

An alternative description of mass transfer through thick oxide films

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An alternative approach for deriving macroscopic mass transfer expressions in the tradition of Wagner's theory is presented. Starting from a microscopic definition of defect formation energies and carrier species concentrations, the oxygen permeability of α -Al₂O₃ thick films under different partial pressures is analyzed. Our formulation reproduces results from permeation experiments that mimic the growth of oxide films on metal alloys, and is more intuitive than previous methods because all micro- and macroscopic factors are directly related to each other.

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Growth of thick α -Al₂O₃ films on metallic substrates under (aggressive) oxidation conditions at high temperatures is not only a widely investigated instance of high-temperature corrosion of metals [1] but also one of the central factors influencing the performance of thermal barrier coatings (TBCs) [2]. The basic description of such phenomena has been based on Wagner's seminal work [3–6], introduced three-quarters of a century ago, where the parabolic rate of growth is derived from a consideration of the diffusion of ions and electronic carriers produced on each side of the scale. The parabolic rates have been widely used in phenomenological analyses of TBCs, e.g., to calculate stress distributions during oxidation, to quantify relevant degradation processes [7–10], and to compare the growth rates on various substrate alloys [11].

Quantum theoretical calculations based on density functional theory (DFT) can be used to evaluate the energetics of fundamental steps in the oxidation process, such as chemical reactions and diffusion barriers. For example, formation energies of point defects in α -Al₂O₃ have been calculated for bulk [12,13] and grain boundary systems [14]. Although these microscopic quantities are expected to be used to evaluate a macroscopic one by virtue of Wagner's theory [15,16], the connection to a macroscopic description based on the theory exhibits ambiguities. In this paper, in order to bridge the gap between formulas describing micro- and macroscopic phenomena, we develop a formalism starting from expressions for the formation energies, focusing particularly on oxygen permeation experiments of α -Al₂O₃ wafers [17,18]. These experiments are useful for

studying the effect of oxide scales on metallic surfaces because the reduced side can be thought of as approximating the interface between scale and metal.

In the oxygen permeation measurements (shown schematically in Figure 1(a)), oxygen permeation is induced by an oxygen partial pressure gradient across the two faces, labeled I ($x = 0$) and II ($x = L$). Diffusion of defects occurs preferentially at grain boundaries [17,18], which has been confirmed by secondary ion mass spectrometry measurements of oxygen diffusion in sapphire [19] and microstructural examination of oxidation of metals [20]. The permeability behavior has been interpreted in terms of two distinct mechanisms depending on the oxygen pressures (see Figure 1):



for $P_{\text{O}_2}^{\text{I}} = 10^{-7} - 10^{-5}$ Pa and $P_{\text{O}_2}^{\text{II}} = 1$ Pa, and



for $P_{\text{O}_2}^{\text{I}} = 1$ Pa and $P_{\text{O}_2}^{\text{II}} = 10^3 - 10^5$ Pa. This behavior means that the predominant vacancy type contributing to mass transfer changes depending on the magnitude of the pressures; this switchover has been postulated to be caused by band-gap reduction at grain boundaries [14].

Here we derive an expression for the permeability starting from the definition of the formation energies of oxygen and aluminum vacancies, namely,

$$\begin{aligned} E_{\text{f},\text{V}_\text{O}^{2+}} &= E_{\text{V}_\text{O}^{2+}} - E_{\text{Pris.}} + \mu_\text{O} + 2\mu_\text{e} \\ &= \Delta E_{\text{f},\text{V}_\text{O}^{2+}} + \mu_\text{O} + 2\mu_\text{e} \end{aligned} \quad (3)$$

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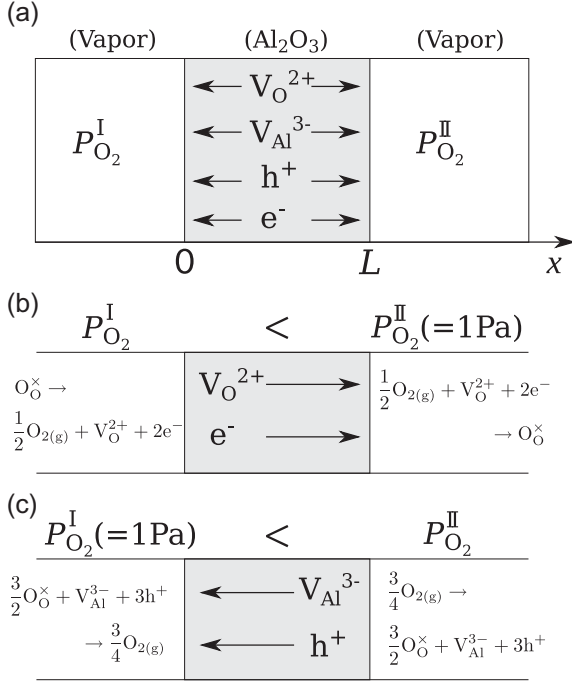


Figure 1. (a) Schematic of the oxygen permeation experiment setup, with different oxygen partial pressures, P_{O_2} , on either side of a polycrystalline Al_2O_3 wafer. (b, c) Permeation mechanisms involving diffusion of oxygen and aluminum vacancies, respectively.

and

$$\begin{aligned} E_{f, V_{Al}^{3-}} &= E_{V_{Al}^{3-}} - E_{Pris.} + \mu_{Al} - 3\mu_e \\ &= \Delta E_{f, V_{Al}^{3-}} - \frac{3}{2}\mu_O - 3\mu_e, \end{aligned} \quad (4)$$

respectively [21]. $E_{V_O^{2+}}$, $E_{V_{Al}^{3-}}$, and $E_{Pris.}$ are energies of crystalline systems including an O, Al, and no vacancy, respectively. μ_O , μ_{Al} , and μ_e are chemical potentials of O atoms, Al atoms, and electrons, respectively, where the Al component is eliminated by using the relation $\mu_{Al_2O_3} = 2\mu_{Al} + 3\mu_O$. All terms except for μ_O and μ_e are expressed in terms of ΔE_f for simplicity.

Using the formation energies, concentrations of each vacancy can be obtained from

$$C_{V_O^{2+}} = N_O \exp(-\beta E_{f, V_O^{2+}}) \quad (5)$$

and

$$C_{V_{Al}^{3-}} = N_{Al} \exp(-\beta E_{f, V_{Al}^{3-}}) \quad (6)$$

where $\beta = (k_B T)^{-1}$. Here, N_O and N_{Al} are the numbers of lattice sites of oxygen and aluminum, respectively. We note that the vacancy concentrations defined here depend not only on μ_O but also on μ_e .

The concentration of electronic carriers, i.e., conduction electrons and holes, introduced at high temperatures can be expressed in terms of the electronic density of states (DOS), labeled ρ , as

$$\begin{aligned} C_e &\simeq \sum_{i=CBM}^{\infty} \rho(\varepsilon_i) \exp(-\beta(\varepsilon_i - \mu_e)) \\ &= N_e \exp(\beta(\mu_e - \varepsilon_{CBM})) \end{aligned} \quad (7)$$

and

$$\begin{aligned} C_h &\simeq \sum_{i=VBM}^{-\infty} \rho(\varepsilon_i) \exp(-\beta(\mu_e - \varepsilon_i)) \\ &= N_h \exp(-\beta(\mu_e - \varepsilon_{VBM})), \end{aligned} \quad (8)$$

respectively. Here, ε_{CBM} and ε_{VBM} are the energy levels of the conduction band minimum (CBM) and valence band maximum (VBM), respectively. For a band gap E_g , $\varepsilon_{CBM} = \varepsilon_{VBM} + E_g$. N_e and N_h are the effective number of states in the conduction and valence bands, respectively.

In our formulation, the vacancies diffuse perpendicular to the surfaces of α - Al_2O_3 wafers (Figure 1), and Fick's first law, as given by $J_i = -D_i dC_i/dx$, is simply applied. D_i is the diffusion coefficient of defect species i ; note that it is the diffusion coefficients of vacancies that are handled here rather than those of (marked) atoms. This leads to the following equations:

$$J_{V_O^{2+}} = \beta C_{V_O^{2+}} D_{V_O^{2+}} \left(\frac{d\mu_O}{dx} + 2 \frac{d\mu_e}{dx} \right), \quad (9)$$

$$J_{V_{Al}^{3-}} = -\frac{3}{2} \beta C_{V_{Al}^{3-}} D_{V_{Al}^{3-}} \left(\frac{d\mu_O}{dx} + 2 \frac{d\mu_e}{dx} \right), \quad (10)$$

$$J_e = -\beta C_e D_e \frac{d\mu_e}{dx}, \quad (11)$$

and

$$J_h = \beta C_h D_h \frac{d\mu_e}{dx}. \quad (12)$$

Here, ε_{VBM} and ε_{CBM} are assumed to be independent of the position in the wafer. We will return to this point later.

The charged-particle fluxes under a steady-state balance to give $\sum_i q_i J_i = 0$ at any arbitrary point in the wafer, where q_i is the charge of species i . From this flux-balance equation and Eqs. (9)–(12), together with Nernst-Einstein relations $\beta C_i D_i = \sigma_i / q_i^2$,

$$\frac{d\mu_e}{dx} = -\frac{\sigma_{V_O^{2+}} + \sigma_{V_{Al}^{3-}}}{2\sigma_{tot}} \frac{d\mu_O}{dx} \quad (13)$$

where σ is the electrical conductivity. Using Eq. (13), the fluxes of O and Al vacancies can be rewritten as

$$J_{V_O^{2+}} = \beta C_{V_O^{2+}} D_{V_O^{2+}} \left(\frac{\sigma_e + \sigma_h}{\sigma_{tot}} \right) \frac{d\mu_O}{dx} \quad (14)$$

and

$$J_{V_{Al}^{3-}} = -\frac{3}{2} \beta C_{V_{Al}^{3-}} D_{V_{Al}^{3-}} \left(\frac{\sigma_e + \sigma_h}{\sigma_{tot}} \right) \frac{d\mu_O}{dx}, \quad (15)$$

respectively. $\sigma_e / \sigma_{tot} (= t_e)$ and $\sigma_h / \sigma_{tot} (= t_h)$ are the transference numbers of electrons and holes, respectively. Hereon we abbreviate $t_e + t_h$ as t_{eh} .

The permeability of gaseous oxygen, \mathcal{P} , is the sum of contributions from the two mechanisms in Eqs. (1) and (2): 1/2 and 3/4 oxygen molecules are transferred per O and Al vacancy, respectively. Since the permeation predominantly occurs at grain boundaries, \mathcal{P} is given by

$$\begin{aligned} \mathcal{P}L &= \delta S_{GB} \int_0^L \left(-\frac{1}{2} J_{V_O^{2+}} + \frac{3}{4} J_{V_{Al}^{3-}} \right) dx \\ &= -\frac{\delta S_{GB}}{2} \beta \int_1^{II} t_{eh} \left(C_{V_O^{2+}} D_{V_O^{2+}} + \frac{9}{4} C_{V_{Al}^{3-}} D_{V_{Al}^{3-}} \right) d\mu_O, \end{aligned} \quad (16)$$

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