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Interface Stability During the Oxidation of Binary Alloys

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ABSTRACT

The stability of a planar alloy/scale interface during the diffusion-controlled oxidation of a homogeneous, single-phase binary alloy depends on both the thermodynamic and transport properties of the system under consideration. A criterion is presented that can be employed to predict the stability of a planar alloy/scale interface for the specified reaction temperature, alloy composition, and chemical potential of the oxidant when only one component of the alloy is oxidized, anion diffusion predominates in the scale, and the solubility of oxygen in the alloy is essentially zero. A planar alloy/scale interface (a single-phase scale) is the preferred growth morphology if diffusion in the oxide phase is the rate-limiting step of the oxidation reaction. An uneven alloy/scale interface (a two-phase scale) is expected if diffusion in the alloy phase is the rate-determining step. This stability criterion is equivalent to the criterion derived by Wagner for the case of predominant cation diffusion in the scale.

INTRODUCTION

The high-temperature oxidation of a U-base alloy can result in the formation of a two-phase product layer (oxide + alloy) on the surface of the alloy.[1] For example, the high-temperature oxidation of U-Nb alloys has resulted in the formation of surface scales that consist of two zones.[2] As shown in Fig. 1, a two-phase zone exists adjacent to the alloy; it comprises stringers of uranium dioxide and Nb-rich alloy, the long axes of which are aligned perpendicular to the surface of the alloy. The second zone is a compact layer of oxide that exists between the gas phase and the two-phase zone. The second zone might contain some oxides of niobium, which could be formed during the initial stage of oxidation and by oxidation of the tips of the Nb-rich stringers.[2] The formation of the two-phase scales can be ascribed to the preferential oxidation of one component of the alloy under conditions for which a planar alloy/scale interface is not stable. The stability of a planar alloy/scale interface depends on both the thermodynamic and transport properties of the system under consideration.

The purpose of this paper is to present a criterion for the stability of a planar alloy/scale interface that can be employed to rationalize the formation of two-phase scales on U-base alloys. This paper closely follows an earlier analysis of Wagner[3] for the stability of a planar alloy/scale interface during the oxidation of binary alloys that contain a noble metal; however, the present work differs from Wagner's analysis because anions, instead of cations, are supposed to be the more mobile ions in the growing scale. As one might expect intuitively, based on Wagner's earlier work,[3] the criterion that is developed in this paper is equivalent to the criterion for the case of predominant cation diffusion in the oxide phase. However, the mathematical analysis for the case of predominant anion diffusion is not available in the literature, and thus, the details of such an analysis are presented in this paper.

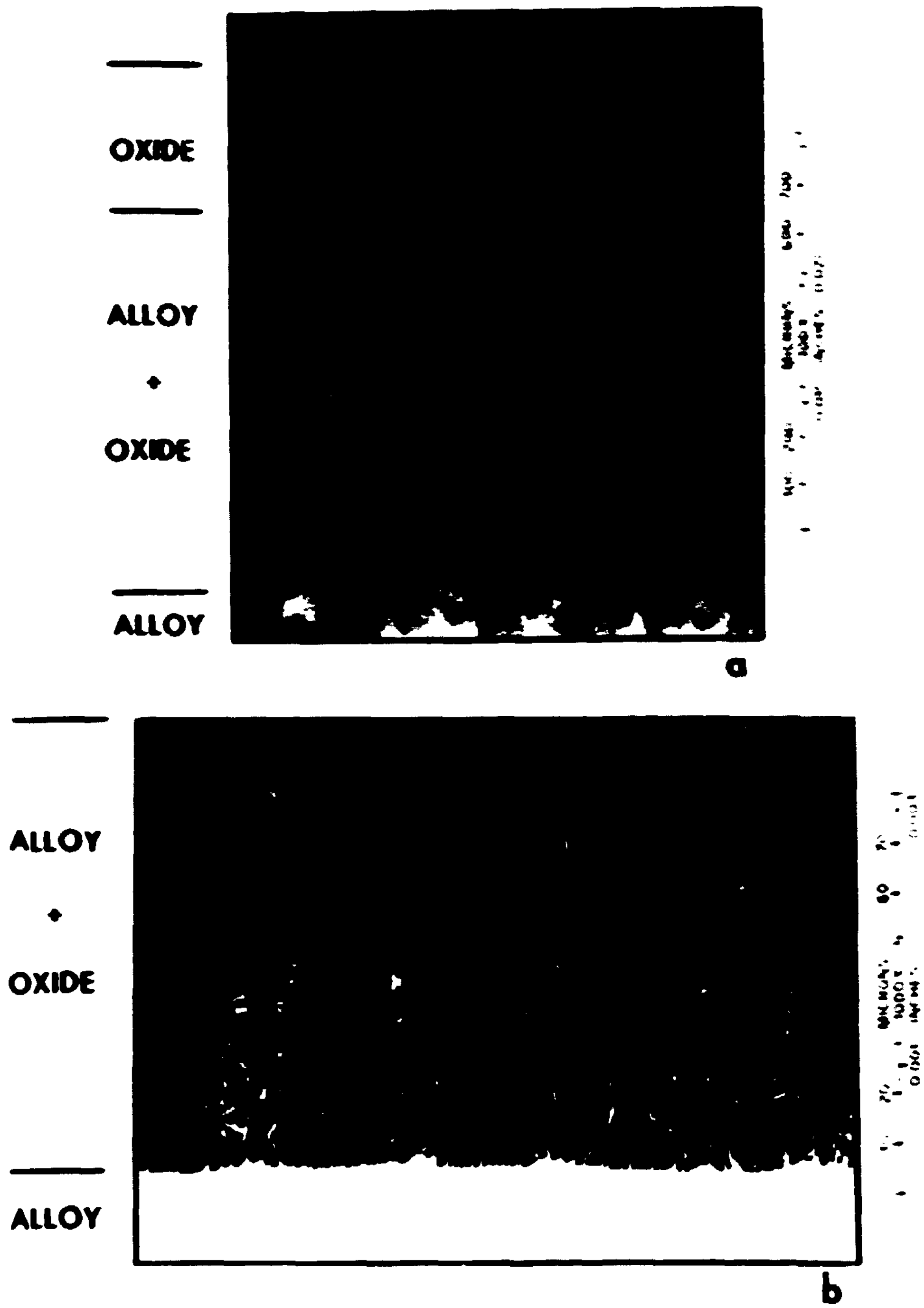

Fig. 1. Scales formed on a U-21a/o Nb alloy: (a) 840 min [illegible]°C and 0.05 Torr oxygen, 100x; (b) 90 min at 1100°C and 0.05 Torr oxygen, 1000x. After Cathcart, et al.[2]

THE STABILITY OF A PLANAR ALLOY/SCALE INTERFACE

A criterion is developed in this section to predict the stability of a single-phase scale (a planar alloy/scale interface) during the oxidation of an alloy under idealized conditions. The purpose is to develop a model that can demonstrate the effect of the system variables on interface stability during oxidation, thereby leading to a better understanding of the mechanisms of oxidation for more complex cases. Because numerous assumptions are introduced, the final equations are only semi-quantitative.

The oxidation of an ideal alloy solid solution, A-B, in which component B is a noble metal. is considered. Component A is selectively oxidized to form the oxide AO_{ν_r}, a compound semiconductor that exhibits predominant anion diffusion. The subscript ν_r is the oxygen-to-metal ratio for the oxide in coexistence with pure metal A; a subscript ν is employed for other oxygen-to-metal ratios. It is possible that component A can be selectively oxidized even if component B is not a noble metal. In this case, the absolute value of the free energy of formation AO_{ν_r} must be much larger than the absolute value of the free energy of formation of the lowest oxide of component B, AO_{ν_r} must grow much faster than the oxides of component B during the initial stages of oxidation, and the concentration of B in the alloy must be relatively low.

In order to determine the stability of a planar alloy/scale interface, the relative rates of movement of different regions of a slightly perturbed alloy/scale interface are examined. A sine-wave perturbation of the alloy/scale interface, as shown in Fig. 2, is employed for this model.[3] Diffusion in both the alloy and oxide phases must be considered.

The flux of component A in the alloy in the x-direction is given by

$$j_A'(x) = -\tilde{D}\ \frac{\partial c_A'}{\partial x} \qquad (1)$$

where $\tilde{D}$ is the interdiffusion coefficient for the alloy, c_A' is the concentration of A in moles/cm^3, and x is the distance from the original

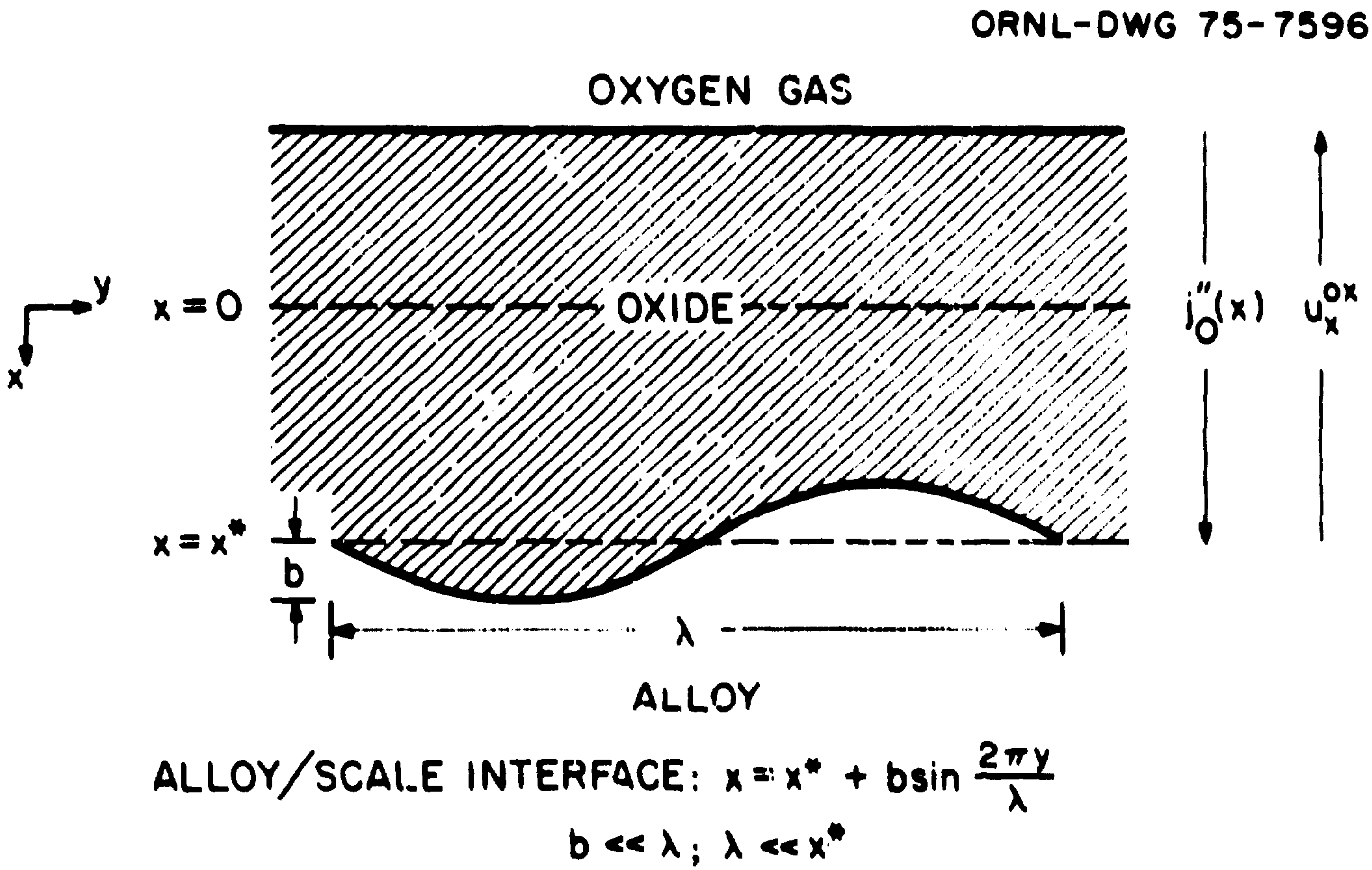

Fig. 2. Schematic representation of a cross section through a single-phase oxide scale on an alloy with an uneven alloy/scale interface.

surface of the alloy. If the alloy is an ideal solid solution, then

$$a_A = N'_A = c'_A V' \quad (2)$$

where a_A is the activity of component A, with pure A as the reference state, N'_A is the mole fraction of A in the alloy, and V' is the molar volume of the alloy, which is assumed to be independent of composition.

When Eq. (2) is inserted into Eq. (1), one obtains

$$j'_A(x) = -\frac{\tilde{D}}{V'} \frac{\partial a_A}{\partial x} \quad (3)$$

An analogous equation can be derived for the flux of component A in the y-direction; therefore, when $\tilde{D}$ is assumed to be independent of composition, Fick's second law can be written as

$$\frac{\partial c'_A}{\partial t} = \frac{1}{V'}\frac{\partial a_A}{\partial t} = -\frac{\partial}{\partial x} j_A(x) - \frac{\partial}{\partial y} j'_A(y) = \frac{\tilde{D}}{V'}\left[\frac{\partial^2 a_A}{\partial x^2} + \frac{\partial^2 a_A}{\partial y^2}\right] \quad (4)$$

It is assumed that the diffusivity of the anions is much greater than the diffusivity of the cations in the oxide. Therefore, the diffusion-controlled oxidation of the alloy requires transport of oxygen anions through the scales from the scale/gas interface to the alloy/scale interface, where additional oxide is formed. If the oxide is a compound semiconductor, then the flux of anions in the positive x-direction with respect to the original surface of the alloy (x = 0) is given by[4]

$$j''_O(x) = -D^s_O\, c''_O \left(\frac{\partial \ln a_O}{\partial x}\right) + u^{ox}_x\, c''_O \quad (5)$$

where D_O^s is the self diffusion coefficient for anions in the scale, c_O'' is the concentration of oxygen in the scale in moles/cm^3, and u_x^{ox}, which is measured with respect to x = 0, is the velocity of the oxide that is caused by the expansion of the scale in the negative x-direction. Expansion of the oxide scale occurs whenever the molar volume of the oxide is greater than the molar volume of the metal from which it forms.

The self diffusion coefficient for oxygen in AO_ν is assumed to exhibit the following dependence on the activity of oxygen:

$$D_O^s = D_O^\circ a_O^m \qquad (6)$$

where m is a constant that can be positive (p-type electronic conductor) or negative (n-type electronic conductor), and D_O° is the self diffusion coefficient of oxygen anions when the activity of oxygen is unity. The concentrations of anions and cations in AO_ν are related to the molar volume of AO_ν, V'', which is assumed to be independent of composition, as follows:

$$c_A'' = 1/V'' \; ; \quad c_O'' = \nu/V'' \qquad (7)$$

Insertion of Eqs. (6) and (7) into Eq. (5) yields

$$j_O''(x) = -\frac{D_O^\circ \nu}{mV''}\left(\frac{\partial a_O^m}{\partial x}\right) + \frac{\nu u_x^{ox}}{V''} \qquad (8)$$

A similar equation can be derived for the flux of oxygen anions in the y-direction.

If the oxide deforms plastically and its molar volume remains constant (incompressible fluid) then the velocity components that arise because of plastic deformation must have zero divergence.[5] Thus,

$$\frac{\partial}{\partial x} u_x^{ox} + \frac{\partial}{\partial y} u_y^{ox} = 0 \qquad (9)$$

Equation (9) is a relationship between the velocity components that arise from the plastic deformation of the oxide. Plastic deformation of the oxide is required because $V''/V' > 1$ and the local rate of oxide formation varies along the irregular alloy/scale interface. The velocity components in Eq. (9) are not necessarily equal to the velocity components for the movement of the alloy/scale interface, although the two velocities are related (see below). In the case of predominant cation diffusion in the scale, the velocity of the alloy/scale interface toward the center of the alloy (a Kirkendall effect) is equal to the velocity of the scale owing to plastic deformation because continuous adhesion of the oxide to the alloy is assumed.[3]

If quasi-steady-state growth of the oxide is assumed, then $\partial c_O''/\partial t \cong 0$, and it follows from Eqs. (8) and (9) that

$$\frac{\partial c_O''}{\partial t} = -\frac{\partial}{\partial x} j_O''(x) - \frac{\partial}{\partial y} j_O''(y) = \frac{D^*_O v}{mV''} \left(\frac{\partial^2 a_O^m}{\partial x^2} + \frac{\partial^2 a_O^m}{\partial y^2}\right) \cong 0 \qquad (10)$$

The locus of the alloy/scale interface is given by

$$x = x^* + b \sin\left(\frac{2\pi y}{\lambda}\right) \qquad (11)$$

where x^* defines the position of an average interface, b is the amplitude of the sine-wave profile and λ is the wavelength (see Fig. 2). It is assumed throughout that

$$b \ll \lambda$$

and $\qquad (12)$

$$\lambda \ll x^*;$$

i.e., the perturbation is supposed to be very small relative to the thickness of the scale.

In order to determine the stability of a planar alloy/scale interface, an expression must be derived for the drift velocity of the perturbed alloy/scale interface as a function of position along the interface. The drift velocity of the alloy/scale interface in the positive x-direction, measured with respect to the original surface of the alloy, is designated as u_x.

The concentration of oxygen at the alloy/scale interface changes discontinuously from c_O'' to c_O'. Application of the principle of the conservation of mass yields

$$j_O''(x) - j_O'(x) = u_x\,(c_O'' - c_O') \qquad (13)$$

$$\text{at} \quad x = x^* + b \sin\left(\frac{2\pi y}{\lambda}\right)$$

where $j_O''(x)$, which is given by Eq. (5), is the total flux of oxygen that arrives at the alloy/scale interface, and $j_O'(x)$ is the flux of oxygen in the alloy in the positive x-direction. If the solubility of oxygen in the alloy is assumed to be virtually zero, then Eq. (13) becomes

$$j_O''(x) = u_x\,c_O'' \qquad (13a)$$

$$\text{at} \quad x = x^* + b \sin\left(2\pi y/\lambda\right)$$

Insertion of Eq. (13a) into Eq. (8) yields, with the aid of Eq. (7),

$$u_x^{ox} = u_x + \frac{D_0^*}{m}\left(\frac{\partial a_0^m}{\partial x}\right)$$

$$\text{at} \quad x = x^* + b \sin (2\pi y/\lambda). \qquad (14)$$

Application of the principle of the conservation of mass to the transfer of component A from the alloy to the oxide yields

$$j'_A(x) - j''_A(x) = \dot{u}_x (c'_A - c''_A)$$

$$\text{at} \quad x = x^* + b \sin (2\pi y/\lambda) \qquad (15)$$

Although the diffusional flux of cations in the scale is assumed to be essentially zero, there does exist a flux of cations in the oxide with respect to $x = 0$ because of the expansion of the oxide. Hence,

$$j''_A(x) = u_x^{ox} c''_A \qquad (16)$$

Component B is not oxidized; therefore, the flux of B in the scale is zero. However, as component A is selectively oxidized, component B must diffuse in the alloy toward the center of the alloy. From the principle of the conservation of the mass it follows that

$$j'_B(x) = u_x c'_B$$

$$\text{at} \quad x = x^* + b \sin (2\pi y/\lambda). \qquad (17)$$

If the molar volume of the alloy is independent of composition, then

$$j'_A\,(x) = -j'_B\,(x) \tag{18}$$

Substitution of Eqs. (16), (17), and (18) into Eqs. (14) and (15) yields

$$u_x = -\frac{V'}{V''}\,\frac{D_O^{\circ}}{m}\,\frac{\partial a_O^m}{\partial x} \tag{19}$$

$$\text{at} \quad x = x^* + b\,\sin\,(2\pi y/\lambda)$$

Upon insertion of Eq. (19) into Eq. (13) and the use of Eq. (8), one obtains

$$u_x^{ox} = (1 - V'/V'')\,\frac{D_O^{\circ}}{m}\left(\frac{\partial a_O^m}{\partial x}\right) \tag{20}$$

$$\text{at} \quad x = x^* + b\,\sin\,(2\pi y/\lambda).$$

Division of Eq. (19) by Eq. (20) yields

$$u_x^{ox} = -\left[V''/V' - 1\right]u_x \tag{20a}$$

Note that $u_x = u_x^{ox}$ only if $V''/V' = 2$. The minus sign appears in Eq. (20a) because the alloy/scale interface moves in the positive x-direction and the oxide expands in the negative x-direction. Equations (20a), which yields the ratio of the thicknesses of the oxide on either side of $x = 0$, can also be derived by simply considering the volume changes that occur when a given amount of metal is converted to oxide and irregularities at the alloy/scale interface are small.

Substitution of Eqs. (2), (3), (7), (16), and (20) in Eq. (15) yields

$$u_x \frac{a'_A}{V'} = -\frac{D^*_O}{V''m}\left(\frac{\partial a^m_O}{\partial x}\right)_{oxide} - \frac{\tilde{D}}{V'}\left(\frac{\partial a_A}{\partial x}\right)_{alloy} \qquad (21)$$

$$\text{at} \quad x = x^* + b \sin (2\pi y/\lambda)$$

Upon combination of Eqs. (2), (3), (17), and (18) one obtains

$$u_x(1 - a_A) = \tilde{D}\,(\partial a_A/\partial x)_{alloy} \qquad (22)$$

$$\text{at } x = x^* + b \sin (2\pi y/\lambda)$$

If Eqs. (21) and (22) or Eqs. (21) and (19) are combined and u_x is eliminated, one obtains the following condition:

$$\frac{\tilde{D}}{V'}\left(\frac{\partial a_A}{\partial x}\right)_{alloy} = -(1 - a_A)\ \frac{D^*_O}{V''m}\left(\frac{\partial a^m_O}{\partial x}\right)_{oxide} \qquad (23)$$

$$\text{at } x = x^* + b \sin (2\pi y/\lambda)$$

In order to obtain an expression for the local rate of movement of the alloy/scale interface, differential equations (4) and (10) must be solved in accordance with the boundary condition expressed by Eq. (23). The solutions of differential equations (4) and (10) can be written as the sum of two terms:

$$a_A = F'(x,t) + f'(x,y,t) \quad \text{if } x > x^* + b \sin(2\pi y/\lambda) \tag{24a}$$

and

$$a_O^m = F''(x,t) + f''(x,y,t) \quad \text{if } x < x^* + b \sin(2\pi y/\lambda) \tag{24b}$$

where $F'(x,t)$ and $F''(x,t)$ represent known solutions of Eqs. (4) and (10), respectively, for a planar alloy/scale interface. The terms $f'(x,y,t)$ and $f''(x,y,t)$ are perturbation functions, which represent the difference between the solutions for a sine-wave profile of the alloy/scale interface and a planar interface.

Wagner[3] introduced approximations for the perturbation functions that are independent of time:

$$f' = v'C' \, b \, \exp\left[-\frac{2\pi(x - x^*)}{\lambda}\right]\sin\left(\frac{2\pi y}{\lambda}\right) \quad \text{if } x > x^* + \quad \sin(2\pi y/\lambda) \tag{25}$$

and

$$f''_{\epsilon} = v''C''b \exp\left[\frac{2\pi(x - x^*)}{\lambda}\right]\sin\left(\frac{2\pi y}{\lambda}\right) \quad \text{if } x < x^* + b\sin(2\pi y/\lambda) \tag{26}$$

where the products bC' $\left(= b\,\frac{\partial F'}{\partial x}\right)$ and bC'' $\left(= b\,\frac{\partial F''}{\partial x}\right)$ give the amplitudes of the activity perturbations for $x = x^*$ at the corresponding time t^*, and v' and v'' are proportionality constants. At large distances from the average interface ($x \gg x^*$), the perturbation functions are essentially equal to zero, and the solutions of Eqs. (4) and (10) are given by the planar interface solutions. This must be the case because the perturbations at the interface are assumed to be very small. At the average interface ($x = x^*$), the perturbation functions assume the form of a sine wave.

Although the perturbation functions cannot be independent of time, it is assumed that they are essentially stationary with respect to the average interface and that their magnitudes change only slowly. Wagner[2] showed that the use of the time-independent forms of the perturbation functions, Eqs. (25) and (26), are reasonable approximations for $f'(x,y,t)$ and $f''(x,y,t)$ if

$$u_x \ll \frac{2\pi\tilde{D}}{\lambda} \tag{27}$$

or

$$\lambda \ll \frac{2\pi\tilde{D}}{u_x} \tag{28}$$

Thus, the use of Eqs. (25) and (26) as approximations for the perturbation functions in the further development of a criterion for the stability of a planar alloy/scale interface requires that the wave length of the sine-wave profile be sufficiently small to satisfy Eq. (28).

At large distances from the average alloy/scale interface, the perturbation functions are zero, and the solutions of Eqs. (4) and (10) are given by the solutions for a planar interface. As an approximation for the planar interface solutions, $F'(x,t)$ and $F''(x,t)$, the first two terms of a Taylor's Series for the $F(x,t)$ about the point $x = x^*$ at $t = t^*$ are employed. Thus, with the aid of Eqs. (25) and (26), particular solutions for differential Eqs. (4) and (10) at $t = t^*$ can be written as:

$$a_A \cong a_A^* + C' \left\{ (x - x^*) + v' b \exp\left[\frac{-2\pi(x - x^*)}{\lambda}\right] \sin\left(\frac{2\pi y}{\lambda}\right) \right\} \quad \text{for } x > x^* + b \sin(2\pi y/\lambda) \tag{29}$$

and

$$a_O^m \cong (a_O^*)^m + C'' \left\{ (x - x^*) - v'' b \exp\left[\frac{2\pi(x - x^*)}{\lambda}\right] \sin\left(\frac{2\pi y}{\lambda}\right) \right\} \quad \text{for } x < x^* + b \sin(2\pi y/\lambda) \tag{30}$$

where a_A^* and a_O^* are the activities of A and O at the average interface plane ($x = x^*$).

In order to calculate the activities of A and O at the alloy/scale interface, Taylor's Series expansions are used for the exponential functions in Eqs. (29) and (30) and Eq. (11) is employed to yield:

$$a_A^i \approx a_A^* + C' (1 + v') b \sin\left(\frac{2\pi y}{\lambda}\right) \qquad (31)$$

and

$$\left[a_O^i\right]^m \approx \left[a_O^*\right]^m + C''(1 - v'') b \sin\left(\frac{2\pi y}{\lambda}\right) \qquad (32)$$

where a_A^i and a_O^i are the activities of A and O at the locus of the alloy/scale interface, which is given by Eq. (11). Terms involving powers of b that are greater than or equal to two are disregarded, because, according to Eq. (12), the magnitude of b is very small.

Because only small deviations from a planar interface are considered, $a_O^i \approx a_O^*$. Upon rearrangement of Eq. (32) one obtains

$$\frac{a_O^i}{a_O^*} = \left[1 + \frac{C''(1 - v'')}{\left[a_O^*\right]^m} b \sin\left(\frac{2\pi y}{\lambda}\right)\right]^{1/m} \qquad (33)$$

If $a_O^i/a_O^* \approx 1$, the first two terms of a series expansion can be used as an approximation for the right-hand-side of Eq. (33) to yield

$$a_O^i \approx a_O^* \left[1 + \frac{C''(1 - v'')}{m\left[a_O^*\right]^m} b \sin\left(\frac{2\pi y}{\lambda}\right)\right] \qquad (34)$$

when power of b greater than unity are disregarded.

Equations (29-31) can be substituted in the boundary equation, Eq. (23). Then, when Taylor's Series expansions are employed for the exponential functions and powers of b greater than unity are disregarded, one obtains

$$\frac{\tilde{D}C'}{V'} + \frac{D_0^{\circ}C''}{m\,V''}\,(1 - a_A^{*}) = \left\{\frac{\tilde{D}C'}{V'}\,\frac{2\pi v' b}{\lambda} + \frac{D_0^{\circ}C''}{m\,V''}\left[(1 - a_A^{*})\left(\frac{2\pi v'' b}{\lambda}\right) + (1 + v')\,bC'\right]\right\}\sin\left(\frac{2\pi y}{\lambda}\right) \tag{35}$$

Equation (35) is of the form (A + B) = (C + D) f(y), where A, B, C, and D are constants and y is a variable. This equation can be satisfied only if (A + B) = 0 and (C + D) = 0. Therefore,

$$\frac{\tilde{D}C'}{V'} = -\frac{D_0^{\circ}C''}{m\,V''}\,(1 - a_A^{*}) \tag{36}$$

and

$$\frac{\tilde{D}C'\,2\pi v' b}{\lambda V'} = -\frac{D_0^{\circ}C''}{m\,V''}\left[(1 - a_A^{*})\,\frac{2\pi v'' b}{\lambda} + (1 + v')\,bC'\right] \tag{37}$$

Because λ must be sufficiently small to satisfy Eq. (28), the first term in the brackets on the right-hand-side of Eq. (37) is much larger than the second term. Hence,

$$\frac{\tilde{D}C' v'}{V'} \cong -\frac{D_0^{\circ}C''}{m\,V''}\,(1 - a_A^{*})\,v'' \tag{38}$$

When corresponding sides of Eqs. (36) and (38) are divided, one obtains

$$\nu' = \nu'' \tag{39}$$

If local thermodynamic equilibrium is maintained at the alloy/scale interface, then it follows that

$$a_A^i(\text{alloy}) = a_A^i(\text{oxide}) \tag{40}$$

and

$$a_O^i(\text{alloy}) = a_O^i(\text{oxide}) \tag{41}$$

At each point in the oxide scale, the activities of metal and oxygen are related by $a_A a_O^{\nu_o} = K$, where K is a constant at constant temperature and total hydrostatic pressure if the chemical potential of the compound is independent of the composition of the oxide over the composition range of interest. Therefore,

$$a_A^*(a_O^*)^{\nu_o} = K \tag{42}$$

and

$$a_A^i(a_O^i)^{\nu_o} = K \tag{43}$$

Equations (40-43) are strictly valid only in the case of a planar alloy/scale interface. If the alloy/scale interface is uneven, then the contribution of the surface free energy to the total free energy change should be included. However, because of the large volume free energy changes for the oxidation of metals such as uranium, the surface free energy effect can be ignored except for very small values of λ, or, in view of Eq. (12), except for very thin scales. In like manner, the effect of stresses on the free energy change is also ignored. Stress effects such as stress-assisted diffusion and cracking of the scale are assumed not to be present. Combination of Eqs. (42) and (43) yields

$$\frac{a_O^i}{a_O^*} = \left(\frac{a_A^*}{a_A^i}\right)^{1/q} \tag{44}$$

When Eq. (44) is compared with Eq. (33), one finds

$$a_A^i(\text{oxide}) = a_A^* \left[1 + \frac{C''(1 - \nu'')}{m\left[a_O^*\right]^m} b \sin\left(\frac{2\pi y}{\lambda}\right)\right]^{-q} \tag{45}$$

Insertion of Eqs. (31) and (45) into Eq. (40) yields

$$\frac{\nu C''(1 - \nu'')}{m(a_O^*)^m} = -\frac{C'(1 + \nu')}{a_A^*} \tag{46}$$

When Eq. (39) is used in Eq. (46), one can solve for ν' and ν'':

$$\nu' = \nu'' = \frac{(q + 1)}{(q - 1)} \tag{47}$$

where

$$q = \frac{a_A^* \nu_c C''}{m(a_O^*)^m C'} \qquad (48)$$

The ratio C''/C' can be obtained from Eq. (36); substitution in Eq. (48) yields

$$q = -\nu_c \frac{N_A'^*}{(1 - N_A'^*)} \frac{\tilde{D}}{(D_O^s)^*} \frac{V''}{V'} \qquad (49)$$

where $(D_O^s)^*$ is the self-diffusion coefficient for oxygen anions at $x = x^*$ $(a_O = a_O^*)$ and $N_A'^*$ $(= a_A^*)$ is the mole fraction of component A at $x = x^*$.

The local rate of movement of the alloy/scale interface toward the center of the alloy is given by Eq. (22). Substitution of Eqs. (29) and (31) in Eq. (22), and evaluation at $x = x^*$ yields

$$u_x^* = \frac{\tilde{D}C'}{1 - a_A^*} \qquad (50)$$

where u_x^* is the velocity of the average alloy/scale interface. Insertion of Eqs. (29) and (31) into Eq. (22) yields, when Taylor's Series expansions are used for the exponential functions and powers of b greater than unity are ignored,

$$u_x - u_x^* = \left[u_x \frac{C'(1 + v')}{(1 - a_A^*)} - u_x^* \frac{2\pi v''}{\lambda}\right] b \sin \frac{2\pi y}{\lambda} \qquad (51)$$

If λ is very small, then the second term in brackets in Eq. (51) is much larger than the first term. Therefore,

$$u_x - u_x^* = - u_x^* \frac{2\pi\gamma' b}{\lambda} \sin\left(\frac{2\pi y}{\lambda}\right) \qquad (52)$$

Equations (47) and (49) are similar, and Eq. (52) is identical, to the corresponding equations that Wagner[2] derived for the case of predominant cation diffusion in the oxide. The same type of analysis for the stability of a planar alloy/scale interface is applicable here.

In regions of the scale where the local thickness exceeds the average thickness ($\sin \frac{2\pi y}{\lambda} > 0$), the sign of γ' (or γ'') determines whether the local interface velocity is greater or less than the average interface velocity. If $\gamma' > 0$, then $u_x < u_x^*$, and the perturbations at the alloy/scale interface should decrease as the reaction proceeds; a flat interface (a single-phase scale) is stable. On the other hand, if $\gamma' < 0$, then $u_x > u_x^*$ and the amplitude of the perturbations at the alloy/scale interface should increase as the reaction proceeds; that is, a flat interface is unstable with respect to a serrated or wavy interface. A two-phase scale, which comprises B-rich alloy and AO_ν, is expected to form on the alloy.

The sign of γ' depends on the value of q, which is defined by Eq. (49). All of the constants in Eq. (49) are positive quantities, and $N_A'^*$ is always less than unity. Therefore, q is always a negative quantity. Hence, $\gamma' > 0$, and a flat interface is stable, when $|q| > 1$; $\gamma' < 0$, and a flat interface is <u>not</u> stable when $|q| < 1$.

The application of the criterion for the stability of a planar alloy/scale interface requires that values of $N_A'^*$ and $(D_O^s)^*$ be known so that q can be calculated. Values of $N_A'^*$ and $(D_O^s)^*$ can be obtained from equations derived by Wagner[6] for the oxidation of a binary alloy with a flat alloy/scale interface. Wagner's model[6] allows one to calculate a parameter, α, which is equal to the parabolic rate constant for the oxidation of the alloy divided by the parabolic rate constant for the oxidation of the pure metal, A, as a function of alloy composition at a given temperature and oxygen potential. When α is equal to unity, then the rate-limiting step of the oxidation reaction must be diffusion in the oxide phase; that is, the alloy oxidizes at the same rate as the pure metal, and thus, diffusion processes in the alloy have essentially no effect on the rate of oxidation. Conversely, if α is less than unity, then the rate of oxidation of the alloy must be limited by diffusion in the alloy phase.

If the rate of oxidation of the alloy were limited by diffusion in the oxide ($\alpha = 1$), then $(D_O^s)^* \ll \tilde{D}$ and $N_A'^*$ should not differ greatly from the bulk alloy composition (the oxygen potential at the alloy/scale interface should be virtually equal to Π_{O_2}, the oxygen potential for coexistence of pure A and AO_{ν_o}). Furthermore, $V'' > V'$ and $\nu_o \geq 1$. Therefore, according to Eq. (49), the absolute value of q is greater than unity; that is, a planar alloy/scale interface is stable when the rate-limiting step of the growth of the single-phase scale shown in Fig. 2 is diffusion in the oxide phase.

If the rate of oxidation of the alloy were limited by diffusion in the alloy phase ($\alpha < 1$), then $\tilde{D} \ll (D_O^s)^*$ and $N_A'^* \ll 1$ (the oxygen potential at the alloy/scale interface should not differ greatly from the ambient oxygen potential). Therefore, according to Eq. (49), the absolute value of q is less than unity. A serrated alloy/scale interface (a two-phase scale) is the stable growth morphology when the rate-limiting step of the growth of the single-phase scale shown in Fig. 2 is diffusion in the alloy phase. During steady-state growth of the two-phase scale the oxygen potential at the growth front of the oxide should be virtually equal to Π_{O_2}/N_A^b, where N_A^b is the mole fraction of component A in the bulk alloy. At the growth front, atoms of component B are supposed to move only short distances in the y-direction in order to allow penetration of oxide into the alloy. The rate of penetration of oxide into the alloy should be approximately equal to the rate of thickening of the oxide on pure metal A, as long as N_A^b does not differ greatly from unity.[3] This assumes that effects of growth stresses on the rate of oxidation are negligible.

Wagner[3] pointed out that a value of $|q|$ greater than unity is a necessary but not sufficient condition for the stability of a planar alloy/scale interface. Other factors, such as interfacial tension, stresses in the scale and in the alloy, fast transport along interfaces, and the grain size of the alloy could affect the morphology of the scale. For example, interface tension would counteract the tendency to form an uneven interface, while differences in molar volumes of the alloy and the scale would favor an uneven interface if this morphology minimized the overall stress in the system.

The criterion for the stability of a planar interface has been applied to the oxidation of U-Nb alloys at elevated temperatures. The results of these experiments, which are in qualitative agreement with the criterion, will be presented in a future publication.

SUMMARY

Analytical expressions have been derived to predict the stability of a planar alloy/scale interface during the oxidation of binary alloys when anion diffusion predominates in the oxide scale. Only one component of the alloy is supposed to be oxidized, and the solubility of oxygen in the alloy is supposed to be zero. According to the stability criterion, a planar alloy/scale interface (a single-phase scale) is the preferred growth morphology if diffusion in the oxide phase is the rate-limiting step of the oxidation reaction. A serrated alloy/scale interface (a two-phase scale) is expected to develop during oxidation if diffusion in the alloy phase is the rate-determining step of the oxidation reaction.

This stability criterion is equivalent to the criterion derived by Wagner[3] for the case of predominant cation diffusion in the scale. The criterion can be applied to the oxidation (sulfidation, etc.) of any binary alloy as long as the assumptions that were employed in the model are valid for the system under consideration.

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