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Oxygen Solubility and a Criterion for the Transition from Internal to External Oxidation of Ternary Alloys

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Smith's model is expanded in order to derive expressions to quantitatively describe the oxygen-solubility behavior in ternary alloys as a function of alloy composition. Multicomponent-diffusion theory is used to establish a criterion for the onset of internal oxidation beneath the external scale when oxidizing conditions favor formation of the oxide of the least-noble metal in a ternary alloy. The oxygen-solubility model and the criterion are applied to the oxidation of Ni–Cr–Al alloys in 76 torr of oxygen at 1100 and 1200°C, predicting the minimum Al concentrations required to form a protective Al_2O_3 *scale. It shows that sufficient Cr additions would significantly reduce the oxygen solubility and also alter the oxygen distribution in the ternary alloys, avoiding the oxygen supersaturation necessary for the onset of internal oxidation. These two factors make it easier to establish the protective* Al_2O_3 *scale.*

KEY WORDS: oxygen solubility; external-scale formation; ternary alloy; Ni–Cr–Al.

INTRODUCTION

The establishment of protective scales on binary alloys is facilitated by the presence of a third element, where the added component is one forming an oxide of intermediate stability compared to the base metal and protective oxides. The minimum bulk concentrations of the least-noble metal in ternary

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alloys, being required to form the protective oxide scales, are much lower than those in the binary alloys. To explain this *third-element effect*, it is usually assumed that the addition of the third element can act as an oxygen getter, blocking oxygen diffusion and reducing its solubility or diffusion flux into the alloys.[1] However, data of oxygen solubility in solid alloys as a function of alloy composition are usually not available because of the difficulty of these experiments. This fact limits the application of a thorough theoretical approach to the oxidation of alloys. To overcome this difficulty, one may use a method given by Smith[2] to estimate the variation of oxygen solubility with alloy composition, using the Gibbs–Duhem equations for the oxide and alloy in equilibrium and the Wagner formalism for the activity coefficients. Unfortunately, Smith's model focused only on solubility in binary alloys.

Criteria to explain a transition from internal oxidation to exclusive growth of a protective scale are significant to design of heat-resistant alloys. A limiting condition has been determined by Wagner[3] from analysis of the diffusion processes for the onset of an internal-oxidation zone beneath the external scale when oxidizing conditions favor the formation of the oxide of the less-noble metal in a binary alloy. It is postulated that internal oxidation occurs if diffusion causes the product of the metal and oxygen concentrations to exceed the solubility product of the oxide in the alloy behind the scale/alloy interface. By this means a minimum concentration of the less-noble metal in the binary alloy, above which internal oxidation will not occur, can be defined in terms of the metal and oxygen solubility product and diffusivities in the alloy, and the parabolic rate constant for the external-scale growth. This criterion based upon the premise that the binary alloy exhibited ideal or Henrian solution behavior was expanded by Smeltzer and Whittle[4] to include nonideal solution behavior.

The purpose of this paper is to expand Smith's model in order to include the oxygen-solubility behavior in a ternary alloy as a function of alloy composition, and to expand Wagner's analysis for the onset of internal oxidation beneath the external scale when oxidizing conditions favor formation of the oxide of the least-noble metal in ternary alloys. Attempts will be made to apply these theoretical analyses to a typical example of ternary alloy oxidation and the *third-element effect*, the oxidation Ni–Cr–Al alloys in 76 torr of oxygen at 1100 and 1200°C.

THEORETICAL ANALYSIS

Oxygen Solubility

For a four-component system of solutes 1, 2, 3, and solvent 4 at constant temperature and pressure, one may apply the Gibbs–Duhem equation for phases I and II in equilibrium ($\mu_i^{I}=\mu_i^{II}$) as

$$N_1^{I}\,d\mu_1+N_2^{I}\,d\mu_2+N_3^{I}\,d\mu_3+N_4^{I}\,d\mu_4=0 \tag{1}$$

$$N_1^{II}\,d\mu_1+N_2^{II}\,d\mu_2+N_3^{II}\,d\mu_3+N_4^{II}\,d\mu_4=0 \tag{2}$$

Recalling that $\sum N_i=1$ and subtracting Eq. (2) from Eq. (1), one obtains

$$\begin{aligned}&(N_1^{II}-N_1^{I})(d\mu_1-d\mu_4)+(N_2^{II}-N_2^{I})(d\mu_2-d\mu_4)\\&\quad+(N_3^{II}-N_3^{I})(d\mu_3-d\mu_4)=0\end{aligned} \tag{3}$$

For a dilute solution, if Wagner formalism is assumed to be applicable, one obtains

$$d\mu_1=RT\left[\frac{dN_1}{N_1}+\varepsilon_1^1\,dN_1+\varepsilon_1^2\,dN_2+\varepsilon_1^3\,dN_3\right] \tag{4}$$

$$d\mu_2=RT\left[\frac{dN_2}{N_2}+\varepsilon_1^2\,dN_1+\varepsilon_2^2\,dN_2+\varepsilon_2^3\,dN_3\right] \tag{5}$$

$$d\mu_3=RT\left[\frac{dN_3}{N_3}+\varepsilon_1^3\,dN_1+\varepsilon_2^3\,dN_2+\varepsilon_3^3\,dN_3\right] \tag{6}$$

$$d\mu_4=RT[-dN_1-dN_2-dN_3] \tag{7}$$

where in the case of the solvent, component 4, it is assumed that if N_1, N_2, and N_3 approach zero, then $N_4\rightarrow 1$, in which case Raoultian ideality is achieved and the activity coefficient of the solvent $\gamma_4=1$. Substituting these four equations into Eq. (3) and simplifying gives

$$\begin{aligned}&\left[\frac{a}{N_1}-bN_1-cN_2-dN_3+e\right]dN_1+\left(\frac{f}{N_2}-cN_1-gN_2-hN_3+j\right)dN_2\\&\quad+\left(\frac{l}{N_3}+dN_1-hN_2-mN_3+p\right)dN_3=0\end{aligned} \tag{8}$$

where $a=N_1^{II}$, $b=(1+\varepsilon_1^1)$, $c=(1+\varepsilon_1^2)$, $d=(1+\varepsilon_1^3)$, $e=(1+\varepsilon_1^1)N_1^{II}+(1+\varepsilon_1^2)N_2^{II}+(1+\varepsilon_1^3)N_3^{II}-1$, $f=N_2^{II}$, $g=(1+\varepsilon_2^2)$, $h=(1+\varepsilon_2^3)$, $j=(1+\varepsilon_2^2)N_2^{II}+(1+\varepsilon_1^2)N_1^{II}+(1+\varepsilon_2^3)N_3^{II}-1$, $l=N_3^{II}$, $m=(1+\varepsilon_3^3)$, $p=(1+\varepsilon_3^3)N_3^{II}+(1+\varepsilon_1^3)N_1^{II}+(1+\varepsilon_2^3)N_2^{II}-1$. In Eq. (8), the mole fractions refers to phase I. The superscript I has been dropped for visual clarity.

If phase II is a small phase field in which the solubility of component 3 and 4 are very small, then N_3^{II} and $N_4^{II}\rightarrow 0$. This describes the condition of a stoichiometric compound of the type M_xO_y, when O and M are components 1 and 2 and $N_1^{II}=y/(x+y)$ and $N_2^{II}=x/(x+y)$. Referring to Eq. (8), one can determine by integration the precise equation defining the effect of adding component 3 on the solubility of 1 in phase I when N_2 is fixed. The integrated result is

$$a \ln N_1 - \frac{bN_1^2}{2} - cN_1N_2 - 2dN_1N_3 + eN_1 - hN_2N_3 - \frac{mN_3^2}{2} + pN_3 = q \tag{9}$$

where q is an integration constant. Now for $N_1 \ll 1$, Eq. (9) may be simplified by neglecting the second and fifth terms so that

$$a \ln N_1 - cN_1N_2 - 2dN_1N_3 - hN_2N_3 - \frac{mN_3^2}{2} + pN_3 = q \tag{10}$$

To find the value of q, let $N_2 = N_3 = 0$ (and thus $N_1 = N_1^\circ$, the solubility of 1 in phase I for the 1–4 binary) in Eq. (10) to yield

$$q = a \ln N_1^\circ \tag{11}$$

Thus the solubility equation is

$$\begin{aligned} N_1^{\mathrm{II}} \ln N_1 - [(1+\varepsilon_1^2)N_2 + 2(1+\varepsilon_1^3)N_3]N_1 &= \frac{(1+\varepsilon_3^3)}{2} N_3^2 \\ &\quad + (1+\varepsilon_2^3)(N_2 - N_2^{\mathrm{II}})N_3 - (1+\varepsilon_3^3)N_1^{\mathrm{II}}N_3 + N_3 + N_1^{\mathrm{II}} \ln N_1^\circ \end{aligned} \tag{12}$$

For another case when N_3 is fixed, the dependence of the solubility of 1 in phase I on the concentration of 2 can be given by Eq. (8) as

$$\left(\frac{dN_1}{dN_2}\right)_{N_3} = \frac{\begin{array}{l} -N_2^{\mathrm{II}} + (1+\varepsilon_2^2)[(N_2)^2 - N_2N_2^{\mathrm{II}}] \\ \qquad + (1+\varepsilon_1^2)N_2(N_1 - N_1^{\mathrm{II}}) + (1+\varepsilon_2^3)N_2N_3 + N_2 \end{array}}{\begin{array}{l} N_1^{\mathrm{II}} - (1+\varepsilon_1^1)[(N_1)^2 - N_1N_1^{\mathrm{II}}] \\ \qquad - (1+\varepsilon_1^2)N_1(N_2 - N_2^{\mathrm{II}}) - (1+\varepsilon_1^3)N_1N_3 - N_1 \end{array}} \, \frac{N_1}{N_2} \tag{13}$$

At the minimum solubility of 1 in phase I, $(dN_1/dN_2)_{N_3} = 0$. Therefore N_2^m, at which the minimum solubility of 1 occurs, would satisfy the equation given by

$$\begin{aligned} &-N_2^{\mathrm{II}} + (1+\varepsilon_2^2)(N_2^m)^2 + (1+\varepsilon_1^2)N_1N_2^m \\ &\quad + (1+\varepsilon_2^3)N_2^mN_3 - (1+\varepsilon_2^2)N_2^mN_2^{\mathrm{II}} - (1+\varepsilon_1^2)N_2^mN_1^{\mathrm{II}} + N_2^m = 0 \end{aligned} \tag{14}$$

Thus N_2^m would be a function of the concentration of component 3.

For a ternary A–B–C alloy plus oxygen system, if 1, 2, 3, and 4 refer respectively to oxygen, the most reactive metal B, the third element C, and the solvent A, one may use the above theory to quantitatively describe the oxygen solubility behavior in the alloy beneath a stoichiometric oxide scale of BO_ν as a function of alloy composition. In particular, one can quantitatively determine whether the addition of the third element C into the A–B alloy does or does not reduce the oxygen solubility in the alloy or plotting Eq. (12).

The Criterion for the Transition from Internal to External Oxidation

A simple diffusion model is shown schematically in Fig. 1. An external scale of oxide $(BCA)O_\nu$ forms on a dilute A–B–C ternary alloy, and the quaternary oxide is assumed to contain a negligible concentration of the solvent metal A and alloying element C so that its composition corresponds closely to that of the binary oxide BO_ν. For convenience, we designate 1 as oxygen, 2 as the least-noble metal B, 3 as the third alloying element C, and 4 as the solvent metal A.

The diffusion of alloying elements A, B, and oxygen in the A–B–C alloy is determined by Fick's second law in matrix form:

$$\frac{\partial(N)}{\partial t}=[D]\frac{\partial^2(N)}{\partial x^2} \tag{15}$$

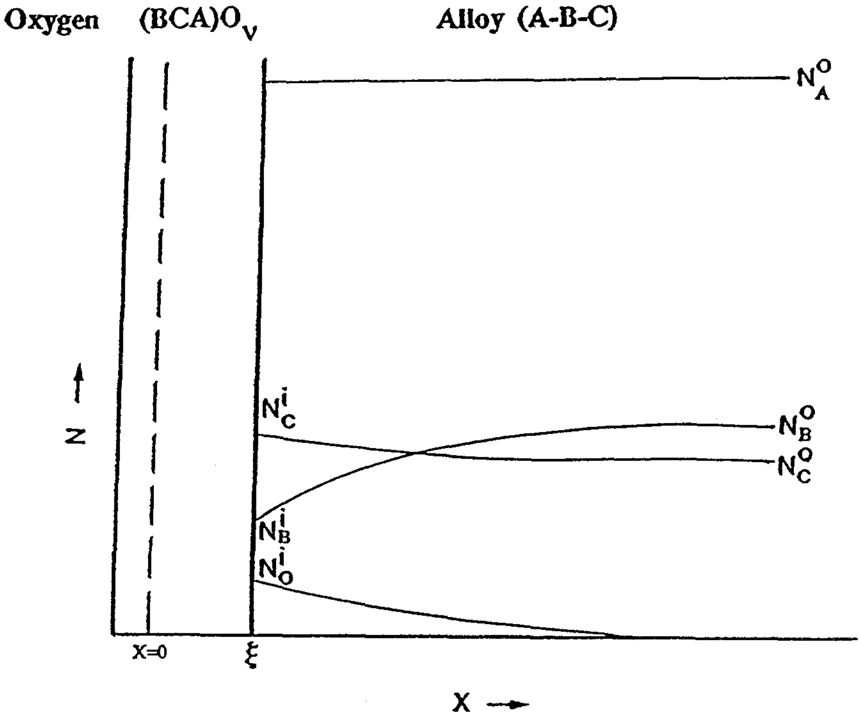

Fig. 1. An oxidation model for a dilute A–B–C alloy.

The general method for solving Eq. (15) is given by Toor[5] for constant diffusion coefficients. Assuming that $[D]$ may be diagonalized by a nonsingular matrix $[\theta]$ and letting

$$(\psi)=[\theta]^{-1}(N) \tag{16}$$

and operating on Eq. (16) by $[\theta]^{-1}$ one obtains

$$\frac{\partial(\psi)}{\partial t}=[\theta]^{-1}[D][\theta]\frac{\partial(\psi)}{\partial x^2} \tag{17}$$

which represents the set of scalar diffusion equations

$$\frac{\partial\psi_k}{\partial t}=D_k\frac{\partial^2\psi_k}{\partial x^2} \qquad (k=1,2,3) \tag{18}$$

where D_k are the eigenvalues of $[D]$ obtained by solving the characteristic equation of $[D]$. The solution of Eq. (18) is then

$$\psi_k=U_k+W_k\,\mathrm{erf}\left(\frac{x}{2\sqrt{D_k t}}\right) \qquad (k=1,2,3) \tag{19}$$

where U_k and W_k are constants defined by initial and boundary conditions. Since $[\psi]=[\theta]^{-1}[N]$, the result is that

$$N_j=\sum_{k=1}^{3}\theta_{jk}U_k+\sum_{k=1}^{3}\theta_{jk}W_k\,\mathrm{erf}\left(\frac{x}{2\sqrt{D_k t}}\right). \tag{20}$$

The oxide scale of BO_v is assumed to grow by diffusion of either or both oxygen or B in the oxide, so that the scale may thicken according to a parabolic growth law:

$$\xi=(2kt)^{1/2} \tag{21}$$

Therefore the concentration gradient of the diffusing species at the scale–alloy interface will be given by differentiation of Eq. (20):

$$\left.\frac{\partial N_j}{\partial x}\right|_{\xi}=\frac{1}{(\pi t)^{1/2}}\sum_{k=1}^{3}\theta_{jk}W_k\frac{\exp(-k/2D_k)}{D_k^{1/2}}, \qquad j=1,2,3 \tag{22}$$

To evaluate the constant W_k in Eqs. (20) and (22), one may consider that the various diffusion species are conserved at the scale–alloy interface, viz., mass balance should be applied. The flux equation of these species toward the interface may have the usual form:

$$J_j = -\sum_{k=1}^{3} \frac{D_{jm}}{V_a} \frac{\partial N_m}{\partial x}\bigg|_{\xi}$$

$$= -\frac{1}{(\pi t)^{1/2}} \sum_{k=1}^{3} \frac{D_{jm}\theta_{mk}W_k}{V_a} \frac{\exp(-k/2D_k)}{D_k^{1/2}} j, \qquad m=1, 2, 3 \tag{23}$$

where V_a is the molar volume of the alloy. This would result in very complicated calculations. We therefore apply Morral's diffusion analysis[6] by introducing a square-root diffusivity matrix $[r]$, with $[r][r]=[D]$. At the scale–alloy interface, it yields.

$$\frac{1}{V_a}(v - N_1^i)\frac{d\xi}{dt}$$

$$= \frac{1}{V_a(\pi t)^{1/2}}[-r_{11}N_1^i + r_{12}(N_2^\circ - N_2^i) + r_{13}(N_3^\circ - N_3^i)] \tag{24}$$

$$\frac{1}{V_a}(1 - N_2^i)\frac{d\xi}{dt} = \frac{1}{V_a(\pi t)^{1/2}}[-r_{21}N_1^i + r_{22}(N_2^\circ - N_2^i) + r_{23}(N_3^\circ - N_3^i)] \tag{25}$$

where the r terms are the elements of the square-root diffusivity matrix, and N_j° and N_j^i are the bulk and interfacial concentration of species j, respectively.

For the alloy phase, one may assume that the difference between bulk and interfacial concentrations of the solvent is quite small. Therefore

$$N_3^\circ - N_3^i = N_1^i - (N_2^\circ - N_2^i) - (N_4^\circ - N_4^i) \tag{26}$$

where $N_1^\circ = 0$ and $N_4^\circ \approx N_4^i$. Thus, substitution of Eqs. (21) and (26) into Eqs. (24) and (25) yields

$$N_1^i = \frac{[r_{12} - r_{13} + (r_{22} - r_{23})v](\pi k/2)^{1/2}}{(r_{23} - r_{21})(r_{12} - r_{13}) - (r_{13} - r_{11})(r_{22} - r_{23})} \tag{27}$$

$$N_2^i = N_2^\circ - f(r, k) = N_2^\circ - \frac{[r_{11} - r_{13} - (r_{21} - r_{23})v](\pi k/2)^{1/2}}{(r_{23} - r_{21})(r_{12} - r_{13}) - (r_{13} - r_{11})(r_{22} - r_{23})} \tag{28}$$

Then according to Eqs. (16) and (19), we obtain

$$W_k = \frac{(\theta_{3k}^c - \theta_{1k}^c)N_1^i + (\theta_{3k}^c - \theta_{1k}^c)f(r, k)}{|\theta| \operatorname{erfc}[(k/2D_k)^{1/2}]} \tag{29}$$

where $|\theta|$ is the determinant of $[\theta]$, and θ_{1k}^c, θ_{2k}^c, and θ_{3k}^c are the cofactors of elements θ_{1k}, θ_{2k}, and θ_{3k}, respectively.

Let a_2 be the chemical activity of B in the alloy, and a_1 the chemical activity of oxygen in the alloy. In equilibrium with BO_v we have

$$a_2 a_1^v = K^{-1} \tag{30}$$

where K is the equilibrium constant for the reaction

$$B(\text{alloy}) + v\text{O}(\text{alloy}) = \text{BO}_v \tag{31}$$

Consider now the concentration profiles B and oxygen which are depicted by Fig. 1 where the external-oxide scale forms and grows without an internal-oxidation zone. Equation (30) must be satisfied at the alloy–oxide interface. However, to ensure that no internal oxidation occurs inside the alloy, we must have $a_2 a_1^v < K^{-1}$ as we move into the alloy, which means at the interface[3]

$$\left(\frac{\partial \ln a_2 a_1^v}{\partial x}\right)_{x=\xi} \leq 0 \tag{32}$$

Defining the activity coefficients of all elements according to the Wagner formalism for dilute and real solutuion behavior of the A–B–C alloy,

$$\ln \gamma_j = \ln \gamma_j^0 + \varepsilon_j^1 N_1 + \varepsilon_j^2 N_2 + \varepsilon_j^3 N_3, \qquad j = 1, 2, 3 \tag{33}$$

The criterion is then obtained from Eqs. (32) and (22) as

$$\sum_{k=1}^{3} \left[\left(\varepsilon_1^2 + v\varepsilon_1^1 + \frac{v}{N_1^i}\right)\theta_{1k} + (\varepsilon_2^3 + v\varepsilon_1^3)\theta_{3k} + \left(\varepsilon_2^2 + v\varepsilon_1^2 + \frac{1}{N_2^i}\right)\theta_{2k}\right] F_k \leq 0 \tag{34}$$

where

$$F_k = \frac{W_k \exp(-k/2D_k)}{(D_k)^{1/2}}, \qquad k = 1, 2, 3 \tag{35}$$

Substituting Eq. (28) into Eq. (34) yields

$$N_2^\circ \geq f(r, k) - \left\{\sum_{k=1}^{3} \left[\left(\varepsilon_1^2 + v\varepsilon_1^1 + \frac{v}{N_1^i}\right)\theta_{1k} + (\varepsilon_1^2 + v\varepsilon_1^2)\theta_{2k} \right.\right.$$
$$\left.\left. + (\varepsilon_2^3 + v\varepsilon_1^3)\theta_{3K}\right] F_k\right\}^{-1} \sum_{k=1}^{3} \theta_{2k} F_k \tag{36}$$

Thus, Eq. (36) may be utilized to define the critical bulk concentration of solute B above which no internal oxidation occurs and an exclusively external BO_v scale forms on the ternary alloy in terms of diffusivities of the alloying element and oxygen within the alloy, the parabolic rate constant for the external scale growth, and the activity coefficients or interaction parameters of B, C, and oxygen.

APPLICATION TO THE OXIDATION OF Ni–Cr–Al ALLOYS

Giggens and Pettit[7] have experimentally studied the oxidation characteristics of Ni–Cr–Al alloys and determined the minimum bulk Al concentrations necessary to form and grow a protective Al_2O_3 scale on the alloys isothermally oxidized at 1000, 1100, and 1200°C. They have found that Cr enables the formation of a continuous, external layer of Al_2O_3 on Ni–Cr–Al alloys at lower Al concentrations than would be necessary if the Cr were not present in the alloy. Similar results on this ternary alloy system have been obtained by many other investigators.[8–11] The experimental data are sufficient to permit the construction of "oxide maps" which delineate the composition ranges for formation of different types of oxide scales at a particular isotherm. Such oxide maps, however, only represent a summary of empirical and experimental data.

The criterion for the transition from internal to external oxidation on ternary alloys, developed in this study, is used to predict the minimum Al bulk concentrations for the exclusive formation of external Al_2O_3 scales on Ni–Cr–Al alloys at 1100 and 1200°C. Values for the interdiffusion coefficients of the ternary alloy system at both temperatures are taken from measurements by Nesbitt and Heckel.[12] Values of interdiffusion coefficients involving oxygen and alloying elements are usually not available experimentally because of the very low solubility of oxygen in metals and alloys and the strong interaction between oxygen and the alloying elements. However, for dilute alloys these interdiffusion coefficients may be estimated based on the knowledge of tracer or self-diffusion coefficients of oxygen and solutes in the base metal as well as thermodynamic interaction parameters of the alloy plus oxygen system.[13] The values of the tracer of self-diffusion coefficient of oxygen in Ni at 1100 and 1200°C are taken as 2.1×10^{-8} and 7.6×10^{-8},[14] of Cr in Ni as 1.3×10^{-10} and 3.9×10^{-10},[15] and of Al in Ni as 1.0×10^{-10} and 5.0×10^{-10},[16] respectively. The values of oxygen solubilities in Ni at the two temperatures are taken from the measurements by Smithells and Ransley[17] and by Seybolt,[18] and are then modified using Eq. (12) to include the effect of Al and Si additions into the ternary alloys. The values of thermodynamic interaction parameters, $\varepsilon_{\mathrm{O}}^{\mathrm{Cr}}$ and $\varepsilon_{\mathrm{O}}^{\mathrm{Al}}$, were experimentally measured[19] in the nickel melts at 1600°C as -46 and -116, respectively. Experimental data on the other interaction parameters in nickel are not available directly. However, they may be calculated using the appropriate thermodynamic properties of the limiting binary systems in a regular solution model given by Lupis,[20] which is proper in this study because all the limiting binary systems of the Ni–Cr–Al–O system do exhibit regular or subregular solution behavior at high temperatures.[21–22] Accordingly, the values of $\varepsilon_{\mathrm{O}}^{\mathrm{O}}$, $\varepsilon_{\mathrm{Al}}^{\mathrm{Al}}$, $\varepsilon_{\mathrm{Al}}^{\mathrm{Cr}}$, and $\varepsilon_{\mathrm{Cr}}^{\mathrm{Cr}}$ obtained at 1600°C are 2, 106, 37, and 65, respectively.

Values for the parabolic rate constants k_C for the growth of external Al_2O_3 scales on Ni–Cr–Al alloys at 1100 and 1200°C were taken directly from the measurement of Giggens and Pettit.[7]

At 1200°C, the minimum Al bulk concentrations N_{Al}^* predicted from Eq. (36) are found to depend on Cr bulk concentrations in the range of 0–35 at.% as shown in Fig. 2. With increasing the Cr concentrations from 0 to about 22 at.%, the value of N_{Al}^* is decreased, whereas further increase in the Cr bulk concentration results in the increase of N_{Al}^*. The data points in Fig. 2 correspond to the compositions of alloys experimentally studied by Giggens and Pettit.[7] Open squares and solid circles indicate the alloys that have been found to exhibit internal oxidation of Al and the exclusive external Al_2O_3 scale formation, respectively. Similar results as above are obtained for the oxidation of Ni–Cr–Al alloys at 1100°C. Figure 3 shows the predicted values of N_{Al}^* and data points of the experimental observations by Giggens and Pettit.[7] It is clear from Figs. 2 and 3 that the predicted values of N_{Al}^* agree well with the experimental observations at both temperatures.

The only attempt to predict values of N_{Al}^* for the formation of exclusive external Al_2O_3 scales on Ni–Cr–Al alloys has been made by Nesbitt.[23] In his analysis the diffusion of oxygen into the alloys was neglected and only the ternary interdiffusion effect on the Al flux from the alloy to the scale–

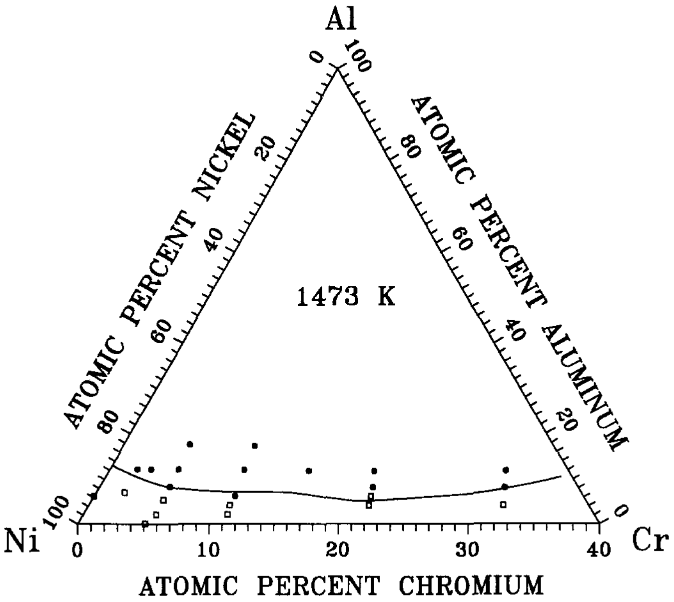

Fig. 2. Predicted minimum Al concentrations for Al_2O_3 scale formation on Ni–Cr–Al alloys at 1200°C.

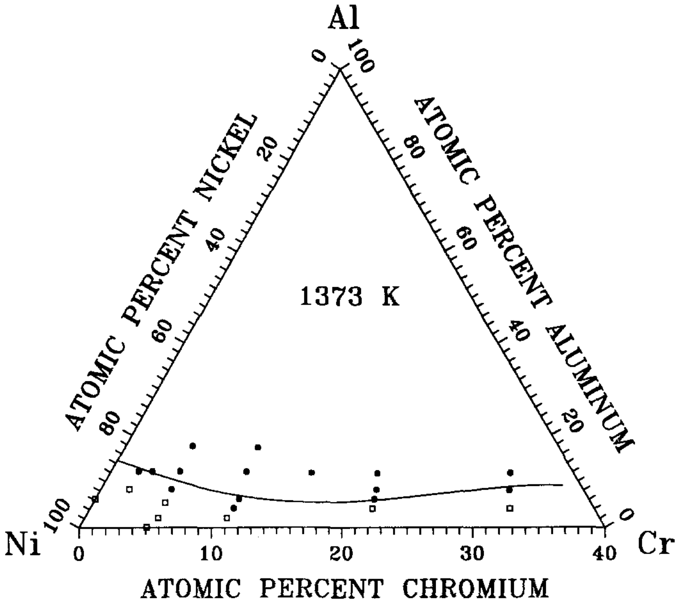

Fig. 3. Predicted minimum Al concentrations for Al_2O_3 scale formation on Ni-Cr-Al alloys at 1100°C.

alloy interface was taken into account. By assuming the mole fraction of Al at the scale–alloy interface to be zero, he predicted the value of N_{Al}^* by equating the maximum possible flux of Al with the rate of Al consumption due to the oxidation at the scale–alloy interface. The predicted values of N_{Al}^* at 1200°C ranged from 3 to 6 at.% for Cr bulk concentrations in the range of 0–40 at.%. In this study, we have also used Nesbitt's method to calculate N_{Al}^* for Ni–Cr–Al alloys at 1100°C. Obtained values of N_{Al}^* range from 2 to 4 at.% in the same bulk concentration range of Cr as above. These predicted values of N_{Al}^* are actually similar to those for binary Ni–Al alloys, if the same method is applied to the oxidation of Ni–Al alloys. They are much lower than those observed experimentally. The results of Nesbitt's analysis indicate clearly that the beneficial effect of Cr additions on the formation of external scale of Al_2O_3 cannot be accounted for by the ternary interdiffusion effect. Because the ternary diffusion coefficients affecting the diffusion of Al in dilute Ni–Cr–Al alloys (D_{AlAl} and D_{AlCr}[12]) and the parabolic rate constants for external Al_2O_3 scale growth[7] are not significantly affected by Cr concentration, the diffusion flux of Al in the alloy to the scale–alloy interface will not be significantly affected by Cr addition either. In fact, one may calculate the flux of Al to the scale–alloy interface using Eq. (23). As shown in Fig. 4, the difference between the Al flux to the scale–

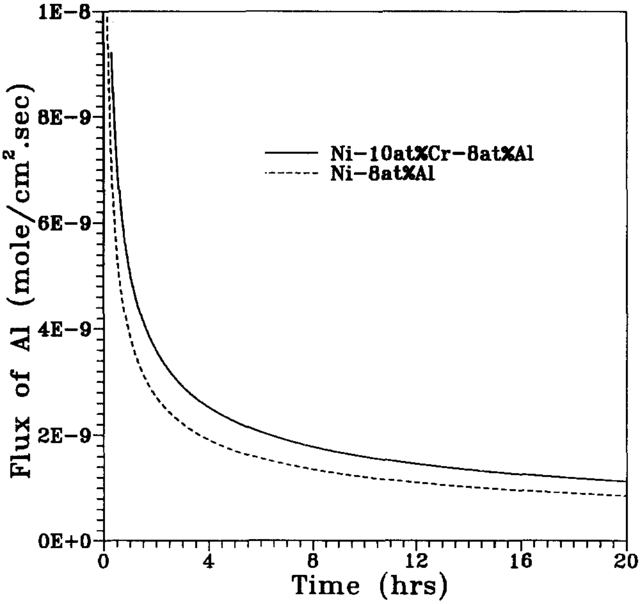

Fig. 4. The Al flux to the scale/alloy interface from Ni–8 at.% alloys with or without Cr additions at 1200°C.

alloy interface of a Ni–10 at.% Cr–8 at.% Al alloy and that of a Ni–8 at.% Al alloy is very small.

According to Wagner's hypothesis[1] for the getting effect in the oxidation of ternary alloys, one may consider that the Cr acts as a getter of oxygen to prevent internal oxidation of Al. During the very initial oxidation, oxides of Ni, Cr, and Al are all formed. If sufficient Cr is present in the alloy, the initial formed NiO will be reduced by Cr through the reaction

$$3NiO + 2Cr\ (\text{in alloy}) = Ni\ (\text{in alloy}) + Cr_2O_3 \qquad (37)$$

In this manner a continuous layer of Cr_2O_3 is formed in the alloy, and this reduces the oxygen activity to such a low level that Al in the alloy can now be selectively oxidized to build up a continuous Al_2O_3 scale. However, it has been experimentally found[7–11] that the amount of Cr in Ni–Cr–Al alloys, required to act as a getter, would not be sufficient to form a continuous Cr_2O_3 external scale in the absence of Al. For instance, Giggens and Pettit[7] found that in order to form an external Al_2O_3 scale on Ni–Cr–Al alloys containing 8 at.% Al at 1200°C, the minimum Cr bulk concentration in addition would be 5 at.%. On the other hand, it has been found that at 1200°C, continuous Cr_2O_3 external scales form only on binary Ni–Cr alloys with more than approximately 20 at.% Cr.[24] Obviously, one should therefore reconsider the role of Cr as a secondary getter. Using the oxygen-solubility model developed in this study, it is now possible for us to quantitatively examine the oxygen-solubility model developed in this study, it is now possible for us to quantitatively examine the oxygen-solubility behavior in Ni–Cr–Al alloys as a function of Cr and Al concentrations. When $N_{Al} = 0.08$, the dependence of the oxygen solubility in the alloys on Cr concentrations at 1200°C is obtained using Eq. (12) and shown in Fig. 5. Because of thermodynamic interactions, the addition of Cr up to 0.05 mole fraction can reduce the oxygen solubility in the alloys dramatically, whereas the gradient of the decrease with larger Cr concentrations is very small. This suggests that the gettering effect of Cr does not necessarily require the Cr concentration high enough to establish a continuous Cr_2O_3 external scale.

At a fixed Cr concentration, the dependence of oxygen solubility in Ni–Cr–Al alloys on the Al concentration at 1200°C is also calculated using Eq. (13) and is shown in Fig. 6. The gradient of the change has large negative values at small Al concentrations, but it remains to be almost constant (~0.011) at N_{Al} larger than 0.02. It is interesting that, although the addition

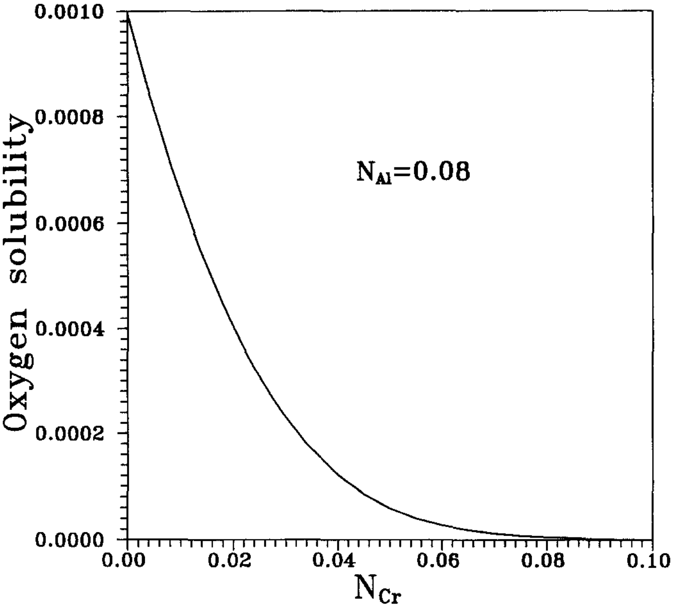

Fig. 5. Oxygen solubility in the Ni–Cr–Al alloys as a function of Cr concentration at 1200°C.

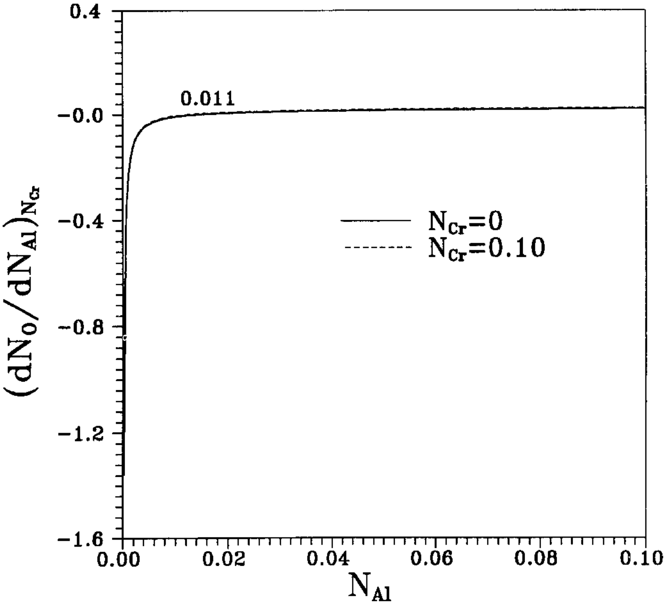

Fig. 6. The dependence of oxygen solubility in Ni–Cr–Al alloys on Al concentrations at 1200°C.

of Cr into the ternary alloys will reduce the oxygen solubility in the alloys, it does not significantly affect the dependence of the oxygen solubility on N_{Al}.

The ternary extension of Wagner's criterion, established in this study, for the presence or absence of internal oxidation is essentially based on the activity gradients of metal and oxygen and their relationships to oxygen supersaturation in the alloys. In the case of binary alloys, Smeltzer and Whittle[4] have demonstrated that Wagner's criterion is equivalent to the relationship between the diffusional-composition path and the oxygen-solubility curve in the alloy–oxygen isotherm. The distributions of oxygen and the solute elements are not independent of each other but are interrelated. Because its concentration is small, the influence of oxygen on the distribution of solute elements may be neglected. However, the distribution of the solute elements should have a very significant effect on the oxgyen distribution, especially where there is strong thermodynamic interaction. Accordingly, the diffusion of oxgyen in the Ni–Cr–Al alloys will depend not only on its own concentration gradient but also on the gradients of Cr and Al. It is also expected that the Cr addition will have an influence on the slope of the virtual diffusion path at the alloy side of the scale–alloy interface,

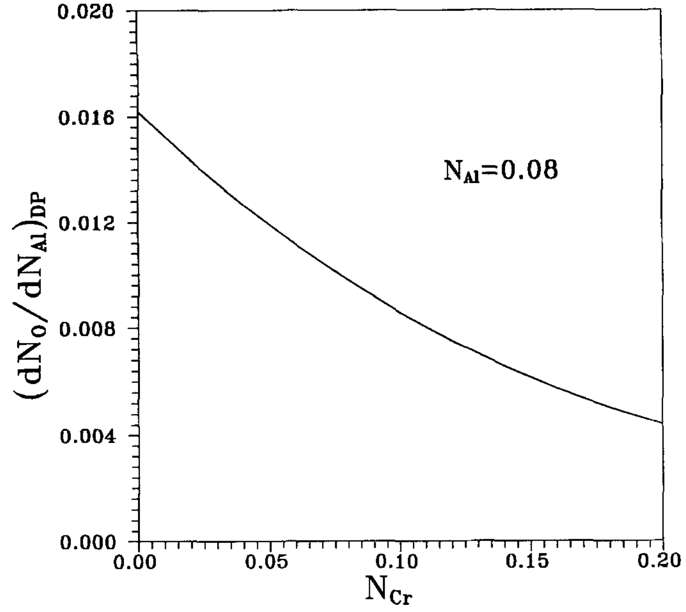

Fig. 7. The change of the slope of the diffusion path at the scale/alloy interface as a function of Cr concentration at 1200°C.

$(dN_O/dN_{Al})_{DP}$. According to Eqs. (22) and (35), we have

$$\left(\frac{dN_O}{dN_{Al}}\right)_{DP} = \left(\frac{\partial N_O}{\partial x} \bigg/ \frac{dN_{Al}}{dx}\right)_{x=\xi} = \frac{\sum_{k=1}^{3} \theta_{1k}F_k}{\sum_{k=1}^{3} \theta_{2k}F_k} \tag{38}$$

where 1 and 2 refer to oxygen and Al, respectively. As shown in Fig. 7, the slope of the diffusion path decreases significantly with increasing Cr bulk concentrations in the Ni–Cr–Al alloys containing 8 at.% Al at 1200°C. Referring to Fig. 6, one finds from Fig. 7 that in order to force the diffusion path to contact the tangent of the oxygen-solubility surface, the Cr bulk concentration in the alloys has to be not less than 5 at.%. In this manner the slope of the diffusion path will be equal to or smaller than the gradient of the oxygen-solubility surface (0.011). Therefore, the diffusion path will not lead to oxygen supersaturation and internal-oxide precipitation.

This effect of the Cr addition may be seen more clearly from Eq. (36). Letting all interaction parameters be zero in Eq. (36), one obtains the criterion for exclusive, external-scale formation as

$$N_2^{\circ} \geq f(r, k) - \frac{N_1^i}{v} \frac{\sum_{k=1}^{3} \theta_{2k}F_k}{\sum_{k=1}^{3} \theta_{1k}F_k} \tag{39}$$

Therefore one can expect from Fig. 7 that the minimum Al bulk concentration required for the exclusive Al_2O_3 external scale should decrease with increasing Cr bulk concentrations in the Ni–Cr–Al alloys. The gettering effect of Cr on the minimum Al concentration may not be seen distinctly from Eq. (39) because the oxygen interfacial concentration (N_1^i) is also included in F_k terms.

It is thus apparent that the beneficial effect of Cr addition on the oxidation of Ni–Cr–Al alloys can be attributed to that through thermodynamic interactions: (i) a sufficient Cr addition reduces the oxygen solubility in the alloys; and (ii) the sufficient Cr addition also alters the oxygen distribution in the ternary alloys and avoids the oxygen supersaturation necessary for the onset of internal oxidation in the alloys. These two factors make it easier to establish a continuous Al_2O_3 external scale on ternary Ni–Cr–Al alloys.

The use of thermodynamic interaction parameters at the molten state for the calculations in this study is an unfortunate situation. However, we have found that the absolute values of these interaction parameters would increase only by less than a factor of 2 if the temperature is extrapolated from the state of melt (i.e., 1600°C) to 1200 or 1100°C, and this temperature effect would only cause changes in the predicted values of the minimum Al for the exclusive Al_2O_3 external scale formation of less than 1.5 at.%. Some doubts may also be given rise to the use of Wagner formalism of activity coefficients for Ni–Cr–Al alloys containing concentration of Al as high as 16 at.% and of Cr as high as 30 at.%. This may be justified by the following facts: (i) the activity of Cr in Ni–Cr alloys shows only a slight deviation from the ideal below 25 at.% Cr over the temperature range of 1000–1400°C;[25] (ii) Al activity corresponds to Henrian solution behavior below 17 at.% Al in Ni–Al alloys between 700 and 1200°C;[26] and (iii) the deviation of Al activity from the ideal decreases on passing from the Ni–Al binary system to the ternary Ni–Cr–Al system and the effect of addition of Cr on the activity of Al is small in ternary Ni–Cr–Al alloys.[27]

SUMMARY

Smith's model has been expanded to quantitatively describe the oxygen-solubility behavior in an A–B–C alloy beneath a stoichiometric oxide scale of BO_ν as a function of alloy composition. Attempts are also made to establish a criterion for the onset of internal oxidation beneath the external-oxide scale of BO_ν when oxidizing conditions favor the formation of the oxide of the least-noble metal B in the A–B–C ternary alloy.

The minimum Al concentrations required to form a protective Al_2O_3 scale on Ni–Cr–Al alloy in 76 torr of oxygen at 1100 and 1200°C have been predicted. Sufficient Cr additions would significantly reduce the oxygen

solubility and also alter the oxygen distribution in the ternary alloy, avoiding the oxygen supersaturation necessary for the onset of internal oxidation. These two factors make it easier to establish the protective Al_2O_3 scale.

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