

Defects and Transport Properties of Metal Oxides

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The paper gives an overview of different types of defects and defect structures in metal oxides and transport properties such as diffusion and electrical conductivity. Point defects (vacancies, interstitials, impurity and dopant ions, hydrogen ions, a.o.) and corresponding defect structures are described by defect equations and equilibria. Oxides of common use metals and which are of particular interest in many aspects of high-temperature oxidation of metals, e.g., cobalt and nickel oxides, chromia, alumina and silica, are used as examples in describing defect structures and transport properties.

KEY WORDS: metal oxides; defects; defect structures; diffusion; electrical conductivity.

INTRODUCTION

It is a great pleasure to contribute to this special issue of *Oxidation of Metals* in honor of Professor David L. Douglass. He has been a leading figure in the field of high-temperature corrosion, and has as editor since its start some 25 years ago made *Oxidation of Metals* the leading publication in this important field. I have followed his work for more than 30 years and have greatly appreciated and benefited from his extensive knowledge. We will be looking forward to many more contributions from Professor Douglass in the years to come.

When metals react with gaseous oxygen, under most conditions they will form a solid oxide film or scale on the metal surface. Depending on the reaction conditions—temperature, gas composition, oxygen activity of the gas, time, etc.—the oxide films or scales may have varying forms, microstructure and morphology. For many systems—and particularly during the initial

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oxidation—the oxide films or scales may be dense and continuous, but after more extended reaction such scales usually develop microcracks or microchannels or may rupture and break up.¹

Different transport processes take place during the film-scale growth. When the films/scales are continuous, the reactants—metal and oxygen—are separated and the reaction may only proceed through a solid-state diffusion of the reacting atoms or ions and associated transport of electrons through the films/scales. At high temperatures such scales may also creep and plastically deform and recrystallization and grain growth are also common phenomena. When alloys are oxidized, different oxides may be formed and these may in turn react by solid-state diffusion and form more complex oxides. All in all, diffusional transport processes may govern the overall oxidation process and may also play an important role in many of the gradual changes that take place during scale growth.¹

Diffusional transport of atoms or ions and transport of electrical charges take place because of the presence of imperfections or defects in solids. A knowledge of defect structures and how defects facilitate solid-state diffusion is fundamental to an understanding of high-temperature oxidation. At any temperature solids contain different structural and compositional defects and these are often divided into three main groups: (i) point defects, (ii) line defects (dislocations) and (iii) plane defects, e.g., grain boundaries, phase boundaries and external surfaces.

This paper presents a short overview of different types of defects that may be encountered in metal oxides and of transport properties, particularly diffusion, of metal oxides. The literature contains countless publications and reports on defects and defect-dependent properties of metal oxides and a comprehensive review of this extensive field is not possible in a limited space. Defects and diffusional properties are therefore exemplified for a few selected oxides which also are of interest in relation to the high temperature oxidation of metals: CoO, NiO and Cr₂O₃. CoO probably represents the best-understood oxide system at this time, while NiO appears to be the only oxide for which a comprehensive study has been made of the relative importance of lattice, grain boundary and dislocation diffusion. Cr₂O₃ is an important oxide as it forms protective scales on numerous high-temperature alloys, but its defect structure and transport properties are still subject to considerable discussion. Properties of alumina and silica are also briefly mentioned.

POINT DEFECTS

If the imperfection is limited to one structural or lattice site and its immediate vicinity, it is termed a point defect. For metal oxides such point defects comprise (i) vacant lattice sites (vacancies) and (ii) extra atoms that

occupy the interstices between the regular sites (interstitials). These point defects may comprise both oxygen and metal vacancies and interstitials. Impurity and dopant atoms are also considered as point defects.

Nonstoichiometry and Predominant Point Defects

In principle, an oxide will contain all types of point defects, but a particular type will usually predominate in an oxide depending upon its composition and deviation from stoichiometry. By way of example, nickel and cobalt monoxide are both metal deficient and their formulas should thus be written Ni_{1-y}O and Co_{1-y}O , respectively, where y is a small fraction of one. Due to their deviation from stoichiometry in the form of metal deficiency, the predominant defects in these oxides are metal vacancies. Other oxides may be oxygen deficient (e.g., ZrO_{2-y}) or contain excess oxygen (e.g., UO_{2+y}) or excess metal (e.g., Zn_{1+y}O at high zinc activities) and in these cases the predominant defects are oxygen vacancies, oxygen interstitials and metal interstitials, respectively. Point defects are also present in oxides when they have stoichiometric composition.

Charges on Defects

Point defects may be neutral or charged.¹⁻³ For point defects it is generally convenient to describe the charge relative to the ideal, perfect crystal (containing no defects) rather than in terms of real charges. This relative charge is termed the effective charge of the defect. In terms of this reference system charged metal vacancies have negative effective charge while charged oxygen vacancies have positive effective charge. For interstitial ions the effective charges are equal to the real charges, and thus interstitial metal ions have positive and interstitial oxygen ions negative effective charge.

Defect Notation

Many important properties of metal oxides are dependent upon the concentrations of defects. Thus diffusion is proportional to the product of the concentration of the point defect and the mobility of the defect and electrical conductivity is proportional to the product of the concentration of charge carriers, their individual charge and their mobilities. To interpret such properties, it is then necessary to know the concentration of point defects and electronic defects as a function of temperature and oxygen activity. To achieve this, it is necessary to have a notation to describe the various defects and to be able to write equations for the formation of the defects which relates their concentrations to temperature and the oxygen activity.

Various systems of notation to describe point defects have been proposed in the literature.¹⁻⁴ The most widely adopted system is that due to Kröger and Vink.⁴ In this system a defect indicated by the major symbol and the site that it occupies by a subscript. Thus a metal atom on a regular metal lattice site in the oxide MO is written as M_M and correspondingly an oxygen ion on a normal oxygen lattice site is written as O_O . Vacancies are denoted by V and oxygen and metal vacancies are written V_O and V_M , respectively. A subscript "i" denotes an interstitial position, and by way of example, an oxygen interstitial ion is written as O_i .

Special symbols are also used to describe effective charges. A positive effective charge is indicated by a superior dot, and a negative effective charge by a superior prime. Thus an oxygen vacancy with two positive effective charges is written $V_O^{2\cdot}$, and a metal vacancy with one negative effective charge V_M' . Zero effective charge is indicated by an "x" added as a superscript. A neutral metal vacancy is thus written V_M^x .

Defect Equations and Equilibria

Under most experimental conditions, point defects in nonstoichiometric oxides are created or annihilated by adding or removing oxygen from the oxides. This is illustrated by considering defect equations and corresponding equilibria for the formation of different defects. When writing defect reactions, it is necessary to take into account mass balance and electroneutrality as for conventional chemical reactions, but in addition, the ratio of the number of regular cation and anion sites must remain constant. It is also useful to envisage that the point defects are dissolved in the solid.

If oxygen from the ambient oxygen gas is incorporated in an oxide by forming an oxygen ion on a normal lattice site, an equivalent number of metal lattice sites must be formed to conserve the ratio of metal to oxygen lattice sites in the oxide. For the oxide $Co_{1-y}O$, for instance, this reaction may be written



Thus for $Co_{1-y}O$, a cobalt vacancy is formed for each oxygen atom that is incorporated into the oxide. In this equation the cobalt vacancy is assumed to be singly charged and to conserve the overall electroneutrality of the crystal a positively charged electron hold, h^* , is formed as compensation.

For low defect concentration such defect reactions may be treated in terms of the law of mass action, and Eq. (1) then takes the form

$$[V_{Co}][h^*] = K_1 p_{O_2}^{1/2} \quad (2)$$

where K_1 is the equilibrium constant. When the concentrations of defect and atoms are expressed as site fractions, the concentration of O_O is essentially equal to unity as the concentration of oxygen vacancies can be considered to be negligibly small.

In further considerations of the defect concentrations and their dependence on the oxygen activity one makes use of the electroneutrality condition for the crystal, i.e., that the sum of the positive effective charges is equal to the sum of the negative effective charges. If singly charged cobalt vacancies and electron holes are the predominant defects in $Co_{1-y}O$, the electroneutrality condition is then given by

$$[V'_{Co}] = [h^*] \quad (3)$$

When Eqs. (2) and (3) are combined, it is seen that the concentration of cobalt vacancies and electron holes are given by

$$[V'_{Co}] = [h^*] = K_1^{1/2} p_{O_2}^{1/4} \quad (4)$$

Thus the concentrations of the cobalt vacancies and electron holes will increase according to this model with increasing oxygen pressure and be proportional to $p_{O_2}^{1/4}$.

The temperature dependence of the $[V'_{Co}]$ is in this case given by that of $K^{1/2}$. The equilibrium constant can be expressed in terms of the standard entropy, ΔS_1° , and standard enthalpy, ΔH_1° , of formation of the cobalt vacancies according to Eq. (1):

$$K_1 = \exp\left(\frac{\Delta S_1^\circ}{R}\right) \exp\left(-\frac{\Delta H_1^\circ}{RT}\right) = K_{01} \exp\left(-\frac{\Delta H_1^\circ}{RT}\right) \quad (5)$$

Experimentally the electrical conductivity and the nonstoichiometry have been found to be approximately proportional to $p_{O_2}^{1/4}$ at near-atmospheric oxygen pressures and following the above model this suggests that singly charged cobalt vacancies are the most important defect in high-purity $Co_{1-y}O$. This will be further discussed below.

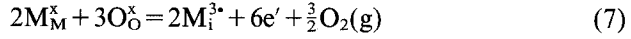
$Ni_{1-y}O$ has the same type of defect structure as $Co_{1-y}O$, but the concentration of nickel vacancies is smaller than that of cobalt vacancies in $Co_{1-y}O$ by more than an order of magnitude. From the observed oxygen pressure dependencies, it is furthermore concluded that the nickel vacancies are both singly and doubly charged.

Other defect structures involving other types of defects may be treated by following the same general procedure. One starts by writing the proper equation for defect formation and then uses the law of mass action coupled

with the overall electroneutrality condition. By way of examples, the formation of doubly charged oxygen vacancies in any oxide may be written



and the formation of triply charged interstitial metal ions in M_2O_3 is



Other defects structure situations that may be considered are the formation of Schottky and Frenkel defect pairs. The formation of Schottky defects in the oxide MO may be written



where nil represents the perfect crystal.

The formation of Frenkel defects is written



Intrinsic Electronic Equilibrium

In addition to the equilibria involving point defects, one must also take into account the intrinsic excitation of electrons



which equilibrium is given by



Impurities and Dopants

In addition to the native defects, dissolved impurity and dopant atoms are also considered to constitute point defects. If the impurity and dopant ions have a valence different from those of the native ions of the oxide and are present in sufficiently large concentrations, their primary effect on the defect structure and defect concentrations is to influence the electroneutrality condition.

Defect Associates, Defect Cluster and Extended Defects

In the above considerations it has been assumed that the points defects are single and unassociated. This assumption is only valid at very low defect concentrations, and as a rule of thumb the defects are considered to be unassociated when defect concentrations as expressed in mole fractions are smaller than 0.01–0.001. At higher defect concentrations point defects will tend to associate or cluster into larger units. In some structures defects may order and form extended planar defects or shear structures.

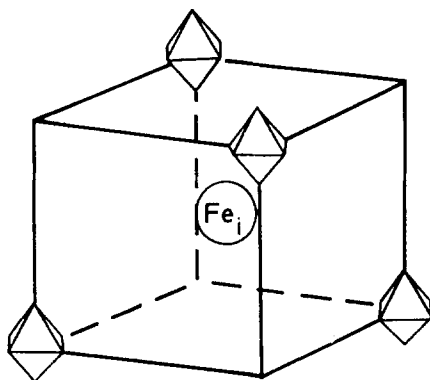


Fig. 1. The basic unit for defect clusters in Fe_{1-y}O comprising four vacancies and one interstitial ion.

Defect Associates

The formation of defect associates and defect clustering is basically due to coulombic interaction between the point or electronic defects having opposite effective charges. Simple pair clusters may arise from the interaction of a dopant ion and a point defect, e.g., between a dopant ion with a negative effective charge and an oxygen vacancy, which has positive effective charge. This type of defect association has been observed in many systems, an extensively studied system is, for instance, zirconia stabilized by doping with lower valent cations (e.g., Y^{3+} , Ca^{2+} a.o.).^{3,5}

Defect Clusters

For phases with large deviations from stoichiometry, larger aggregates are formed.^{1,3,5,6} An extensively studied case is wustite, Fe_{1-y}O . This oxide never has a stoichiometric composition, rather the values of y range from 0.05 to 0.15 depending upon the temperature and oxygen activity. The defects in this oxide are termed defect clusters and they consist of iron vacancies and interstitials in ratios ranging from 3:1 to 4:1. A number of different cluster compositions have been proposed, but the basic cluster unit is considered to be a cluster of four metal vacancies tetrahedrally surrounding a metal interstitial as illustrated in Fig. 1.^{1,3,5-9} More complex units may be formed by the sharing of faces, edges and corners of the 4:1 units. Other examples of defect clusters are found in oxides with fluorite structures. An example in case is uranium dioxide which may have a relatively large excess of oxygen, UO_{2+x} , in which the value of x may be as large as 0.15. In this

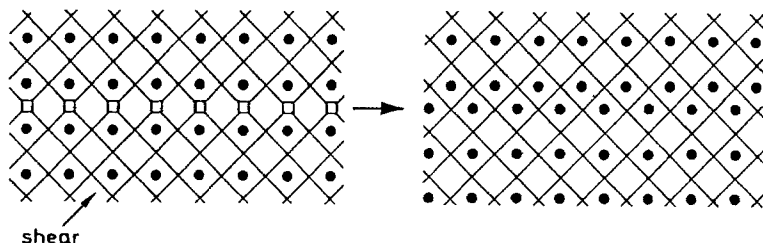


Fig. 2. Schematic illustration of an extended defect and the formation of shear planes. The black circles represent the metal atoms, the oxygen atoms are located at the intersections of the mesh while the squares represent the oxygen vacancies. (a) illustrates the alignment of oxygen vacancies and (b) the elimination of oxygen vacancies and the formation of a shear plane.

case the defect clusters are concluded to consist of oxygen interstitials and vacancies.¹⁰

Extended Defects

Extended defects are present in several oxide phases, including the extensively studied phases TiO_2 and WO_3 . Extended defects may be considered to form through the ordering and subsequent elimination of point defects in the form of planar defects.⁶ This process is schematically illustrated in Fig. 2 in which oxygen vacancies are assumed to be aligned and then eliminated in the form of a shear plane. This process is concluded to be responsible for the formation of a homologous series of oxide structures in several oxide systems, e.g., $\text{Ti}_n\text{O}_{2n-1}$.⁶

Infinitely Adaptive Structures

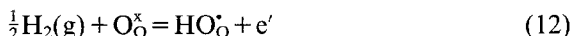
Some groups of oxides also possess the so-called infinitely adaptive structures.¹¹ In these cases, changes in nonstoichiometry do not take place by the formation of single point defects or extended defects. Rather the phase adjusts to changes in nonstoichiometry or composition through vernier-type structures. An example in case is $\text{L-Ta}_2\text{O}_5$.¹¹⁻¹³ This oxide is oxygen deficient, and the monophasic structure is maintained through the creation or elimination of oxygen sites in the oxygen sublattice upon changing the oxygen activity, while the number of tantalum sites remain unchanged.

Hydrogen Defects

About 20 years ago hydrogen and water vapor were not generally considered to affect bulk properties of metal oxides at high temperatures, and in studies of properties of metal oxides at high temperatures and reduced

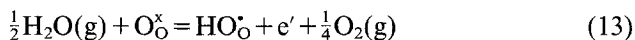
oxygen activities, oxides were often equilibrated in $H_2 + H_2O$ mixtures. However, in more recent years a number of studies have demonstrated that hydrogen may dissolve in metal oxides at high temperatures and significantly affect their defect structure and defect-dependent properties. Some oxides may even become hydrogen ion conductors under proper conditions.¹⁴⁻¹⁶

At high temperatures hydrogen dissolves in metal oxides as protons, and when this takes place from ambient $H_2(g)$ this dissolution may be written



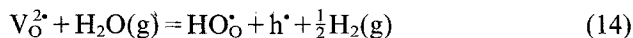
As indicated by this equation the dissolved proton is associated with an oxide ion and thus converts an oxide ion to an hydroxide ion (having a positive effective charge) on a normal oxygen site.

Protons may alternatively be dissolved from ambient water vapor according to the equation



As seen from this equation the concentration of dissolved protons is dependent on both the activities of water vapor and oxygen (or hydrogen and oxygen activity).

Relatively large concentrations of hydrogen may be dissolved in oxides doped with lower valent cations and with oxygen vacancies as the predominant native point defect. In this case the interaction of water vapor may be written



From this equation it is seen that upon reaction with water vapor the oxygen vacancies are gradually filled up and at the same time protons dissolve in the oxide.

An Example: Hydrogen Defects in Cr_2O_3

An example of the effect of hydrogen defects on the electrical conductivity of a porous chromia specimen at 450–1000°C is shown in Fig. 3.¹⁷ The chromia specimen was a *p*-type conductor, in all probability due to the presence of Mg impurities in the chromia. The specimen was exposed to an atmosphere of $H_2 + 2\% H_2O$ and the electrical ac conductivity was measured at different total gas pressures of the gas mixture. By this procedure the oxygen activity at each temperature was constant while the hydrogen activity was changed. Figure 3 shows the electrical conductivity as a function of the hydrogen activity at constant oxygen activity. As seen the *p*-conductivity decreases with increasing hydrogen activity at the lower temperatures. This

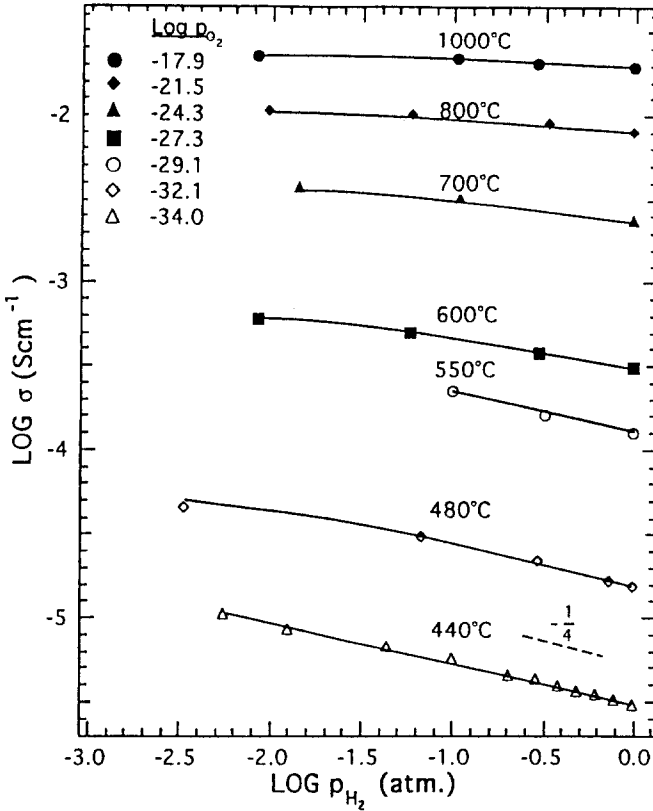


Fig. 3. The electrical conductivity of chromia in the temperature range 440–1000°C as a function of the hydrogen activity under conditions where the oxygen activity at each temperature is constant. The major aliovalent impurity in the chromia specimen was magnesium.¹⁷

may qualitatively be explained by assuming that the important defects comprise the Mg'_{Cr} -impurity atoms, the protonic defects, and the electron holes. The electroneutrality condition in this case is given by

$$[h^*] + [\text{HO}'_{\text{O}}] = [\text{Mg}'_{\text{Cr}}] \quad (15)$$

When the concentration of the protonic defects is increased with increasing hydrogen activity, the electron hole concentration is correspondingly decreased. The effect of hydrogen becomes increasingly important the lower the temperature, and this suggests that the dissolution of hydrogen in chromia at constant hydrogen activity increases with decreasing temperature.

DIFFUSIONAL PROPERTIES

Solid-state diffusion takes place because of the presence of defects in solids. Point or (lattice) defects, i.e., vacancies and interstitials, are responsible for lattice diffusion. Diffusion also takes place along line defects (dislocations) and plane defects which include grain boundaries, interphase boundaries and inner and outer surfaces. Diffusion is faster along line and plane defects than in the lattice, and they are therefore often termed high diffusivity or easy diffusion paths. The relative importance of the different diffusion processes depend on a number factors: microstructure, grain size, porosity that may be present, temperature, activities of the constituent atoms in the oxide, etc. As illustrated below, grain boundary and dislocation diffusion have smaller activation energies than that of lattice diffusion and thus become increasingly important the lower the temperature in oxide specimens with constant grain size and dislocation density.

Mechanisms of Lattice Diffusion

Lattice diffusion takes place through the migration of point defects. The diffusion mechanism is termed vacancy diffusion if an atom on a normal site jumps into an adjacent unoccupied lattice site. Through this mechanism the atoms move in the opposite direction to that of the vacancies. This mechanism has been demonstrated for oxides with either metal or oxygen vacancies, e.g., in Co_{1-y}O , zirconia a.o.¹

In metals small interstitially dissolved atoms such as H, C, N, and O diffuse by jumping from one interstitial site to one of its neighboring interstitial sites. This mechanism is termed the interstitial mechanism. Such a mechanism has not been demonstrated for the native ions in metal oxides, as these ions are too large to permit such a movement. However, native ions may move by another interstitial-type mechanism called the interstitialcy mechanism. In this an interstitial ion pushes one of its neighbors on normal lattice site into another neighboring interstitial position and the ion occupies the lattice site of the displaced atom. This mechanism was originally demonstrated for AgBr.^{3,18} As regards metal oxides it has, for instance, been shown to be apply to transport of interstitial iron ions in single crystals of Fe_3O_4 .¹⁹

The vacancy and interstitialcy mechanisms are the ones that are generally considered in metal oxides, but other, more special, mechanisms may apply in special cases. By way of example, the diffusion of lithium in rutile parallel to the *c*-axis has been reported to be larger by a factor of 10^8 than that perpendicular to the *c*-axis.²⁰ Crystallographically this observation can be explained by assuming that the diffusion takes place along channels in the rutile structure in the *c*-direction. This mechanism has been termed "chimney

diffusion.²¹ Other structures may also provide channels for rapid diffusion of small atoms.

The diffusion mechanism of more complex defect clusters, e.g., in wustite, is still a matter of conjecture. The motion of a 4:1 cluster will require two distinct jumps in close sequence, and one may ask if the probability of such sequenced jumps is sufficiently high to explain the rapid diffusion that is found in wustite.²² Another point of view is that the defect clusters coexist in a dynamic equilibrium with single defects and that the overall diffusion processes really involve diffusion of single defects. Further studies are necessary to clarify this question.

Diffusion Coefficients

Vacancy Diffusion

Diffusion in crystalline solids involves jumps of atoms, ions and defects between definite sites in the crystal structure. In description of atomic diffusion statistical random-walk models are used to relate how far atoms will move from their original sites after having made a large number of jumps. Through this approach the self-diffusion coefficient (the diffusion of the native, constituent atoms in an homogeneous oxide) for vacancy diffusion in a cubic structure can be expressed by^{1-3,23,24}

$$D = \alpha a_0^2 \omega N_d \quad (16)$$

where α is a geometrical factor, a_0 the lattice parameter, ω the jump frequency of an atom or ion to an adjacent vacancy and N_d is the fraction of the total number of lattice sites that are vacant.

The mole fraction N_d may be expressed as

$$N_d = \exp\left(-\frac{\Delta G_d^\circ}{RT}\right) = \exp\left(\frac{\Delta S_d^\circ}{R}\right) \exp\left(-\frac{\Delta H_d^\circ}{RT}\right) \quad (17)$$

where ΔG_d° , ΔS_d° and ΔH_d° denote the standard molar free energy, entropy and enthalpy of formation of the defects, respectively. If the concentration of defects in oxides is a function of the oxygen activity, an activity dependent term must also be included in this equation.

On the basis of the theory of activated complexes, ω may be expressed as

$$\omega = K v \exp\left(-\frac{\Delta G_m}{RT}\right) = K v \exp\left(\frac{\Delta S_m}{R}\right) \exp\left(-\frac{\Delta H_m}{RT}\right) \quad (18)$$

where K is the transmission coefficient which represents the probability that an atom with sufficient energy to make a jump actually completes the jump and ν is a frequency factor. ΔG_m is the free energy change for the activated process and ΔS_m and ΔH_m the corresponding changes in entropy and enthalpy.

By combining Eqs. (16)–(18) the expression for the self-diffusion coefficient is given by

$$\begin{aligned} D &= \alpha \nu a_0^2 K \exp \left[\left(\frac{\Delta S_d^\circ + \Delta S_m}{R} \right) \exp \left(-\frac{\Delta H_d^\circ + \Delta H_m}{RT} \right) \right] \\ &= D_0 \exp \left(-\frac{\Delta H_d^\circ + \Delta H_m}{RT} \right) \end{aligned} \quad (19)$$

From this equation the activation energy is determined by the enthalpies of both the defect formation, ΔH_d° , and the motion of the defects, ΔH_m . However, when the experiment is carried out in such a manner that the defect concentration is constant and independent of temperature (e.g., by doping), then the activation energy is given by only that for the motion of the defects.

For dilute solutions of defects the diffusion coefficient for the defect, D_d , is not dependent on the defect concentration but is related to the random diffusion coefficient for the atom or ion through the equation

$$D = D_d N_d \quad (20)$$

It is also important to realize that when the diffusivity is measured by use of tracers, the tracer self-diffusion coefficient, D_{tr} , is not necessarily equal to that of the atoms but they are related through the correlation coefficient, f :

$$D_{tr} = fD \quad (21)$$

This coefficient allows for the fact that successive jumps of a tracer atom may be correlated when defects move randomly in a structure. The value of f depends on the lattice geometry and the diffusion mechanism, and measurements of f may thus be used to establish the diffusion mechanism in a solid.

Hydrogen Diffusion

Hydrogen that is dissolved in oxides as hydroxide ions on normal oxygen site diffuses by moving from one oxygen site to a neighboring oxygen site.^{15,16}

EXAMPLES OF DEFECTS AND DIFFUSION IN SOME METAL OXIDES

The literature contains innumerable references to studies of defects and defect-dependent properties of metal oxides. A general feature of the overall results and their interpretation is that there exist considerable discrepancies and even confusion. For most oxide systems it has not as yet proved possible to advance defect models that provide an overall consistent interpretation of nonstoichiometry and transport properties such as electrical conductivity, diffusion a.o. There are probably many reasons for this: insufficient characterization of microstructure and porosity of specimens, of impurity contents before and after the experimental studies, of possible effects of water vapor/hydrogen defects on the defect structure, insufficient control of activities of oxygen and other components in the ambient gas a.o. In interpretation of the defect structures of metal oxides it is also common to use ideal, dilute solution models that do not take into account such aspects as defect interactions and associations. Studies of diffusional properties also require careful experimental work where it is important to delineate the relative importance of lattice diffusion, dislocation and grain boundary diffusion. There are few comprehensive data available of such aspects. In view of this state of affairs and to illustrate some main features, defect structures and diffusional properties will only be discussed for a few selected metal oxides in the following.

Cobalt Monoxide, Co_{1-y}O

Cobalt monoxide is one of the most extensively studied oxides and data are available on nonstoichiometry, electrical conductivity, self-diffusion for both cobalt and oxygen, high-temperature creep a.o. In the author's opinion this is probably the best-understood oxide at this stage of development.^{1,3}

CoO is approximately stoichiometric at its decomposition pressure which ranges from 10^{-12} atm O_2 at 950°C to 10^{-6} atm at 1450°C . At higher oxygen activities the oxide is metal deficient and the concentration of cobalt vacancies increases with increasing oxygen pressure. As a measure of the nonstoichiometry and defect concentration, the value of y in CoO_{1-y} is about 0.01 at 1150°C and 1 atm O_2 .^{1,3,25-28}

At near-atmospheric oxygen pressures ($1-10^{-4}$ atm O_2) and in the temperature range $950-1350^\circ\text{C}$ the nonstoichiometry, electrical conductivity and self-diffusion coefficient of cobalt is approximately proportional to $p_{\text{O}_2}^{1/4}$. This oxygen pressure dependence is not exactly obeyed over the whole temperature and oxygen pressure region, thus close to atmospheric oxygen pressure and at the lower temperatures a somewhat higher oxygen pressure dependence tending towards $p_{\text{O}_2}^{1/3}$ is observed.

Nonstoichiometry has been studied by thermogravimetry. Under conditions where the deviation is proportional $p_{\text{O}_2}^{1/4}$, the value of the equilibrium constant for formation of cobalt vacancies with one effective charge (K_1 in Eqs. (2) and (4) is given by

$$K_1 = 10^{-2} \exp\left(-\frac{54 \text{ kJ/mol}}{RT}\right) \quad (22)$$

where the defect concentration is expressed in terms of y and Co_{1-y}O is given by (1). Thus the standard enthalpy of formation of singly charged cobalt vacancies according to Eq. (1) is $\Delta H_1^\circ = 54 \text{ kJ/mol}$.

Under conditions when the electrical conductivity is proportional to $p_{\text{O}_2}^{1/4}$, the product of the electrical conductivity (conductivity due to the electron holes) and the absolute temperature is reported to have an activation energy of 56 kJ/mol :¹

$$\sigma T = \text{constant} \cdot \exp\left(-\frac{56 \text{ kJ/mol}}{RT}\right) \quad (23)$$

From Eqs. (4), (5) and (22) the activation energy (enthalpy) for the temperature dependence of the electron hole concentration is $54/2 = 27 \text{ kJ/mol}$. The difference between the observed activation energy and the enthalpy associated with the concentration of electron holes, $56 - 27 = 29 \text{ kJ/mol}$ is concluded to reflect the mobility of the electron holes, μ_h . Furthermore, this implies that electron holes are small polarons that move by a hopping mechanism.

The mobility can be calculated from the nonstoichiometry and conductivity data. By way of example, at 1350°C and $p_{\text{O}_2} = 0.1 \text{ atm}$ the value of y is $8 \cdot 10^{-3}$ and the conductivity $25 \text{ ohm}^{-1} \text{ cm}^{-1}$ and from the relation $\sigma = e\mu_h[h^*]$ the value of the mobility is $0.38 \text{ cm}^2 \text{ s}^{-1} \text{ volt}^{-1}$.

Reported values of the cobalt tracer diffusion coefficient in CoO in air at temperatures from 1000 to 1600°C are shown in Fig. 4.^{25,28-30} The results are in remarkably good agreement and the tracer self-diffusion coefficient can be expressed as

$$D_{\text{Co}}^{\text{tr}} = 5 \cdot 10^{-3} \exp\left(-\frac{160.6 \text{ kJ/mol}}{RT}\right) \quad (24)$$

The self-diffusion coefficient decreases with decreasing oxygen pressure and at $5 \cdot 10^{-3} \text{ atm. O}_2$, where the self-diffusion coefficient is approximately

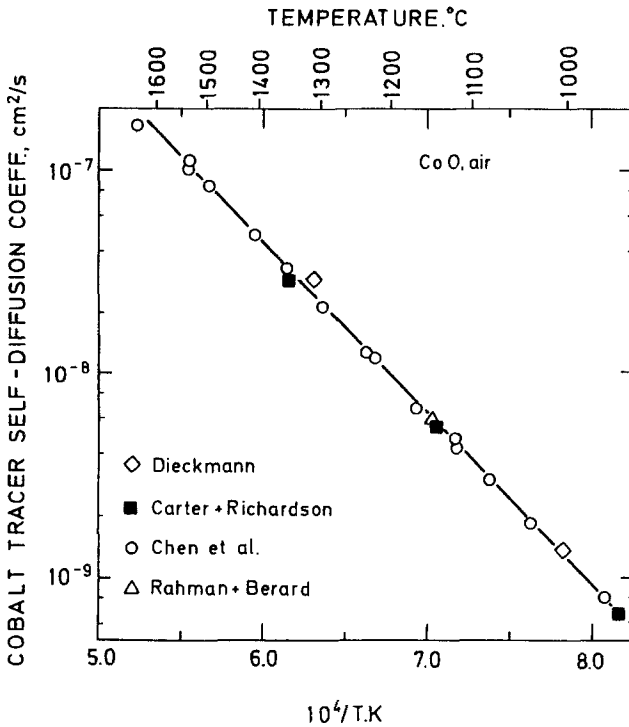


Fig. 4. Literature values of the cobalt tracer self-diffusion coefficient in CoO in air or $p_{O_2} = 0.21$ atm as a function of the reciprocal absolute temperature. Results after Carter and Richardson,²⁵ Dieckmann,²⁸ Chen *et al.*,²⁹ and Rahman and Berard.³⁰

proportional to $p_{O_2}^{1/4}$, the value is given by

$$D_{Co}^{tr} = 1.66 \cdot 10^{-3} \exp\left(-\frac{166 \text{ kJ/mol}}{RT}\right) \quad (25)$$

CoO has the NaCl structure, and for vacancy diffusion in this structure the value of the correlation coefficient is $f=0.78$. Thus the self-diffusion coefficient for random cobalt diffusion is given by

$$D_{Co} = \frac{1}{0.78} D_{Co}^{tr} \quad (26)$$

If one makes use of Eq. (20) the D_{Co} is related to the self-diffusion coefficient for the vacancies themselves, $D_{V'_{Co}}$, and the vacancy concentration, y , i.e.,

$$D_{Co} = y \cdot D_{V'_{Co}} \quad (27)$$

By combining the proper values of D_{Co} and y , the value of the self-diffusion coefficient for the vacancies is given by

$$D_{V_{\text{Co}}} = 10^{-1} \exp\left(-\frac{134 \text{ kJ/mol}}{RT}\right) \quad (28)$$

Self-diffusion of oxygen in CoO. It is smaller than that of the cobalt diffusion by several orders of magnitude.^{31,32} It has been reported to increase with increasing oxygen activity and this suggests that the important oxygen defects are oxygen interstitials.

NICKEL OXIDE, Ni_{1-y}O

Ni_{1-y}O and Co_{1-y}O have similar properties. Both oxides possess the halite structure and both are metal-deficient. However the metal deficiency in NiO, y in Ni_{1-y}O , is 10–100 times smaller than that in Co_{1-y}O . At 1 atm O_2 at high temperatures (900–1300°C) the value of y can be expressed as³

$$y = \text{const} \cdot \exp\left(-\frac{80 \text{ kJ/mol}}{RT}\right) \quad (29)$$

By way of example, the value of y at 1 atm O_2 at 900°C is approximately $y = 10^{-4}$. This small deviation from stoichiometry and the correspondingly small defect concentrations make it necessary to use high-purity samples in order to avoid effects of impurities. Thus for $y = 10^{-4}$ a level of aliovalent impurities of 100 ppm may greatly affect the observed defect-dependent properties.

The many studies of the electrical conductivity show discrepancies. The oxide is a p -conductor like CoO and the conductivity increases with increasing oxygen pressure. However, the oxygen pressure dependence reported by various investigators range from $p_{\text{O}_2}^{1/6}$ to $p_{\text{O}_2}^{1/4}$ and these oxygen pressure dependencies suggest that the nickel vacancies are partially singly and doubly charged.^{1,3}

Studies of nickel tracer self-diffusion in NiO by Volpe and Reddy³³ show that the oxygen pressure dependence ranges from $p_{\text{O}_2}^{1/5}$ to $p_{\text{O}_2}^{1/6}$. This again suggests that the vacancies are singly and doubly charged. Studies by Atkinson and Taylor³⁴ at 1 atm. O_2 are in good agreement with those of Volpe and Reddy and for the temperature range 500–1400 the diffusion coefficient can be expressed as

$$D_{\text{Ni}}^{\text{tr}} = 2.2 \cdot 10^{-2} \exp\left(-\frac{245 \text{ kJ/mol}}{RT}\right) \quad (30)$$

As the enthalpy associated with the value of γ amounts to 80 kJ/mol, the activation energy for the mobility of the nickel vacancies amounts to $245 - 80 = 165$ kJ/mol. As mentioned above, the corresponding value for cobalt vacancies is 135 kJ/mol.

The self-diffusion of oxygen is smaller than that for nickel by several orders of magnitude.³⁵⁻³⁷ It has also been reported that self-diffusion of oxygen increases with increasing oxygen pressure and if this is correct, this result suggests that the oxygen defects are oxygen interstitials.

NiO appears to be the only oxide for which a comprehensive study has been made of the importance of grain boundary and dislocation diffusion of nickel relative to that of lattice diffusion. The study was made by Atkinson and Taylor³⁴ and their results are shown graphically in Fig. 5. The dislocation diffusion coefficient was reported to have the value

$$D_{\text{disl}} = 0.26 \exp\left(-\frac{192 \text{ kJ/mol}}{RT}\right) \quad (31)$$

and that for grain boundary diffusion

$$D_{\text{gb}}\delta = 3 \cdot 10^{-8} \exp\left(-\frac{171 \text{ kJ/mol}}{RT}\right) \quad (32)$$

where δ is the grain boundary width which they estimated to be about $7 \cdot 10^{-8}$ cm.

The relative importance of lattice, grain boundary and dislocation is similar to that found in metals. Atkinson and Taylor also found that nickel diffusion along grain boundaries and dislocations had approximately the same oxygen pressure dependence as that for lattice diffusion. That suggests that the diffusion along grain boundaries and dislocations in their high-purity specimens takes place by the vacancy mechanism.

CHROMIA, Cr₂O₃

Chromia and chromia-rich oxides form protective scales on a large number of high-temperature alloys, the so-called chromia formers. For this reason numerous studies have been carried out in order to contribute to the elucidation of the defect structure and transport properties of chromia. Even so an unequivocal interpretation of the properties of chromia has as yet proved elusive.^{1,3}

Nonstoichiometry in Cr₂O₃ is very small and no reliable data have been reported for temperatures where the oxide has its primary uses (<1200°C).^{1,3}

At high temperatures, >1000–1200°C depending on the purity of the chromia, the oxide is an intrinsic electronic conductor.^{17,38} Under these

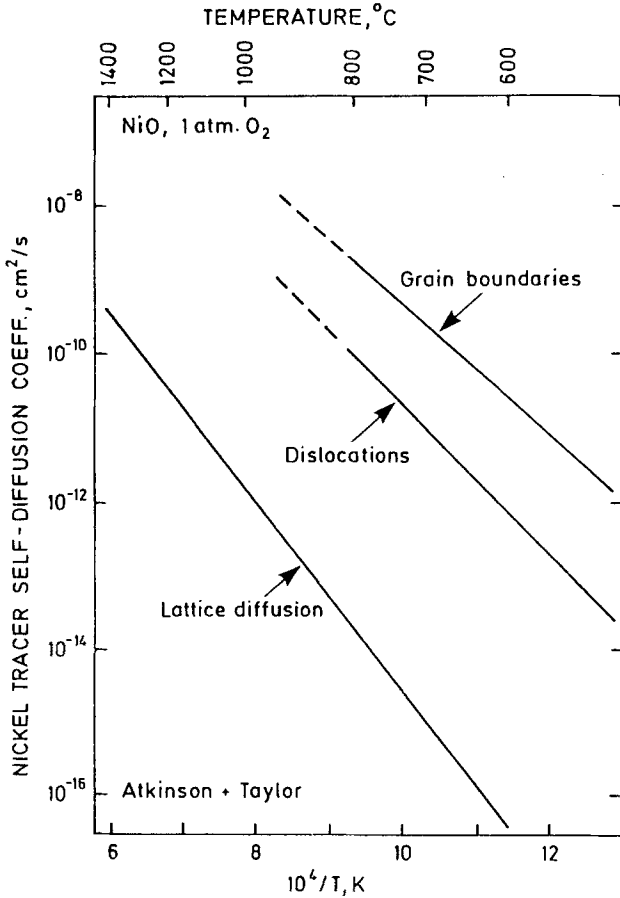


Fig. 5. The nickel tracer self-diffusion for lattice, grain boundary and dislocation diffusion in NiO. Results after Atkinson and Taylor.³⁴

conditions the electroneutrality condition is given by

$$[e'] = [h^{\bullet}] = K_i^{1/2} \tag{33}$$

At lower temperatures it is concluded that the oxide is an extrinsic conductor. If the dominant impurities have one negative effective charge, e.g., Ml'_{Cr} , and these are compensated by the formation of electronic defects, the oxide is a *p*-type conductor. If the dominant impurity or dopant has a positive effective charge, the oxide becomes an *n*-type conductor. These aspects have recently been discussed in more detail elsewhere.³⁸

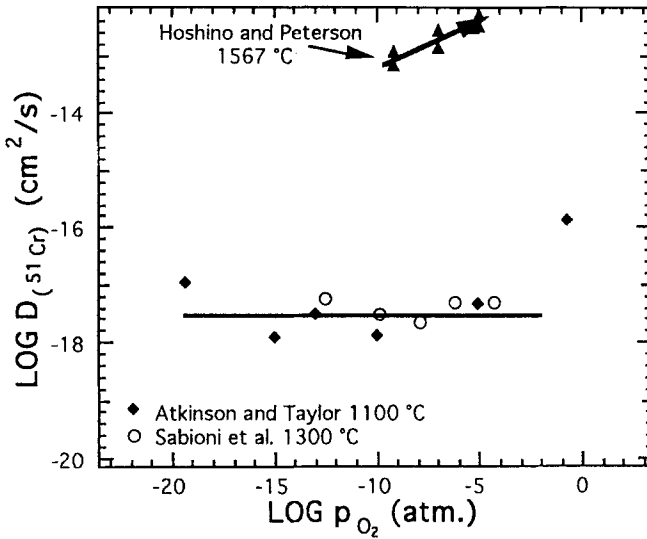


Fig. 6. Literature values of the chromium self-diffusion coefficient in single crystals of chromia. Results after Hoshino and Peterson (1567°C),⁴⁰ Sabioni *et al.* (1300°C)⁴¹ and Atkinson and Taylor (1100°C).³⁹

Self-diffusion of both chromium and oxygen have been studied in mono- and polycrystalline chromia. Reported values of self-diffusion for chromium in single crystalline chromia are summarized in Fig. 6.³⁹⁻⁴¹ The results of Atkinson and Taylor³⁹ at 1100°C and by Sabioni *et al.* at 1300°C⁴¹ are of the same magnitude. The Atkinson and Taylor data suggest that the self-diffusion coefficient goes through a minimum at about 10^{-10} – 10^{-15} atm O_2 . If these results reflect lattice diffusion, this indicates that the dominant type of chromium defect change with oxygen pressure, e.g., from chromium interstitials at the lower oxygen activities to chromium vacancies at near-atmospheric oxygen activities. Another important feature is that the chromium self-diffusion coefficient is extremely small and has a value of about 10^{-17} $cm^2 s^{-1}$. If an average diffusion distance is estimated using the relation $x \sim (Dt)^{1/2}$, one finds that the value of x is approximately 20 Å (2 nm) for a diffusion anneal of 1 h.

Oxygen self-diffusion has also been measured in both single crystals and polycrystalline chromia.^{1,42-45} The oxygen self-diffusion coefficient in single crystals is—as for chromium self-diffusion—of the order of 10^{-17} $cm^2 s^{-1}$ at 1100–1300°C.^{44,45} For polycrystalline materials the reported values are several orders of magnitude larger than for single crystals, and this is probably due to much faster grain boundary diffusion in polycrystalline material.⁴⁵

These small values suggest that long time periods will be necessary to reach point defect equilibria in chromia, and recent results have also demonstrated that it even takes weeks to equilibrate highly porous chromia specimens at 1200°C.¹⁷ In view of this slow diffusion, it is doubtful if it is possible in practice to reach and measure equilibria involving chromium and oxygen point defects in chromia.

A possible reason for the slow diffusion is that the point defect concentrations are small due to the predominant electronic equilibrium. Let us illustrate this by formation of chromium vacancies and the corresponding defect equilibrium:



$$[\text{V}_{\text{Cr}}^{3'}] = K_{\text{V}_{\text{Cr}}}\text{[h}^{\bullet}]^{-3}p_{\text{O}_2}^{3/4} \quad (35)$$

If the dominant defect equilibrium is that of the intrinsic electronic equilibrium and the electroneutrality condition can be approximated by $[\text{e}'] = [\text{h}^{\bullet}] = K_i^{1/2}$, then the concentration chromium vacancies is given by

$$[\text{V}_{\text{Cr}}^{3'}] = K_{\text{V}_{\text{Cr}}}K_i^{-3/2}p_{\text{O}_2}^{3/4} \quad (36)$$

Qualitatively, the relatively high concentration of electronic defects reduces the concentration of point defects. This may be illustrated by a Kröger-Vink diagram proposed for chromia where it is assumed that intrinsic electronic equilibrium dominates and that the point defects comprise oxygen and chromium interstitials and vacancies (Fig. 7). Near the stoichiometric composition the defect concentrations may be extremely low, and accordingly under these conditions diffusional transport will become correspondingly slow.

As discussed above, hydrogen defects also becomes an important aspect of the defect structure of chromia in ambient atmospheres containing hydrogen.

Defects and Diffusional Transport in Other Oxides

From the point of view of high-temperature corrosion, alumina (Al_2O_3) and silica (SiO_2) are also particularly important in achieving high corrosion resistance of alloys and these are. Both oxides form highly protective scales on alloys. Protective scales of both oxides provide even better protection than chromia at high temperatures.

Despite its importance in high-temperature corrosion, the defect structure of $\alpha\text{-Al}_2\text{O}_3$ is not definitely known.^{1,3} Studies of oxygen diffusion in single crystals of alumina and of oxygen and aluminum in polycrystalline material have been reported. Oxygen diffusion in polycrystalline alumina is faster than in single crystals, in all probability due to more rapid grain boundary diffusion in the polycrystalline material. The slow diffusion in alumina is at least partially due to the low point defect concentrations in

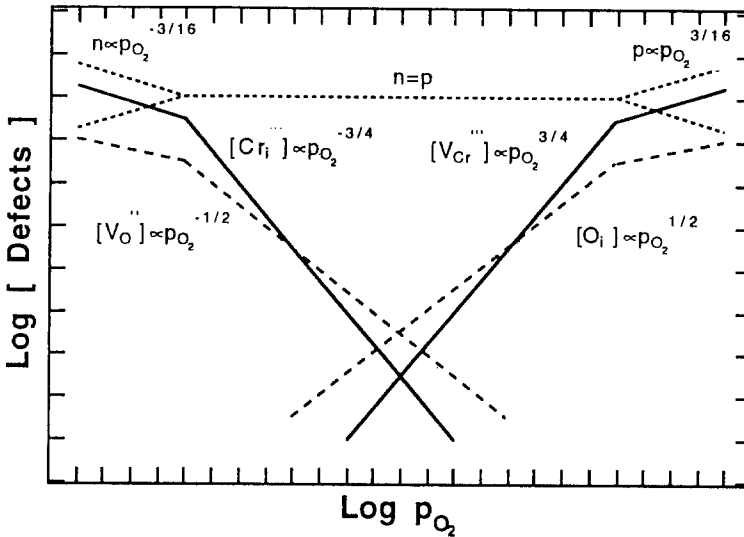


Fig. 7. Kröger-Vink diagram involving chromium and oxygen vacancies and interstitials for a defect structure situation in chromia where intrinsic electronic equilibrium predominates at near-stoichiometric compositions.

this oxide. Qualitatively, this is, in turn, due to the high lattice energy and a large band gap (about 10 eV) for alumina.

In the oxidation of silicon and of many silicides at high temperatures the oxide scale consists of amorphous silica or quartz glass. The parabolic rate constant for the oxidation of silicon is reported to be proportional to p_{O_2} and this in turn suggests that the diffusing species through the silica layer are oxygen molecules that are moving without interacting with the silica network.¹⁸ O tracer diffusion studies have confirmed that the oxidation takes place by inward oxygen diffusion.⁴⁶

The presence of water vapor in the ambient atmosphere increases the oxidation rate of silicon and the oxidation rate increases with increasing water vapor content. This is illustrated in Fig. 8 which compares the parabolic rate constant for oxidation of silicon in dry and wet oxygen.⁴⁶ The detailed mechanistic aspects of this effect of water vapor is not understood, but in gross terms the increased rate of diffusional transport in the presence of water vapor can be correlated with the modifying effect that OH groups have in breaking up the network structure of silica.

Diffusional Transport in Oxides and Growth of Oxide Scales

For many years after C. Wagner in 1933 advanced his theory for high-temperature parabolic oxidation of metals it was assumed in interpretations

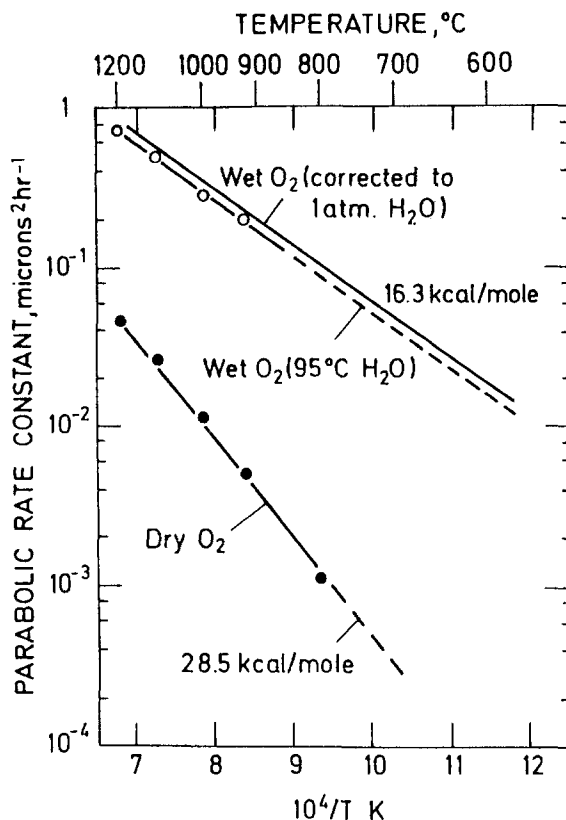


Fig. 8. The parabolic rate constant for oxidation of silicon in dry and wet oxygen. Results after Deal and Grove.⁴⁶

of oxidation mechanisms that the solid-state diffusional transport comprised lattice diffusion only. However, the Wagner theory only represents an ideal case in which it is assumed that the scales are dense and continuous and adhere to the metal over the entire metal surface. As briefly described above scale growth involves many other aspects such as formation of pores and cavities, microcracks and microchannels in the scales, a.o.

With respect to solid-state diffusional transport in growing oxide scales it seems safe to conclude that lattice diffusion is the predominating mode of diffusion in scales with relatively large defect concentrations, e.g, in Fe_{1-y}O, CoO at high temperatures (>800°C), NiO at very high temperatures (>1200°C) a.o. For oxides with low defect concentrations and correspondingly slow lattice diffusion, grain boundary diffusion becomes the important mode of diffusion in the scales. This has, for instance, been demonstrated

for the oxidation of nickel; in this case Atkinson and Taylor have demonstrated the importance of rate-determining grain boundary diffusion of nickel at reduced temperatures ($<1000^{\circ}\text{C}$).³⁴

In all probability grain boundary diffusion is also the rate-determining mode of diffusional transport in growth of chromia and alumina scales. When these oxides grow as scales on alloys, their grain boundaries are probably enriched in atoms or have segregations of oxides of other components from the alloy. Thus the grain boundaries of chromia and alumina scales grown on different alloys may in these terms have quite different compositions and diffusional properties. Thus to explain and interpret diffusional properties of oxides and their growth as oxide scales it is necessary to have a much better understanding of the compositions and "structures" of grain boundaries in oxides. This represents an important challenge for the future in the field of "defects and transport properties in oxides."

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