A model for double oxidation

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1 The model

This is 1D model of the vacancy-mediated oxygen diffusion on a fixed lattice. There are three species, ^{16}O, ^{18}O and vacancies. Electric fields, electrons and holes, cation diffusion and electric fields are all ignored in this preliminary version. Our model, shown schematically in Fig. 1, assumes that the atoms and vacancies lie on planes on (x, z), and can hop into neighbouring planes at a distance $\pm a$ along the y axis.
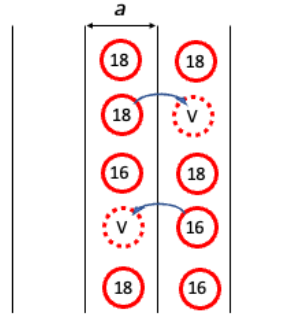

Figure 1: Schematic diagram of the simplest model with vacancy-mediated hops.

$p_{16}(y)$ and $p_{18}(y)$ denote the probability that a site at y is occupied by ^{16}O or ^{18}O respectively. It is occupied by a vacancy with probability p_V. The sum rule for any site is therefore

$$p_V(y) + p_{16}(y) + p_{18}(y) = 1. \tag{1}$$

It will also be useful to convert the probabilities of site occupancy to a number per unit volume, which is achieved by multiplying the site occupancy for species i, p_i, by the number of sites per unit volume, $1/\Omega$. Thus the number of i per unit volume is

$$\rho_i = p_i/\Omega. \tag{2}$$

We consider the flux of oxygen isotopes and vacancies, a positive value means the flux is to the right, in the $+y$ direction.

Now we introduce jump probabilities in an infinitesimal interval of time dt:

$p \times dt$ = probability that, if a site is occupied by an atom of oxygen and a vacancy occupies a site to the right, the atom will jump into the vacancy in the time interval dt.

For simplicity we assume the hopping probabilities are equal for the two isotopes. If $n_i^+(y)$ atoms on an area A hop to the right and $n_i^-(y)$ hop to the left per second, the flux $J_i(y)$ of either isotope is given by

$$J_i(y) = [n_i^+(y) - n_i^-(y + a)]/A.$$

(3)

Now we can express the numbers hopping as follows. The number of sites on a plane of area A is

$$N = A \cdot a/\Omega \tag{4}$$

where, as in (2), Ω is the volume per site in the lattice. Hence

$$n_i^+(y) = p \times p_i(y)Np_V(y + a), \tag{5}$$
$$n_i^-(y + a) = p \times p_i(y + a)Np_V(y) \tag{6}$$

from which, inserting (4), (5) and (6) into (3), to first order in the Taylor expansion in a:

$$J_i(y) = \frac{pa}{\Omega}\left[p_i(y)p_V(y) + p_i(y)\frac{\partial p_V(y)}{\partial x}a - [p_i(y)p_V(y) + \frac{\partial p_i(y)}{\partial x}a\, cv(y)]\right]$$
$$= \frac{pa^2}{\Omega}\left[p_i(y)\frac{\partial p_V(y)}{\partial x} - \frac{\partial p_i(y)}{\partial x}p_V(y)\right]. \tag{7}$$

2   Fluxes and the oxygen diffusion coefficient

Let's now make the connection between the microscopic properties $\{p, a, \Omega\}$ and the diffusion coefficient of oxygen. Firstly, note that we can interpret the label i in eqn. (7) as referring to ^{16}O, ^{18}O, or the total oxygen. For the total oxygen we have from the sumrule (1)

$$p_V(y) + p_O(y) = 1, \tag{8}$$

and hence

$$\frac{\partial p_V}{\partial y} + \frac{\partial p_O}{\partial y} = 0. \tag{9}$$

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Using these relations, we can replace the terms involving p_V in eqn. (7) to express J_O as

$$\begin{aligned}
J_O(y) &= -\frac{pa^2}{\Omega}\frac{\partial p_O(y)}{\partial y} \\
&= -pa^2\frac{\partial \rho_O(y)}{\partial y} \\
&\equiv -D_O\frac{\partial \rho_O(y)}{\partial y},
\end{aligned} \tag{10}$$

which is Fick's law, identifying the factor pa^2 as equal to the diffusion coefficient of oxygen, D_O. We now need an equivalent expression for the fluxes of ^{16}O and ^{18}O. Interpreting J_i in (7) as referring to ^{16}O we can rewrite it as:

$$J_{16} = \rho_{16}J_O\Omega - D_O p_V\frac{\partial \rho_{16}}{\partial y} \tag{11}$$

and similarly for J_{18}:

$$J_{18} = \rho_{18}J_O\Omega - D_O p_V\frac{\partial \rho_{18}}{\partial y}. \tag{12}$$

We can check that these formulae are consistent with the total oxygen flux, Eqn. (10), by adding them:

$$\begin{aligned}
J_{16} + J_{18} &= (\rho_{16} + \rho_{18})J_O\Omega - D_O p_V\left(\frac{\partial \rho_{16}}{\partial y} + \frac{\partial \rho_{18}}{\partial y}\right) \\
&= (p_{16} + p_{18})J_O - D_O p_V\left(\frac{\partial \rho_O}{\partial y}\right) \\
&= (p_{16} + p_{18})J_O + p_V J_O \\
&= J_O.
\end{aligned} \tag{13}$$

How can we understand equations (11) and (12)? Recalling the relation (2) for the number of atoms or vacancies per unit volume, the first term in (12) for example is $p_{18}J_O$, which is very nearly the proportion of the total oxygen flux that is carried by ^{18}O, the exact proportion being $p_{18}J_O/p_O$. The second term is harder to interpret. At first sight one might think it is negligible, since the factor $p_V \ll 1$. However, if ρ_{18} is of the same order of magnitude as ρ_O, which is probably the case in the region of scale of width L that we use to estimate the diffusion coefficient, then we can infer that

$$p_V D_O\frac{\partial \rho_{18}}{\partial y} \approx p_V D_O\rho_{18}/L \tag{14}$$

and p_V/L may be the same order of magnitude as the gradient of p_V, in which case the last term is the same order of magnitude as the first. We might have anticipated this anyway, when we saw how the first and last terms in (11) and (12) combine when we add them.

3 The diffusion equation, Fick's second law

Finally here's some uncomfortable news. If we assume that J_O is constant, in a quasi-steady-state situation, it seems that ρ_{16} and ρ_{18} obey Fick's second law with the same diffusion coefficient as the total oxygen scaled by the local value of p_V! This is not what we hoped for. Here's the proof. Since it applies equally to either isotope, I shall drop the isotope suffices for simplicity and start with flux equation (11) or (12) in the form:

$$\frac{J}{\Omega D_O} = \rho \frac{\partial \rho_V}{\partial y} - \rho_V \frac{\partial \rho}{\partial y}. \tag{15}$$

Taking its divergence, i.e. the x derivative in this 1D case:

$$\frac{1}{\Omega D_O} \frac{\partial \rho}{\partial t} = -\rho \frac{\partial^2 \rho_V}{\partial y^2} - \frac{\partial \rho}{\partial y} \frac{\partial \rho_V}{\partial y} + \frac{\partial \rho_V}{\partial y} \frac{\partial \rho}{\partial y} + \rho_V \frac{\partial^2 \rho}{\partial y^2} \tag{16}$$

In the steady-state of oxygen diffusion, the second derivative of ρ_V vanishes and we find

$$\frac{\partial \rho}{\partial t} = p_V D_O \frac{\partial^2 \rho}{\partial y^2}. \tag{17}$$

4 Conclusion from simplest model

Our assumption has been that a low concentration of oxygen vacancies, with a positive gradient through the scale towards the alloy, mediates the diffusion of oxygen. Let us suppose that the supply of ^{16}O is instantaneously replaced by ^{18}O, without disturbing the quasi-steady state distribution of the total oxygen concentration and the complementary concentration of vacancies. We find that the concentration of ^{18}O evolves with an effective diffusion coefficient, which is not the constant diffusion coefficient of oxygen D_O, but $p_V D_O$. The quasi-steady state means that $p_V(y)$ is a linear function of x, so the solution of the diffusion equation will be non-standard. Furthermore, the standard assumption that p_V is less than 10^{-3} means that this effective, spatially-varying diffusion coefficient would be orders of magnitude less than D_O. But Andy's heroic extraction of an oxygen diffusion coefficient from TOF-SIMS data suggests that the ^{18}O is really diffusing much faster than the above analysis implies. In fact its diffusion rate appears to be consistent with that of total oxygen, within an order of magnitude. Could it be that the diffusion mechanism is in fact interstitial?

5 Generalisation drawing on the Mishin-Borchardt analysis

See Mishin and Borchardt[1, 2]

The approach and notation of these these authors cleverly avoids assuming a vacancy mechanism for the diffusion, so I'll follow their approach, if not entirely the same notation, here. We introduce the excess of isotope fractions compared to
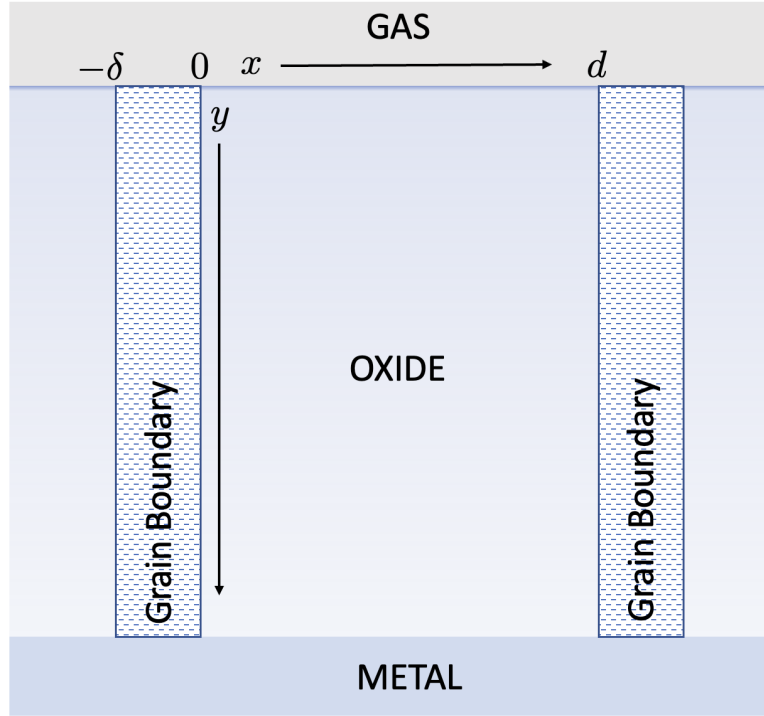

Figure 2: Schematic diagram of the geometry, following ref.

naturally occuring isotope fractions:

$$c_i = \frac{p_i}{p_O} - \left(\frac{p_i}{p_O}\right)_{\text{natural}} \tag{18}$$

where $i = 16, 18$ as before. The second term is included for completeness, but for ^{18}O it is relatively small and can be of no importance in the final analysis. Nevertheless, let us keep it and call it ϵ, which will preserve the symmetry of the final equations for isotope flux. Let us first show the equivalence of the above fluxes (11) and (12) to eqn. (10) of ref. [1], which I'll refer to as eqn. (MB10). We can write (11) and (12) as:

$$J_i = p_i J_O - \frac{1}{\Omega} D_i p_V \nabla p_i. \tag{19}$$

In practice we might assume as before that the diffusion coefficients of the isotopes

are the same, $D_i = D_O$. Now we substitute $p_i \rightarrow (c_i + \epsilon)p_O$:

$$J_i = c_i p_O J_O + \epsilon p_O J_O - \frac{1}{\Omega} D_i p_V \nabla p_i \tag{20}$$

$$= c_i p_O J_O + \epsilon p_O J_O - \frac{1}{\Omega} D_i p_V (p_O \nabla c_i + c_i \nabla p_O + \epsilon \nabla p_O) \tag{21}$$

$$= c_i p_O J_O + \epsilon p_O J_O + p_V c_i J_O + p_V \epsilon J_O - D_i p_V \rho_O \nabla c_i \tag{22}$$

$$= \epsilon J_O + c_i J_O - D_i p_V \rho_O \nabla c_i \tag{23}$$

$$J_i^* = c_i J_O - D_i p_V \rho_O \nabla c_i. \tag{24}$$

In the last line we introduce the flux of excess isotope as defined by MB.
This transformation has made the interpretation of terms much clearer. The first term $c_i J_O$ is exactly the quantity of excess isotope that is being carried along by the flux of diffusing oxygen, which can be referred to as the "drift" term. It is not related to the exchange of isotope atoms that is also taking place, mediated by vacancies in this picture. That is taken care of by the second term, which also shows the effective diffusion coefficient of the isotope, referred to by MD as D_O^* or simply D :

$$D \equiv D_O p_V. \tag{25}$$

The factor that differentiates D from D_O, in this case the vacancy concentration p_V, is generalised by MD and referred to as the correlation factor f. They do note that D is strongly dependent on position through the scale. To differentiate grain boundary and bulk lattice diffusion, MD introduce a prime on the GB quantities.
The interpretations of the two terms in eqn. 24 suggests it should apply to a more general model, not restricted to vacancy mediated transport. Other diffusion mechanisms would lead to the same separation of drift diffusion terms. Furthermore, the same equations apply to diffusion of the metal, with J_M replacing J_O etc.

5.1 Time-dependence

I wish I'd read or realised this before, equations (MB2) and (MB3) elegantly solve the moving boundaries problem, the only assumption being that the fluxes are divergenceless through the scale, i.e. they only depend on time, not position. I note that the thickness L in eqn. (MB3) is explicitly time-dependent. I had never appreciated this before, although it's now obvious. I'd previously thought that the solution was a quasi-stationary one, whereas in fact it is exact, but only if there is no lateral growth or shrinkage of the scale by creation or annihilation of crystal at the GBs. Furthermore, it leads to the exact parabolic growth law with the constant given by eqn. (MB4). Beautiful. The same assumption means that there can be no flux of oxygen or aluminium in or out of the GB, so the flux lines are parallel to the GB, which justifies (MB1) and (MB6). Boundary velocities in my notation are:

$$V_1 = [\nu J_M' + (1 - \nu)J_M]/\rho_M$$
$$V_2 = [\nu J_O' + (1 - \nu)J_O]/\rho_O \tag{MB6}$$

E and the thickness of the scale grows as

$$\frac{\mathrm{d}L}{\mathrm{d}t} = V_2 - V_1. \tag{26}$$

MB did not consider electric fields, so let us include an electric field E normal to the surface so that the flux equations (MB3) become

$$J_i = \frac{D_i \rho_i}{k_{\mathrm{B}}T} \left(-\nabla \mu_i + z_i E\right) \tag{27}$$

where z_i is the charge (atomic units) on the ion oxygen or aluminium. If there is a space-charge throughout the scale, $E(y)$ is a function of y just as the other three variables, D_i, μ_i and ρ_i are, for each element.

5.2 Chemical potentials

Before we can go further, there is an issue about chemical potentials that needs to be settled. That is the use of the Gibbs-Duhem equation, which appears in MB and other sources. Let's look first at what the simplest vacancy-mediated model that I started with says. Consider the following paradox. If the fluxes of O and Al were constant across the scale and only driven by Fick's law and the local gradient of vacancies, as in the simplest model I started with, then, as we have seen, in the quasi-steady state, the vacancy concentrations would vary linearly across the scale and the fluxes would be constant in space. For a low vacancy concentration, the chemical potential of O and Al (designated metal M) take the form (see my lecture notes on ideal solutions):

$$\begin{aligned} \mu_{\mathrm{O}} &= \mu_{\mathrm{O}}^{\circ} + k_{\mathrm{B}}T \ln p_{\mathrm{O}} \\ &= \mu_{\mathrm{O}}^{\circ} - k_{\mathrm{B}}T p_{\mathrm{VO}} \\ \mu_{\mathrm{M}} &= \mu_{\mathrm{M}}^{\circ} + k_{\mathrm{B}}T \ln p_{\mathrm{M}} \\ &= \mu_{\mathrm{M}}^{\circ} - k_{\mathrm{B}}T p_{\mathrm{VM}} \end{aligned} \tag{28}$$

Remember the p are site occupancy, not pressure!

References

[1] Yu. Mishin and G. Borchardt. Theory of oxygen tracer diffusion along grain boundaries and in the bulk in two-stage oxidation experiments. Part I: formulation of the model and analysis of type A and C regimes. *Journal de Physique III France*, 3:863–881, 1993.

[2] Yu. Mishin and G. Borchardt. Theory of oxygen tracer diffusion along grain boundaries and in the bulk in two-stage oxidation experiments. Part II : analysis of type B regime. *Journal de Physique III France*, 3:945–960, 1993.