THE ISOTOPE EFFECT IN DIFFUSION AND ITS USE
IN STUDIES OF METAL OXIDES

W. K. Chen and N. L. Peterson

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W. K. Chen and N. L. Peterson
Materials Science Division
Argonne National Laboratory
Argonne, Illinois 60439

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Abstract

Application of the isotope mass effect in diffusion to the studies of defects and diffusion in nonstoichiometric metal oxides will be presented. Experimental results on CoO, NiO, Fe$_{1-x}$O, and (Co,Ni)O solid solutions will be used in the discussion.

Introduction

Studies of diffusion in solids have increased our understanding of the formation, interaction and migration of defects in solids. In addition to providing information about the diffusion-related phenomena, such as sintering, high-temperature creep, corrosion, and oxidation, diffusion data can be particularly useful in testing the defect models for nonstoichiometric compounds. Traditionally, for such compounds, the defect concentration is expressed as a function of thermodynamic variables based on a proposed defect model. The model is tested by comparing the expression thus obtained with the experimentally observed data [1,2]. In metal-deficient transition metal oxides, M$_{1-x}$O, cation vacancies are usually the predominant nonstoichiometric defect. From the reaction,

$$\frac{1}{2} \, O_2 (g) + \alpha M^{2+} + O^{2-} + V_M^{\alpha} + \alpha M^{3+}, \tag{1}$$

one can express the concentration of cation vacancy as

$$[V_M^{\alpha}] = \frac{K_1 p_{O_2}^{1/2(\alpha+1)}}{M^{2+} \, O^{2-}}. \tag{2}$$

Here $O_2$ is an oxygen molecule in the gas phase, $M^{2+}$ and $O^{2-}$ are a cation and an oxygen ion on their respective lattice sites, $V_M^{\alpha}$ is a cation vacancy with an $\alpha$ negative charge relative to the lattice, $M^{3+}$ is a lattice cation with a localized electron hole $h$, $K_1$ is the equilibrium constant for reaction (1), and $p_{O_2}$ is the equilibrium oxygen partial pressure. Thus, from the approximation $D = [V_M^{\alpha}] D_v$, where $D$ and $D_v$ are the diffusion coefficients of cation self-diffusion and vacancy diffusion, respectively, one can test the proposed defect model by comparison of the above prediction with the measured functional dependence of $D$ with respect to $p_{O_2}$. This type of evaluation is often

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hampered by the presence of impurities when the defect concentration is sufficiently dilute or by the defect-defect interaction when the defect concentration is sufficiently large. Thus, it is desirable to have independent kinetic data to confirm the proposed defect model.

The Bardeen-Herring [3] correlation factor has been shown to be useful for characterization of the diffusion mechanism in metals [4]. One method of determining the correlation factor in diffusion is the measurement of isotope mass effect in diffusion [4]. In the present report, we review the use of isotope effect in diffusion for the studies of defect and diffusion in oxides. Following an introduction to correlation and isotope effect for self- and solute diffusion in simple oxide, we discuss (1) cation self-diffusion in CoO, NiO, and Fe_{1-x}O; (2) effect of solute additions on solute and self-diffusion in NiO; and (3) cation self-diffusion in (Co,Ni)O solid solutions. These materials have the NaCl structure and are characterized by metal deficiency at high temperatures. The value of $x$ in M_{1-x}O is $<10^{-3}$ for NiO, $<10^{-2}$ for CoO, and 0.05-0.15 for Fe_{1-x}O. For solid solution (Co,Ni)O, the deviation from stoichiometry depends on the composition for a given temperature and oxygen potential.

**Correlation factors in diffusion**

Diffusion in a crystal is known to take place by a continual migration of diffusing species via an endless succession of jumps from site to site in the crystal. In an isotropic crystal (e.g., cubic crystal), the diffusion coefficient may be written in the general form [5]

$$D = \frac{1}{6} \left< R^2 \right>/t$$  \hspace{1cm} (2)

where $< R^2 >$ is the square of the vector displacement R of a diffusing specie in time t, averaged over all possible migration paths. If the total n jumps occur in time t, each R is the vector sum of n individual atom jump vectors r. If each jump is the same length, then for a large n,

$$< R^2 > = \left< \left( \sum_{i=1}^{n} r_i \right)^2 \right> = nr^2 \left[ 1 + 2 (< \cos \theta_1 > + < \cos \theta_2 > + \ldots) \right],$$  \hspace{1cm} (3)

where $< \cos \theta_j >$ is the average value of the cosine of the angle between a given jump and the jth following jump.

For random atomic jumps, (i.e., the direction of any jump is always at random and independent of the direction of the previous jumps), all $< \cos \theta >$ in (3) average to zero and $< R^2 > = nr^2$. Equation (2) becomes

$$D = \frac{1}{6} r^2 \Gamma,$$  \hspace{1cm} (4)

where $\Gamma = \frac{n}{t}$ is the average jump frequency. If the jump direction of a given atom depends on the direction of a previous jump, all $< \cos \theta >$ are no longer zero and $< R^2 > = nr^2 f$, where

$$f = 1 + 2 (< \cos \theta_1 > + < \cos \theta_2 > + \ldots),$$  \hspace{1cm} (5)
and $f$ is the correlation factor. Then Eq. (2) becomes

$$D = \frac{1}{6} r^2 T f.$$  \hspace{1cm} (6)

For self-diffusion in those crystal structures where atomic migration can be described by a single jump frequency, the correlation factor is a geometrical constant determined by the lattice geometry and the diffusion mechanism. The value of $f$ has been calculated for several diffusion mechanisms in a number of crystal lattices [6,7]. Thus, direct measurement of $f$ may lead to an identification of the diffusion mechanism.

The correlation factor is no longer a geometrical constant for the diffusion of an impurity atom in a crystal. The presence of an impurity atom in an otherwise pure crystal will change the jump frequencies of the neighboring solvent atoms to the values different from that found in the absence of impurity atom. Thus, the correlation factor for impurity diffusion $f_4$ depends on the relative jump frequencies of solute and solvent atoms. More detailed considerations show that the value of $f_4$ for impurity diffusion by the vacancy mechanism in a cubic lattice is given by [8]

$$f_4 = \frac{H}{2\omega_2 + 2H},$$  \hspace{1cm} (7)

where $\omega_i$ is the average jump frequency of an impurity atom, and $H$ is the effective escape frequency with which the vacancy escapes its nonrandom position with respect to the impurity. For impurity diffusion in the fcc lattice by a vacancy mechanism, the effective escape frequency $H$ is given by [8]

$$H = 2\omega_1 + 7 \sigma \omega_3.$$  \hspace{1cm} (8)

Here $\omega_1$ is the exchange frequency of a vacancy, which is nearest neighbor to an impurity atom, with any of the four solvent atoms that are also nearest neighbors to the impurity; $\omega_3$ is the exchange frequency of a vacancy, which is nearest neighbor to an impurity, with any of the seven solvent atoms adjacent to the vacancy but not nearest neighbors to the impurity; and $\sigma$ is a known function of $\omega_4/\omega_0$, where $\omega_4$ is the vacancy jump frequency for the reverse of a $\omega_3$ jump, and $\omega_0$ is the solvent-vacancy exchange frequency in the pure solvent. Thus, $H$ contains only the solvent-vacancy exchange frequencies that are influenced by the presence of the impurity atom. Since the temperature dependence of the various $\omega_i$'s will, in general, be different, the value of $f_4$ will vary with temperature. The values of $f$ and $f_4$ can be inferred from measurements of the isotope effect for self- and impurity diffusion in an otherwise pure solvent.

As impurity atoms are added to the solvent, those solvent atoms neighboring impurity atoms will jump with a frequency $\omega_1$, $\omega_3$, or $\omega_4$ rather than $\omega_0$. Lidiard [9] was the first to derive correctly the average solvent-atom jump frequency as a function of impurity content $c$ in terms of the various $\omega_i$'s. He found that the diffusion coefficient of the solvent in a dilute solid solution could be written as
\[ D_s(c) = D_s(0) (1 + bc), \quad (9) \]

where \( D_s(c) \) and \( D_s(0) \) are the diffusion coefficients of a solvent atom in the solid solution with solute content \( c \) and in the pure solvent, respectively; and \( b \) is a constant for a given dilute solid solutions at a given temperature. The ratio of the impurity diffusion coefficient \( D_i(0) \) to the solvent diffusion coefficient in the otherwise pure solvent is given by [9]

\[ \frac{D_i(0)}{D_s(0)} = \frac{f_i \omega_2}{\omega_0} \exp \left( -\frac{-\Delta g}{RT} \right) \quad (10) \]

and

\[ f_i = 1 - \left[ 4 f/(b + 18) \right] \left( D_i(0)/D_s(0) \right), \quad (11) \]

where \(-\Delta g\) is the association energy of the impurity-vacancy and, therefore, \( \omega_i/\omega_0 = \exp \left( -\frac{-\Delta g}{RT} \right) \). A measurement of \( D_i(0), D_s(0), \) and \( b \) will give a value of \( f_i \) for impurity diffusion in the pure solvent within the framework of the Lidiard theory.

In deriving Eq. [11], Lidiard assumed that all solvent jumps in the dilute solid solutions have a correlation factor \( f \) as in the pure solvent. Howard and Manning [10] have removed this assumption and found that, for a given set of values of \( D_i(0), D_s(0), \) and \( b \), a range of possible values of \( f_i \) exist, and that unique values of \( \omega_i/\omega_0, \omega_s/\omega_i, \) and \( \omega_i/\omega_s \) correspond to each value of \( f_i \). Hence, given experimental values of \( D_i(0), D_s(0), b, \) and \( f_i \), a unique set of jump frequency ratios may be obtained.

**Isotope mass effect in diffusion**

For tracer diffusion in solids, the correlation factor \( f \) or \( f_i \) can be implied from an accurate measurement of the relative diffusion rates of two isotopes of the same element. The isotope effect in diffusion has been expressed by Schoen [11], and later by Tharmalingam and Lidiard [12], as

\[ 1 - \frac{D_\beta}{D_\alpha} = f \]

\[ 1 - \left( \frac{T_\beta}{T_\alpha} \right) = \Delta K \left[ 1 - \left( \frac{m_\alpha}{m_\beta} \right)^{1/2} \right] \quad (12) \]

where the subscripts \( \alpha \) and \( \beta \) pertain to two isotopes with masses \( m_\alpha \) and \( m_\beta \), respectively. The ratio of average jump frequencies in Eq. (12) is given by Mullen [13] as

\[ 1 - \frac{T_\beta}{T_\alpha} = \Delta K \left[ 1 - \left( \frac{m_\alpha}{m_\beta} \right)^{1/2} \right]. \quad (13) \]
Here $\Delta K$ is the fraction of the total translational kinetic energy, at the saddle point, in the jump direction associated with the migrating atom. From Eqs. (12) and (13), the general expression for the isotope mass effect in diffusion becomes

$$\frac{1-(D_B/D_A)}{1-(m_A/m_B)^{1/2}} = f\Delta K$$

(14)

For those cases in which only one atom undergoes an atomic displacement during the jump process and its jumping motion is not coupled with the surrounding atoms, the value of $\Delta K$ will be unity, otherwise it will be less than unity. For diffusion mechanisms that involve the simultaneous motion of $n$ atoms in the jump process, the mass of the isotopes in Eq. (14) must be replaced by the expression $(n-1)m + m_1$, where $m$ is the average mass of the nontracer atoms [14].

From Eq. (14), the value of $f\Delta K$ can be determined by measuring the relative diffusion coefficients of two isotopes of the same element. For self-diffusion, the measured value of $f\Delta K$ and the allowed values of $f$ and $\Delta K$ may permit an unambiguous determination of the diffusion mechanism and thus provide a unique value of $\Delta K$. In the case of impurity diffusion, the value of $f_1$ can be determined from the measured value of $f\Delta K$ and the value of $\Delta K$ obtained from the self-diffusion experiment.

Experimental

The diffusivities of $^{55}$Co and $^{60}$Co in CoO [14], $^{57}$Ni, $^{66}$Ni, $^{55}$Co, and $^{60}$Co in NiO [16,17], $^{52}$Fe and $^{59}$Fe in Fe$_{1-x}$O [18], and $^{60}$Co and $^{57}$Ni in (Co, Ni)O [19] were measured as a function of temperature and/or composition by the tracer-sectioning technique. The oxide single crystals were grown by the Verneuil process in an arc-imaging furnace. The starting material was commercially available powder of purity 99.999%. For the boundary conditions used in the diffusion experiments, the specific activity $C$ may be expressed as a function of the penetration distance $X$ by the equation

$$C = C_0 \exp \left(-\frac{X^2}{4Dt}\right),$$

(15)

where $C_0$ is a constant, and $t$ is the time of the diffusion annual.

The isotope effect for diffusion was measured by the simultaneous diffusion of isotopes $\alpha$ and $\beta$ of the same element. The ratio of specific activities $C_\alpha/C_\beta$ as a function of penetration distance (i.e., $C_\alpha$) can be expressed from Eq. (15) as

$$\ln \left(\frac{C_\alpha}{C_\beta}\right) = \text{Const.} - \left[1 - \left(\frac{D_\beta}{D_\alpha}\right)\right] \ln C_\beta.$$  

(16)
The value of $1 - (D_{60}/D_{55})$ and thus $fAK$ [from Eq. (14)] may be accurately
determined from a plot of $\ln(C_{55}/C_{60})$ versus $\ln C_{60}$ without being influenced
by possible errors that arise from sectioning and the time and temperature
of annealing. The ratio of the specific activities ($C_{55}/C_{60}$) was determined
in each section to within 0.1% by a half-life separation of the $\gamma$ activ-

For an accurate comparison of the diffusivities of $^{60}$Co and $^{57}$Ni in
a given sample, the two tracers were also diffused simultaneously in the
dilute and concentrated solid solutions of (Co,Ni)O crystals and analyzed
in the manner of Eq. (16).

Results and discussion

Cation self-diffusion in CoO and NiO

Figure 1 shows typical penetration plots for the diffusion of $^{60}$Co
in CoO [15]. Since the data obey Eq. (15) over two to three decades in
activity, the diffusion coefficients determined from the slopes of these
curves represent bulk diffusion. The cation self-diffusion coefficient
in CoO as a function of temperature is shown in Fig. 2 and may be ex-
pressed as $D = (5.0 \pm 0.4) \times 10^{-3} \exp \left[-(38,890 \pm 230)/RT\right]$ cm$^2$/s. The

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Cation self-diffusion in Fe$_{1-x}$O

Thermodynamic data of Darken and Curry [23] indicate that the Fe$_{1-x}$O phase extends over a wide range of composition. The closest approach to stoichiometry is Fe$_0.95$O, and the deviation from stoichiometry may be as high as Fe$_0.84$O [23]. In view of this large defect concentration, a simple defect model that does not include defect clustering would appear to be inappropriate for this oxide. Using neutron and x-ray diffraction techniques, Roth [24] and Koch and Cohen [25] have proposed that the basic defect structure in Fe$_{1-x}$O is clusters of vacancies on octahedral cation sites grouped about occupied tetrahedral cation sites. Although the precise configuration of the defect clusters is not well defined, and probably depend on temperature, they form a region resembling the spinel structure of Fe$_3$O$_4$. From a structural point of view, the vacancies in the defect clusters are expected to be less effective in the ionic migration process. "Free vacancies" that are in coexistence with the defect clusters are thought to be the major defect responsible for the cation diffusion process. Although the concentration of "free vacancies" depends upon the total fraction of vacant sites and temperature, they are not expected to be linearly related to the deviation from stoichiometry.

Figure 4 [18] shows the cation diffusivity in Fe$_{1-x}$O single crystals or coarse-grained polycrystals as a function of the deviation from stoichiometry. The diffusivity decreases at 802°C and increases slightly at 1200°C with an increase in x and is rather insensitive to any change in x at 1003°C. The data of Himmel et al. [26] are shown to be in fair agreement with the data of Ref. [18]. The general trend shown in Fig. 4 is also consistent with the Mössbauer line broadening for $^{57}$Fe in Fe$_{1-x}$O reported by Greenwood and Howe [27] and Anand and Mullen [28]. The temperature dependence of the cation diffusivity in Fe$_0.94$O is well described by the Arrhenius expression, with $D_0 = 8.6 \times 10^{-3}$ cm$^2$/s, and $Q = 29.35 \pm 0.3$ kcal/mole in the temperature range 700-1350°C [18]. These experimental observations appear to confirm the "free-vacancy" model as presented in the preceding paragraph.

Figure 5 [18] shows the values of $f$AK, which were measured by the simultaneous diffusion of $^{52}$Fe and $^{59}$Fe in Fe$_{1-x}$O at various temperatures, plotted as a function of deviation from stoichiometry. The values of $f$AK appear to be independent of temperature at a given composition, but the values decrease with an increase in deviation from stoichiometry. The change in the values of $f$AK can be attributed to the change in the values of the correlation factor $f$, if one assumes the value of $\Delta K$ to be a constant, as in the cases of NiO and CoO.

The smaller value of $f$AK in Fe$_{1-x}$O (Fig. 5) relative to NiO and CoO and the decrease in $f$AK with an increase in vacancy concentration tend to suggest that divacancies and possibly higher-order vacancy clusters are contributing to cation diffusion in Fe$_{1-x}$O. If the properties of divacancies relative to monovacancies are the same as in fcc metals, the divacancy contribution to diffusion will be more important at low temperatures than at high temperatures in a material containing a temperature-independent
concentration of defects, i.e., Fe\textsubscript{0.94}O. Thus, the observed linear Arrhenius plot for Fe\textsubscript{0.94}O requires a proper balance between binding and migration energies of the various vacancy groups, if more than one kind of vacancy-type defect contributes significantly to cation diffusion. The temperature independence of the value of \(f_{AK}\) at a given composition (Fig. 5) also tends to discount the possibility of joint contribution by the various vacancy groups.

Thus, on the basis of our experimental observations, the cation diffusion in Fe\textsubscript{1-x}O can best be described in the following manner. The Fe ions diffuse via "free vacancies" that are in coexistence with defect clusters of the Roth-type [24] or Koch-Cohen-type [25]. The concentration of "free vacancies" depends on temperature and deviation from stoichiometry. The macroscopic diffusion rate of "free vacancies" decreases with an increase in the deviation from stoichiometry [29,30] because the number of available neighboring sites for a vacancy jump decreases as a result of a site-blocking effect [31-33]. The experimentally measured correlation factor for cation diffusion in Fe\textsubscript{1-x}O (Fig. 5) apparently reflects the consequences of both tracer- and vacancy-correlated jumps. At 1003\(^\circ\)C (Fig. 4) for example, the tracer diffusivity is insensitive to an increase in the deviation from stoichiometry, because an increase in the concentration of "free vacancies" is nearly offset by a decrease in the vacancy mobility and by an increase in the correlation effects (i.e., a decrease in the value of the correlation factor).

**Effect of cobalt additions on cobalt and nickel diffusion in NiO**

The experimental results to be presented provide information about various vacancy jump processes in the vicinity of an impurity atom through the expressions (7-11).

The experimental values of \(f_{Co}\Delta K\) deduced from measurements of the simultaneous diffusion of \(\text{\textsuperscript{55}}Co\) and \(\text{\textsuperscript{60}}Co\) in NiO, increase from 0.45 ± 0.001 at 1179\(^\circ\)C to 0.61 ± 0.01 at 1649\(^\circ\)C [16]. The correlation factor \(f_{Co}\) can be determined from the product \(f_{Co}\Delta K\) by assuming that \(\Delta K\) for cobalt impurity diffusion is the same as that for nickel self-diffusion in NiO (\(\Delta K = 0.78\)). The value of \(f_{Co}\) thus obtained is plotted as a function of temperature in Fig. 6 [17].

The diffusion coefficients for both cobalt and nickel diffusion in \((\text{Co}_{x}\text{Ni}_{1-x})\text{O}\) crystals at a given temperature increase linearly with the cobalt concentration (up to \(c = 0.015\)) at precisely the same rate [17]. The equal enhancement for both solvent and solute diffusivities is also demonstrated by the fact that the ratio of cobalt and nickel diffusivities are independent of composition at a given temperature [17].

At this point, one should be reminded of the basic assumptions made by Lidiard [9] in arriving at Eqs. (9)-(11), i.e., (1) solute additions do not alter the free energy of formation of vacancies in the system, (2) vacancy-solute interactions are limited to nearest-neighbor cation sites, (3) the correlation factor for solvent jumps near the impurity is
unchanged by the presence of the impurity, and (4) no overlapping of the sphere of influence of the solute atoms in the solid solution occurs. Within this framework, the theory has successfully explained the effect of solute additions on self-diffusion in metallic systems, but it does not predict the enhancement of solute diffusivity.

However, in addition to the solute-vacancy interactions considered by Lidiard [9], the effect of solute on charge neutrality and thus on defect concentration must also be considered in oxide systems. Since the third ionization energy for Co$^{3+}$ is smaller than that for Ni$^{3+}$, the concentration of cation vacancies must vary with cation composition at a given temperature in a dilute oxide solid solution (Co$_c$Ni$_{1-c}$)O to conserve charge neutrality. Thus, vacancy concentration may vary linearly with cation composition. The combined effects of the vacancy-solute interactions given by Lidiard [9] and the change in vacancy concentration in a solid solution results in the enhancement factors $b_1 = b + b_v$ and $b_2 = b_v$ for the diffusion of the solvent ($b_1$) and solute ($b_2$), respectively. Here $b_v$ is the contribution to the enhancement of diffusivity by the increased vacancy concentration. Since the experimental results show that $b_1 = b_2$ and $D_1/D_8$ are constant values independent of Co concentration at a given temperature, the enhancement of both cobalt and nickel diffusivities is inferred to be caused primarily by the increased concentration of cation vacancies in the dilute solid solution. Thus, the vacancy-solute interactions, and therefore their contribution to the enhancement of solvent diffusion, are negligible (i.e., $b \approx 0$). These conclusions suggest that $\Delta g < RT$ and $\omega_o = \omega_1 = \omega_3 = \omega_4 \neq \omega_2$. Using these conditions, $\omega_2/\omega_0$ and $D_{Co}/D_{Ni}$ in pure NiO were calculated as a function of temperature from the measured values of $f_{Co}$ only, using Eqs. (7) and (11). These values are shown in Fig. 7 [17]. The energy term in the temperature dependence of $D_{Co}/D_{Ni}$ is $AQ = Q_2 - Q_1$, where $Q_2$ and $Q_1$ are the activation energies for cobalt and nickel tracer diffusion in NiO, respectively. The direct experimental values of $Q_2$ [19] and $Q_1$ [16] give $AQ = -6.7$ kcal/mole, which is in good agreement with $-6.32$ kcal/mole deduced from the line in Fig. 7. Furthermore, the experimental values of $D_{Co}/D_{Ni}$ determined from the simultaneous diffusion of $^{60}$Co and $^{57}$Ni in NiO at 1382 and 1496°C are in good agreement with the line in Fig. 7 deduced from the values of $f_{Co}$. Thus, a self-consistent view of cobalt diffusion in NiO can be developed with $\omega_0 = \omega_1 = \omega_3 = \omega_4 \neq \omega_2$ and an impurity-vacancy interaction energy $\Delta g < RT$. This concept will be discussed in terms of the concentrated solid solution (Co,Ni)O.

Cation self-diffusion in (Co,Ni)O solid solutions

In a solid solution (A$_c$B$_{1-c}$)$_0$, the tracer diffusivity of component cation A, which is termed $D_A$, at cation fraction c can be expressed as

$$D_A = a^2 \left[ v'_M \right] \omega_{A'}}_A$$  \hspace{1cm} (17)
Here \( a \) is the lattice constant, \( \omega_A \) is the average exchange frequency of a vacancy and a tracer \( A \), and \( f_A \) is the correlation factor for tracer \( A \). In the limit of a random distribution of cations \( A \) and \( B \) in the solid solution and no interaction between the vacancies and a particular species, an expression similar to Eq. (17) can be given for component \( B \) with the subscript changed from \( A \) to \( B \). Thus, one obtains

\[
\frac{D_A}{D_B} = \frac{\omega_A f_A}{\omega_B f_B}
\]  (18)

In the solid solution, the successive jumps of vacancies are correlated. After exchange with a cation \( A \), the vacancy is still a neighbor of this cation \( A \). If \( \omega_A \) is larger than the average vacancy jump frequency, the vacancy, after the exchange with a cation \( A \), has a greater than random probability of making a reverse jump, by reexchange with the cation \( A \). Similarly, a smaller than random probability exists of reexchange with a slow diffusing cation \( B \) (with \( \omega_B \) smaller than the average vacancy jump frequency). Taking correlated jumps of vacancies into account, the correlation factors \( f_A \) and \( f_B \) in a random solid solution with a cubic structure is expressed as \([8,34]\)

\[
f_A = 1 - \frac{2 (D_A/D_B)}{(M_o + 2)[c(D_A/D_B) + (1 - c)]}
\]  (19a)

and

\[
f_B = 1 - \frac{2}{(M_o + 2)[c(D_A/D_B) + (1 - c)]}
\]  (19b)

where \( M_o = 7.15 \) for an fcc lattice. From Eqs. (18) and (19), the value of \( D_A/D_B \) can be calculated from the knowledge of \( \omega_A/\omega_B \) and vice versa. In the previous subsection, it was concluded that the enhancement of cobalt and nickel diffusivities in a dilute solid solution is primarily due to the increased concentration of cation vacancies, and the vacancy-solute interactions are negligible. Extending this concept to the concentrated solid solutions, one expects \( \omega_{Co}/\omega_{Ni} \) to be a constant value independent of cation composition \( c \) for a given temperature. To test the validity of this ideal situation, the value of \( \omega_{Co}/\omega_{Ni} (= 2.9) \) at 1300°C is obtained from Fig. 7(b). The value of \( D_{Co}/D_{Ni} \) as a function of \( c \) at 1300°C is calculated by means of Eqs. (18) and (19), with \( \omega_{Co}/\omega_{Ni} = 2.9 \). Figure 8 shows that the measured values of \( D_{Ni} \) [19] are in excellent agreement with the values calculated from \( D_{Co}/D_{Ni} \) and the measured values of \( D_{Co} \).

Thus, it may be concluded that (1) CoO and NiO form a reasonably ideal quasi-binary solid solution over the entire range of composition at temperatures above \( \approx 1000°C \); (2) the predominant nonstoichiometric defect in \((Co_cNi_{1-c})O\), similar to their end members, is a cation vacancy, the
concentration of which is a function of cation composition; (3) the cation self-diffusivities of both Co and Ni in the solid solution are primarily controlled by the concentration of cation vacancies. The ratio $\omega_{\text{Co}}/\omega_{\text{Ni}}$ is nearly constant over the entire range of composition at a given temperature.

References


Fig. 1. Log of specific activity vs. penetration distance squared for the diffusion of $^{60}$Co in CoO in air. From Ref. [15].
Fig. 2. Log D vs. 1/T for cation self-diffusion in CoO in air. From Refs. [15,20].
Fig. 3. In ($C_{55}/C_{60}$) vs. ln ($C_{60}$) plots for caption self-diffusion in COO at 11.5 (C$_{55}$/C$_{60}$) increases from bottom to top and in (C$_{60}$) decreases from left to right. From Ref. [15].
Fig. 4. $D$ vs. deviation from stoichiometry for diffusion of $^{59}\text{Fe}$ in Fe$_{1-x}$O. From Ref. [18]. The data of Himmel et al. [26] at 983°C are shown for comparison.
Fig. 5. The values of $f\Delta K$ vs. deviation from stoichiometry for Fe diffusion in Fe$_{1-x}$O. From Ref. [18].
Fig. 6. \( \log f_{Co} \) vs. \( 1/T \) for cobalt diffusion in NiO. From Ref. [17].
Fig. 7. Temperature dependence of (a) $\frac{D_{\text{Co}}}{D_{\text{Ni}}}$ (△) and (b) $\omega_2/\omega_0$ (△) as calculated from measured values of $f_{\text{Co}}$. Experimental data from the simultaneous diffusion of $^{60}\text{Co}$ and $^{57}\text{Ni}$ (/5/) are also shown. From Ref. [17].
Fig. 8. Experimental values of $D_{Co}(\Omega)$ and $D_{Ni}(\Delta)$ vs. $c$ in $(Co_Ni_{1-c})O$ at 1300°C in air, from Ref. [19], compared with the calculated values of $D_{Ni}(---)$ using $\omega_{Co}/\omega_{Ni} = 2.9$. 

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