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U.S. Nuclear Regulatory Commission  
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Subject: Submittal of Missing Appendices in the Intermediate Milestone—Passive Dissolution of Container Materials— Modeling and Experiments, IM 01402.571.230

Dear Ms. Bloomer:

Appendices A and B of the subject report were inadvertently left out when report was submitted to you. Please add appendices to report. If you have any questions regarding this report, please feel free to contact Osvaldo Pensado at (210) 522-6084.

Sincerely yours,



Vijay Jain  
Element Manager  
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VJ:jg  
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## **APPENDIX A**

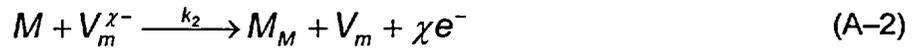
### **DERIVATION OF THE POTENTIAL DEPENDENCE OF THE PASSIVE CURRENT DENSITY**

1

## DERIVATION OF THE POTENTIAL DEPENDENCE OF THE PASSIVE CURRENT DENSITY

This appendix justifies the statement that the passive current density is independent of the applied potential if the rate of charge transport through the oxide film via cation vacancies is negligible with respect to the rate of charge transport via oxygen vacancies and cation interstitials.

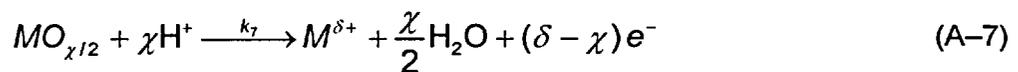
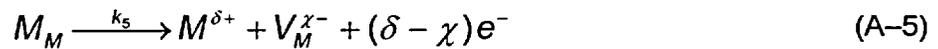
In the original Point Defect Model (Macdonald, 1992), it is proposed that for a passive metal,  $M$ , forming an oxide of stoichiometric composition,  $MO_{\chi/2}$ , the fundamental charge transfer reactions controlling the dissolution of the metal at the metal-film interface are (an additional reaction with respect to the original model has been added to account for interstitial dissolution)



where

$\chi$	—	oxidation state of the metal
$M_i^{\chi+}$	—	cation interstitial in the oxide
$V_m$	—	vacancy in the metal
$e^-$	—	electron
$V_M^{\chi-}$	—	cation vacancy in the oxide
$M_M$	—	metal in the oxide lattice
$V_O^{2+}$	—	oxygen vacancy in the oxide
$k_p$	—	rate constant, $p = 1, 2, 3, \dots, 7$

On the other hand, at the film-solution interface the fundamental charge transfer reactions are



where

- $\delta$  — oxidation state of cation in solution
- $H^+$  — hydrogen ion
- $H_2O$  — water molecule
- $O_o$  — oxygen in the oxide lattice

The reaction in Eq. (A-3) results in the formation of oxide volume, which can be expressed in mathematical form for a one-dimensional system as

$$\frac{dL_+}{dt} = \Omega k_3 \quad (A-8)$$

where

- $\Omega$  — molar volume of the oxide {in units of  $cm^3/mol$  [ $ft^3/mol$ ] assuming that  $k_3$  is in units of  $mol/(cm^2 s)$  [ $mol/ft^2s$ ]}
- $L$  — oxide thickness at time  $t$

On the other hand, the rate of film dissolution is controlled by the reaction in Eq. (A-9)

$$\frac{dL_-}{dt} = -\Omega (a_{H^+})^n k_7 \quad (A-9)$$

where

- $a_{H^+}$  — activity of hydrogen ion
- $n$  — reaction order with respect to the hydrogen ion activity

Therefore, the expression defining the overall film growth is

$$\frac{dL}{dt} = \Omega k_3 - \Omega (a_{H^+})^n k_7 \quad (A-10)$$

Under the steady-state condition,  $dL/dt = 0$ , the rate constants  $k_3$  and  $k_7$  are related as

$$k_3 = (a_{H^+})^n k_7 \quad (A-11)$$

Equation (A-11) is significant because it can be used to relate the potential drop at the metal-film interface,  $\phi_{mf}$ , to the potential drop at the film-solution interface,  $\phi_{fs}$ , using the formalism of the Point Defect Model. The Point Defect Model postulates (Macdonald, 1992) that the potential drop at the film-solution interface is proportional to the total applied potential to the system,  $V$ , that is,

$$\phi_{fs} = \alpha V + V_o \quad (A-12)$$

where  $V_0$  is a constant. The Point Defect Model proposes that the rate constants follow an exponential dependence with respect to the change in potential energy; that is,

$$k_3 = k_3^0 e^{\alpha_3 \frac{F}{RT} \chi \phi_{mif}} \quad (\text{A-13})$$

where

- $k_3^0$  — a reference rate constant
- $\alpha_3$  — transfer coefficient, positive and less than one
- $F$  — Faraday's constant
- $R$  — ideal gas constant
- $T$  — absolute temperature

Similarly, for the reaction in Eq (A-7), the rate constant is defined as

$$k_7 = k_7^0 e^{\alpha_7 \frac{F}{RT} (\delta - \chi) \phi_{f/s}} \quad (\text{A-14})$$

where

- $k_7^0$  — a reference rate constant
- $\alpha_7$  — transfer coefficient

From Eq. (A-11), a relationship between the potential drop at the metal-film interface,  $\phi_{mif}$ , and the potential drop at the film-solution interface,  $\phi_{f/s}$ , is derived

$$\phi_{mif} = \frac{\alpha_7 (\delta - \chi)}{\alpha_3 \chi} \phi_{f/s} + \frac{RT}{\alpha_3 \chi F} \ln \left( a_{H^+}^n \frac{k_7^0}{k_3^0} \right) \quad (\text{A-15})$$

For steady-state conditions, the potential drop at the metal-film interface is proportional to the corresponding drop at the film-solution interface, which is assumed proportional to the total applied potential. Note that if there is no change in the oxidation state of the cation transferred from oxide film to the solution (i.e.,  $\delta = \chi$ ), the potential drop at the metal-film interface is independent of the applied potential.

If  $I$  is the current density {in units of  $A/cm^2$  [ $A/ft^2$ ]} vector, conservation of charge requires that

$$\nabla \cdot I = -\frac{\partial \rho}{\partial t} \quad (A-16)$$

where  $\rho$  is the charge density {expressed in units of  $Coulomb/cm^3$  [ $Coulomb/ft^3$ ]}. Under steady-state conditions, the right side of Eq. (A-16) is zero. Therefore, at steady state and for a one-dimensional problem, the current density is independent of the spatial coordinate. For the case  $\delta = \chi$ , the current density at the metal-film interface (which is the same at any point in the system) is computed as

$$I = \chi F (k_1 + k_3) + \chi F a_{V_M^-} k_2 \quad (A-17)$$

where  $a_{V_M^-}$  is the cation-vacancy activity in the proximity of the metal-film interface. Note that if the rate of charge transport via cation vacancies is negligible with respect to the rate of charge transport of cation interstitials or oxygen vacancies (i.e.,  $k_2 \ll k_1, k_3$ ), Eq. (A-17) reduces to

$$I \approx \chi F (k_1 + k_3) \quad (A-18)$$

Likewise  $k_3$ ,  $k_1$  is dependent on the potential drop at the metal-film interface,  $\phi_{mf}$ . The drop  $\phi_{mf}$  has been argued to be independent of the applied potential for the case  $\delta = \chi$ . Therefore, Eq. (A-18) implies that the current density is independent of the applied potential, if cation interstitials or oxygen vacancies are the predominant charge carriers.

If, on the other hand, cation vacancies are the dominant charge carriers, Eq. (A-17) becomes

$$I \approx \chi F a_{V_M^-} k_2 = \chi F k_5 = \chi F k_5^0 e^{\alpha_5 \frac{F}{RT} \chi \phi_{fs}} \quad (A-19)$$

where

- $\alpha_5$  — transfer coefficient
- $k_5^0$  — a reference rate constant

The second equality results from requiring that the rate of cation vacancy creation, from Eq. (A-5), be the same as the rate of cation vacancy annihilation, from Eq. (A-2). The third equality in Eq. (A-19) is the exponential expansion of the rate constant as dictated by the Point Defect Model. Because the potential drop  $\phi_{fs}$  is assumed proportional to the total applied potential, it follows that for systems in which cation vacancies are the predominant charge carriers, the passive current density is an exponential function of the applied potential

A discussion of the more complex alloy system is presented as follows. In developing the model in Chapter 5<sup>1</sup> for the dissolution of nickel-chromium-molybdenum alloys, it was assumed that cations do not experience a change in oxidation state in the transfer from the oxide to the solution. Consistent with arguments in this appendix, it was assumed in Chapter 5<sup>2</sup> that the potential drop at the metal-film interface is independent of the applied potential. Under steady-state conditions, the current density at the metal-film interface is computed as

$$I = F \left[ \chi a_{Cr} \left( k_1^{Cr} + k_3^{Cr} + a_{V_{Cr}^{z-}} k_2^{Cr} \right) + \delta a_{Ni} \left( k_1^{Ni} + k_3^{Ni} + a_{V_{Cr}^{z-}} k_2^{Ni} \right) + \xi a_{Mo} k_1^{Mo} \right] \quad (A-20)$$

where

- $\chi, \delta, \xi$  — oxidation state of chromium, nickel, and molybdenum, respectively
- $a_M$  — atomic fraction of element  $M$  ( $= Cr, Ni, Mo$ )
- $k_n^M$  — rate constant, the superscript  $M$  ( $= Cr, Ni, Mo$ ) and subscript  $n$  ( $= 1, 2, 3$ ) are used to label particular species and reactions. See Chapter 5<sup>3</sup> for additional details in the notation
- $a_{V_{Cr}^{z-}}$  — activity of cation vacancies at the metal-film interface

Experimentally it is known that the passive current density for Alloy 22 is independent of the applied potential over a wide range up to the potential for transpassive dissolution (Dunn, et al., 1999, 2000). According to the assumptions in Chapter 5<sup>4</sup>, this independence is possible only if the rate of cation vacancy transport is negligible with respect to the rate of interstitial or oxygen vacancy transport (i.e.,  $a_{V_{Cr}^{z-}} k_2^{Cr} \ll k_1^{Cr}, k_3^{Cr}$  and  $a_{V_{Cr}^{z-}} k_2^{Ni} \ll k_1^{Ni}, k_3^{Ni}$ ). In other words, using steady-state constraints, it can be argued (similar to other arguments developed in this appendix) that the terms  $a_{V_{Cr}^{z-}} k_2^{Cr}$  and  $a_{V_{Cr}^{z-}} k_2^{Ni}$  are functions of the applied potential; therefore, these terms should not be important contributors to the current density for the Alloy 22 system. Equation (5-16) follows from this observation. The predominant charge carriers, consistent with the Point Defect Model, should be cation interstitials or oxygen vacancies. Chapter 5<sup>5</sup> provides additional arguments in favor of the interstitial transport mechanism.

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<sup>1</sup>Pensado, O., D S Dunn, G A Cragnolino, and V Jain. "Passive Dissolution of Container Materials, Modeling, and Experiments" San Antonio, Texas: CNWRA Unpublished report, 2002.

<sup>2</sup>Ibid

<sup>3</sup>Pensado, O., D S Dunn, G A Cragnolino, and V Jain. "Passive Dissolution of Container Materials, Modeling, and Experiments" San Antonio, Texas: CNWRA Unpublished report, 2002.

<sup>4</sup>Ibid

<sup>5</sup>Ibid

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Dunn, D.S, Y.-M. Pan, and G.A, Cragnolino. "Stress Corrosion Cracking, Passive, and Localized Corrosion of Alloy 22 High-Level Radioactive Waste Containers." Proceedings of the Corrosion 2000 Conference. Paper No 00206. Houston, Texas: NACE International 2000.

Dunn, D.S., Y.-M. Pan, and G.A. Cragnolino. "Effects of Environmental Factors on the Aqueous Corrosion of High-Level Radioactive Waste Containers—Experimental Results and Models." CNWRA Report 99-004. San Antonio, Texas: CNWRA 1999.

Macdonald, D.D. "The Point Defect Model for the Passive State." *Journal of Electrochemical Society*. Vol. 139. pp. 3,434–3,449. 1992.

## **APPENDIX B**

### **FINITE DIFFERENCE IMPLEMENTATION OF THE SOLD-STATE DIFFUSION PROBLEM**

## FINITE DIFFERENCE IMPLEMENTATION OF THE SOLID-STATE DIFFUSION PROBLEM

This appendix provides a detailed discussion of the finite difference implementation of the constitutive equation and mass conservation equation describing the transport of vacancies and atoms in the alloy.

In Chapter 5<sup>1</sup> it was discussed that the constitutive equation for the diffusion of vacancies in the metal is

$$J_v = -\frac{1}{c_v^o} \sum_A D_A c_A \nabla c_v + \frac{c_v}{c_v^o} \sum_A D_A \nabla c_A \quad (\text{B-1})$$

where

$J_v$	—	flux of vacancies
$c_A$	—	concentration of specie $A$ ( $A = \text{Ni}, \text{Cr}, \text{Mo}$ )
$D_A$	—	diffusion coefficient for element $A$ in the bulk of the alloy
$c_v$	—	concentration of vacancies in the alloy
$c_v^o$	—	equilibrium concentration of vacancies at a reference temperature

Mass conservation demands that

$$\frac{\partial c_v}{\partial t} = -\nabla \cdot J_v = \frac{1}{c_v^o} \sum_A D_A c_A \nabla^2 c_v - \frac{c_v}{c_v^o} \sum_A D_A \nabla^2 c_A \quad (\text{B-2})$$

If it is assumed that the vacancy concentration is negligible with respect to the atom concentration in the alloy, Eq. (B-2) can be approximated as

$$\frac{\partial c_v}{\partial t} \approx \frac{1}{c_v^o} \sum_A D_A c_A \nabla^2 c_v = D_{\text{eff}} \nabla^2 c_v \quad (\text{B-3})$$

The effective diffusion coefficient,  $D_{\text{eff}}$ , is not constant but nearly constant if the concentration of vacancies is negligible. Without requiring that the concentration of vacancies be negligible, but requesting the diffusion coefficient be similar (i.e.,  $D_{\text{Ni}} \cong D_{\text{Cr}} \cong D_{\text{Mo}} = D$ ) and the total sites in the alloy be constant (i.e.,  $c_{\text{Ni}} + c_{\text{Cr}} + c_{\text{Mo}} + c_v = c_T$ ), Eq. (A-2) can be simplified, without additional approximations, into

$$\frac{\partial c_v}{\partial t} = -\nabla \cdot J_v = \frac{c_T}{c_v^o} D \nabla^2 c_v = D_{\text{eff}} \nabla^2 c_v \quad (\text{B-4})$$

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<sup>1</sup>Pensado, O, D S Dunn, G.A Cragnolino, and V Jain "Passive Dissolution of Container Materials, Modeling, and Experiments" San Antonio, Texas CNWRA Unpublished report, 2002

The effective diffusion coefficient,  $D_{\text{eff}}$ , is a constant. Results reported in Chapter 5<sup>2</sup> are based on Eq. (B-4). The finite difference equations implemented to integrate a one-dimensional representation of Eq. (B-4) are described next.

Let the timestep and position step of the finite difference implementation be represented as  $\Delta t$  and  $\Delta x$ . Let the dimensionless parameter  $\lambda$  be defined as

$$\lambda = D_{\text{eff}} \frac{\Delta t}{\Delta x^2} \quad (\text{B-5})$$

The parameter,  $\lambda$ , must be less than or equal to 0.5 to guarantee convergence of the finite difference computations. For the sake of simplicity in the notation, concentrations are referred to with two subscripts,  $c_{i,j}$ . The first subscript,  $i$ , tracks the time step and the second subscript,  $j$ , tracks the position. Superscripts  $v$  (for vacancies), Ni, Cr, and Mo are used to differentiate the particular species being considered (e.g.,  $c_{i,j}^v$  or  $c_{i,j}^{\text{Ni}}$ ). The metal-oxide interface is located at the spatial step  $j = 0$ . The spatial steps range from  $j = 0$  to  $j = N$ . A free boundary in the metal is constructed at the position step  $j = N$ . The temporal steps start at  $i = 0$  (initial time).

## B.1 Finite Difference Equations to Determine Vacancy Concentrations

At the  $i^{\text{th}}$  timestep, the total vacancies in the system,  $c_i^{vT}$ , is defined as

$$c_i^{vT} = \sum_{j=0}^N c_{i,j}^v \quad (\text{B-6})$$

The total vacancies injected into the system,  $inj_i$ , as a result of the alloy dissolution process, between the time steps  $i$  and  $i + 1$ , is computed as

$$inj_i = \frac{\Delta t}{c_T \Delta x} \sum_A k_1^A c_{i,0}^A \quad (\text{B-7})$$

The symbol  $k_1^A$  ( $A$ —Ni, Cr, and Mo) represents rate constants for the reactions in Eqs. (5-1), (5-2), and (5-3) in Chapter 5.<sup>3</sup>

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<sup>2</sup>Pensado, O, D S Dunn, G.A Cragnolino, and V Jain "Passive Dissolution of Container Materials, Modeling, and Experiments." San Antonio, Texas CNWRA Unpublished report, 2002.

<sup>3</sup>Ibid

A free boundary is constructed at the position step  $j = N$ . A free boundary can release or receive vacancies depending on the concentration gradient and Fick's law. The number of vacancies leaving the system,  $e_j$ , between the time steps  $i$  and  $i + 1$ , is computed as

$$e_j = \lambda (c_{i,N-1}^v - c_{i,N}^v) \quad (\text{B-8})$$

If the system between the position step  $j = 0$  and  $j = N$  was a closed system, all vacancies injected to the system would remain in the system, and, for that particular case, by definition,  $e_j = 0$ .

Equations (B-6), (B-7), and (B-8) allow the computation of the total vacancies at the time step  $i + 1$  to be

$$c_{i+1}^{vT} = c_i^{vT} + inj_i - e_j \quad (\text{B-9})$$

Concentrations at positions  $j = 1, \dots, N-1$ , for a new timestep,  $i + 1$ , are computed from a first-order finite difference representation of Eq. (B-4)

$$c_{i+1,j}^v = c_{i,j}^v + \lambda (c_{i,j-1}^v - 2c_{i,j}^v + c_{i,j+1}^v) \quad j = 1, \dots, N-1 \quad (\text{B-10})$$

At the spatial step,  $j = N$  (the free boundary), the vacancy concentration is computed according to logarithmic extrapolation

$$c_{i+1,N}^v = \frac{(c_{i+1,N-1}^v)^2}{c_{i+1,N-2}^v} \quad (\text{B-11})$$

Finally, the concentration of vacancies at the metal-film interface,  $j = 0$ , at the new timestep,  $i + 1$ , is computed by requesting conservation of mass

$$c_{i+1,0}^v = c_{i+1}^{vT} - \sum_{k=1}^N c_{i+1,k}^v \quad (\text{B-12})$$

Note that from Eq. (B-12), it follows that  $c_{i+1}^{vT} = \sum_{j=0}^N c_{i+1,j}^v$ , which guarantees, by induction, that

Eq. (A-6) is valid for all timesteps. Equation (B-7) requires determination of the atom concentrations at the interface. Therefore, the complete coupled diffusion problem must be solved to compute the concentration of vacancies. Note also that finite difference computations of two simulations having the same kinetic parameters will be identical if  $\lambda$  and the ratio,  $\Delta t/\Delta x$ , are the same for both simulations. In other words, simulations having constant ratios of  $\Delta t/\Delta x$  and  $D_{\text{eff}}/\Delta x$  will yield identical results.

## B.2 Finite Difference Equations To Determine Atom Concentrations

Concentrations at a new timestep,  $i + 1$ , for the position steps  $j = 1, \dots, N-1$  are computed as

$$c_{i+1,j}^A = c_{i,j}^A + (c_{i,j}^v - c_{i+1,j}^v) F_{i,j}^A \quad j = 1, \dots, N-1 \quad (\text{B-13})$$

The second term on the right side of Eq. (B-13) is the decrease in the concentration caused by the diffusive transport of vacancies. The factor  $F_{i,j}^A$  satisfies  $F_{i,j}^{Ni} + F_{i,j}^{Cr} + F_{i,j}^{Mo} = 1$  to be consistent with the assumption  $c_{Ni} + c_{Cr} + c_{Mo} + c_v = c_T$ . This factor is defined later in this appendix. It is straightforward to demonstrate by induction that if  $c_{i,j}^{Ni} + c_{i,j}^{Cr} + c_{i,j}^{Mo} + c_{i,j}^v = c_T$ , then Eq. (B-13) guarantees that the total number of sites is a constant for any later timestep.

The concentration at the free interface,  $j = N$ , is computed by logarithmic extrapolation and corrected to enforce that the total number of sites is a constant

$$c_{i+1,N}^A = (c_T - c_{i+1,N}^v) \frac{(c_{i+1,N-1}^A)^2 / c_{i+1,N-2}^A}{\sum_B (c_{i+1,N-1}^B)^2 / c_{i+1,N-2}^B} \quad (\text{B-14})$$

Finally, the concentration at the interface,  $j = 0$ , is computed as follows

$$c_{i+1,0}^A = \sum_{j=0}^N c_{i,j}^A - \frac{c_{i,0}^A}{c_T} k_1^A \frac{\Delta t}{\Delta X} + e_{j_i} \times F_{i,N}^A - \sum_{j=1}^N c_{i+1,j}^A \quad (\text{B-15})$$

Equation (B-15) is consistent with the conservation of the mass requirement that the total atoms ejected from the system at the metal-film interface complements the atoms remaining in the system, or, in mathematical representation

$$\sum_{j=0}^N c_{i+1,j}^A = \sum_{j=0}^N c_{i,j}^A - \frac{c_{i,0}^A}{c_T} k_1^A \frac{\Delta t}{\Delta X} + e_{j_i} \times F_{i,N}^A \quad (\text{B-16})$$

Equation (B-13) through (B-16) are general and independent of the relative magnitude of diffusion coefficients. If it is assumed that the solid-state diffusion coefficients are similar, a simplified expression for the factor  $F_{i,j}^A$  can be derived. The constitutive equation for the diffusion of atoms is

$$J_A = -\frac{D}{c_v^0} (c_v \nabla c_A - c_A \nabla c_v) \quad (\text{B-17})$$

Let  $J_{i,j}^{A \text{ in}}$  and  $J_{i,j}^{A \text{ out}}$  be the flux of atoms jumping in and out of the spatial element,  $j$ . From Eq. (B-16), it follows that

$$J_{i,j}^{A \text{ in}} \propto c_{i,j}^v (c_{i,j+1}^A - c_{i,j}^A) - c_{i,j}^A (c_{i,j+1}^v - c_{i,j}^v) \quad (\text{B-18})$$

and

$$J_{i,j}^{A \text{ out}} \propto c_{i,j}^v (c_{i,j}^A - c_{i,j-1}^A) - c_{i,j}^A (c_{i,j}^v - c_{i,j-1}^v) \quad (\text{B-19})$$

Let  $\Delta c_{i,j}^A$  be the increase in concentration caused by diffusion transport. For  $j = 1 \dots N-1$  the following relationship holds

$$\Delta c_{i,j}^A \propto J_{i,j}^{A \text{ in}} - J_{i,j}^{A \text{ out}} \propto c_{i,j}^v (c_{i,j+1}^A - 2c_{i,j}^A + c_{i,j-1}^A) - c_{i,j}^A (c_{i,j+1}^v - 2c_{i,j}^v + c_{i,j-1}^v) \quad (\text{B-20})$$

The fraction,  $F_{i,j}^A$ , can be immediately derived from Eq. (B-20) for  $j = 1 \dots N-1$

$$F_{i,j}^A = \frac{c_{i,j}^v (c_{i,j+1}^A - 2c_{i,j}^A + c_{i,j-1}^A) - c_{i,j}^A (c_{i,j+1}^v - 2c_{i,j}^v + c_{i,j-1}^v)}{-c_T (c_{i,j+1}^v - 2c_{i,j}^v + c_{i,j-1}^v)} \quad j=1, \dots, N-1 \quad (\text{B-21})$$

The denominator in Eq. (B-21) is obtained by adding the numerator for nickel, chromium, and molybdenum, and assuming the total concentration is a constant equal to  $c_T$ . Finally, the factor  $F_{i,N}^A$  needed in Equation (B-15) is computed as

$$F_{i,N}^A = \frac{c_{i,N}^v (c_{i,N}^A - c_{i,N-1}^A) - c_{i,0}^A (c_{i,N}^v - c_{i,N-1}^v)}{-c_T (c_{i,N}^v - c_{i,N-1}^v)} \quad (\text{B-22})$$

Equation (B-21) is a postulated equation, that is suggested by Eq. (B-20). Likewise, in Eq. (B-20), the denominator in Eq. (B-21) is obtained by adding the numerator for Ni, Cr, and Mo and assuming the total concentration is a constant equal to  $c_T$ .

The system of equations in this appendix is valid provided that the diffusion coefficients in the bulk of the alloy are similar for all alloy components. If this assumption is not valid, it may be possible the existence of enhanced transport of one of the alloy components toward the interface. Equations developed in this appendix can be extended to address the case of dissimilar diffusion.