MASS TRANSPORT THROUGH POLYCRYSTALLINE MICROSTRUCTURES

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ABSTRACT

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Mass transport properties are important in polycrystalline materials used as protective films. Traditionally, such properties have been studied by examining model polycrystalline structures, such as a regular array of straight grain boundaries. However, these models do not account for a number of features of real grain ensembles, including the grain size distribution and variations in grain shape. In this study, a finite difference scheme is developed to study transient and steady-state mass transport through realistic two dimensional polycrystalline microstructures. Comparisons with the transport properties of traditional model microstructures provide regimes of applicability of such models. The effects of microstructural parameters such as average grain size are examined.

INTRODUCTION

It has long been acknowledged that grain boundary diffusion often dominates the effective diffusivity of solutes in real materials. Grain boundary diffusion affects various applications in different ways. For example, in protective films, one might be interested in time for an environmental specie to penetrate the film and attack an intolerant material beneath. In a diffusion barrier, one might be interested in the steady state flux of a contaminant through the film. In applications in which corrosion properties are composition dependent, the penetration of species into the material along grain boundaries determines the lifetime of the specimen. Different issues are important in each case, and no currently available solution treats all cases.

The calculation of grain boundary diffusion behavior in real materials has proven to be a difficult problem. Solutions to grain boundary diffusion problems often use simplifying assumptions that restrict either the geometries that can be solved or the regimes of their applicability. To overcome these restrictions, we have developed a flexible finite difference technique that can be applied to a variety of microstructures, boundary conditions, and time regimes. We have utilized this technique to study diffusion in simulated microstructures over a wide range of time scales.

In this paper, we will describe this model, present some results for model and realistic microstructures, and compare to applicable analytic results.

BACKGROUND

We will not go into the specifics of the numerous analytical solutions to grain boundary diffusion problems here. For an in-depth description of many of the solutions to such problems, refer to Kaur and Gust¹.

Analytic treatments of grain boundary diffusion and the penetration into surrounding grains usually assume a single boundary or an array of boundaries normal to a surface held at constant composition. The first such solution was proposed by Fisher² for a semi-infinite slab of material. Refinements³ and extensions have been proposed to Fisher's solution, including solutions for cases of samples having finite size^{4,5} and slanted boundaries.⁶ None of these models treats the complicated topology encountered in most polycrystals.

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Levine and MacCallum⁷ proposed a different approach to the problem by solving the diffusion into a sample via a given volume fraction of high diffusivity boundary material coupled with diffusion into an average-shape grain. They found that the logarithm of the average concentration in a serial sample of a polycrystal varied as depth to the 6/5 power. Since all grain boundaries are combined into a single volume fraction of boundary material, grain boundary connectivity is again ignored.

Purely numerical methods have also been applied to the study of grain boundary problems. Levine and Losee⁸ used a Monte Carlo method to simulate the diffusion of impurities in grain boundaries. Their method was unique in that it explicitly allowed for equilibrium grain boundary segregation of impurity diffusants. Holloway et al.⁹ used a finite difference method to solve the case of grain boundary diffusion along straight boundaries in thin films and compared their results to an analytic solution of the same problem. Gui et al.¹⁰ verified the transmission-line-matrix method for the solution of model grain boundary diffusion problems for which analytic solutions were available as well as applying the technique to other simple geometries.

METHOD

To set up diffusion problems, we mapped the desired microstructure onto a square diffusion lattice and applied the appropriate boundary conditions. A discretized microstructure is typically described by assigning each site in a lattice an index that identifies the site as a member of a particular grain. The grid lines separating grain sites become paths for the transport of matter along their length. The paths are assigned effective diffusivities corresponding to either that of a grain boundary if the path is a line boundary between dissimilar sites in the grain lattice, or that of the bulk if the path is a line boundary between similar sites. In this scenario, grain boundaries have no effect on transverse diffusion. A schematic showing the mapping in an idealized structure is shown in figure 1. We then applied either periodic or closed boundary conditions to the edges of the lattice, and infinite or finite source/sink concentration boundary conditions as required.

To model diffusion in realistic microstructures, we applied our technique to two-dimensional microstructures created using a Monte Carlo Potts model¹¹. By using microstructures at various stages of grain growth, we were able to examine the effects of grain size on both the effective diffusivities and the penetration behavior.

Diffusion along each path in the lattice takes place according to the usual diffusion equation

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) \quad (1)$$

where C is the concentration, t is time, x and y are spatial coordinates, and D is the appropriate diffusion coefficient (bulk or boundary) for the path. We use the Crank-Nicholson discretization to obtain an implicit finite difference expression for equation (1) which is second-order accurate in the time and space discretization¹². In this scheme, the diffusion along a given path depends on the concentration at neighboring paths. We then used an Alternating Direction Implicit (ADI) algorithm to integrate equation (1). This method is stable for large timesteps, but in order to model all diffusion regimes accurately, i.e. short time as well as long-time, we used an adjustable timestep to minimize transient artifacts at short times (by using short timesteps) while being able to model steady state behavior with minimal computation (by using long timesteps). The ADI implementation of the Crank-Nicholson scheme treats one dimension implicitly and the other dimension explicitly for half of each timestep, then reverses the dimensions for the second half of each timestep. A limitation of this method became apparent in the modeling of grain boundary

diffusion. At points where the diffusion coefficient becomes discontinuous in the direction of the flux, such as at a grain boundary trijunction, very long timesteps cause a spike in the transient concentration during the first half of each timestep that must be accurately counteracted in the second half of each timestep to a precision unattainable by the algorithm. Unchecked, this error can result in a pile-up of solute at these points. Thus, in order to maintain the stability of the calculation at long times, the size of the spike had to be limited to an acceptable value by limiting the length of the timestep.

Figure 1. The method by which a grain growth lattice is mapped to a diffusion lattice. Note that diffusivities along grain boundaries correspond to the grain boundary coefficient, diffusivities across grain boundaries correspond to the bulk coefficient.

RESULTS

We validated our simulation technique by comparing to analytic results. The first comparisons were made for a single-crystal slab with an infinite source opposite either an infinite sink or a diffusion barrier. As figure 2 shows, the finite difference calculations give results that are in excellent agreement with the analytic solutions for both cases.

Figure 2. Comparison of finite difference calculation results to analytic results for the solution of diffusion through a 400x400 finite slab (a) with the conditions $D=1$, $C(t=0,x,y)=0$, $C(t>0,x=0,y)=1$, $C(t>0,x=400,y)=0$, and (b) with the conditions $D=1$, $C(t=0,x,y)=0$, $C(t>0,x=0,y)=1$, $J_x(t>0,x=400,y)=0$.

We then simulated diffusion for the case of multiple grain boundaries running through a finite slab, as reported by Gilmer and Farrell^{4,5}, and compared our results to their solutions. When using precisely the parameters they reported, we found quantitative disagreement between the two models, despite qualitative similarity. We found that good agreement could be obtained if we doubled the length scale (i.e. grain boundary width and separation) in our films. This agreement is shown in figure 3. It appears that there may be a factor of two discrepancy in the length scale definitions of the models.

Figure 3. Comparison of finite difference calculation results to semi-analytic results reported by Gilmer and Farrell for the solution of diffusion into a finite slab 200 units thick with equally spaced grain boundaries normal to the surface and a ratio of boundary to bulk diffusivity $D_b/D_g = 1000$. The analytic results use a boundary separation $L=200$ units and a grain boundary width $\delta=1$. The finite difference results use $L=400$ and $\delta=2$. Dashed lines and open symbols correspond to the case of diffusion into a film with a diffusion barrier on the back side. Solid lines and closed symbols correspond to the case of diffusion into a film with a high diffusivity surface on the back side.

We also used our technique to study the grain boundary diffusion through realistic microstructures. The effect of grain size on the effective diffusivity in simulated microstructures was investigated by examining the steady-state diffusion through finite slabs. The results of this study are shown in figure 4. A law-of-mixing diffusion coefficient $D_{eff} = D_b \delta / 2\bar{r}$ is also plotted for comparison. The law of mixing expression should be valid when $D_b \delta \gg D_g$, where D_g is the diffusion coefficient in the grain bulk; D_b is the grain boundary coefficient, δ is the grain boundary width, $\bar{r}$ is the average grain size, and the constant $1/2$ compensates for the indirect path of grain boundary diffusion. The simulation data shows that the effective diffusivity varies inversely with grain size as predicted by the law of mixing. However, D_{eff} is smaller than the law of mixing predicts at all grain sizes. As the grain size increases, D_{eff} decreases faster than the law of mixing predicts. This may be the result of statistically significant "bottlenecks" to diffusion in the grain boundary structure that may arise when grain sizes approach the size the diffusion lattice.

It was not possible to compare the penetration behavior obtained from our simulations to the $6/5$ power law behavior found by Levine and MacCallum. Even with relatively large 400×400 lattices, variation in the concentration profile resulting from the finite size of the grains

dominates any long-range average behavior. Graphs of the penetration concentration profile into the polycrystalline structures with different average grain sizes are shown in figure 5.

Figure 4. Effective diffusion coefficient as a function of grain size for a simulated microstructure on a 400x400 lattice with $D_b=10^{-1}$ and $D_g=10^{-6}$. The law of mixing function $D_{eff} = D_b \delta / 2 \bar{r}$ is shown for comparison.

Figure 5. Penetration into simulated polycrystalline microstructures. $D_g=10^{-6}$, $D_b=10^{-1}$, (a) $\bar{r}=10$, (b) $\bar{r}=30$.

CONCLUSIONS

We have implemented a flexible finite difference technique based on the Crank-Nicholson scheme that uses the Alternating Direction Implicit (ADI) method to provide stability for long timesteps. Our implementation uses a variable timestep to maintain a desired precision for both short-time and long-time regimes of diffusion.

We find excellent quantitative agreement with analytic results for one-dimensional diffusion problems. There is some discrepancy between the results obtained by our method and those obtained in the solution of idealized grain boundary diffusion problems published by Gilmer and

Farrell^{4,5}. Since the results can nearly be made equivalent by scaling length scales in one dimension by a factor of two in our simulation, this discrepancy may result from a difference in the interpretation of the modeled geometry.

In simulations of grain boundary diffusion in realistic microstructures, we find that the effective diffusivity varies with the inverse of average grain size. We see deviations from this scaling as the grain size approaches the same order of magnitude as our finite lattice.

Greater resolution is required to model thinner grain boundaries. Real microstructures contain grain boundaries with thicknesses that are at most 10^{-3} of the average grain diameter. In our simulations, grain boundary thicknesses are at least 10^{-3} of the average grain diameter. Thus, more realistic simulations will require the use of larger diffusion lattices.

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