



Full length article

A model for time-dependent grain boundary diffusion of ions and electrons through a film or scale, with an application to alumina

M.P. Tautschnig^{a,*}, N.M. Harrison^b, M.W. Finnis^{a,c}^a Department of Physics, Imperial College London, London SW7 2AZ, UK^b Department of Chemistry, Imperial College London, London SW7 2AZ, UK^c Department of Materials, Imperial College London, London SW7 2AZ, UK

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ABSTRACT

A model for ionic and electronic grain boundary transport through thin films, scales or membranes with columnar grain structure is introduced. The grain structure is idealized as a lattice of identical hexagonal cells – a honeycomb pattern. Reactions with the environment constitute the boundary conditions and drive the transport between the surfaces. Time-dependent simulations solving the Poisson equation self-consistently with the Nernst-Planck flux equations for the mobile species are performed. In the resulting Poisson-Nernst-Planck system of equations, the electrostatic potential is obtained from the Poisson equation in its integral form by summation. The model is used to interpret alumina membrane oxygen permeation experiments, in which different oxygen gas pressures are applied at opposite membrane surfaces and the resulting flux of oxygen molecules through the membrane is measured. Simulation results involving four mobile species, charged aluminum and oxygen vacancies, electrons, and holes, provide a complete description of the measurements and insight into the microscopic processes underpinning the oxygen permeation of the membrane. Most notably, the hypothesized transition between *p*-type and *n*-type ionic conductivity of the alumina grain boundaries as a function of the applied oxygen gas pressure is observed in the simulations. The range of validity of a simple analytic model for the oxygen permeation rate, similar to the Wagner theory of metal oxidation, is quantified by comparison to the numeric simulations. The three-dimensional model we develop here is readily adaptable to problems such as transport in a solid state electrode, or corrosion scale growth.

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1. Introduction

Thin films of insulating material at metal – gas and metal – liquid interfaces accomplish a range of service functions in materials technology. Common examples are functional ceramics in electronics, energy related applications and sensors. Thin films formed by surface oxidation of a metal can have either beneficial or corrosive effects. Alumina and chromia formed by thermal oxidation are examples of protective oxide films, which find application in thermal barrier coatings, and can be engineered for durability by additions of rare earth elements [1–4]. They can also grow in an uncontrolled manner, adhering weakly to the metal and allowing corrosion to proceed. Metal oxidation is a heterogeneous process, consisting of multiple steps, involving the dissociation of molecular

oxygen, transport through the growing oxide layer, and the reaction between oxygen and metal atoms. Generally speaking a growing oxide layer on the metal surface requires either metal atoms, normally ions, to be transported to the oxide – gas interface to sustain the oxidation reaction, or alternatively oxygen atoms or ions to be transported through the oxide to the metal – oxide interface to sustain an internal oxidation reaction. Furthermore, the transport is usually thought to be effected by diffusion of cation or anion vacancies. Both processes may proceed, depending on the material under consideration and on the environmental conditions such as temperature and oxygen partial pressure, P_{O_2} . While the slowest process is rate-determining for consecutive processes, like dissociation of oxygen molecules and their transport through the oxide, the fastest process is rate-determining for parallel processes, like bulk and grain boundary diffusion through the oxide. The measured oxygen and aluminum diffusion coefficients in α -alumina are found to be several orders of magnitude greater at the grain boundaries than in the bulk material [5–7]. The fact that grain boundaries

* Corresponding author.

E-mail address: mpt13@imperial.ac.uk (M.P. Tautschnig).

provide the dominant transport mechanism underlines the importance of including their geometric and transport properties in a realistic model of the process. Since vacancies in strongly ionic oxides such as alumina or chromia are charged species relative to the perfect crystal, the fluxes of these species carry an electric current, which in the usual scenario of steady-state growth is not sustainable, unless compensated by an equal and opposite current of electrons or holes, as described by the classic model of Wagner [8,9]. The prediction of the growth behaviour of thin films, and its influence on the material or device performance, requires us to describe the mixed ionic, electronic transport through the films, while taking their grain boundary structure into account.

Because of the widespread importance of alumina films [10], and since it is a relatively well characterized material, we focus on alumina films for the validation of our modelling approach. Moreover, a recent series of permeation experiments for α -alumina polycrystal membranes, e.g. Ref. [11], conducted for different combinations of applied oxygen gas pressures at high temperatures, provides an ideal test case for our transport model. These experimental results will be summarized briefly in the following section.

1.1. Brief review of oxygen permeation and diffusion experiments

Permeation rates of oxygen through a polycrystalline membrane of alumina have been reported in the literature [11,12], and cover a range of oxygen partial pressures. Scanning Electron Microscope (SEM) imaging of the films prepared under different applied pressures strongly suggests that mass transfer occurs along grain boundaries. The thermodynamic driving force in these experiments is the difference in the oxygen chemical potential between the two membrane surfaces $\Delta\mu_{\text{O}_2} = k_{\text{B}}T\ln(P_{\text{O}_2}^{\text{II}}/P_{\text{O}_2}^{\text{I}})$. Fig. 1 shows a schematic of membrane permeation experiments.

The experiments included nominally pure α -alumina polycrystals [11,13], doped α -alumina polycrystals [14–17], and nominally pure α -alumina bicrystals [18], with temperatures of $\sim 1700 - 2000$ K. A simple analysis of the permeation rate data in Ref. [11], assumed a model of one-dimensional, steady-state diffusion, in which either Al or O is transported by vacancy migration, depending on the absolute magnitude of the applied oxygen pressure.

In the non-doped polycrystalline alumina experiments [11], when applying high oxygen pressures at surface (II), $P_{\text{O}_2}^{\text{hi}} = 10^3 - 10^5$ Pa, while keeping surface (I) at $P_{\text{O}_2}^{\text{l}} = 1$ Pa, grain boundary ridges formed on the $P_{\text{O}_2}^{\text{hi}}$ surface and grain boundary trenches were observed on surface (I). Applying a low oxygen pressure at surface (II), $P_{\text{O}_2}^{\text{lo}} = 10^{-5} - 10^{-8}$ Pa, while keeping surface (I) at $P_{\text{O}_2}^{\text{l}} = 1$ Pa, no grain boundary ridges are formed and only grain boundary trenches are observed. Since the oxygen

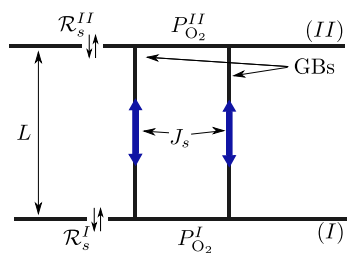


Fig. 1. Schematic of the membrane permeation experiments where mass transfer occurs by grain boundary transport. Different oxygen gas partial pressures, $P_{\text{O}_2}^{\text{l}}$ and $P_{\text{O}_2}^{\text{hi}}$, are applied on the surfaces.

permeation rates of a single-crystal alumina wafer were below the measurable limit and as the visible surface growth and “dissolution” proceeds at grain boundaries it is reasonable to assume that grain boundaries dominate the transport [11]. The oxygen permeation rates, P , for fixed $P_{\text{O}_2}^{\text{l}} = 1$ Pa were found to follow distinct power laws [11]; in the limit of $P_{\text{O}_2}^{\text{II}} = P_{\text{O}_2}^{\text{hi}}$,

$$P \propto (P_{\text{O}_2}^{\text{II}})^{3/16}, \quad (1)$$

and in the limit of $P_{\text{O}_2}^{\text{II}} = P_{\text{O}_2}^{\text{lo}}$,

$$P \propto (P_{\text{O}_2}^{\text{II}})^{-1/6}. \quad (2)$$

The power laws and the pressure dependent formation of the grain boundary ridges have led to the interpretation of the experiments in terms of, aluminum vacancy transport being dominant in oxygen chemical potential gradients with high oxygen pressure magnitude, $P_{\text{O}_2}^{\text{II}} = P_{\text{O}_2}^{\text{hi}}$, and oxygen vacancy transport being dominant in the case of $P_{\text{O}_2}^{\text{II}} = P_{\text{O}_2}^{\text{lo}}$.

Indeed, the rational power laws appear in the theory as a direct consequence of the +3 and –2 ionic charges of the ions, assuming that the negative of these charges is carried by each vacancy, with a counter-current of electrons or holes, and no time-dependence of the fluxes (the steady-state assumption) or net local charge densities within the grain boundaries. These assumptions are discussed further in section 4.1. Furthermore, only aluminum vacancy transport can lead to ridge formation, which is observed by SEM imaging in the case of $P_{\text{O}_2}^{\text{II}} = P_{\text{O}_2}^{\text{hi}}$, supporting the above interpretation. The switch-over in dominant point defect species in the grain boundary has been termed “ $p - n$ transition” in the literature [5,19].

The diffusion coefficients determined from alumina bicrystal experiments with $P_{\text{O}_2}^{\text{II}}/P_{\text{O}_2}^{\text{l}} = 10^5$ Pa/1 Pa for several distinct grain boundary types have been found compatible with those measured in polycrystalline samples [18]. The bicrystal diffusion coefficients were calculated from the grain boundary ridge volume and a caveat regarding this approach is that the formation of the ridges on the $P_{\text{O}_2}^{\text{hi}}$ side does not necessarily imply an exactly equivalent mass transport from the opposite side of the membrane, since oxide can be displaced by formation of internal pores in the subsurface region of the crystals, as has indeed been observed in some polycrystal permeation experiments [14].

1.2. Scope of the paper

The above level of analysis leaves several open questions, e.g. does the grain boundary diffusion mechanism, with the associated inhomogeneity of fluxes and electric fields, map accurately onto a 1D diffusion problem? And what are the magnitude and roles of the surface and interface charges, the electric fields, currents, space charges, and transients that are all believed to be present in a three-dimensional film, traversed by grain boundaries?

To address these questions we have modelled the transport of oxygen through a planar film by making an idealized representation of the grain structure, in which we suppose the grains to be columnar, with identical and perfectly hexagonal cross sections, see Fig. 2. We describe in this paper the set of coupled reaction-diffusion equations we have used to model the oxygen permeability across the membrane, our method of solving them, and the results we have obtained for the model alumina membrane. Within this geometry, grain boundary transport through the film of charged cation and anion vacancies, electrons, and holes is

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