ISSN : 0974 - 7486 Volume 9 Issue 12

Trade Science Inc.

Materials Science

An Indian Journal

Feature Article

MSAIJ, 9(12), 2013 [471-476]

Semi-empirical calculation of coefficients of bulk oxygen self-diffusion in binary metal oxides

Evgenia Vykhodets

Ural Federal University, 620002, Yekaterinburg, (RUSSIA)

E-mail: Evgenia.vykhodets@gmail.com

ABSTRACT

The results of semi-empirical calculations of the coefficients of bulk oxygen self-diffusion in binary metal oxides are presented. The vacancy mechanism of oxygen ion diffusion using thermal equilibrium and structural vacancies in the oxygen sublattice of these oxides is considered. The calculations are based on the empirical relationships for vacancy formation and migration enthalpies in oxide systems, which are obtained by analyzing the most reliable experimental data on bulk oxygen diffusion in oxides. Using the proposed model, the diffusion coefficients can be calculated with accuracy of one order of magnitude and the diffusion activation enthalpy – with an error of about 10%.

KEYWORDS

Diffusion;
Oxide;
Structural vacancies;
Activation enthalpy.

Metal oxides are important functional materials, and, therefore, the experimental data on their oxygen self-diffusion coefficients are of interest. This issue is considered in a large number of studies. However, the available experimental data are scattered and for many oxide systems they are lacking. Besides, there are no reliability criteria for such data. This state of the research of diffusion in binary oxides was noted in the reviews already in 1968 and 1972[1,2], but no radical changes took place since then.

The lack of data concerning oxygen diffusion coefficients D is due mainly to a very strong effect of impurities in the cationic subsystem of the oxides on the values of D. In the absence of structural vacancies in the oxygen sublattice, the temperature dependence of diffusion coefficients D is described by the Arrhenius expression[2]

$$D = D_0 \exp(-Q / kT) \text{<Eq 1>} \quad \textbf{(1)}$$

where D_0 is a frequency factor; Q is the activation enthalpy of diffusion; k is the Boltzmann constant; and Ò is absolute temperature. Usually, it is assumed[2] that

$$Q = Q_f + Q_m \quad \textbf{(2)}$$

where Q_f and Q_m are oxygen vacancy formation and migration enthalpies.

When an oxide is doped with cations having lower valance than the basis metal, structural vacancies are formed in the oxygen sublattice by the charge compensation mechanism, and in this case the temperature dependence of diffusion coefficients is of a more complicated character than that described by expression (1). Figure 1 displays a typical D (T) dependence for such case[1], where three temperature intervals can be distinguished. At $T > T_1$, diffusion is due mainly to thermal equilibrium vacancies, and the $D(T)$ dependence is described by expression (1). At $T < T_2$, diffusion is due mostly to structural vacancies, and the $D(T)$ dependence in this interval is also described by the Arrhenius expression, but the frequency factor and the activation enthalpy have other values than in expression (1). For $T < T_2$, the $D(T)$ dependence takes the form[2]

$$D = c_V D_{os} \exp(-Q_m / kT) \quad \textbf{(3)}$$

where c_V is the concentration of structural vacancies in the oxygen sublattice of the oxide; and $c_V D_{0s}$ is the frequency factor for diffusion due to structural vacancies. Expressions (1, 2) are written neglecting the correlation effects. Relationships $D_{0s} H'' D_0$ and $c_V D_{0s}$ « D_0 are usually true. At $T_2 < T < T_1$, the contributions to D from diffusion by thermal equilibrium and structural vacancies become comparable, and in this case the numerical values of diffusion activation energy will be intermediate between Q and Q_m. By analogy, the frequency factor in this case will have intermediate values between D_0 and $c_V D_{0s}$.

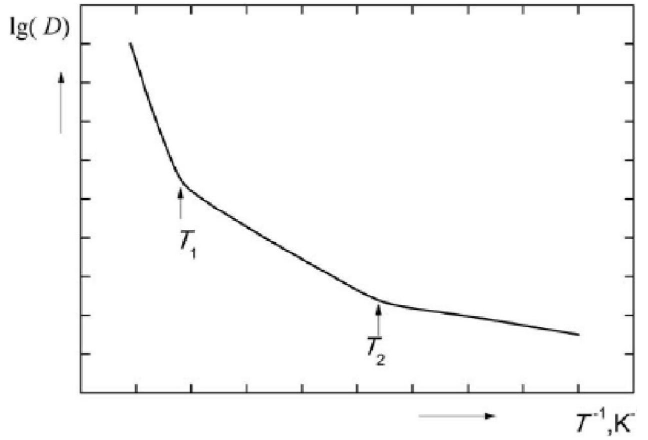

Figure 1 : A typical temperature dependence of bulk oxygen diffusion coefficients for binary oxides containing structural vacancies in the oxygen sublattice[1]

The concentration is of the same order of magnitude as the concentration of impurities in the cationic subsystem of the oxides. Since the value of in binary oxides MO_x is determined by uncontrollable doping of the cationic subsystem of the oxides, the concentration is small. In many cases, the concentration of impurities is so small that it cannot be determined by modern analytical methods. From expressions (1-3) it follows that the diffusion coefficients for one and the same oxide in one and the same temperature interval may differ in different studies by several orders of magnitude only because the values of T_1 and T_2 in those works are different. Usually, in diffusion experiments, the values of these temperatures are not known since they are determined not only by diffusive properties of oxides (parameters Q_f, Q_m, D_0, and D_{0s}), but also by uncontrollable doping of the cationic sublattice. The above analysis is therefore simplified. This discrepancy of data between different works may be caused also by many other reasons, for example, by the contribution to mass transfer associated with diffusion in cracks, grain boundaries, and dislocations, by point defects in the diffusion zone which trap diffusing atoms, as well as by incorrect indirect methods for measuring diffusion coefficients etc.

In this work, we propose a method for calculating the oxygen bulk diffusion coefficients in binary oxides, which is based on expressions (1-3), some theoretical and experimental results for frequency factors in solids, as well as on empirical regularities for enthalpies Q_f and Q_m in metal oxides. The empirical regularities were obtained only from reliable experimental data taking into account two criteria of their reliability. The minimal requirement was the use of the trace elements in diffusion experiments and direct methods for measuring the concentration profiles of tracers after diffusion annealing[3]. In case of oxygen diffusion, ^{18}Î tracers and secondary ionic mass spectrometry (SIMS) or nuclear reaction analysis (NRA) for measuring the concentration profiles were usually used. In the studies of the last 20 years, the experimental data on oxygen self-diffusion in oxides usually meet this requirement.

Numerous studies of diffusion in metals resulted in one more reliability criterion of experimental data. It was first introduced in work[4]. This criterion imposes severe restrictions on the frequency factor value during interstitial diffusion mechanism. Formerly, the Zener theory[4] cast doubt on many experimental data on hydrogen, oxygen, carbon, and nitrogen diffusion in metals, and the results obtained after 1950 were not contradictory to this theory in general[3]. Later, it was established that reliable experimental data on diffusion due to thermal equilibrium vacancies in metals also meet the Zener theory. In our opinion, the concepts of the Zener theory have a general character and can be used also for analysis of coefficients of oxygen bulk diffusion in oxides. Based on the Zener criterion, we considered that only those experimental data are reliable, for which the values of the frequency factor D_0 are within the range from 10^{-7} to 10^{-3} m^2/s. Note that this restriction concerns only the data on diffusion due to thermal equilibrium vacancies and it does not apply to the data on diffusion by structural vacancies. As mentioned above, the frequency factor values during diffusion by structural vacancies are smaller than D_0.

Let us first consider the regularities of the experimental data on migration enthalpy $Q_{m.}$ Expression (3) and Figure 1 show that with an increase in the concentration of structural vacancies, , the temperature range, in which diffusion by oxygen structural vacancies prevails, expands. This is why the most reliable data on migration enthalpy Q_m can be obtained by examining diffusion in oxide systems with a priori high concentrations of structural vacancies, . It is obvious that binary oxides with an uncontrollable content of impurities in the cationic sublattice fail to meet this condition. Typical representatives of oxides with a high concentration of structural oxygen vacancies are YSZ oxides (yttrium-doped cubic zirconium dioxides) and perovskites of the ABO_3 family, where A or B cations are partially replaced by cations with smaller valence. Analysis of experimental diffusion data for these systems showed that in all cases, irrespective of the crystal lattice type and the chemical composition of the oxide, see for example studies[5-10], the values of oxygen bulk diffusion activation enthalpy are close to each other and amount to $Q_m = (1.1\pm0.1)$ eV. In this analysis, only the data obtained by SIMS method were considered. In view of this result, the same value of Q_m is assumed to be typical of all binary metal oxides. In principle, close values of Q_m for different oxides are not surprising. In the elastic model of potential diffusion barrier[3], this result is due to identical radii of diffusing atoms in different crystals and to close values of their elastic constants.

Further, let us consider the regularities of vacancy formation enthalpy Q_f in oxides. Currently, no systematic data on this issue are available. There are several works dealing with empirical correlations between vacancy formation enthalpy and some other well studied properties of oxides, for example, formation and atomization enthalpy of compounds. Based on the analysis of these correlations it was concluded[2] that for different oxides of the same metal, enthalpy Q_f is expected to increase when the value of x in MO_x decreases. In this study, we also examined the correlation between the values of Q_f and x, but found these values from diffusion data taking into consideration expression (2) and the aforesaid result: according to the most reliable investigations, $Q_m = 1.1$ eV for different oxides.

TABLE 1 and Figure 2 demonstrate experimental Q data for binary oxides MO_x. Although a large number of works are devoted to oxygen diffusion in oxides, we used only seven of them for finding the correlation between the values of Q_f and $\tilde{o}$ since only in those works the experimental results meet the above reliability criteria for experimental data. Note that the criteria of experimental data selection consisted in using direct methods for measuring diffusion coefficients and the Zener theory for measuring the frequency factor D_0 during diffusion by thermal equilibrium vacancies. These criteria can hardly be considered very stringent. The absence of representative sampling of experimental data on diffusion by thermal equilibrium vacancies is likely to be due to strong influence of impurities on oxygen diffusion coefficients. Figure 2 exhibits a monotonous dependence of the diffusion activation enthalpy Q (and consequently the vacancy formation enthalpy Q_f) on the value of index x in MO_x. As mentioned above, a similar correlation was predicted in work[2], but there the case in point was oxides of the same metal rather than oxides of different metals. At present, the available data are of course insufficient to make conclusions about the accuracy and universality of the discovered correlations. We can only note that for four oxides MO_2, their diffusion activation enthalpies are close amounting to $Q = (2.5 \pm 0.2)$ eV.

Figure 3 displays temperature dependences of the coefficients of bulk oxygen diffusion D in oxides calculated with expression (1). The calculated data refer to diffusion due to thermal equilibrium vacancies and are given for oxides with the chemical composition MO, $MO_{1.5}$, MO_2, and $MO_{2.5}$. The lower level of the calculated D values approximately corresponds to the minimal values of oxygen diffusion coefficients, which can be measured by modern techniques. This level was achieved in particular in study[10]. The parameters of the temperature dependence (frequency factor D_0 and diffusion activation enthalpy Q) are given in the caption. Note that in all cases, the same value of the frequency factor, $D_0 = 6\cdot10^{-6}$ m^2/s, is used in the calculations. The most reliable calculated results in Figure 3 are likely to be those for the oxides with the chemical composition MO_2. For such oxides, the experimental data of four different studies are listed in TABLE 1 and the divergence between the calculated and experimental data is not greater than one order of magnitude. An important point is that the calculated results presented in Figure 3 can be used as a benchmark when it is impossible to obtain the data on diffusion by thermal equilibrium vacancies experimentally, for example, for oxides in which structural vacancies exist at any temperatures.

TABLE 1 : Parameters of temperature dependence for reliable data on oxygen diffusion coefficients in binary metal oxides

Oxide	Index x in MO_x	Measured temperature interval, °C	Diffusion activation enthalpy Q, Ev	Frequency factor D_0, m^2/s	Reference
CoO	1	1100-1500	4.47	$8.6\cdot10^{-5}$	[11]
Fe_2O_3	1.5	900-1250	3.38	$2.04\cdot10^{-4}$	[12]
ZrO_2	2	450-980	2.29	$2.5\cdot10^{-7}$	[10]
TiO_2	2	900-1300	2.6	$2\cdot10^{-7}$	[13]
IrO_2	2	600-765	2.73	$2.8\cdot10^{-6}$	[14]
ThO_2	2	1099-1644	2.27	$5.67\cdot10^{-7}$	[15]
Nb_2O_5	2.5	800-1200	2.14	$1.72\cdot10^{-6}$	[16]

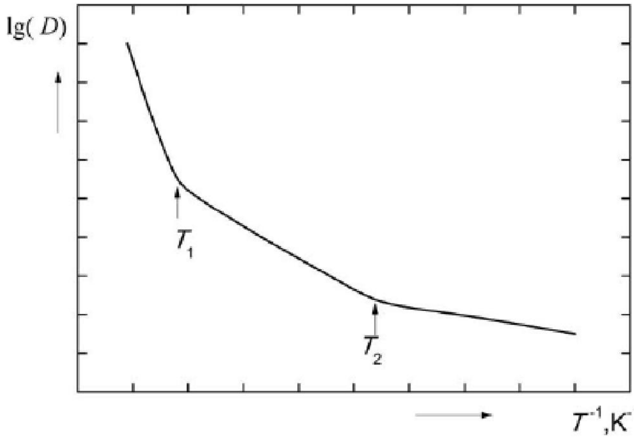

Figure 2: Activation enthalpy Q of oxygen diffusion in binary oxides as a function of the values of index x in MO_x (empirical dependence).

Figure 4 depicts the calculated $D(T)$ dependences for the oxides containing structural vacancies in the oxygen sublattice. These dependences are of the same form as the $D(T)$ curves in Figure 1. Specifically, the calculated results are shown in Figure 4 for MO_2 at = 0 (line 1), =10^{-8} (line 2), and =10^{-6} (line 3). The parameters of the calculated curves are given in the caption. The dotted lines in Figure 4 are the $D(T)$ dependences for the temperature intervals in which the contributions to D due to diffusion by thermal equilibrium vacancies and by structural vacancies are comparable. Note the following main characteristics of the $D(T)$ dependences on Figure 4. In the absence of structural vacancies, the $D(T)$ dependence is due to diffusion by thermal equilibrium vacancies and it is described by the Arrhenius equation. In the presence of structural vacancies, the lg$D$ versus T^{-1} dependences have inflections, and, as mentioned above, three temperature intervals can be distinguished. It is seen that even at very low concentrations of structural vacancies (= 10^{-6}) their influence on the bulk oxygen diffusion coefficients is very strong. In this case, the $D(T)$ dependence corresponding to diffusion by thermal equilibrium vacancies can be observed experimentally only at temperatures $T > T_3$ H" 1200 K. At lower temperatures, the $D(T)$ values in the oxides containing structural vacancies will be higher than those in the oxide without impurity atoms in the cationic sublattice. As the temperature lowers, the ratios of the corresponding diffusion coefficients increase. For example, at temperatures below 700 K these ratios will be 4 orders of magnitude or greater. From Figure 3 it is obvious that the effect of impurities on the oxygen diffusion coefficients increases when the index x in MO_x decreases. In the framework of the discussed model for oxides with the chemical composition MO, diffusion by thermal equilibrium vacancies at = 10^{-6} can be observed experimentally only at $T > 2500$ K.

The above analysis shows that the experimental values of D will correspond to oxygen bulk diffusion by thermal equilibrium vacancies only at high temperatures and low concentrations of impurities. In other cases, the experimental D values in real crystals should be higher than in oxides containing no impurities, see Figure 4. Accordingly, the experimental values of diffusion activation enthalpy and frequency factor in real crystals should be lower than in oxides without impurities. In principle, these results can be verified experimentally. In this connection we have analyzed the available literature data on oxygen diffusion coefficients in binary oxides, which were not included in TABLE 1. We considered only the data obtained by direct methods for measuring the concentration profiles of tracers. This condition was considered to be the minimal criterion of reliability of experimental data. No limitations on the frequency factor value were imposed in the analysis. The analysis showed that the above regularities for the diffusion coefficient, activation enthalpy, and frequency factor are not always fulfilled. The experimental data on oxygen diffusion in the binary oxides MgO[17], Cr_2O_3[18], CoO[19], NiO[20], and ZnO[21] did not contradict the model or were in satisfactory agreement with it. At the same time, some other data obtained for UO_2[22], Al_2O_3[23], CdO[24], and ZnO[25] oxides were in conflict with the model. In particular, these works reported overestimated frequency factors: $1.2\cdot10^{-1}$, $2.06\cdot10^{-2}$, $3.8\cdot10^{-2}$, and $6.5\cdot10^{7}$ m^2/s, respectively. Such data may be indicative in some cases of the model inadequacy; for example, the correlation effects were not taken into account. Their consideration may change essentially the theoretical results in case of strong interaction of oxygen ions with impurity atoms. It is not ruled out that some experiments were performed in the conditions when the concentration of structural vacancies was a function of temperature. These issues require additional experimental and theoretical examination.

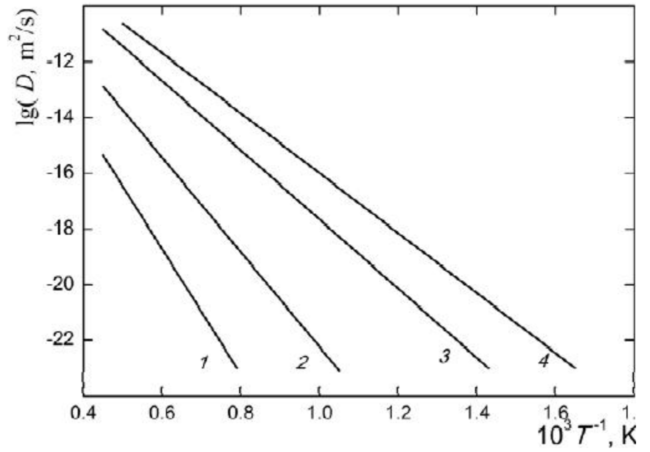

Figure 3 : Results of calculation with expression (1) of the dependence of coefficients of bulk diffusion D on the reciprocal absolute temperature T^{-1} for diffusion by thermal equilibrium vacancies: 1 – MO oxides, $Q = 4.5$ eV; 2 – $MO_{1.5}$ oxides, $Q = 3.4$ eV; 3 – MO_2 oxides, $Q = 2.5$ eV; 4 – $MO_{2.5}$ oxides, $Q = 2.15$ eV; $D_0 = 6\cdot10^{-6}$ m^2/s in all cases.

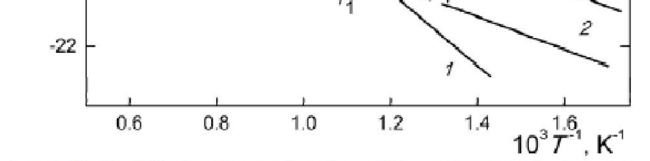

Figure 4 : Coefficients of bulk diffusion D as a function of the reciprocal absolute temperature T^{-1} for MO_2 oxides: 1 – calculation with expression (1) for diffusion by thermal equilibrium vacancies, $Q = 2.5$ eV, $D_0 = 6\cdot10^{-6}$ m^2/s; 2 and 3 – calculation with expression (3) for diffusion by structural vacancies, $D_{0s} = 6\cdot10^{-6}$ m^2/s; $C_V = 10^{-8}$ and 10^{-6} for lines 2 and 3, respectively.

ACKNOWLEDGEMENT

The work was supported by the Russian Foundation for Basic Research (grant 12-03-31736)

REFERENCES

[1] P.A.Harrop; J.Material Science, **3**, 206 **(1968)**.
[2] P.Cofstad; Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides,Wiley-Interscience, NY **(1972)**.
[3] V.B.Vykhodets, T.E.Kurennykh, A.S.Lakhtin, A.Ya.Fishman; Solid State Phenomena, **138**, 119 **(2008)**.
[4] C.A.Wert, C.Zener; Phys. Rev., **76**, 1169 **(1949)**.
[5] M.Runde, J.L.Routbort, J.N.Mondy, S.J.Rothman, C.L.Wiley, X.Xu; Physical Review B, **46**, 3142 **(1992)**.
[6] J.H.Park, K.C.Goretta, N.Murayma; Physica C, **312**, 269 **(1999)**.
[7] M.C.Kim, S.H.Park, H.Haneda, J.Tanaka, T.Mitsuhasi, S.Shirasaki; J.Materials Science Letters, **9**, 102 **(1990)**.
[8] P.S.Manning, J.D.Surman, J.A.Kilner; Solid State Ionics, **93**, 125 **(1996)**.
[9] Solmon,C.Monty, M.Filal, G. Petot-Ervas, C. Petot; Solid State Phenomena, **41**, 103 **(1995)**.
[10] U.Brossman, G.Knoener, H.-E.Schaefer, R.Wurschum; Rev.Adv.Mater.Sci., **6**, 7 **(2004)**.
[11] J.L.Routbort, S.J.Rothman; J. of Physics and Chemistry of Solids, **47**, 883 **(1986)**.
[12] W.S.Hagel; Trans AIME, **236**, 179, **(1966)**.
[13] R.Haul, G.Dumbgen; J.Physics and Chemistry of Solids, **26**, 1 **(1965)**.

[14] C.U.Pinnow, I.Casko, N.Nagel, T.Mikolajick, C.Dehm, F.Jahnel, M.Seibt, U.Geuer, K.Samwer; O_2, J. Applied Physics, **91**, 1707 **(2002)**.

[15] K.Ando, J.Oishi, T.Tsuji, Y.Hidaka, K.Shiba, J.Nuclear Materials, **120**, 99 **(1984)**.

[16] W.K.Chen, R.A.Jackson; J.Chemical Physics, **47**, 1144 **(1967)**.

[17] Oishi, W.D.Kingery; J.Chem.Phys., **33**, 905 **(1957)**.

[18] W.C.Hagel; J.Am.Ceram.Soc., **48**, 70 **(1965)**.

[19] W.K.Chen, R.A.Jackson; J.Phys.Chem.Solids, **30**, 1309 **(1969)**.

[20] C.Dubois, C.Monty; J. Philibert,Phil.Mag., **46**, 419 **(1982)**.

[21] G.W.Tomlins, J.L.Routbort, T.O.Mason; J.Am.Ceram.Soc., **81**, 869 **(1998)**.

[22] A.B.Auskern, J.Belle; J.Nucl.Mater., **3**, 311 **(1961)**.

[23] D.Prot, C.Monty, Phyl.Mag., **73**, 899 **(1996)**.

[24] R.Haul, D.Just; J.Appl.Phys., **33**, 487 **(1962)**.

[25] W.G.Moore, E.J.Williams; Disc.Farad.Soc., **28**, 86 **(1959)**.