}$$

(2) $$\boxed{C^V_{i+1,j} = C^V_{ij} + \frac{1}{C_V^0}\left(D^{Ni}C^{Ni}_{ij} + D^{Cr}C^{Cr}_{ij} + D^{Mo}C^{Mo}_{ij}\right)\frac{\Delta t}{\Delta x^2}\left(C^V_{ij-1} - 2C^V_{ij} + C^V_{ij+1}\right)}$$

Note that Equation (2) reduces to Equation (1) (page 185) when $D^{Ni} = D^{Cr} = D^{Mo}$ and C_V is small (i.e., $C_T \approx C_{Ni} + C_{Cr} + C_{Mo}$)

Equation (2) is correct, although the procedure to derive it is not

In general:

$$J_V = -\frac{1}{C_V^0}\left(\sum_A D^A C_A\right)\nabla C_V + \frac{1}{C_V^0}C_V\left(\sum_A D^A \nabla C_A\right)$$

$$-\nabla\cdot J_V = \frac{1}{C_V^0}\left(\sum_A D^A \nabla C_A\right)\nabla C_V + \frac{1}{C_V^0}\left(\sum_A D^A C_A\right)\nabla^2 C_V$$
$$-\frac{1}{C_V^0}\left(\sum_A D^A \nabla C_A\right)\nabla C_V - \frac{C_V}{C_V^0}\left(\sum_A D^A \nabla^2 C_A\right)$$

$$= \frac{1}{C_V^0}\left(\sum_A D^A C_A\right)\nabla^2 C_V - \frac{C_V}{C_V^0}\left(\sum_A D^A \nabla^2 C_A\right)$$

Now C_V is small, then

$$-\nabla\cdot J_V \sim \frac{1}{C_V^0}\left(\sum_A D^A C_A\right)\nabla^2 C_V$$

Thus $$\frac{\partial C_V}{\partial t} \approx \frac{1}{C_V^0}\left(\sum_A D^A C_A\right)\nabla^2 C_V$$ this equation is consistent with (2)

3/8/2002 CAY

$$\frac{\partial C_V}{\partial t} \approx \frac{1}{C_V^0}\left(\sum_A D^A C_A\right)\nabla^2 C_V$$

Thus $C^V_{i+1,j} = C^V_{ij} + \frac{1}{C_V^0}\left(\sum_A D^A C_A\right)\frac{\Delta t}{\Delta x^2}\left(C^V_{i,j-1} - 2C^V_{ij} + C^V_{ij+1}\right)$
which is equivalent to Equation 2.

$$J=0: \quad C^A_{i+1,0} = C^A_{i,0} - \frac{C^A_{i,0}}{C_T}K^A\frac{\Delta t}{\Delta x} + \left(C^V_{i,0} + \text{vacancies injected} - C^V_{i+1,0}\right)\left(\text{Fraction}_{i+1,0}\right)$$

$$J=1:N \rightarrow C^A_{i+1,j} = C^A_{ij} + \left(C^V_{ij} - C^V_{i+1,j}\right)\text{Fraction}_{i+1,j}$$

$$J=0 \rightarrow C^A_{i+1,0} = C^A_{i,0} - \underbrace{\frac{C^A_{i,0}}{C_T}K^A\frac{\Delta t}{\Delta x}}_{\text{atoms A ejected}} + \underbrace{\left[C^V_{i,0} + \text{vacancies injected} - C^V_{i+1,0}\right]}_{\text{atoms jumping in from } X=1}\text{Fraction}(A)_{i+1,0}$$

$$J=1\cdots N \rightarrow C^A_{i+1,j} = C^A_{ij} + \underbrace{\left(C^V_{ij} - C^V_{i+1,j}\right)}_{\text{vacancies injected to element } ij}\text{Fraction}(A)_{i+1,j}$$

The definitions are very consistent:

$$J=0 \rightarrow \sum_A C^A_{i+1,0} = \sum_A C^A_{i,0} - \underbrace{\sum_A \frac{C^A_{i,0}}{C_T}K^A\frac{\Delta t}{\Delta x}}_{\text{vacancies injected}} + C^V_{i,0} + \text{vacancies injected} - C^V_{i+1,0}$$

$$\sum_A C^A_{i+1,0} = C_T - C^V_{i+1,0} \Rightarrow C^V_{i+1,0} + \sum_A C^A_{i+1,0} = C_T \quad \checkmark$$

$$J=1\cdots N \rightarrow \sum_A C^A_{i+1,j} = \sum_A C^A_{ij} + C^V_{ij} - C^V_{i+1,j} = C_T - C^V_{i+1,j}$$
$$\Rightarrow \sum_A C^A_{i+1,j} + C^V_{i+1,j} = C_T \quad \checkmark$$

The only requirement is that $\sum_A \text{Fraction}(A)_{ij} = 1$

For functions in life2.m, vacancyDiffusion.m, and vacancyDiffusionC.m I selected

$$\text{Fraction}(A)_{i+1,0} = \frac{C^A_{i,1}}{\sum_B C^B_{i,1}}$$

$$\text{Fraction}(A)_{i+1,j} = \frac{C^A_{is}}{\sum_B C^B_{ij}}$$

3/8/2002 OA

My selection of the fraction(A) was not adequate.
It seems appropriate in the limit $C_v \to 0$, but in general it is not

In the algorithm in vacancyDiffusion.m, the update algorithm obeys

$$C^A_{i+1,j} = C^A_{ij} + R_{ij}\frac{C^A_{ij}}{\sum_K C^K_{ij}}$$

$i=0 \quad C^A_{0,j} = C^A_0$

$$C^A_{1,j} = C^A_0 + R_{ij}\frac{C^A_0}{C^A_0+C^B_0+C^C_0} = C^A_0\left(1 + R_{ij}\frac{1}{C^A_0+C^B_0+C^C_0}\right)$$

$$\Rightarrow C^B_{1,j} = C^B_0\left(1 + R_{ij}\frac{1}{C^A_0+C^B_0+C^C_0}\right)$$

$$C^C_{1,j} = C^C_0(\ \ldots\ )$$

Therefore $\dfrac{C^A_{ij}}{C^A_{ij}+C^B_{ij}+C^C_{ij}} = \dfrac{C^A_0}{C^B_0+C^C_0+C^A_0} = \dfrac{C^A_0}{C_T}$

and so forth

$$C^A_{ij} = C^A_0\,\xi, \quad C^B_{ij} = C^B_0\,\xi, \quad C^C_{ij} = C^C_0\,\xi$$

$$C^A_{i+1,j} = C^A_{ij} + R_{i+1,j}\frac{C^A_{ij}}{\sum_K C^K_{ij}} = C^A_{ij}\left(1 + R_{i+1,j}\right) = C^A_0\,\xi\left(1+R_{i+1,j}\right)$$

Consequently $\dfrac{C^A_{ij}}{C^A_{ij}+C^B_{ij}+C^C_{ij}} = \dfrac{C^A_0}{C_T} \quad \forall_{ij}$

My technique is not appropriate to describe diffusion profiles in the bulk of the alloy. The fraction

$\dfrac{C^A_{ij}}{C^A_{ij}+C^B_{ij}+C^C_{ij}}$ = initial atom fraction for all times and positions

A flat line should result, and that is indeed obtained from vacancyDiffusion.m and vacancyDiffusionC.m and like2.m.

3/7/2002 OA

The trick to get a more correct description is improving the fraction, $Fraction(A)_{ij}$ defined on page 189.

$$J_A = -\frac{D}{C^0}\left(C_V \nabla C_A - C_A \nabla C_V\right) \qquad A = Ni,\ Cr,\ Mo$$

The fact that I did not derive diffusion profiles is not due to having selected identical diffusion coefficients, as I have explained on page 190.
I will still assume that $D^{Ni} = D^{Cr} = D^{Mo}$

$$J_A\big|_{ij} \propto C^V_{ij}\left(C^A_{ij+1} - C^A_{ij}\right) - C^A_{ij}\left(C^V_{ij+1} - C^V_{ij}\right)$$

($C^A_{ij+1} - C^A_{ij} > 0$, $C^A_{ij} > 0$)

$$\sum_A J^A_{ij} \propto C^V_{ij}\left(\sum_A C^A_{ij+1} - \sum_A C^A_{ij}\right) - \left(C^V_{ij+1} - C^V_{ij}\right)\sum_A C^A_{ij}$$

($\sum_A C^A_{ij+1} = C_T - C^V_{ij+1}$, $\sum_A C^A_{ij} = C_T - C^V_{ij}$, $\sum_A C^A_{ij} = C_T - C^V_{ij}$)

$$\sum_A J^A_{ij} \propto C^V_{ij}\left(C^V_{ij} - C^V_{ij+1}\right) + \left(C^V_{ij} - C^V_{ij+1}\right)\left(C_T - C^V_{ij}\right)$$

$$= C_T\left(C^V_{ij} - C^V_{ij+1}\right)$$

$$F^A_{ij} = \begin{cases} \dfrac{C^A_{ij}}{\sum_B C^B_{ij}} & \text{if } C^V_{ij} = C^V_{ij+1} \qquad j < x\,\text{Partition} + 1 \\ \dfrac{C^V_{ij}\left(C^A_{ij+1} - C^A_{ij}\right) - C^A_{ij}\left(C^V_{ij+1} - C^V_{ij}\right)}{C_T\left(C^V_{ij} - C^V_{ij+1}\right)} & \text{if } C^V_{ij} \neq C^V_{ij+1},\ j < x\,\text{Part}+1 \end{cases}$$

$$C^A_{ij} \overset{\text{opp. 3/11/02}}{=} \left(C_T - C^V_{ij}\right)\frac{\left(C^A_{ij-1}\right)^2}{C^A_{ij-2}}\frac{1}{\sum_B \frac{\left(C^B_{ij-1}\right)^2}{C^B_{ij-2}}} \qquad \text{if } j = x\,\text{Partition} + 1$$

$$C^A_{ij} = \left(C_T - C^V_{ij}\right)\frac{\left(C^A_{ij-1}\right)^2}{C^A_{ij-2}}\frac{1}{\sum_B \frac{\left(C^B_{ij-1}\right)^2}{C^B_{ij-2}}} \qquad j = x\,\text{Partition} + 1 = N$$

→ extrapolation formula, corrected to make sure that $\sum_B C^B_{ij} + C^V_{ij} = C_T$
compare to the extrapolation formula on page 186.

3/14/2002 OA

I programmed the equations on page 191 and they lead to inconsistent results. The equations were programmed in vacDiffSameV1.m
The inconsistency is due to a conceptual error.

It is not true that $\Delta C \propto J$

The relationsip that is true is $\boxed{\Delta C \propto J_{in} - J_{out}}$

This change affects the selection of the fractions F_{ij}^A
The equations on page 189 are right still.

F_{ij}^A are three numbers such that $\sum_A F_{ij}^A = 1$

Equations on page 189 remain right provided that $\sum_A F_{ij}^A = 1$.

$$C_{i+1,0}^V = C_{i+1}^{VT} - \sum_{j=1}^{N} C_{i+1,j}^V$$

C_{i+1}^{VT}: total # of vacancies at $i+1$; $\sum_{j=1}^{N} C_{i+1,j}^V$: vacancies from $j=1$ onward

$$C_{i+1}^{VT} = \text{injected}(x_{j=0}) - \text{ejected}(j=N) + \underbrace{C_i^{VT}}_{\text{previous \# of vacancies}}$$

$$C_{i+1,0}^V = C_{i,0}^V + \text{inj}(j=0) - \text{diffusing away}(j=0)$$

$$\Rightarrow \text{Diffusing away}(j=0) = C_{i,0}^V + \text{injected}(j=0) - C_{i+1,0}^V$$

$$\text{Diffusing away}(j=0) = \underset{j=0}{\text{Diffusing in}(N_i)} + \underset{j=1}{\text{Diffusing in}(C_r)} + \underset{j=2}{\text{Diffusing in}(M_o)}$$

$$\text{Diffusing in}(N_i) = -J_{i0}^{N_i} = +\frac{D}{C_v}\left(C_v \nabla C^{N_i} - C^{N_i} \nabla C_v\right)$$

$$-J_{i0}^{N_i} \propto \underbrace{C_{i0}^V\left(C_{i1}^{N_i} - C_{i0}^{N_i}\right)}_{>0} - \underbrace{C_{i0}^{N_i}\left(C_{i1}^V - C_{i0}^V\right)}_{>0}$$

$$-J_{i0}^{N_i} - J_{i0}^{C_r} - J_{i0}^{M_o} \propto C_{i0}^V\left(C^T - C_{i1}^V - C^T + C_{i0}^V\right) - \left(C^T - C_{i0}^V\right)\left(C_{i1}^V - C_{i0}^V\right)$$

$$C_{i0}^V\left(C_{i0}^V - C_{i1}^V\right) - \left(C^T - C_{i0}^V\right)\left(C_{i1}^V - C_{i0}^V\right) = C^T\left(C_{i0}^V - C_{i1}^V\right)$$

$$J_{i0}^V = -J_{i0}^{N_i} - J_{i0}^{C_r} - J_{i0}^{M_o} \propto \underbrace{C^T\left(C_{i0}^V - C_{i1}^V\right)}_{>0} > 0 \Rightarrow \text{makes sense}$$

3/14/2002 OA

$$\text{Diffusing in}(N_i)\big|_{i0} = \text{Diffusing away}(V)\big|_{i0} \frac{C_{i0}^V\left(C_{i1}^{Ni} - C_{i0}^{Ni}\right) - C_{i0}^{Ni}\left(C_{i1}^V - C_{i0}^V\right)}{C^T\left(C_{i0}^V - C_{i1}^V\right)}$$

With such a definition $\sum_A \text{Diffusing in}(A)_{i0} = \text{Diffusing away}(V)_{i0}$

$$F_{i0}^A \equiv \frac{C_{i0}^V\left(C_{i1}^A - C_{i0}^A\right) - C_{i0}^A\left(C_{i1}^V - C_{i0}^V\right)}{C^T\left(C_{i0}^V - C_{i1}^V\right)} > 0$$

On page 189 we had

$$C_{i+1,0}^A = C_{i0}^A - \frac{C_{i0}^A}{C^T} K_i^A \frac{\Delta t}{\Delta x} + \left[C_{i0}^V + \text{injected}(j=0) - C_{i+1,0}^V\right] F_{i0}^A$$

$$F_{i0}^A = \begin{cases} \dfrac{C_{i0}^V\left(C_{i1}^A - C_{i0}^A\right) - C_{i0}^A\left(C_{i1}^V - C_{i0}^V\right)}{C^T\left(C_{i0}^V - C_{i1}^V\right)} & \text{if } C_{i0}^V \neq C_{i1}^V \\ ? & \text{if } C_{i0}^V = C_{i1}^V \end{cases}$$

If $C_{i0}^V = C_{i1}^V$, we can do in general

$$C_{i+1,0}^A = \frac{\left(C_{i,0}^A\right)^2}{C_{i-1,0}^A} \quad \text{extrapolation in time, predictor}$$

The predictor is then corrected as

$$C_{i+1,0}^A = \left(C^T - C_{i+1,0}^V\right) \frac{\frac{\left(C_{i0}^A\right)^2}{C_{i-1,0}^A}}{\sum_B \frac{\left(C_{i0}^B\right)^2}{C_{i-1,0}^B}}$$

Predictor Corrector Only if $C_{i0}^V \neq C_{i1}^V$ ~~3/14/2002~~ $C_{i0}^V = C_{i1}^V$

$C_{i0}^V = C_{i1}^V$ only happens probably in the 1st time step.

$$F_{ij}^A = \begin{cases} \dfrac{C_{ij}^V\left(-C_{ij-1}^A + 2C_{ij}^A - C_{ij}^A\right) - C_{ij}^A\left(-C_{ij-1}^V + 2C_{ij}^V - C_{ij}^V\right)}{C^T\left(C_{ij-1}^V - 2C_{ij}^V + C_{ij+1}^V\right)} & \text{if } C_{ij+1}^V + C_{ij-1}^V \neq 2C_{ij}^V \\ \text{Stop computations if } C_{ij+1}^V + C_{ij-1}^V = 2C_{ij}^V & \end{cases}$$

$j \leq N-1$

For $j = N$, we extrapolate and then correct:

$$C_{i+1,N}^A = \left(C^T - C_{i+1,N}^V\right) \frac{\frac{\left(C_{i+1,N-1}^A\right)^2}{C_{i+1,N-2}^A}}{\sum_B \frac{\left(C_{i+1,N-1}^B\right)^2}{C_{i+1,N-2}^B}}$$

predictor–corrector

SUBMITTED TO QA: 3/21/2002

4/8/2002 OPA

Note that all finite difference equations depend on two parameters:

$\lambda \equiv D\frac{\Delta t}{\Delta x^2}$ and an $\frac{\Delta t}{\Delta x}$ & computations at interface

Thus, for any simulation, if λ and $\frac{\Delta t}{\Delta x}$ are identical, the output of the computations is the same. We can take advantage of this property of the system to find the diffusion coefficient from fitting to experimental data.

$$\Delta t = \min\left(tmStpCt \cdot C_T^2 \frac{\Delta x}{K_1^{Ni} C_{Ni}^\circ + K_1^{Cr} C_{Cr}^\circ + K_1^{Mo} C_{Mo}^\circ}, tmStpCt \cdot \frac{\Delta x^2}{D} \right)$$

↳ selection in the algorithm

$\Delta t = \min$ (kinetic time, diffusion time)

$$\text{Kinetic time} = p \cdot C_T^2 \frac{\Delta x}{K_1^{Ni} C_{Ni}^\circ + K_1^{Cr} C_{Cr}^\circ + K_1^{Mo} C_{Mo}^\circ}$$

$$\text{diffusion time} = p \cdot \frac{\Delta x^2}{D}$$

$$\frac{\text{Kinetic time}}{\text{diffusion time}} = \frac{C_T^2 \cdot D}{\Delta x \left(K_1^{Ni} C_{Ni}^\circ + K_1^{Cr} C_{Cr}^\circ + K_1^{Mo} C_{Mo}^\circ \right)} = \frac{D}{\Delta x} \frac{C_T^2}{K_1^{Ni} C_{Ni}^\circ + K_1^{Cr} C_{Cr}^\circ + K_1^{Mo} C_{Mo}^\circ}$$

When the above ratio OPA 4/8/2002 < 1 ⇒ diffusion is slower than kinetics

OPA 4/8/02 > 1 ⇒ kinetics is slower than diffusion

CASE 1:

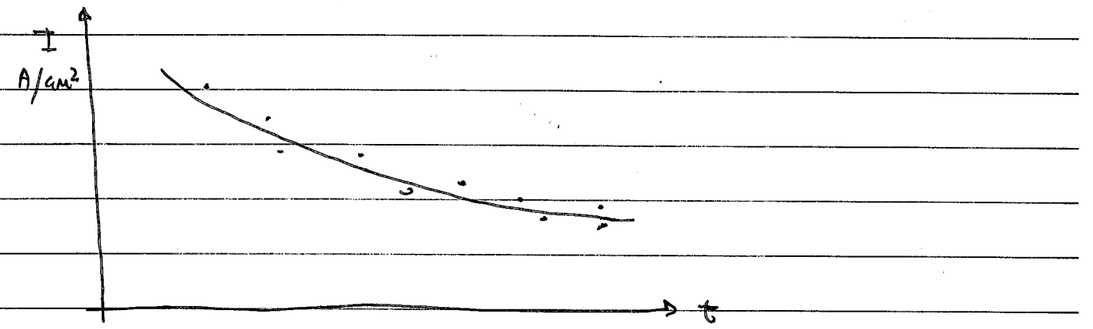
Assume $\Delta t = p \cdot \frac{\Delta x^2}{D}$

$\lambda = D\frac{\Delta t}{\Delta x^2} = p =$ tmStpCt ⇝ input to program

Under which circumstances $\frac{\Delta t}{\Delta x}$ = constant?

$$\boxed{\frac{\Delta t}{\Delta x} = p \cdot \frac{\Delta x}{D}}$$ If $\frac{\Delta x}{D}$ is a constant, then the same outcome is produced regardless of the exact values of D and Δx.

Approach to curve fitting:



The only possibility to have agreement is:

Say that at $\underbrace{(t_1, I_1)}_{\text{experimental}}$ and $\underbrace{(t_1', I_1')}_{\text{model}}$ both points have the same values of the current. Then, in order for (t_1, I_1) to be derived from the model, the following relationship must hold:

$$t_1 \frac{D}{\Delta x^2} = \underbrace{t_1' \frac{D'}{\Delta x'^2}}_{\text{original simulation values}} = t_1''$$ ⇝ dimensionless time.

Thus $\frac{D}{\Delta x^2} = \frac{t_1''}{t_1}$ & known value

$\frac{D}{\Delta x^2} = \frac{P}{\Delta t}$ $\quad \frac{D}{\Delta x} = \left(\frac{t_1''}{t_1}\right)\Delta x = \frac{D'}{\Delta x'} \Rightarrow \Delta x = \left(\frac{t'}{t_1''}\right)\frac{D'}{\Delta x'}$ & size of interpoint

$D = \left(\frac{t_1''}{t_1}\right)\Delta x^2 = \left(\frac{t_1''}{t_1}\right)\left(\frac{t'}{t_1''}\right)^2\left(\frac{D'}{\Delta x'}\right)^2 = \left(\frac{t'}{t_1''}\right)\left(\frac{D'}{\Delta x'}\right)^2$ & diffusion coefficient.

4/8/2002 OA

$$\Delta x = \frac{t_1}{t_1''}\frac{D'}{\Delta x'} = \frac{t_1 D'}{\Delta x'}\left(\frac{1}{\frac{t_1' D'}{\Delta x'^2}}\right) = \frac{t_1}{t_1'}\Delta x'$$

$$\boxed{\Delta x = \frac{t_1}{t_1'}\Delta x'}$$ ⇝ this implies that results depend on the value of Δx adopted

⟹ not really ⟹ If $\frac{D}{\Delta x}$ is a constant, the same output is produced. That is the only requirement!

$$D = \frac{t_1}{\frac{t_1' D'}{(\Delta x')^2}}\left(\frac{D'}{\Delta x'}\right)^2 = \frac{t_1}{t_1'} D'$$

Thus Δx and D can be derived easily from t_1 and t_1'

Case 3 Let $Kc = K_1^{N_1} C_{N_1}^{\circ} + K_1^{Cr} C_{Cr}^{\circ} + K_1^{Mo} C_{Mo}^{\circ}$

$$\Delta t = p\, C_r^2 \frac{\Delta x}{Kc}$$

$$\lambda = D\frac{\Delta t}{\Delta x^2} = \frac{D}{\Delta x^2} p\, C_r^2 \frac{\Delta x}{Kc} = \frac{p\, C_r^2}{Kc}\frac{D}{\Delta x}$$

$\lambda = ct \iff \frac{D}{\Delta x}$ is constant

If $\frac{D}{\Delta x}$ is constant $\Rightarrow \frac{D}{\Delta x}\frac{\Delta t}{\Delta x} = \lambda$ and $\frac{\Delta t}{\Delta x}$ is constant as well

How do we compare results?

From first line $\frac{t}{\Delta x} = \frac{t_s}{\Delta x_s} \Rightarrow t = \frac{\Delta x}{\Delta x_s} t_s$

$$\frac{t}{D} = \frac{t_s}{D_s} \Rightarrow t = \frac{D}{D_s} t_s \iff \frac{\Delta x}{\Delta x_s} = \frac{D}{D_s}$$

$$\iff \frac{\Delta x}{D} = \frac{\Delta x_s}{D_s}$$

5/29/2002 OA

$\xi = \frac{t_s^{\circ}}{t^{\circ}}$ at t° is such that

$$I_{exp}(t^{\circ}) = I_{simulated}(t_s^{\circ})$$

$$\xi = \frac{t_s^{\circ}}{t^{\circ}}$$

To match the experiment, the scale must be changed:

New scale: $t = \frac{1}{\xi} t_s$

$$D = \frac{1}{\xi} D' \qquad \Delta x = \frac{1}{\xi} \Delta x'$$

values from the simulation

Formulas to change scale:

$I_{exp}(t^{\circ}) = I_{simulated}(t_s^{\circ})$

$\xi = \frac{t_s^{\circ}}{t^{\circ}}$, $D = \frac{1}{\xi} D^{S}$, $\Delta x = \frac{1}{\xi}\Delta x^{S}$, $t = \frac{1}{\xi} t_s$

6/19/2002 OAJ

IM 20.1402.571.230

Passive Dissolution of Container Materials, Modeling and Experiments

O. Pensado, D. Dunn, G. Cragnolino, and V. Jain

I polished the set of equations for the description of the solid-state diffusion problem. I went through a couple of iterations

vacDifSameV2.m : improved equations to update atom concentrations, consistent with equations on pages 192-193

vacDifSameV21.m : corrects error in vacDifSameV2.m that results in mass not being conserved

vacDifSameV3.m : same as vacDifSameV21.m but cleaner

vacDifSameV3b.m : corrects error in vacDifSameV3.m. In vacDifSameV3.m, atom concentrations at the interface are obtained as extrapolation of bulk values, which is incorrect. In vacDifSameV3b.m, interface concentrations are consistent with the conservation of mass requirement.

The complete development process of the functions in the above files is documented at vacDif.m.zip ;

~~to be submitted to QA records~~.

It is complicated to have a clear exposition of the equations by hand; thus I decided to write an appendix for the report referred at the top.

6/19/2002 OAJ

In the appendix of the report, I detail the finite difference equations to address the solid state diffusion problem. The reader of this notebook is referred to that appendix for a clearer exposition.

I have been analyzing data generated by Darrell Dunn to describe the transient decrease in time of the passive current density. The data, and analyzes are summarized in the following files:

comp6.nb → contains input data, and data treatment

exp.nb → treatment of experimental data to be put in adequate format and graphic display.

TDep.nb → treatment of experimental data to derive an activation energy

Results of the computations in comp6.nb have been compressed in the zip file comp6runs.zip

Abundant readme files are provided with the electronic documentation accompanying this notebook to facilitate the reader searching for information. The electronic files above referred to will also be submitted to the QA records as part of the IM 20.1402.571.230 report.

7/19/2002 QAP

Objective. Documenting relevant computations in the report IM 20.1402-571.230
Passive Dissolution of Container Materials, Modeling and Experiments.
O. Pensado, D. Dunn, G. Craynolino, V. Jain

The set of files referred to on page 199 are a complete documentation of computations in the above report. It is intended to submit to QA all of the files used so that an informed reader or reviewer could reproduce the computations.

In this notebook and the continuation notebook 534 a roadmap of the computations is provided to find more easily the computations in the electronic files.

THIS NOTEBOOK OPR, 7/19/02 IS CONTINUED ON NOTEBOOK 534

I have reviewed this scientific notebook and find it in agreement with QAP-001
Darrell Dunn for V. Jain
1/14/2004

OPR 7/19/2002

I have reviewed this scientific notebook and find it in agreement with QAP-001.
There is sufficient information regarding methods used for conducting tests, acquiring and analyzing data so that another qualified individual could repeat the activity.

1/20/04