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An Extension of Wagner's Analysis of Competing Scale Formation

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Wagner's criterion to predict the minimum concentration of solute ($N^0_{B(min)}$) necessary for the exclusive formation of its scale has been modified to incorporate both thermodynamic and kinetics requirements. The analysis presented here involves a receding alloy/scale interface for which the composition of the alloy at this interface is governed by thermodynamic equilibrium between the two competing scale phases and the base alloy. This is a more rigorous analysis than that of Wagner's, who assumed the alloy/scale interface to be immobile and the solute composition at the interface to be zero. A comparison is made between values of $N^0_{B(min)}$ found experimentally and those predicted by Wagner's and the present criterion for a number of alloy-gas systems. It is shown that the criterion developed in the present analysis can often provide a better approximation of the actual $N^0_{B(min)}$. The expressions derived from the present analysis have been extended also in a semiquantitative manner to provide a criterion for the minimum amount of solute in the alloy required for the transition from internal to external scale formation.

KEY WORDS: Competitive scale growth; exclusive-scale formation; moving boundary.

INTRODUCTION

When an alloy reacts with a gas, such as oxygen or sulfur, the characteristics of the scale which forms are dependent on a number of factors. In particular, the concentration of the alloying constituents and their affinity for the gas greatly affect what the phase constitution of the resulting scale will be. Wagner[1-4] has treated several different cases in a series of publications. The

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variable in his treatments was often the affinity the alloying constituents had for the oxidant. For example, he treated such cases as the oxidation of a binary alloy containing a noble metal[1] and of an alloy whose constituents had a similar affinity for the oxidant.[2] One of the cases of most practical importance that Wagner discussed was the formation of competing scale phases,[3] in which a critical concentration of solute necessary for the exclusive formation of its own scale could be calculated. Wagner's treatment of this case was greatly simplified by the assumptions: (1) the element whose scale formed exclusively on the alloy had a much higher affinity for the gas than that of the other elements, so that its concentration at the alloy/scale interface was practically zero; and (2) the movement of the alloy/scale interface due to metal consumption was negligible.

In the case of oxidation, where alloys usually contain either aluminum, chromium, or silicon in order to form a homogeneous scale of Al_2O_3, Cr_2O_3, or SiO_2, the simplifying assumptions employed in Wagner's treatment are valid. This is because these oxides are both extremely stable and slow-growing in comparison to the oxides of the other alloying constituents. However, in the case of sulfidation, the contrary is often encountered. The stabilities of the sulfides of the alloying constituents are usually very close to one another, and their growth rates are very high.[5] Under these conditions the simplifying assumptions adopted by Wagner are inadequate.

This paper gives a rigorous analysis of the competing scale growth case that allows for a much broader understanding of alloy scaling. The analysis is essentially a modification of Wagner's original treatment. As such, the basic concepts and techniques used here are in accordance with those of Wagner. We will be concerned primarily with the exclusive formation of a competing scale phase; however, it will be shown that the formulated equations can be extended to the treatment of the transition from internal to external scale formation.

ANALYSIS

Thermodynamics of Competing Scale Growth

Extensive reviews on the thermodynamics of alloy oxidation have been given by Whittle,[6] and Douglass.[7] In this paper, only the important aspects necessary for the subsequent analysis will be presented. It should be stressed that the term oxidation will be used throughout this paper in a generic sense, rather than being strictly the reaction of a metal with oxygen. In other words, the term oxidation will be used to mean simply the reaction of a metal with a gas to form a product. Thus, for clarity, we will say that the metal is reacting with an oxidant X_2, which could be O_2, S_2, or some other reactive gas.

Consider an alloy AB in which B has a greater affinity for the oxidant than A. The oxidation reaction for the alloy constituents can be written as

$$A(\text{alloy}) + \tfrac{1}{2}X_2 = AX \tag{1}$$

for A, and

$$B(\text{alloy}) + \tfrac{1}{2}X_2 = BX \tag{2}$$

for B. It will be assumed that AX and BX are insoluble in each other and, in order to simplify the analysis, formation of a mixed phase such as a spinel phase $A_{1+x}B_{2-x}O_4$ ($A = \text{Co, Ni, Fe}$; $B = \text{Cr, Al}$) will not be considered.

If each of the above reactions are at equilibrium, one can write for reaction (1)

$$\frac{a_A P_{X_2}^{1/2}}{a_{AX}} = K_1 \tag{3}$$

and for reaction (2)

$$\frac{a_B P_{X_2}^{1/2}}{a_{BX}} = K_2 \tag{4}$$

where the a's are the thermodynamic activities of either the alloying element or the scale, and the K's are the temperature-dependent equilibrium constants.

The activity of the scale phase is typically assumed to be equal to one. The activities of the alloying constituents A and B are proportional to their respective atomic fractions, N_i, so that $a_i = \gamma_i N_i$. The proportionality constant, γ, is referred to as the activity coefficient. Also, since we are dealing with atomic fractions, we can write $N_A + N_B = 1$. With these relationships, together with Eq. (3) and (4), one finds that equilibrium exists between two oxides of stoichiometry AX and BX at

$$P_{X_2}^e = \left(\frac{K_1}{\gamma_A} + \frac{K_2}{\gamma_B}\right)^2 \tag{5}$$

and

$$N_B^e = \frac{1}{(K_1/K_2)(\gamma_B/\gamma_A) + 1} \tag{6}$$

This is shown Schematically in Fig. 1. For a given binary alloy system at a particular temperature, N_B^e is constant. Thus, on a strictly thermodynamic basis, alloys with composition $N_B < N_B^e$ will form AX preferentially. Whereas, alloys with composition $N_B > N_B^e$ will form BX preferentially.

If a regular-solution model was employed to solve for γ_A and γ_B,[8] Eqs. (5) and (6) could be written in terms of oxide-dissociation pressures

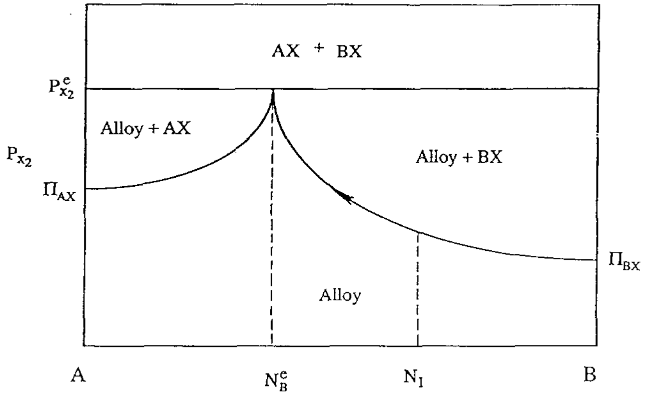

Fig. 1. A schematic stability diagram for an *A–B* alloy system.

and the regular-solution model parameter Ω. Without going into the analysis, simple algebraic manipulation of Eq. (6) yields

$$\ln\frac{\Pi_{AX}}{\Pi_{BX}}=2\ln\frac{1-N^e_B}{N^e_B}-\frac{2\Omega}{RT}(1-2N^e_B) \tag{7}$$

where Π is the dissociation pressure of the indicated phase, and Ω is the bonding parameter of the regular solution. The relationship between N^e_B and the left-hand side of Eq. (7) for various values of Ω is shown in Fig. 2. It can be seen in this figure that a larger Ω gives a higher N^e_B for a given ratio Π_{AX}/Π_{BX}. This is a direct result of stronger bonding between *A* and *B*; which decreases the activity of *B* (as well as *A*) in the alloy. In other words a larger Ω, and hence a larger bond strength between *A* and *B*,

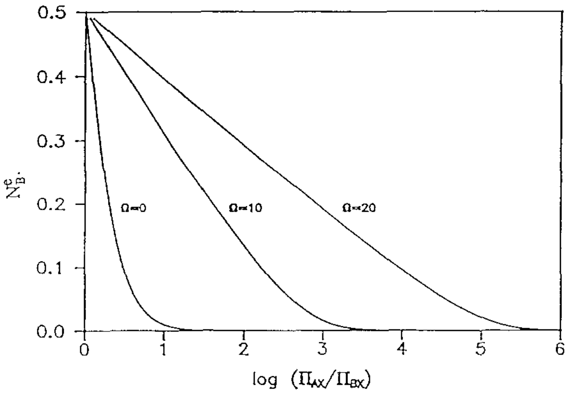

Fig. 2. The effect of the ratio Π_{AX}/Π_{BX} on the value of N^e_B for various values of the bonding parameter Ω in the alloy.

decreases the affinity of B for the oxidant. This is an interesting result, because it shows that not only should the ratio Π_{AX}/Π_{BX} be large to more easily facilitate the exclusive formation of BX, but also the strength of the bond between A and B in the alloy should be relatively weak. It is recalled that in Wagner's analysis of exclusive scale formation he assumed N_B^e to be negligible. Indeed, since he was considering the alloy to be reacting with oxygen to form either Al_2O_3, Cr_2O_3, or SiO_2, this assumption had no consequence. For example, N_{Cr}^e is approximately equal to 10^{-9} at 1000°C, when NiO and Cr_2O_3 are the competing scale phases in the Ni-Cr-O_2 system. It is interesting to note that if the mixed phase $NiCr_2O_4$ is considered to be competing with the Cr_2O_3, rather than NiO, the magnitude of N_{Cr}^e increases only marginally to a value of approximately 10^{-7}.[8] The only instance when N_B^e will be an important parameter in the determination of the amount of solute required for the exclusive formation of its scale is when the two competing scale phases have very similar stabilities. If the ratio of the dissociation pressures of the two competing scales differs by more than three orders of magnitude N_B^e will very likely be negligible. This can be shown with the Cu-Ni-O_2 system, where at high temperature $\Pi_{Cu_2O} \approx 1000\Pi_{NiO}$.[9] Using the activity data determined by Rapp and Maak[10] for a range of Cu-Ni alloys at 700 and 1000°C, and solving for N_{Ni}^e by iteration, it is found that N_{Ni}^e is 0.0017 at 700°C and 0.018 at 1000°C. These values are quite low, and it is reasonable to infer from this that competing scale phases exhibiting greater differences in stability than that between NiO and Cu_2O would give negligible values of N_B^e. Significant values of N_B^e (i.e., 0.01-0.1) are expected for a number of alloy-S_2 systems. This is because it is generally accepted that the stability of most sulfides are very similar.[5,11] However, due to the large number of stable sulfides for a given alloy-S_2 system, and the lack of accurate thermodynamic data of these sulfides, values of N_B^e cannot be calculated with very much confidence.

The preceding treatment was restricted to the framework of equilibrium thermodynamics. However, due to kinetic factors, equilibrium is realistically rarely obtained during an oxidation reaction. For example, referring to Fig. 1, if kinetics processes are disregarded, an alloy with composition N_1 will form BX exclusively on its surface. However, if kinetics processes are taken into account, and it is assumed that interdiffusion within the alloy is slow to the extent that the supply of B to the alloy/scale interface is less than the consumption of B due to scale growth, B will deplete locally at the BX/alloy boundary. This behavior is indicated by the arrow in Fig. 1, where it can be seen that the boundary concentration of B will eventually decrease to a value N_B^e, at which point the simultaneous formation of AX and BX will occur. Thus, after an initial transient period, and in the context of ideal behavior, the final composition at the alloy/scale interface will be N_B^e. This will be maintained by self-adjustments of the volume fractions of AX and BX within the scale to keep the supply rates of both A and B equal to their consumption rates.

Solution to the Diffusion Equation

To consider kinetic factors during scale growth, we must set up the diffusion equation and the proper boundary conditions which would apply within the alloy for the situation of exclusive BX formation:

$$\frac{\partial N_B}{\partial t} = D\frac{\partial^2 N_B}{\partial x^2} \tag{8}$$

$$D\frac{\partial C_B}{\partial x}\bigg|_{x=\mathscr{X}} + C_B(x=\mathscr{X})\frac{d\mathscr{X}}{dt} = \frac{1}{V_{AB}}\frac{d\mathscr{X}}{dt} \tag{9}$$

$$N_B(x=\infty) = N_B(t=0) = N_B^0 \tag{10}$$

where D is the interdiffusion coefficient of the alloy which is assumed to be independent of composition, N_B^0 is the alloy composition of B in the bulk, $C_B = N_B/V_{AB}$, V_{AB} is the equivalent molar volume of the alloy, and $\mathscr{X}$ is the position of the alloy/scale interface with reference to the original alloy interface (i.e., $x=0$). Thus, $\mathscr{X}$ is the depth of the metal consumption zone (MCZ), which is related to the parabolic rate constant for the growth of BX by

$$\mathscr{X} = \frac{V_{AB}}{V_{BX}}\sqrt{2k_p t} \tag{11}$$

where V_{BX} is the equivalent molar volumes of the scale BX, and k_p is the parabolic rate constant of BX in units of cm^2/sec. The physical situation represented by the above equations is shown schematically in Fig. 3.

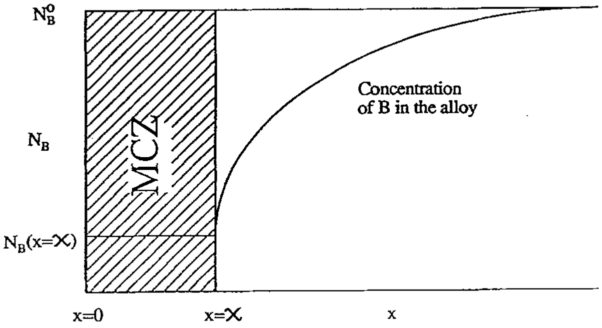

Fig. 3. Schematic set-up for the solution to the diffusion equation to solve for the concentration of B at the moving interface $x=\mathscr{X}$. The shaded region represents the metal-consumption zone (MCZ).

The general solution to a similar moving-boundary problem has been given already by Neumann,[12] who solved for the flux of heat from the moving surface of separation between a solid and a liquid during a solidification process. The solution was for a semi-infinite region $x > 0$ initially at the melting point of the system, and with a surface $x = 0$ maintained at the freezing point. Neumann obtained the solution

$$N_B(x > 0) = C_1 + C_2 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{12}$$

where C_1 and C_2 are constants which can be determined by the boundary conditions. If we let $x \to \infty$ or $t \to 0$, from boundary condition (10), it can be readily determined that $C_1 = N_B^0$. Substituting Eqs. (11) and (12) into (9), one can solve to find

$$C_2 = -[1 - N_B(x = \mathscr{X})]\left(\frac{\pi k_p}{2D}\right)^{1/2} \frac{V_{AB}}{V_{BX}} \exp\left(\frac{V_{AB}^2}{V_{BX}^2} \frac{k_p}{2D}\right) \tag{13}$$

and

$$N_B(x \geq \mathscr{X}) = N_B^0 - \left(\frac{\pi k_p}{2D}\right)^{1/2} \frac{V_{AB}}{V_{BX}} \exp\left(\frac{V_{AB}^2}{V_{BX}^2} \frac{k_p}{2D}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{14}$$

Thus, at $x = \mathscr{X}$ and using Eq. (11)

$$N_B(x = \mathscr{X}) = N_B^0 - [1 - N_B(x = \mathscr{X})]F(u) \tag{15}$$

where

$$F(u) = \sqrt{\pi}\, u \exp(u^2) \operatorname{erfc}(u) \tag{16}$$

with

$$u = \frac{V_{AB}}{V_{BX}} \sqrt{\frac{k_p}{2D}} \tag{17}$$

The $F(u)$ function is in fact the auxiliary function that was used by Wagner[1] initially in his analysis of the diffusion of Ni in Ni–Pt alloys during their oxidation. For that case the auxiliary function was part of the solution to the expression that solved for the concentration of Ni at the displacing alloy/scale interface. The value of u given in Eq. (17) is the same as that used by Wagner, except Wagner assumed $V_{AB} = V_{BX}$. Limiting cases for the solution to the auxiliary function give[3]

$$F(u) = \sqrt{\pi}\, u - 2u^2 + \sqrt{\pi}\, u^3 - 2u^4 + \cdots \qquad \text{if } u \ll 1$$

$$F(u) = 1 - \tfrac{1}{2} u^{-2} + \tfrac{3}{4} u^{-4} - \tfrac{15}{8} u^{-6} + \cdots \qquad \text{if } u \gg 1$$

For the exclusive formation of BX on alloy AB, one must have $N_B(x=\mathscr{X}) > N_B^e$. Therefore, based on the above equations, the minimum concentration of B in the alloy required for the exclusive formation of BX must be that

$$N^0_{B(\min)} > N_B^e + [1 - N_B^e]F(u) \tag{18}$$

The right-hand side of the criterion given in Eq. (18) is the summation of the thermodynamic and the kinetic requirements for the exclusive formation of BX. This criterion can be described qualitatively by saying that the bulk concentration of B necessary to form BX exclusively must be greater than that determined on a strictly thermodynamic basis (N_B^e) by an amount given by the kinetics requirement ($F(u)$). When D is much larger than k_p, u is very small and Eq. (18) can be simplified to

$$N^0_{B(\min)} > N_B^e + [1 - N_B^e]\frac{\sqrt{\pi}\,V_{AB}}{V_{BX}}\sqrt{\frac{k_p}{2D}} \tag{19}$$

Further, when the stability of BX is much greater than that of AX, N_B^e will be very small, so that Eq. (19) can be simplified to

$$N^0_{B(\min)} > \frac{\sqrt{\pi}\,V_{AB}}{V_{BX}}\sqrt{\frac{k_p}{2D}} \tag{20}$$

This criterion is exactly the same as that derived by Wagner.[3] It is interesting to note that Wagner did not use the auxiliary function in his derivation of the criterion shown in Eq. (20). The reason for this is that his simplifying assumptions allowed him to use a much simpler expression for $N_B(x > 0)$—i.e., the Fourier solution to Fick's second law. It should be noted also that Wagner qualified the criterion that he had derived by stating that it was a necessary but not a sufficient[3] criterion because it does not account for the stage of transient scale growth. This stage is characterized by the nucleation of the oxides of both alloying constituents. According to Wagner, the two oxides that nucleate may continue to grow to form a composite scale even when the amount of B in the alloy is greater than that determined by his criterion [Eq. (20)]. In Wagner's analysis of the formation of composite scales[2] he did consider the limiting case of when the volume fraction of the more noble oxide, and hence its thickness, went to zero. The criterion from this limiting case is usually not referenced; perhaps because Wagner did not expand upon it. By this it is meant that it was never explicitly stated as being a criterion. Interestingly, a comparison between Wagner's "limiting-case" criterion and the criterion derived from the present analysis reveals that the two are essentially the same.

The difference between the criterion from present analysis and that of Wagner's can be seen in the comparative plot shown in Fig. 4 of $N^0_{B(\min)}$ vs. $k_p/2D$. Two cases from the present analysis have been considered: one

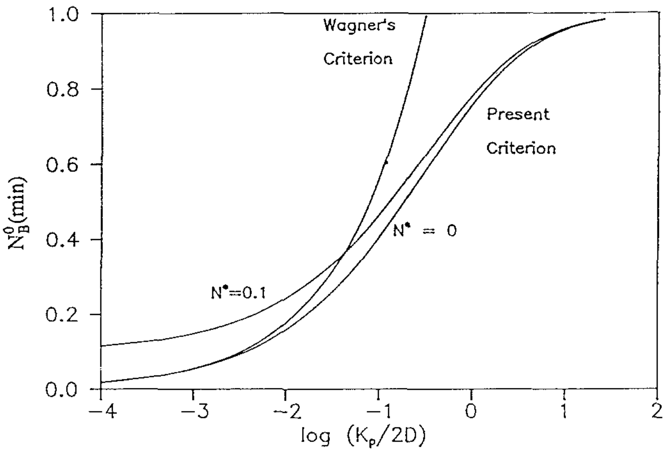

Fig. 4. Comparison between $N^e_{B(\min)}$ obtained from Wagner's analysis and the present analysis as a function of $k_p/2D$ ratios.

when N^e_B is negligible and another when it is not. The equivalent volume of the scale phase and the alloy have been assumed to be equal to each other. Also, because a value of $N^0_{B(\min)}$ greater than unity has no physical meaning, the maximum value of $N^0_{B(\min)}$ has been set at unity. It can be seen in Fig. 4 that for low values of the $k_p/2D$ ratio there is little difference between $N^0_{B(\min)}$ obtained from the two analyses. In fact, the difference is the value of N^e_B which, for low $k_p/2D$ ratios, is essentially equal to $N^0_{B(\min)}$. With larger $k_p/2D$ ratios, the present analysis gives smaller values of $N^0_{B(\min)}$ compared to those obtained from Wagner's analysis. It can be seen that the latter analysis approaches $N^0_{B(\min)} = 1$ quite rapidly, but is unable to give the logical result that, despite the kinetics conditions, *BO* should form exclusively on pure $B(N^0_B = 1)$. Table I presents the results of a number of calculations of $N^0_{B(\min)}$ using the criteria derived from the two analyses for various alloy-gas systems at 1000°C. These calculated values are compared to what is found experimentally. The particular alloy-gas systems chosen were done so that a range of $k_p/2D$ ratios would be represented. It is acknowledged that due to the large variation in k_p values reported in the literature, particularly for Cr_2O_3 growth, and the likely dependence of D on alloy composition these $k_p/2D$ ratios have a significant uncertainty. This is an unfortunate limitation of any type of theoretical analysis that requires the input of empirically determined parameters. For the calculation using the present criterion the value of N^e_B was assumed to be negligible for all of the systems except for Ni-Cu-O_2: where N^e_{Ni} is equal to 0.018. The results of the calculations clearly demonstrate that the criterion from the

Table I. Actual and Calculated Values of $N^0_{B(\min)}$ for Various Alloy-Gas Systems at 1000°C

System A-B-X_2	BX	$k_p(BX)$ $\mathrm{cm^2\,s^{-1}}$	D $\mathrm{cm^2\,s^{-1}}$	$\frac{k_p}{2D}$	$N^0_{B(\min)}$ Wagner's analysis [Eq. (20), $V_{AB} = V_{BX}$]	$N^0_{B(\min)}$ Present analysis [Eq. (18)]	$N^0_{B(\min)}$ Experimental
Fe-Cr-O_2	Cr_2O_3	5.0×10^{-12a}	6.0×10^{-10b}	4.2×10^{-3}	0.11	0.13	0.18-0.24[c]
Co-Cr-O_2	Cr_2O_3	5.0×10^{-12}	5.8×10^{-12d}	0.43	1.0	0.50	0.27-0.33[c]
Ni-Cu-O_2	NiO	6.0×10^{-11e}	2.7×10^{-11f}	1.1	1.0	0.80	≈0.8[g] (at 800°C)
Co-Cr-S_2	Cr_2S_3	1.3×10^{-7h}	5.8×10^{-12}	1.1×10^{3}	1.0	1.0	≈1.0[i]

[a] From Ref. 13. [b] From Ref. 14. [c] From Ref. 15. [d] From Ref. 16. [e] From Ref. 17. [f] From Ref. 18. [g] From Ref. 19. [h] From Ref. 20. [i] From Ref. 21.

present analysis more closely approximates the actual value of $N^0_{B(\min)}$ when the $k_p/2D$ ratio is not very large or very small.

Equation (18) can be regarded as a global expression from which the amount of solute required for the exclusive formation of its own scale can be calculated. By starting with Eq. (18), one can then make the appropriate and simplifying assumptions for the alloy system being considered to obtain a valid expression for the amount of solute required for the exclusive formation of its scale. For example, as indicated in Table I, for the oxidation of Co-Cr alloys in O_2, the stability of Cr_2O_3 is much greater than that of CoO, so that N^e_{Cr} is negligible, but because $k_p(Cr_2O_3)$ is almost equal to D, u is close to unity, and as a result, Wagner's expression is not valid. Instead, the proper expression, based on Eq. (18), is

$$N^0_{Cr(\min)} > F(u) \tag{21}$$

This equation is the same as that derived by Bastow *et al.*[22] These authors extended Wagner's analysis to include recession of the alloy/scale interface and, similar to Wagner, assumed N^e_B to be negligible.

DISCUSSION

We will now further develop the general solutions given in Eq. (15)–(17), along with (18), as it applies to different scaling behaviors. In addition, these equations will be applied to the case of the transition from internal to external scale formation.

Competing Scale Formation

If the electric conductivity is predominantly electronic, the parabolic rate constant for the scale can be expressed as a function of the oxidant pressure at the alloy/scale interface and the scale/gas interface in the manner[23]

$$\begin{aligned} k_p &= k_p^0(P_0^{1/n} - P_i^{1/n}) \qquad &[p\text{-type scale}] \\ k_p &= k_p^0(P_i^{-1/n} - P_0^{-1/n}) \qquad &[n\text{-type scale}] \end{aligned} \tag{22}$$

where P_i and P_0 are the oxidant partial pressures at the alloy/scale and scale/gas interface respectively, n is an integer that is dependent on the point defect structure in the scale, and k_p^0 is a pressure-independent factor. For completeness, Eq. (22) will not be further simplified by assuming that $P_0 \gg P_i$. Based on equilibrium thermodynamics, the pressure at the alloy/scale interface is expressed as a function of the concentration of B at this boundary [i.e., $N_B(x = \mathscr{X})$] by the relationship

$$P_i = \frac{\Pi_{BX}}{(\gamma_B N_B(x = \mathscr{X}))^2} \tag{23}$$

Since k_p is dependent on the oxidant partial pressure at the two scale interfaces, the expression for u can be modified to give

$$u=\frac{V_{AB}}{V_{BX}}\sqrt{\frac{k_p^0 P_i^{1/n}}{2D}\left(\left(\frac{P_0}{P_i}\right)^{1/n}-1\right)} \qquad [p\text{-type scale}]$$
$$u=\frac{V_{AB}}{V_{BX}}\sqrt{\frac{k_p^0 P_0^{-1/n}}{2D}\left(\left(\frac{P_0}{P_i}\right)^{1/n}-1\right)} \qquad [n\text{-type scale}] \tag{24}$$

Consequently, Eq. (18) can be modified to give

$$N^0_{B(\mathrm{min})} > N^e_B + F(\omega\sqrt{P_i^{1/n}}) \qquad [p\text{-type scale}]$$
$$N^0_{B(\mathrm{min})} > N^e_B + F(\omega\sqrt{P_0^{-1/n}}) \qquad [n\text{-type scale}] \tag{25}$$

where

$$\omega=\frac{V_{AB}}{V_{BX}}\sqrt{\frac{k_p^0}{2D}\left(\left(\frac{P_0}{P_i}\right)^{1/n}-1\right)} \tag{26}$$

and P_i is defined by Eq. (23).

Figures 5 and 6 show the graphic results obtained from Eq. (25) for various k_p/D ratios for a p-type and an n-type scale, respectively, assuming $P_i = 10^{-10}$ atm. Any given curve in these two figures represents a boundary above which a homogeneous scale of BX, and below which a heterogeneous mixture of AX and BX (where BX can be internal and/or external) forms on the alloy. Thus, as shown earlier, an increase in the k_p/D ratio for a particular alloy system and scaling environment means that a larger amount of B is required in the alloy for the exclusive formation of BX. Also, the

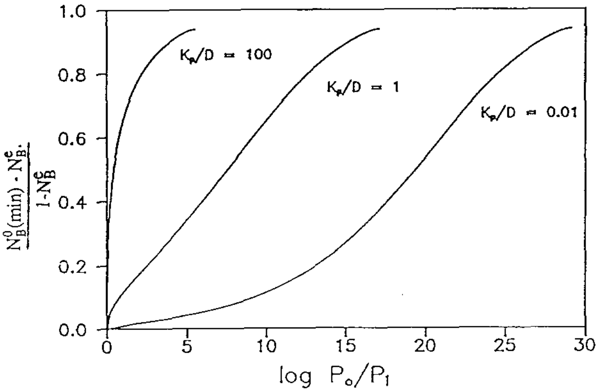

Fig. 5. A plot of N^0_B–N^e_B vs. log (P_0/P_i) for various k_p/D ratios for a p-type scale (P_i was assumed to be 10^{-10} atm).

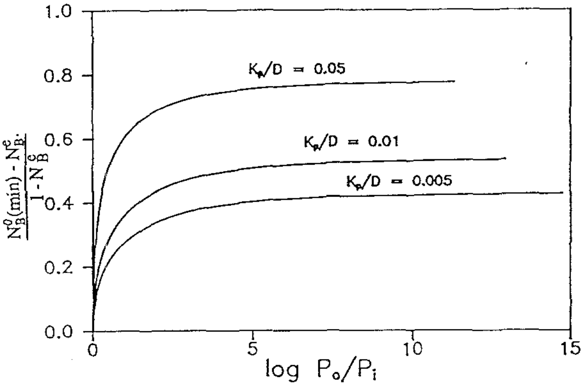

Fig. 6. A plot of $N_B^0 - N_B^e$ vs. $\log(P_0/P_i)$ for various k_p/D ratios for an n-type scale (P_i was assumed to be 10^{-10} atm).

pressure dependence of $N^0_{B(\min)}$ for the two types of scales is quite different. For the formation of a p-type scale, the value of $N^0_{B(\min)}$ is strongly dependent on the external pressure. By contrast, if the external scale to form is n-type, the value of $N^0_{B(\min)}$ is essentially independent of the external pressure.

Transition from Internal to External Scale Formation

We will now extend our analysis to the case of the transition from internal to external scale formation. Our treatment will be somewhat qualitative in the sense that no detailed expressions will be derived.

Formation of an internal reaction product in the form of discrete particles may still be governed by the diffusion equation and boundary conditions given in Eqs. (8)-(10). The only difference from the analysis given above is that instead of referring to $\mathscr{X}$ as the depth of the metal-consumption zone, it will be referred to as the depth of internal-scale formation. We will call this depth $\mathscr{X}_i$ (it should be noted that similar to $\mathscr{X}$, $\mathscr{X}_i$ is measured from the original metal surface—(i.e., $x = 0$). When no external scale forms, $\mathscr{X}_i$ is related to the reaction time and the oxidant diffusion rate in the metal A by the fundamental Wagner equation[4]

$$\mathscr{X}_i = 2\gamma\sqrt{D_0 t} \tag{27}$$

where γ is a constant commonly known as the dimensionless parameter for internal oxidation of alloys. Its value may be determined by means of graphical or numerical methods.[24]

The amount of metal consumed ($\mathscr{X}$) due to internal oxidation can be considered an "equivalent depth." As such, it can be related to the amount of internal reaction product formation, $\mathscr{X}_i$, by the expression

$$\mathscr{X}=\frac{V_{AB}}{V_{BX}}f\mathscr{X}_i=\frac{V_{AB}}{V_{BX}}2f\gamma\sqrt{D_0 t} \tag{28}$$

where f is the volume fraction of BX phase in the internal-reaction-product zone (IRZ). A comparison of Eqs. (28) and (11) reveals that they are equivalent if, for the case of internal-reaction-product formation, we let

$$k_p=k_{p,i}=2D_0(f\gamma)^2 \tag{29}$$

The significance of this relationship is that Eqs. (15)-(17) are also valid solutions for the case of internal scale formation. For example, Eq. (17) would be modified for the case of the transition from internal to external scale formation to give

$$u=f\frac{V_{AB}}{V_{BX}}\gamma\sqrt{\frac{D_0}{D}} \tag{30}$$

Equations (15)-(17) are valid solutions for both internal and external scale formation because phenomenologically these two processes are equivalent in that they both affect the solute concentration profile inside the alloy and the solute concentration at the alloy/scale (or IRZ) boundary in a similar manner.

The transition from internal to external scale formation can be understood in one of two ways. The first and most common way is to assume that there is a critical volume fraction of scale particles within the IRZ. This critical fraction will be denoted f^*. When $f>f^*$, the transport of oxidant through the IRZ will be severely blocked and therefore further internal scale formation will cease. It follows that once a critical volume fraction is determined it will also define a critical k_p^* [Eq. (29)], a critical u^* [Eq. (17)], and a critical $F(u^*)$ [Eq. (16)]. Therefore, from Eq. (15), the critical bulk concentration for the transition from internal to external scale formation is

$$N_B^{0*}=N_B(x=\mathscr{X}_i)+F(u^*) \tag{31}$$

The other way to understand the transition is to assume that there is a critical concentration of B at the IRZ/alloy boundary. This critical concentration will be denoted $N_B^*(x=\mathscr{X}_i)$. When the concentration of B at the boundary is greater than $N_B^*(x=\mathscr{X}_i)$, a considerable flux of B will be set up within the IRZ which will, on the one hand, facilitate the growth of the particles in the IRZ, and on the other hand, provide a certain amount of B to successfully diffuse through the IRZ and arrive at the alloy surface to form an external scale of BX. In this case

$$N_B^{0*} = N_B^*(x = \mathscr{X}_i) + F(u) \tag{32}$$

Although the two approaches used to obtain N_B^{0*} are different, the value obtained will be the same. This is because f^* will in fact occur when the concentration of B at the boundary is $N_B^*(x = \mathscr{X}_i)$.

It is generally found that γ is dependent on the oxidant pressure by Sievert's law[24]

$$\gamma \propto N_X^m \propto P_{X_2}^{m/2} \tag{33}$$

where N_X is the solubility of the oxidant in the alloy and m is a parameter that varies between $\frac{1}{2}$ and 1. The significance of the above relationship is that it shows that the critical concentration for the transition from internal to external scale formation is oxidant pressure-dependent. This result has been shown previously by Rapp[25,26] and it will not be expanded upon here. What is important to understand from the above analysis is that both exclusive scale formation and the transition from internal to external scale formation have been treated by using a general expression given by Eq. (18). Such a broad and unifying treatment is quite novel.

CONCLUSIONS

Alloy oxidation can be understood by analyzing the alloy-oxidant stability diagram. However, the information which can be acquired from such a diagram is limited to strictly thermodynamic considerations. That is, the variation of alloy composition in the region of the alloy/scale interface due to kinetic factors is not taken into account. As it has been shown in this analysis, there are instances when this is not a trivial oversight. For example, in the case of an alloy reacting with S_2, the actual sulfidation status of the alloy is governed by kinetic rather than themodynamic factors. To account for kinetic factors, the general solution to a moving-boundary diffusion equation was employed. By setting the solute flux within the alloy equal to its consumption rate due to the growth of its scale, an expression for the concentration profile of the solute within the alloy was obtained. The beneficial aspect of the expression obtained is that it can be applied universally because it has incorporated both kinetic and thermodynamic factors. Further, the present analysis has unified the treatments of exclusive-scale formation and the transition from internal to external-scale formation. The alloying elements which will have the greatest potential to form their own scale exclusively, and at low solute concentration, are those elements that have a much higher affinity for the oxidant compared to the other alloying component, and a low parabolic rate constant for the growth of its scale. Unfortunately, these requirements cannot always be fulfilled.

REFERENCES

1. C. Wagner, *J. Electrochem. Soc.* **103**, 571 (1956).
2. C. Wagner, *J. Electrochem. Soc.* **103**, 627 (1956).
3. C. Wagner, *J. Electrochem. Soc.* **99**, 369 (1952).
4. C. Wagner, *Z. Elektrochem.* **63**, 772 (1959).
5. S. Mrowec and K. Przybylski, *High Temp. Mat. Processes* **6**, 1 (1984).
6. D. P. Whittle, in *High-Temperature Corrosion, NACE-6*, R. A. Rapp, ed. (National Association of Corrosion Engineers, Houston, Texas 1983), p. 171.
7. D. L. Douglass, in *Selected Topics in High Temperature Chemistry—Defect Chemistry of Solids*, Øivind Johannesen and Arnfinn G. Anderson, eds. (Elsevier, Amsterdam, 1989), p. 185.
8. B. Birks and H. Rickert, *J. Inst. Met.* **91**, 308 (1963).
9. D. R. Gaskell, *Introduction to Metallurgical Thermodynamics*, 2nd ed. (Hemisphere Publ. Corp., New York, 1981), p. 371.
10. R. A. Rapp and F. Maak, *Acta Metall.* **10**, 63 (1962).
11. S. R. Shatynski, *Oxid. Met.* **11**, 307 (1977).
12. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed. (Clarendon Press, Oxford, 1959), p. 285.
13. H. Hindam and D. P. Whittle, *Oxid. Met.* **18**, 245 (1982).
14. D. P. Whittle and G. C. Wood, *J. Electrochem. Soc.* **115**, 133 (1968).
15. G. Wallwork, *Rep. Prog. Phys.* **39**, 401 (1976).
16. A. Green, D. P. Whittle, J. Stringer, and N. Swindells, *Scripta Metall.* **7**, 1079 (1973).
17. A. Atkinson, R. I. Taylor, and A. E. Hughes, *Phil. Mag. A* **45**, 823 (1982).
18. M. Marchukova and P. Mirochkina, *Fiz. Metal. Metalloved.* **32**, 1257 (1971).
19. D. P. Whittle and G. C. Wood, *Corros. Sci.* **8**, 295 (1969).
20. K. Nishida, K. Nakayama, and T. Narita, *Corros. Sci.* **13**, 759 (1973).
21. T. Biegun, A. Bruckman, and S. Mrowec, *Oxid. Met.* **12**, 157 (1978).
22. B. D. Bastow, D. P. Whittle, and G. C. Wood, *Oxid. Met.* **12**, 413 (1978).
23. P. Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides* (Wiley & Sons, New York, 1972).
24. S. Mrowec and T. Werber, *Gas Corrosion of Metals* (National Bureau of Standards and National Science Foundation, Washington, D.C. 1978).
25. R. A. Rapp, *Acta Metall.* **9**, 730 (1961).
26. R. A. Rapp, *Corrosion* **21**, 382 (1965).