



Destabilisation of nanoporous membranes through GB grooving and grain growth



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ABSTRACT

We have used a phase field model to study destabilization of cylindrical pores in a polycrystalline membrane; a key feature in the model is that it incorporates surface diffusion as the mechanism for mass transport. Using a model system in which a cylindrical pore runs through a material in which all the grain boundaries (GBs) are perpendicular to the pore axis, we identify two elementary mechanisms for pore failure. The first one is based just on grain boundary (GB) grooving, which causes a circular trench at the groove, and a constriction of the pore on either side of the GB; as the groove deepens, the constriction narrows, and eventually closes the pore. Pore closure through this mechanism is possible only when the grain size exceeds a critical size (below which the open pore surface acquires an inverse-bamboo morphology), and therefore, it is controlled by grain growth kinetics. In the second mechanism, the groove profiles of unequal sized grains is such that the curvature differences trigger a coarsening-like process in which atoms from the surface of smaller grains are transported to that of larger grains, causing an ever-narrowing constriction there. A simplified model that incorporates these two mechanisms acting in parallel is used to rationalize our observations of pore failure in polycrystalline systems.

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1. Introduction

In a seminal paper, Keller et al. [1] showed that alumina coatings prepared under specific electrochemical conditions are made up of a continuous solid alumina phase, with a nearly periodic array of uniformly sized cylindrical holes with their diameter in the range of 40–300 nm. Since then, such nanoporous oxide membranes have been made of zirconia [2] and titania [3] as well. While such membranes may be used directly in applications (for example, as catalysts [4]) they are being used increasingly as templates for growing a variety of one-dimensional nanostructures made up of other materials (typically, oxides or metals). Examples include ordered arrays of nanowires of TiO₂, Au and Ni [5], nanotubules of ZnO [6], nanodots of Au [7], nanoholes of Pt [8]. In a review of metal oxide nanowires and their applications, Shen et al. [9] have listed the use of anodic alumina as template as one of the “bottom up” methods for making nanowires.

Many application regimes (such as catalysis or template-assisted growth of other materials) may expose the nanoporous anodic oxide membranes to high temperatures, at which diffusive processes (especially surface diffusion) are active. Also, there is

always a driving force that exists for the cylindrical pore to split into spheres. Since the (surface area/ volume) ratio of an infinitely long pore is inversely proportional to its radius, this driving force increases with decreasing pore radius. Thus, the thermal stability of such membranes (i.e., the thermal stability of the nanosized pores in the membranes) is of great scientific and technological interest. Several recent studies have addressed this issue experimentally [10,11,2]. This forms the motivation for our computational work on this problem: what are the possible mechanisms that may destabilize a cylindrical pore, and how long would it take for the pore to be closed due to such mechanisms?

Among the mechanisms of destabilization of cylindrical pores, Rayleigh instability is an obvious one. The classic work of Nichols and Mullins [12] presented analytical results for early stages of destabilization via Rayleigh instability; in a recent paper [13], we used computer simulations based on a phase field model to study the late stages of pore evolution (including its closure) mediated by surface diffusion.

However, the solid in the porous oxide membranes is polycrystalline (especially after exposure to high temperature); thus grain boundary (GB) grooving is another destabilization mechanism leading to pore closure in such membranes. In this mechanism, material from the root of the GB groove is transported to the pore wall where it accumulates, and causes a constriction in the pore;

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with time, the constriction becomes progressively narrower, leading to the eventual closure of the pore. This paper is on our two-part study of pore destabilization triggered by GB grooving, and mediated by surface diffusion.

In the first part, in Section 3, we consider a model system in which all the grain boundaries are normal to the pore axis, and study the role of grain size in the events leading up to pore closure; this part of our work builds on the work by Mullins on GB grooving at a planar surface [14], and its later extension by Klinger and Rabkin to GB grooving of solid cylinders [15]. We then repeat this exercise on a system with grains of different sizes; this reveals a second mechanism for pore closure through grooving. While this first part offers us valuable insights, it still misses a key feature of polycrystalline materials: grain growth. Thus, in the second part of our study, in Section 4, we consider the full problem of pore evolution in the presence of GB grooving and grain growth. As we will see in that section, grain growth has two types of effects: in the first, grain growth is essential when the initial grain size is smaller than the critical size above which GB grooving can do its job of destabilizing and closing a pore; in the second, it can disrupt the formation of the groove by keeping the grain boundary moving. Thus, these two effects lead to an interesting (and non-trivial) relationship between pore closure time and grain growth kinetics. Thus, Section 4 builds on the ideas in Section 3, and elucidates the complex ways in which grain growth both helps and interferes with the processes of pore destabilization and closure.

We have chosen to address our research problem using a computational route based on phase field models. Essentially, these models describe the energy of different types of interfaces, and how (and how fast) they may migrate under a driving force.

There are many good reasons for the use of such models (which also explains their ever increasing popularity in recent decades), and they have been covered well in several reviews (see, for example Refs. [16–18]). The most important among these reasons, in the context of our study, are the following: (a) they capture microstructural instabilities (and we treat Rayleigh instability as one) very well, in the sense that results from phase field simulations on such instabilities are in good quantitative agreement with those from analytical theories, and (b) they can be run right from early stages all the way up to very late stages of microstructural evolution; along the way, if there are topological transitions of features (such as pore splitting, coalescence of droplets, or shrinkage and removal of a grain during grain growth), they are handled gracefully.

As we will see in Section 4, the second feature is very attractive indeed; constrictions in the pore lead eventually to pore closure, and during grain growth, many grains shrink and vanish from the system (as a result of which previously non-neighbouring grains become neighbours).

2. Phase field model and solution technique

Our model is a combination of the Cahn-Hilliard [19] and Fan-Chen [20] models. We designed the model to represent a polycrystalline solid that may co-exist with a vapour phase. To achieve this, we use a density field $\rho(\mathbf{r}, t)$, a vapour phase order parameter $\theta_v(\mathbf{r}, t)$, and a set of grain orientation order parameters $\eta_i(\mathbf{r}, t)$. Thus, the vapour phase is a region in which $(\rho, \theta_v, \{\eta_i\}) = (0, 1, \{0, 0, \dots, 0\})$. Similarly, the first and second grains (for example) are regions in which $(\rho, \theta_v, \{\eta_i\}) = (1, 0, \{1, 0, \dots, 0\})$ and $(1, 0, \{0, 1, \dots, 0\})$, respectively. Large gradients in ρ and θ_v help us in identifying the free surface, and large gradients in η_i represent grain boundaries. We use as many η_i fields as the number of grains in the system. We write the free energy functional in the following form:

$$F = \int_V \left[f_{sv} + \kappa_\theta (\nabla \theta_v)^2 + \sum_i \kappa_i (\nabla \eta_i)^2 \right] dV, \quad (1)$$

where κ_θ and κ_i are the gradient energy coefficients representing the energy cost associated with gradients in θ_v and η_i , respectively. The free energy density $f_{sv}(\rho, \theta_v, \eta_i)$ is written as

$$f_{sv} = \rho^2 [f_s + \theta_v^2] + (1 - \rho)^2 [f_v + s] + W_{sv} \theta_v^2 S. \quad (2)$$

W_{sv} sets the energy barrier height between vapour and solid. We have used the following expressions for the functions f_s and f_v and s :

$$f_s = 0.25 + \sum_{i=1}^n \left[\frac{\eta_i^4}{4} - \frac{\eta_i^2}{2} + \sum_{j>i}^n \epsilon_{ij} \eta_i^2 \eta_j^2 \right] \quad (3)$$

energy barrier between grain i and grain j is set by ϵ_{ij} ,

$$f_v = 0.25 + \frac{\theta_v^4}{4} - \frac{\theta_v^2}{2}, \quad (4)$$

and

$$s = \sum_i (\eta_i^2). \quad (5)$$

This free energy function f_{sv} is a surface with minima which represents the mutual equilibrium between the vapour phase and each of the solid grains. The evolution of the density field variable $\rho(\mathbf{r}, t)$ is governed by the Cahn-Hilliard equation [19].

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \left[M \nabla \left(\frac{\delta F}{\delta \rho} \right) \right] \quad (6)$$

$$M = M_b + 16.0(M_{gb} \phi_{gb} + M_s \phi_s) \quad (7)$$

M is the atomic mobility which is closely related to diffusivity. M_b represents bulk diffusivity, M_{gb} represents grain boundary diffusivity and M_s represents surface diffusivity. ϕ_{gb} is a function of order parameters $\eta_i(\mathbf{r}, t)$ which has non zero values only at grain boundaries and vanishes at all other locations. Similarly, ϕ_s is a function of $\eta_i(\mathbf{r}, t)$ and $\theta_v(\mathbf{r}, t)$ which has non zero values only at the surface. Our approach for incorporating enhanced surface and GB diffusion is similar to that of several others [13,21–25]. A tensorial form for M_s or M_{gb} (so that the atomic mobility *along* and *normal* to the interface may be different; in the extreme case, the mobility normal to the interface may even be made vanishingly small) has been used to implement enhanced surface diffusivity in Refs. [21,26,25]; we have adopted a simpler approach of using an isotropic (scalar) form for M_s and M_{gb} . Our formalism is simpler to code, and leads to faster simulations; in addition, it has been shown to work well in our earlier study on Rayleigh instabilities of cylindrical pores [13].

$$\phi_{gb} = \sum_{i=1}^{n-1} \sum_{j>i} \eta_i^2 \eta_j^2 \quad (8)$$

$$\phi_s = \theta_v^2 \sum_{i=1}^n \eta_i^2 \quad (9)$$

The evolution of the order parameter fields is governed by the Allen-Cahn equation [27].

$$\frac{\partial \theta_v}{\partial t} = -L \left[\frac{\delta F}{\delta \theta_v} \right] \quad (10)$$

$$\frac{\partial \eta_i}{\partial t} = -L \left[\frac{\delta F}{\delta \eta_i} \right] \quad (11)$$

The kinetic coefficient L governs the relaxation rates of the θ and η_i fields; in our simulations, we have used a position-dependent L (just as we did with atomic mobility in Eq. (7)):

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