

Spalling of Protective Oxide Scales

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The bulk mole fraction of an element A in a binary alloy AB required to form (1) a coherent, continuous layer of oxide AO_v , (2) a second layer of AO_v , should the first layer spall from the surface, and (3) further layers of the protective oxide if repeated spalling is likely, is calculated as a function of the ratio of the parabolic rate constant for oxidation to the alloy interdiffusion coefficient. The implications of spalling of the protective oxide layers are also discussed.

INTRODUCTION

The majority of heat-resistant alloys contain at least one element, for example Al, Cr, or Si which, because of its relatively high affinity for oxygen, tends to be selectively oxidized from the alloy. The resulting scale is highly protective because diffusion processes in such oxides are slow. As a result of the selective oxidation, a depletion of the selectively oxidized element (for example, A in a binary alloy AB) is produced at the alloy-oxide interface. In the absence of oxygen solubility and diffusivity, the mole fraction of A at the alloy-oxide interface must not be depleted below that for thermodynamic stability of oxide AO_v in contact with the alloy in order for a continuous layer of the oxide AO_v to be formed.

Generally, although the diffusion coefficient of oxygen may be several orders of magnitude greater than the alloy interdiffusion coefficient,¹ its solubility behind the scale is low because of the high stability of the surface oxide, and the criteria given above are still valid.

Further considerations become necessary if the protective oxide is likely to spall from the alloy surface. This is frequently the case in many industrial applications when oxidation-resistant alloys are required to withstand thermal cycling. Such conditions, and indeed isothermal oxidation itself

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for many systems, promote cracking of the protective oxides, which in turn exposes fresh alloy to the oxidizing gases. This freshly exposed alloy then oxidizes in a manner appropriate to its composition, now different from that of the original alloy, and consequently, for the alloy to be able to re-form the protective oxide, the mole fraction of A at the alloy surface when spalling occurs must also be great enough for a coherent layer of the protective oxide to be formed.

LIMITING COMPOSITION FOR SCALE HEALING

It is assumed that the surface scale grows according to a parabolic rate law, and furthermore, that selective oxidation is complete, that is, no B enters the scale. The instantaneous position of the alloy-oxide interface, Δx , measured from the original alloy surface, is then given by

$$\Delta x = (2kt)^{\frac{1}{2}} \quad (1)$$

where k is the corrosion constant as defined by Wagner,² and is the parabolic rate constant for oxidation in terms of the displacement of the alloy-oxide interface; this corrosion constant is related to the conventional parabolic rate constant of oxidation, k_p , which relates weight gain per unit surface area with time, by

$$k = (2V_A/vM_{O_2})^2 k_p \quad (2)$$

where V_A is the molar volume of the alloy, M_{O_2} the gram molecular weight of oxygen, and v the ratio of oxygen ions to metal cations in the oxide AO_v .

Generally, the oxidation rate is small, and the displacement of the alloy-oxide interface can be neglected. A solution of the general diffusion equation in the underlying alloy, considered as semi-infinite,

$$t > 0, \quad \partial N_A / \partial t = D(\partial^2 N_A / \partial x^2), \quad 0 \leq x \leq \infty \quad (3)$$

under these conditions

$$t = 0, \quad N_A = N_{A,b}, \quad 0 \leq x \leq \infty \quad (4)$$

$$t > 0, \quad D(\partial N_A / \partial x) = (1 - N_{A,i})[d(\Delta x)/dt], \quad x = 0 \quad (5)$$

has been obtained;² N_A , $N_{A,i}$, and $N_{A,b}$ are the mole fractions of A locally at position x (measured from the original alloy surface) at time t , at the alloy-oxide interface and in the bulk alloy, and D is the alloy interdiffusion coefficient. The concentration of A in the alloy is given as

$$t > 0, \quad N_A = N_{A,b} - \left\{ \left(\frac{1}{2} \pi k / D \right)^{\frac{1}{2}} / \left[1 - \left(\frac{1}{2} \pi k / D \right)^{\frac{1}{2}} \right] \right\} (1 - N_{A,b}) \operatorname{erfc}[x/2(Dt)^{\frac{1}{2}}] \quad (6)$$

which reduces at the alloy–oxide interface, $x = 0$, to

$$t > 0, \quad N_{A,i} = [N_{A,b} - (\frac{1}{2}\pi k/D)^{\frac{1}{2}}]/[1 - (\frac{1}{2}\pi k/D)^{\frac{1}{2}}] \quad (7)$$

As indicated earlier, for a coherent layer of the protective oxide AO_v to be formed, $N_{A,i}$ must be greater than that for thermodynamic stability of AO_v in contact with the alloy. This value may be taken as practically zero, since the protective oxide is thermodynamically very stable, and thus the critical bulk mole fraction of A, $(N_{A,b,crit})_I$, is given by

$$(N_{A,b,crit})_I > (\frac{1}{2}\pi k/D)^{\frac{1}{2}} \quad (8)$$

The depletion of A at the alloy–oxide interface, ΔN_A , is given as

$$\Delta N_A = N_{A,b} - N_{A,i} = (1 - N_{A,i})(\frac{1}{2}\pi k/D)^{\frac{1}{2}} \quad (9)$$

and thus in order for a continuous layer of the protective oxide to be re-formed on the surface of the alloy if the initial layer spalls, a second critical bulk mole fraction of A in the alloy is required, which satisfies

$$(N_{A,b,crit})_{II} > (N_{A,b,crit})_I + \Delta N_A \quad (10)$$

or using Eqs. (7), (8), and (9)

$$(N_{A,b,crit})_{II} > 1 - [1 - (\frac{1}{2}\pi k/D)^{\frac{1}{2}}] \quad (11)$$

CONCENTRATION CHANGES IN THE ALLOY AFTER HEALING

It is interesting to inquire into the concentration changes occurring in the alloy after the formation of the second layer of the protective oxide. The concentration of A at the alloy–oxide interface is of particular importance if repeated losses of the protective oxide are expected, as sufficient time must elapse between successive losses of oxide in order for the concentration of A at the alloy–oxide interface to return to the value it had before the loss of the first oxide.

Let the loss of the protective oxide occur at time t^* , then again diffusion in the underlying alloy will be governed by the general diffusion equation

$$t > t^*, \quad \partial N_A / \partial t = D(\partial^2 N_A / \partial x^2), \quad 0 \leq x \leq \infty \quad (12)$$

and the boundary condition at the alloy–oxide interface, $x = 0$, relating the flux of A out of the alloy to the rate of increase in scale thickness is given by

$$t > t^*, \quad D(\partial N_A / \partial x) = [1 - N_{A,i}(t)][k/2(t - t^*)^{\frac{1}{2}}]^{\frac{1}{2}}, \quad x = 0 \quad (13)$$

which is similar to Eq. (5) except that under these conditions $N_{A,i}(t)$ is not constant but a function of time. The initial condition will be given by Eq. (6)

with $t = t^*$

$$t = t^*, \quad N_A = N_{A,b} - \left\{ \left(\frac{1}{2} \pi k / D \right)^{\frac{1}{2}} / \left[1 - \left(\frac{1}{2} \pi k / D \right)^{\frac{1}{2}} \right] \right\} (1 - N_{A,b}) \operatorname{erfc} \frac{1}{2} x (Dt)^{\frac{1}{2}},$$

$$0 \leq x \leq \infty \quad (14)$$

Thus, a solution is required of Eq. (12), subject to the auxiliary Eqs. (13) and (14). Unfortunately, an exact analytical solution under these conditions is not possible. However, an approximate solution may be obtained as is shown in the Appendix; this solution appears to be in reasonable agreement with a solution developed by numerical analysis for typical values of the constants involved.³

The solution is written

$$t > t^*, \quad N_A = N_{A,b} - \frac{\phi}{1 - \phi} (1 - N_{A,b}) \operatorname{erfc} \frac{x}{2[D(t - t^*)]^{\frac{1}{2}}} \\ \times \left[1 + \frac{\phi}{1 - \phi} \times \frac{2}{\pi} \sin^{-1} (t^*/t)^{\frac{1}{2}} \right] \\ + \frac{2}{\pi} \int_0^{(t^*/t - t^*)^{\frac{1}{2}}} \exp \left[-\frac{x^2(1 + u^2)}{4Dt} \right] \frac{du}{1 + u^2} \quad (15)$$

where ϕ replaces $(\frac{1}{2} \pi k / D)^{\frac{1}{2}}$.

CHANGES IN THE INTERFACIAL COMPOSITION AFTER HEALING

The mole fraction of element A at the alloy-oxide interface is the most important factor in determining the likely oxidation behavior. This is obtained from Eq. (15) by putting $x = 0$, as

$$t > t^*, \quad N_{A,i} = \frac{\phi}{1 - \phi} \left[N_{A,b} - \phi - \frac{\phi}{1 - \phi} (1 - N_{A,b}) \times \frac{2}{\pi} \sin^{-1} (t^*/t)^{\frac{1}{2}} \right] \quad (16)$$

Figure 1 shows the variation of the mole fraction of A at the alloy-oxide interface with time for an alloy of given bulk composition ($N_{A,b} = 0.25$) and a ratio of oxidation rate constant to an alloy interdiffusion coefficient of 10^{-2} , in accord with Eqs. (7) and (16). While $t > t^*$, the interface composition is approximately constant, but there is an abrupt decrease when the second protective oxide layer is formed immediately after spalling of the initial layer. As t becomes greater than t^* , the interfacial concentration of A increases, rapidly at first, eventually approaching the value it had before the initial layer spalled from the surface.

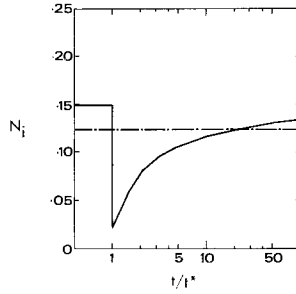


Fig. 1. Variation of the interfacial composition with time when spalling of the protective oxide occurs for $N_{A,b} = 0.25$ and $k/D = 10^{-2}$.

REPEATED SPALLING OF THE PROTECTIVE OXIDE

As indicated earlier, repeated spalling of the protective oxide is a distinct possibility in many systems. The variation of the interfacial composition with time after the formation of the second layer of protective oxide, as shown in Fig. 1, is important then, as the subsequent mode of oxidation will depend on the surface composition at the time of spalling. A third layer of the protective oxide would or would not be formed, depending on whether the interfacial composition of A were above or below the limiting composition for the formation of a protective oxide, as given in Eq. (8). In the example used in Fig. 1, namely, k/D having a value of 10^{-2} , the limiting composition is $N_A = 0.125$ and is shown as the horizontal chain line. During the time interval when the curve representing the interfacial composition of A lies below this horizontal line, a protective oxide layer would not be re-formed. Thus, to a first approximation, it may be said that if the spalling frequency is greater than this time interval, continued protection against high temperature oxidation is unlikely.

Clearly then, there must exist a further category of alloys containing higher bulk mole fractions of A, for which the interfacial concentration does not fall below that necessary for reestablishment of a protective layer. Thus, with these alloys unless the rate of spalling is exceptionally rapid, continued formation of the protective oxide would be expected. This critical bulk mole fraction which permits rapid spalling is easily obtained with the aid of Eq. (16), since at $t = t^*$, $N_{A,i}$ must be greater or equal to ϕ . Thus

$$[\phi/(1 - \phi)][N_{A,b} - \phi - [\phi/(1 - \phi)](1 - N_{A,b})] \geq \phi$$

giving

$$(N_{A,b,crit})_{III} > 1 - (1 - \phi)^3 \quad (17)$$

Thus, there are three critical bulk mole fractions of A in the alloy, given by Eqs. (8), (11), and (17) dividing alloys into four groups. Figure 2 shows how these critical bulk mole fractions vary with the ratio of oxidation rate constant to alloy interdiffusion coefficient, curves I, II, and III representing eqs. (8), (11), and (17) respectively.

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|--|--|
| I. $N_{A,b} < \phi$ | Insufficient A to form the protective oxide. |
| II. $\phi < N_{A,b} < 1 - (1 - \phi)^2$ | Sufficient A to form the protective oxide initially, but not to re-form it. |
| III. $1 - (1 - \phi)^2 < N_{A,b} < 1 - (1 - \phi)^3$ | Sufficient A for healing of the protective scale, but not to cope with rapid spalling. |
| IV. $N_{A,b} > 1 - (1 - \phi)^3$ | Rapid spalling possible. |

Included in Fig. 2 are typical ranges of values of the ratio k/D for Fe-Cr and Ni-Cr alloys. In agreement with the values in the figure, Fe-Cr alloys in the range 12–20 wt. % and Ni-Cr alloys in the range 18–30 wt. % Cr form Cr_2O_3 scales at first, but suffer rapid scaling when the protective oxide spalls from the surface; a new layer of the protective oxide Cr_2O_3 is not immediately re-formed.^{4,5} For Fe-Cr alloys containing less than about 12 wt. % Cr and Ni-Cr alloys with less than about 18 wt. % Cr, a protective scale of Cr_2O_3 is not generally formed, while Fe- or Ni-alloys containing greater than about 20 or 30 wt. % Cr respectively, form multiple layers of Cr_2O_3 .^{6,7}

It must be pointed out that with alloys containing a sufficient concentration of the easily oxidizable element, A, to form the protective oxide, this oxide may not form immediately on exposure of the alloy to the oxidizing environment. Often the establishment of the protective oxide is preceded by a

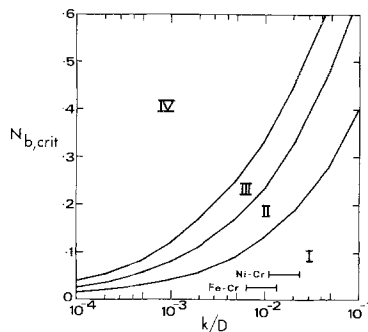


Fig. 2. Critical mole fractions for alloys to withstand repeated spalling of the protective oxide as a function of k/D .

“non-steady state” period when both the elements enter the oxide scale. However, this “non-steady state” period is usually of short duration,¹ and the protective oxide is soon established.

Alloys containing insufficient element A for a new layer of the protective oxide to form on spalling of the initial layer will oxidize in a different manner. Oxide AO_v will still be formed at the surface of the alloy, but this will take the form of a discontinuous precipitate rather than a coherent layer, allowing simultaneous oxidation of the other alloy components. Under these conditions, the scale thickening rate will be much increased and the scale encroach rapidly into the alloy. Furthermore, oxygen dissolution and diffusion into the alloy may now occur as the effective oxygen pressure behind the less stable surface oxide is considerably higher than behind the protective scale. Thus, oxygen diffuses into the alloy into regions where there is a higher local concentration of A, resulting in a higher volume fraction of AO_v being precipitated. Eventually, a coherent layer of AO_v will be possible and healing may occur. However, substantial oxidation can take place before this happens. Calculating the time at which healing occurs under these circumstances is rather more difficult, principally because of the larger number of parameters involved, and the difficulty of assigning values to them in any situation.

APPENDIX

A solution of

$$t > t^*, \quad \partial N_A / \partial t = D(\partial^2 N_A / \partial x^2), \quad 0 \leq x \leq \infty \quad (\text{A.1})$$

is required, subject to the following auxiliary equations

$$t > t^*, \quad D(\partial N_A / \partial x) = [1 - N_{A,i}(t)][k/2(t - t^*)]^{\frac{1}{2}}, \quad x = 0 \quad (\text{A.2})$$

$$t = t^*, \quad N_A = N_{A,b} - \left\{ \left(\frac{1}{2} \pi k / D \right)^{\frac{1}{2}} [1 - \left(\frac{1}{2} \pi k / D \right)^{\frac{1}{2}}] \right\} \\ \times [1 - N_{A,b}] \operatorname{erfc} x / 2(Dt^*)^{\frac{1}{2}}, \quad (\text{A.3})$$

The solution may be written in the form

$$t > t^*, \quad N_A(x, t) = f(x, t) + g(x, t) \quad (\text{A.4})$$

where functions $f(x, t)$ and $g(x, t)$ both satisfy Eq. (A.1) with f or g replacing N_A , and in addition satisfy the following conditions

$$t = t^*, \quad f(x, t^*) = -[\phi / (1 - \phi)](1 - N_{A,b}) \operatorname{erfc} x / 2(Dt^*)^{\frac{1}{2}} \quad (\text{A.5})$$

$$t > t^*, \quad \partial f / \partial x = 0, \quad x = 0 \quad (\text{A.6})$$

$$t = t^*, \quad g(x, t^*) = N_{A,b} \quad (\text{A.7})$$

$$t > t^*, \quad D(\partial g/\partial x) = [1 - f(0, t) - g(0, t)][k/2(t - t^*)]^{1/2}, \quad x = 0 \quad (\text{A.8})$$

where ϕ is equal to the ratio $(\frac{1}{2}\pi k/D)^{1/2}$.

Function $f(x, t)$ has been obtained, and may be written

$$t > t^*, \quad f(x, t) = -[\phi/(1 - \phi)](1 - N_{A,b})(2/\pi) \times \int_0^{(t^*/t - t^*)} \exp[-x^2(1 + u^2)/4Dt][du/(1 + u^2)] \quad (\text{A.9})$$

values of the integral for different arguments of $(t^*/t - t^*)^{1/2}$ and $(x^2/4Dt)$ being tabulated.⁸ Equation (A.9) reduces at $x = 0$ to

$$t > t^*, \quad f(0, t) = -[\phi/(1 - \phi)](1 - N_{A,b})(2/\pi) \sin^{-1} [t^*/t]^{1/2} \quad (\text{A.10})$$

Substitution of Eq. (A.10) into Eq. (A.8) yields

$$t > t^*, \quad D(\partial g/\partial x) = \{1 + [\phi/(1 - \phi)](1 - N_{A,b})(2/\pi) \sin^{-1} [t^*/t] - g(0, t)\} \times [k/2(t - t^*)]^{1/2}, \quad x = 0 \quad (\text{A.11})$$

Thus, the solution is now required of Eq. (A.1), with g replacing N_A , subject to the boundary conditions (A.7) and (A.11). Due to the complexity of the boundary condition (A.11), an exact analytical solution cannot be obtained. However, if it is assumed that the inverse sine function in Eq. (A.11) is invariant with time, an approximate solution may be obtained. Within the region of interest of the present work, this approximate solution appears to agree reasonably well with a numerical solution of the appropriate equations.

The function $g(x, t)$ therefore takes the form

$$t > t^*, \quad g(x, t) = N_{A,b} - [N_{A,b} - g(0, t)] \operatorname{erfc} x/2[D(t - t^*)]^{1/2} \quad (\text{A.12})$$

where $g(0, t)$ is obtained by combining Eqs. (A.12) and (A.11). Thus, the full solution reads

$$t > t^*, \quad g(x, t) = N_{A,b} - [\phi/(1 - \phi)](1 - N_{A,b}) \times [1 + [\phi/(1 - \phi)](2/\pi) \sin^{-1} [t^*/t]^{1/2}] \times \operatorname{erfc} x/2[D(t - t^*)]^{1/2} \quad (\text{A.13})$$

Thus, combining Eqs. (A.9) and (A.13)

$$t > t^*, \quad N_A(x, t) = N_{A,b} - \frac{\phi}{1 - \phi}(1 - N_{A,b}) \left[\operatorname{erfc} \frac{x}{2[D(t - t^*)]^{1/2}} \times \left[1 + \frac{\phi}{1 - \phi} \frac{2}{\pi} \sin^{-1} \left[\frac{t^*}{t} \right]^{1/2} \right] + \frac{2}{\pi} \int_0^{(t^*/t - t^*)} \exp \left[-\frac{x^2(1 + u^2)}{4Dt} \right] \frac{du}{1 + u^2} \right] \quad (\text{A.14})$$

At the alloy-oxide interface, $x = 0$, Eq. (A.14) reduces to

$$t > t^*, \quad N_{A,i}(t) = [1/(1 - \phi)] \{N_{A,b} - \phi - [\phi/(1 - \phi)](1 - N_{A,b}) \\ \times (2/\pi) \sin^{-1} [t^*/t]^{\frac{1}{2}}\} \quad (\text{A.15})$$

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