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May 1983

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THE PARABOLIC GROWTH OF OXIDE SOLID SOLUTIONS
ON BINARY ALLOYS*P. Y. Hou and D. P. Whittle⁺

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Abstract

The growth of oxide solid solutions on binary alloys has been described using the ternary diffusion model put forward by Wagner and subsequently modified by Dalvi and Coates and Bastow, Whittle and Wood. A more refined defect model where the presence of all types of vacancy species within the scales is considered has been adapted to obtain the diffusivities of cations in the scales as a function of oxygen potential and cation composition. In addition, correlation effects on cation jump frequencies have been included to account for additional compositional dependence of the diffusivities. Results have been analyzed for oxidation of Ni-Co to (Ni,Co)O at 1273°K in 1 atm. oxygen. Improved agreement between calculated and experimental cation concentration profiles indicates that this approach is better than arbitrarily assign functional forms to the compositional and oxygen activity dependencies of the diffusivities, and demon-

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⁺Deceased

strates that an accurate as possible a model for the point defect structure of the oxide is required for correct interpretation of the growth of these solid solution types of scales.

Key words: parabolic oxidation, diffusion, defects, Ni-Co alloys.

Introduction

There have been a number of recent analyses of the oxidation of binary alloys which form solid solution scales and whose growth rate is determined by the transport of both cations through the scale, using the ternary diffusion model put forward by Wagner¹, and subsequently modified by Dalvi and Coates² and Bastow, Whittle and Wood³. The growth rate of the solid solution scale depends primarily on the distribution of the two cations through the scale and on the oxygen activity profile. These are calculated from Wagner's transport equations, which in turn allows calculation of the parabolic growth rate of the scale. However, this requires a knowledge of the variation of the self-diffusion coefficients of the two cations through the scale, and in applying Wagner's analysis to practical situations, previous investigators⁴⁻¹¹ have based the compositional and oxygen activity dependence of the cation diffusion coefficients on a somewhat oversimplified model of the defect structure of the oxide solid solution. In addition, some earlier authors⁴⁻⁹ found it necessary to use data from the oxidation experiments themselves in order to establish the boundary conditions for the calculation of the theoretical cation profiles, and as a consequence, the agreement between theoretical and experimental profiles arises partly because the boundary conditions are the same.

More recently, completely independently determined diffusion data and boundary conditions have been used in similar calculations¹⁰⁻¹³ to substantiate

the model. However, in the one case^{10,11} these were still based on a relatively simple defect model for the oxide solid solution, while in the other^{12,13} empirically based relationships were used.

There is now mounting evidence especially when a wide range of oxygen potentials is considered (as in scale growth) that a simple oxide defect model, in which essentially only one type of defect predominates, is not only unjustified, but is likely to produce non-trivial errors in any calculations of transport properties. The purpose of this paper, then, is to provide a more complete description of Wagner's original theory by including a more refined treatment of the real defect structure of the oxide solution growing on a binary alloy. However, it must be appreciated that the present status of knowledge of oxide defect structures, even in pure oxides, is rather limited. Nevertheless, it is hoped that it will become apparent that better defect models are required if alloy oxidation theory is to be understood quantitatively.

Transport equations for scale growth

In essence this follows Wagner's¹ original treatment, and will only be summarized briefly. The reader is referred to the original paper for further details. The growth of a solid solution oxide, (AB)O, on a binary alloy, AB, is considered. The usual assumptions of constant molar volumes, semi-conducting oxides, local thermodynamic equilibrium and negligible cross terms in the transport coefficient matrix are made. The fluxes of A and B in the scale are due to both a concentration gradient and a gradient of electrical potential. However, the details of the driving force need not be considered. The sum of the two cationic fluxes, normalized to a fractional position, $y(=x/x_s$ where x_s is the instantaneous thickness of the surface scale), since diffusion-control prevails, can be equated to the parabolic rate constant.

$$D_A(1-\xi) \left[-\frac{\partial \ln a_{AO}}{\partial \xi} \frac{d\xi}{dy} + \frac{z_A}{z_O} \frac{d \ln a_O}{dy} \right] + D_B \xi \left[-\frac{\partial \ln a_{BO}}{\partial \xi} \frac{d\xi}{dy} + \frac{z_B}{z_O} \frac{d \ln a_O}{dy} \right] = k \quad (1)$$

where D_A , D_B are the self diffusivities of metal cations A and B in the scale, ξ the local equivalent fraction of compound BO in the oxide, a_{AO} , a_{BO} , a_O the activities of AO, BO and oxygen respectively, and z_A , z_B , z_O the valencies of A, B and oxygen respectively.

The systems which have been considered to date have been confined to oxide solutions having the simple cubic, NaCl structure in which $z_A = z_B = z_O$ and in which the psuedo-binary oxide solution approximates to ideal thermodynamic behavior, when $\partial(\ln a_{AO})/\partial \xi$ and $\partial(\ln a_{BO})/\partial \xi$ can be replaced by $-1/(1-\xi)$ and $1/\xi$ respectively. Thus, equation (1) becomes

$$k = (D_A - D_B) \frac{d\xi}{dy} + [D_A(1-\xi) + D_B \xi] \frac{d \ln a_O}{dy} \quad (2)$$

Using the nomenclature and the simplifications referred to above, Wagner's second equation, which is essentially a mass balance equation for one of the components (B), and which is used in conjunction with eqn.(2) to obtain the complete solution, reads

$$yk \frac{d\xi}{dy} = \frac{-d}{dy} \left[D_B \left(\frac{d\xi}{dy} - \xi \frac{d \ln a_O}{dy} \right) \right] \quad (3)$$

All these equations contain the self-diffusion coefficients of the two cations D_A and D_B which are in general, a function of both the oxygen activity and the oxide composition. The form of the dependence is closely related to the type of defect structure present in the oxide, and it may be shown¹⁴ that the form assumed for this function by authors who have solved these equations previously⁴⁻¹¹ is essentially valid if only a single type of defect predominates in the oxide solution. However, it is becoming increasingly clear (see, for example, Kofstad¹⁵), that one type of metal vacancy may dominate at high partial pres-

tures of oxygen, while another type dominates at low values of P_{O_2} . Since the oxide activity through the scale varies over a wide range, from the dissociation pressure of the oxide at the inner alloy/scale interface to the ambient oxygen pressure ($\sim 10^{-7}$ - 1 for oxidation of Ni-Co alloys at 1000°C in 1 atmosphere oxygen, for example), the simple approximation of only a single type of defect is not adequate.

Diffusion coefficients in oxide solid solutions

Initially, it is appropriate to re-consider the assumption made in previous solutions to these equations, namely that the ratio of self-diffusion coefficients of cations A and B in the oxide solution is a constant independent of a_O and ξ . Young et al.¹² and Narita et al.¹³ in recent calculations of the concentration profiles in growing (CoFe)S scales and (CoFe)O and (CoNi)O scales respectively, removed this restriction. However, they used empirical relationships for the dependence of D_A/D_B on composition. Dieckmann and Schmalzried¹⁶ have pointed out that correlation effects between the elementary jumps occur, which make the ratio D_A/D_B dependent on the composition of the oxide solution.

According to Dieckmann and Schmalzried¹⁶, correlation effects are found if the elementary jump frequencies Γ_A of an A-cation into a neighboring vacancy differs from the corresponding jump frequency for a B-cation, Γ_B . This can be taken into account by defining an effective jump frequency Γ_{eff} , to determine the cation diffusivity, and which differs from Γ_i ($i=A$ or B) by a correlation factor which is concentration dependent. Accordingly, the self-diffusion coefficients in an oxide solution (AB)O are written as

$$D_A = \frac{2\Gamma_A f_A a^2 [V]}{f_o} \quad \text{and} \quad D_B = \frac{2\Gamma_B f_B a^2 [V]}{f_o} \quad (4)$$

where Γ_i and f_i are the elementary jump frequencies and correlation factors

respectively, $f_o (=0.782)$ the correlation factor for vacancy diffusion for a pure oxide of the rock salt B1 structure¹⁷, a the elementary jump distance and $[V]$ the atomic fraction of vacant sites. The concentration dependence of the correlation factors may be found¹⁸ from either

$$f_A = 1 - \frac{0.218}{(1-\xi) + \xi(D_B/D_A)} ; \quad f_B = 1 - \frac{0.218}{(1-\xi)(D_A/D_B) + \xi} \quad (5)$$

or

$$f_A^2 + f_A \frac{0.218 - (1-\xi) - \eta_A}{(1-\xi)} + \frac{0.782\eta_A}{(1-\xi)} = 0 ; \quad \eta_A = \frac{\Gamma_B/\Gamma_A}{(\Gamma_B/\Gamma_A) - 1} \quad (6a)$$

$$f_B^2 + f_B \frac{0.218 - \xi - \eta_B}{\xi} + \frac{0.782\eta_B}{\xi} = 0 ; \quad \eta_B = \frac{\Gamma_A/\Gamma_B}{(\Gamma_A/\Gamma_B) - 1} \quad (6b)$$

According to experimental determinations of the tracer diffusivities of both Co and Ni ions in (CoNi)O between 1100 and 1550°C at $P_{O_2} = 0.21$ atmos. by Chen and Peterson¹⁸ and calculations by Dieckmann and Schmalzried¹⁸, when these correlation factors are taken into account, the ratio of elementary jump frequencies, Γ_{Co}/Γ_{Ni} , varies by only 8% over the entire composition range, as opposed to a variation of about 16% in D_{Co}/D_{Ni} . Hence it seems more appropriate to consider Γ_{Co}/Γ_{Ni} as a constant and use eqns.(6) and (4) to find diffusivities as a function of composition, although this correction should only refine the theoretical calculations slightly since there is still a 8% variation in the elementary jump frequencies ratio.

In addition to the concentration dependence of the cation diffusivities through the correlation factors, $[V]$ also depends strongly on oxide composition and oxygen activity. As discussed in an earlier paper¹⁴, vacancies of different effective charges are now considered to exist in these types of non-stoichiometric oxides, with the relative proportions of each depending on oxide composition and oxygen activity. All the vacancies contribute towards the diffusivity and thus $[V]$ in eqn.(4) really represents $\sum[V^z]$, the sum of the

concentrations of the vacancies carrying effective charges $z=0, 1$, and 2 . As given in a previous paper¹⁴, the atomic fractions of the various effectively charged vacancies can be expressed by

$$[V^z] = (K_{V^z}^{AO})^{(1-\xi)} (K_{V^z}^{BO})^\xi a_O \quad (7a)$$

$$[V] = (K_{V^z}^{AO} K_V^{AO})^{(1-\xi)} (K_{V^z}^{BO} K_V^{BO})^\xi \frac{a_O}{[h \cdot]} \quad (7b)$$

$$[V'] = (K_{V^z}^{AO} K_V^{AO} K_{V'}^{AO})^{(1-\xi)} (K_{V^z}^{BO} K_V^{BO} K_{V'}^{BO})^\xi \frac{a_O}{[h \cdot]^2} \quad (7c)$$

where K_i^j ($i=V^z, V, V'$; $j=AO, BO$) are the equilibrium constants for formation of the three types of vacancies according to

$$\frac{1}{2} O_2 = O_O^x + V^z ; \quad V^z = V + h \cdot ; \quad V = V' + h \cdot \quad (8)$$

in the two pure oxides, where V^z , V and V' represent vacancy lattice sites in the cation sub-lattice. The equilibrium constants are related to the free energies of formation of the defects in the two pure oxides by

$$(\Delta G^\circ)_i^j = -RT \ln K_i^j, \quad i = V^z, V, V'; \quad j = AO, BO \quad (9)$$

The concentration of electron holes, $[h \cdot]$, is assumed to be much larger than that of n-type electronic defects, and is given by the simplified electroneutrality condition:

$$[h \cdot] = (K_{V^z}^{AO} K_V^{AO})^{(1-\xi)} (K_{V^z}^{BO} K_V^{BO})^\xi \frac{a_O}{[h \cdot]} + 2(K_{V^z}^{AO} K_V^{AO} K_{V'}^{AO})^{(1-\xi)} (K_{V^z}^{BO} K_V^{BO} K_{V'}^{BO})^\xi \frac{a_O}{[h \cdot]^2} \quad (10)$$

Through solutions of eqns.(7) and (10), $[V]$ is given as a function of a_O and ξ , and together with solution of eqn.(6), can be substituted into eqn.(4) to give D_A and D_B as a function of ξ and a_O .

Solution of the transport equations

Substituting for $d \ln a_o / dy$ from eqn.(2) into eqn.(3) and using $p = D_A / D_B$ where according to eqn.(4)

$$p = \frac{f_A \Gamma_A}{f_B \Gamma_B} \quad (11)$$

and is a function of composition through the term f_A / f_B , gives, after differentiation

$$\begin{aligned} & \frac{d^2 \xi}{dy^2} p D_B [p - (p-1)\xi] + \frac{d\xi}{dy} y k [p - (p-1)\xi]^2 - p k \\ & + p [p - (p-1)\xi] \frac{dD_B}{dy} + \frac{dp}{dy} [D_B \xi + k \xi (1-\xi)] + \left(\frac{d\xi}{dy} \right)^2 D_B p (p-1) = 0 \end{aligned} \quad (12)$$

Using the relationships that

$$D_B = D_B(\xi, a_o) \quad \text{and} \quad p = p(\xi) \quad (13)$$

then gives

$$\begin{aligned} & \frac{d^2 \xi}{dy^2} [p - (p-1)\xi] + \frac{d\xi}{dy} \frac{k}{D_B} \left\{ \frac{y}{p} [p - (p-1)\xi]^2 - 1 + \frac{\partial \ln D_B}{\partial \ln a_o} \right\} \\ & + \left(\frac{d\xi}{dy} \right)^2 \left\{ [p - (p-1)\xi] \frac{\partial \ln D_B}{\partial \xi} + (p-1) \left(1 - \frac{\partial \ln D_B}{\partial \ln a_o} \right) + \frac{d \ln p}{d \ln \xi} \left[1 + \frac{k}{D_B} (1-\xi) \right] \right\} = 0 \end{aligned} \quad (14)$$

Using the same nomenclature, eqn.(2) becomes

$$\frac{k}{D_B} = (p-1) \frac{d\xi}{dy} + [p(1-\xi) + \xi] \frac{d \ln a_o}{dy} \quad (15)$$

Eqns.(14) and (15) are solved numerically using finite difference method, with f_A , f_B and $[V]$ obtained from eqns.(6), (7) and (10), and hence D_B and $\partial \ln p / \partial \ln \xi$ can be obtained from eqns.(4) and (11) respectively. $\partial \ln D_B / \partial \ln \xi$ and $\partial \ln D_B / \partial \ln a_o$ are obtained assuming linear variation within one step length of the finite difference forms of equations (14) and (15).

Additional relationships are required for the solution, as detailed in Wagner's paper¹. These include a mass balance at the scale/gas interface:

$$y = 1, \quad \frac{k}{D_B} = p \left(\frac{d\xi}{dy} \right) \frac{1}{(p-1)(\xi-1)\xi} \quad (16)$$

where the values of the variable p , $d\xi/dy$, D_B and ξ are those pertaining to $y=1$. At the inner alloy/scale interface, because the interdiffusion coefficient in the alloy is very much smaller than the growth rate of the scale, the composition of the scale at $y=0$ is given by¹⁹

$$y = 0, \quad \xi = \frac{p \xi_{all}}{1 + \xi_{all}(p-1)} \quad (17)$$

where again ξ and p refer to values at $y=0$, and ξ_{all} is the equivalent fraction of element B in the bulk alloy. The oxygen activity at $y=0$ is directly related to the oxide composition there, since thermodynamic equilibrium is assumed. Thus,

$$y = 0, \quad a_o = (1-\xi) \exp \left(\frac{\Delta G_{AO}^o}{RT} \right) + \xi \exp \left(\frac{\Delta G_{BO}^o}{RT} \right) \quad (18)$$

where ΔG_{AO}^o and ΔG_{BO}^o are the standard free energies of formation of AO and BO respectively.

The numerical technique for solution is initiated by trial values of the rate constant k and the composition of the oxide at $y=1$ and the equations integrated inward to $y=0$, the procedure being repeated using continuously better estimates of k and $\xi_{y=1}$ until the calculated and actual values of $\xi_{y=0}$ (from eqn.(17)) and $a_{o,y=0}$ (from eqn.(18)) are within 1 and 5% respectively. The step length, Δy , in the finite difference forms of eqns.(14) and (15) is reduced until the result is independent of the step length; it is also independent of the initial estimates.

Data for the NiO-CoO system

Equilibrium constants for the formation of the different ionic defects in CoO have been measured by a number of authors and summarized by Dieck-

mann²⁰.

$$K_{Vz}^{CoO} = 1.6 \times 10^{-2} \exp[-26000(J/mole)/RT] \quad (19a)$$

$$K_V^{CoO} = 2.4 \exp[-51000(J/mole)/RT] \quad (19b)$$

$$K_V^{CoO} = 0.17 \exp[-72000(J/mole)/RT] \quad (19c)$$

Corresponding values from experimental measurements for NiO are not available. Theoretical estimations of these equilibrium constants calculated by Osburn and Vest²¹ using a conduction band model for the pre-exponential terms and a hydrogen atom model for the ionization energies give

$$K_{Vz}^{NiO} = 5.43 \times 10^{11} T^{-3} \exp[-187544(J/mole)/RT] \quad (20a)$$

$$K_V^{NiO} = 1.61 \times 10^{-7} T^{3/2} \exp[-9260(J/mole)/RT] \quad (20b)$$

$$K_V^{NiO} = 4.03 \times 10^{-8} T^{3/2} \exp[-36998(J/mole)/RT] \quad (20c)$$

Chen and Peterson¹⁸ have measured tracer diffusion coefficients in CoO, NiO and in some oxide solutions, (NiCo)O. However, as indicated earlier, rather than fitting their somewhat limited data to an empirical expression¹³, it is more appropriate to utilize the model outlined in the earlier section. Thus, using their measured values of the tracer diffusion coefficients of Ni and Co ions in pure CoO in air ($P_{O_2} = 0.21$ atmos.), given as

$$D_{Co}^{T,CoO}(a_O = 0.46) = 5.0 \times 10^{-3} \exp[-160800(J/mole)/RT] \quad (21a)$$

$$D_{Ni}^{T,CoO}(a_O = 0.46) = 3.3 \times 10^{-2} \exp[-197600(J/mole)/RT] \quad (21b)$$

the ratio of diffusivities of the two cations in pure CoO can be obtained. Then, with a value for the correlation factor for Co diffusion in pure CoO of 0.782, and the corresponding value for Ni diffusion in the same oxide calculated from eqn.(5), the ratio Γ_{Co}/Γ_{Ni} is calculated. Furthermore, using eqn.(6),

$p = \Gamma_A f_A / \Gamma_B f_B$ can be calculated for other compositions. Finally, using the value of $D_{Co}^{T,CoO} = D_{Co}^{CoO} / f_o$ and eqn.(4) with the total vacancy concentration, $\sum[V]$, obtained from eqns.(7) and (10) enables the constant $2\Gamma_{Co} a^2 / f_o$ to be found. Thus, D_{Co} and similarly D_{Ni} can be calculated as functions of oxide composition, oxygen activity and temperature.

Figure 1 shows a typical variation of D_{Co} and D_{Ni} with oxide composition, ξ , at different oxygen activities. Both diffusivities increase with Co content of the oxide and the oxygen activity, primarily due to the concomitant increase in vacancy concentration. However, unlike in the simple defect model used earlier^{10,11}, $\log D_{Co}$ (or $\log D_{Ni}$) is not exactly a linear function of composition. This is shown more clearly in figure 2 which presents $\partial \ln D_{Co} / \partial \xi$ and $\partial \ln D_{Co} / \partial \ln a_o$ as functions of ξ and a_o ; p , the ratio of diffusivities, and which depends only on composition, is also shown. For comparison, the previously used simplified model gave rise to the following expressions:

$$D_{Ni} = p D_{Co}^0 \beta^{\xi-1} a_o^{1/\nu} \quad \text{and} \quad D_{Co} = D_{Co}^0 \beta^{\xi-1} a_o^{1/\nu} \quad (22)$$

where D_{Co}^0 is the diffusivity of Co in pure Co at 1 atmos. O_2 pressure, β is the ratio of the concentration of cation defects (vacancies) in pure CoO to pure NiO at unit oxygen activity, and ν is the effective (average) charge of the vacancies. These expressions give

$$\frac{D_A}{D_B} = p \quad (0.2) \quad \frac{\partial \ln D_{Co}}{\partial \xi} = \ln \beta \quad (4.83) \quad \frac{\partial \ln D_{Co}}{\partial \ln a_o} = \frac{1}{\nu} \quad (0.4) \quad (23)$$

with the actual values used (at 1000°C) given in parenthesis. In comparison, figure 2 indicates that at 1000°C, p can vary within the range 0.2-0.35, $\partial \ln D_{Co} / \partial \xi$ in the range 3.52-5.17 and $\partial \ln D_{Co} / \partial \ln a_o$, 0.39 to 0.48.

As a final point in this section, it is perhaps appropriate to examine how the diffusivities calculated according to this model compare with the experimental data of Chen and Peterson¹⁸. This is shown in figure 3a where the solid

curves represent values calculated from eqns.(4), (6), (7) and (10) using equilibrium constants according to eqns.(19) and (20), and eqn.(21) in conjunction with eqns.(5) and (4) to obtain Γ_{Ni}/Γ_{Co} and $2\Gamma_{Co}a^2/f_o$. The calculated self-diffusion coefficients are converted to tracer diffusion coefficients using the correlation factor (f_o) of 0.782. The agreement falls off rapidly as the NiO content of the solid solution increases, and this is presumably due to the variation in defect concentration with composition, not being adequately expressed by the constants given in eqn.(20). When these equilibrium constants calculated for $T=1573^\circ K$ are reduced in order to obtain a best fit to the experimental results, much better agreement can be obtained. A comparison between experimentally measured tracer diffusivities and the diffusivities calculated using K_{Vz}^{NiO} , K_V^{NiO} and K_V^{CoO} values reduced by 40% is shown in figure 3b.

Calculated concentration profiles in growing NiO-CoO scales

Figure 4 shows the calculated cation profiles across the scales formed on three Ni-Co alloys and compares them with the corresponding profiles determined by electron microprobe analysis²² and those calculated in a previous paper¹⁰. The agreement between the experimentally measured profiles and those calculated in this work shows an improvement over the earlier calculations. The improvement is seen in a better overall fit with each experimental profile. The dip in the previously obtained theoretical profile for Ni-80%Co and Ni-38%Co near the scale/alloy interface cannot be justified by diffusion theories, but such a dip is no longer present in this calculation.

Although theoretically calculated cation profiles using the above analysis show a better agreement with experimental data, the fit is still not perfect. This could be due to several reasons: i) The use of a still incomplete defect model for the oxide, and the limited experimental data on the defect equilibrium

constants; ii) the lack of any theory accounting for the variation of Γ_{Co} or Γ_M as a function of composition; and finally iii) the scatter in the cation concentrations obtained by microprobe analysis.

An additional result of these calculations is the variation in vacancy concentration through the growing scale. Figure 5 shows the total vacancy concentration through the scales on four Ni-Co alloys. The total vacancy gradient through the scale is, of course, related to the growth rate of the oxide. Thus, the overall vacancy gradient across the scale, and the growth-rate, increases with increasing Co content of the alloy.

Concluding remarks

It was not the intention at the outset of this paper to try and improve the agreement between calculated and experimental cation concentration profiles through growing (NiCo)O scales, although this has indeed been achieved. Indeed, the main purpose was to demonstrate that correct interpretation of the growth of these solid solution types of scales really requires an accurate as possible a model for the point defect structure of the oxide, and that this is better approach than that of arbitrarily assigning functional forms to the compositional and oxygen activity dependencies of the diffusivities. Future work should examine the effects, if any, of the possible formation of more complex defects - vacancy/cation complexes - on the compositional dependence of the cation diffusion coefficients. For example, in the CoO-FeO system the ratio of D_{Fe}/D_{Co} is greater than 1 at low oxygen activities and less than 1 at higher oxygen activities¹³. This dependence on oxygen activity cannot be accounted for by the correlation factors introduced in the present analysis, and presumably some type of vacancy clustering²³ must be considered.

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Figure Captions

Figure 1 Variation of D_{Co} and D_{Ni} with oxide composition, ξ , at different oxygen activities.

Figure 2 Variation of $\partial \ln D_{Co} / \partial \xi$ and $\partial \ln D_{Co} / \partial \ln a_O$ as functions of ξ and a_O , and p as a function of ξ .

Figure 3a A comparison between values of D_{Co}^T , D_{Ni}^T and p calculated from theory and those obtained experimentally by Chen and Peterson¹⁸.

Figure 3b A comparison between experimentally measured D_{Co}^T , D_{Ni}^T and p values and those calculated using reduced equilibrium constants for the formation of vacancies in NiO.

Figure 4 A comparison between experimental cation profiles and theoretical profiles calculated in this analysis and in a previous paper¹⁰ in oxide scales formed at 1000°C on Ni-Co alloys containing 10.9%, 38.4% and 80.0% Co respectively.

Figure 5 Variation in vacancy concentration through the scales of Ni-80%Co, Ni-38%Co, Ni-20%Co and Ni-10%Co oxidized under 1 atm. O_2 at 1000°C.

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Fig. 1

Fig. 2

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Fig. 3a

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Fig. 3b

Fig. 4

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Fig. 5

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