The Kirkendall effect in the phase field crystal model

K. R. Elder; K. Thornton; J. J. Hoyt

a Department of Physics, Oakland University, Rochester, MI 48309 b Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109 c Department of Materials Science and Engineering, McMaster University, Hamilton, ON, Canada L8S-4L7

First published on: 16 August 2010
The Kirkendall effect in the phase field crystal model

K.R. Elder\textsuperscript{a*}, K. Thornton\textsuperscript{b} and J.J. Hoyt\textsuperscript{c}

\textsuperscript{a}Department of Physics, Oakland University, Rochester, MI 48309; \textsuperscript{b}Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109; \textsuperscript{c}Department of Materials Science and Engineering, McMaster University, Hamilton, ON, Canada L8S-4L7

(Received 9 January 2010; final version received 29 June 2010)

The Kirkendall effect stems from unequal mobilities of atomic species, which give rise to a net flux of vacancies during interdiffusion in substitutional alloys. In this work, we study a simple binary phase field crystal model to include unequal atomic mobilities and demonstrate that the model captures many phenomena associated with the Kirkendall effect, including the center of mass motion, vacancy supersaturation that can lead to pore formation, and enhanced vacancy concentration near grain boundaries.

Keywords: Kirkendall effect; binary phase field crystal model; crystal growth; computer simulation; microstructure formation

1. Introduction

In a classic experiment, Smigelskas and Kirkendall [1] demonstrated that, in a binary substitutional alloy in which the vacancy-atom exchange rates (or hopping frequencies) are different between the two atomic species, interdiffusion is accompanied by a net flux of vacancies. This phenomenon became known as the Kirkendall effect after Kirkendall’s original observation of marker motion in a diffusion couple [2]. The discovery led to a formulation of the so-called interdiffusion coefficient and an expression for the velocity of material flow based on the difference in the tracer diffusivities of the two components [3]. It also served as an experimental proof that substitutional diffusion is facilitated by vacancies, as was suggested theoretically [4], rather than by mechanisms such as direct exchange of two atoms or rotational swapping of multiple atoms. In the years since the original experiments on Cu/Cu–Zn diffusion couples, the Kirkendall effect, broadly defined herein to refer to effects resulting from the net vacancy flux arising from unequal mobilities of atomic species, has been shown to play a role in a wide variety of materials phenomena. For example, it causes deformation due to the lattice expansion and contraction that result from the net vacancy flux during interdiffusion between two contacting metals or metallic alloys with atomic species having different hopping frequencies [5–9]. In extreme cases, the net vacancy flux can lead to

*Corresponding author. Email: elder@oakland.edu
a supersaturation of vacancies and to the subsequent formation of voids in the material [10–13]. While Kirkendall voiding poses a major concern for the reliability of electronics packaging [14], it has also recently been employed to fabricate hollow core nanorods and nanospheres [15–20], nanostructures that could be useful in designing novel materials for optoelectronics and energy conversion. The Kirkendall effect is also important in structural materials for nuclear energy applications. Under irradiation conditions alloys tend to segregate solute species near grain boundaries, surfaces, and dislocations through a process known as the inverse Kirkendall effect [21–24], which affects their structural integrity. Recently, continuum-level models for simulating interdiffusion have been developed and applied to study various phenomena associated with the Kirkendall effect [25–32]. These models include the effects of elasticity [25,26], discrete vacancy sources/sinks with [30–32] and without [27–29] molar volume changes. All of these works describe the state of the system through continuum variables such as the concentrations of each species. In this paper, we examine the Kirkendall effect using the phase field crystal (PFC) model for a binary alloy [33,34]. The PFC model [39,40] is a computational framework able to describe the dynamics of solids and liquid–solid mixtures over the large time-scale associated with interdiffusion in alloys, while providing atomic-scale resolution. We demonstrate that the model naturally incorporates the Kirkendall effect, just as it includes the elasticity and interfacial anisotropy.

2. Model

Recently a phase field crystal model of a substitutional binary alloy was developed to model elasticity, plasticity, solidification and phase segregation [33]. The model can be written in terms of two fields, the number density difference, \( n = (\rho_A + \rho_B - \rho_\ell)/\rho_\ell \), and the concentration, \( \psi = (\rho_A - \rho_B)/\rho_\ell \), where \( \rho_A, \rho_B \) and \( \rho_\ell \) are the atomic number densities of \( A \) atoms, \( B \) atoms and a reference liquid, respectively. While this model can incorporate atomic species of different sizes, for this study the atoms will be assumed to have equal sizes so the influence of mobility can be studied independently. In this limit, the free energy functional in dimensionless form becomes

\[
F = \int \mathrm{d}\tilde{x} \left[ \frac{\Lambda^0}{2} n - \frac{t}{3} n^3 + \frac{v}{4} n^4 + \gamma \psi + \frac{\omega}{2} \psi^2 + \frac{u}{4} \psi^4 + \frac{K}{2} \left| \nabla \psi \right|^2 \right],
\]

(1)

where \( \Lambda^0 \) is the operator defined by

\[
\Lambda^0 \equiv \Delta B_0 + B_\ell^4 \psi^2 + B_0^c (1 + \nabla^2)^2,
\]

(2)

and \( \Delta B_0 \equiv B_0^\ell - B_0^c \), \( F \equiv \Delta F/(k_B T \rho_\ell \lambda_0^d) \), \( \tilde{x} \equiv \tilde{r}/\lambda \) and \( K \equiv K/\lambda^2 \). All lengths have been non-dimensionalized by \( \lambda \), which simply sets the length-scale. The parameter \( B_0^\ell \) is the dimensionless bulk modulus of the liquid, \( B_0^c \) is proportional to the elastic constants of the crystal, \( K \) is the gradient energy coefficient for the concentration field, and the other parameters \( t, v, \omega, B_\ell^4, \omega, u \) affect the phase diagram; more details can be found in [33]. For this initial study we consider a system in which both atomic species have the same lattice constant. As noted in earlier work [33,34] a concentration-dependent lattice constant can be easily modeled by replacing \( (1 + \nabla^2)^2 \) by \( 1 + 2R^2\nabla^2 + R^4\nabla^4 \) and making \( R \) a function of \( \psi \). For example, \( R = 1 + \alpha \psi \) would
reproduce Vegard’s law as is done in [34]. This model is essentially a simplification of a more complex description such as classical density functional theory [35–37] or the model recently proposed by Jin and Khachaturyan [38].

While it is possible to write down equations of motion for $n$ and $\psi$, for an investigation of the Kirkendall effect, it is more convenient to use the equations of motion for the dimensionless atomic number density of each species, i.e. $n_A \equiv (n + \psi)/2 = \rho_A/\rho_0$ and $n_B \equiv (n - \psi)/2 = \rho_B/\rho_0$. The equations of motion for $n_A$ and $n_B$ then become [33]

$$\frac{\partial n_A}{\partial t} = M_A \nabla^2 \frac{\delta F}{\delta n_A} = M_A \nabla^2 \left[ A^n n - m^2 + v n^3 + \left[ w + B_2^\prime n^2 \right] \psi + u \psi^3 - K \nabla^2 \psi \right]$$

(3)

$$\frac{\partial n_B}{\partial t} = M_B \nabla^2 \frac{\delta F}{\delta n_B} = M_B \nabla^2 \left[ A^n n - m^2 + v n^3 - \left[ w + B_2^\prime n^2 \right] \psi - u \psi^3 + K \nabla^2 \psi \right].$$

(4)

The parameters $M_A$ and $M_B$ are the mobilities of the $A$ and $B$ atoms, respectively. In the following section, numerical simulations based on these equations will be conducted to examine the Kirkendall effect under various initial conditions and mobility differences. For simplicity, the time is non-dimensionalized such that $M_A$ is equal to one, and the $A$ species is taken to be the fast diffuser (i.e. $M_B < M_A$).

Rigorous consideration of the Kirkendall effect in continuum theories requires off-diagonal terms [27–29,41,42] of mobilities that couple the fluxes to the concentrations of other species, as well as concentration-dependent (and thus spatially varying) mobilities. Expressions for such mobilities are available in analytic form for thermodynamically ideal, but kinetically non-ideal binary substitutional alloys [43]. However, as a first step, we assume the above simplified set of equations, which allows us to develop analytical solutions as presented in the Appendix. We also note that the recent dynamic classical density functional calculations of Archer [44] do not indicate off-diagonal terms for such an atomic-scale description.

3. Simulations

To examine the Kirkendall effect, numerical simulations of the dynamical equations were conducted under various conditions in a two-dimensional cell with periodic boundary conditions in a system where the equilibrium crystalline phase in this two-dimensional geometry is a hexagonal structure. The simulations were conducted using a simple Euler algorithm for the time derivatives with $\Delta t = 0.01$ and the usual spherical Laplacian approximation for all spatial gradients with $\Delta x \approx 1$. For simulations in which the crystalline phase completely fills the simulation box, the precise value of $\Delta x$ was always chosen to exactly fit an integer number of atoms in both the $x$ and $y$ directions. The parameters chosen were $(B_0^\prime, B_2^\prime, B_x^\prime, t, v, K, w, u) = (0.7, -1.8, 1.0, 6.1, 0.4, 1.0, 4.0, 4.0)$. For this parameter set, the average value of $n$ at liquid–solid coexistence and the equilibrium lattice constant were determined numerically by equilibrating a single crystal coexisting with a liquid. The average value of $n$ at coexistence is $0.2517$ in liquid and $0.1503$ in solid; the equilibrium lattice constant is $a = 6.927$. The equilibrium state of both liquid and crystalline phases is homogeneous in $\psi$. Other relevant numerical details are given in the appropriate sections.
3.1. **Single crystal: vacancy diffusion**

We first examine a simple case of a single crystal that contains an initial concentration inhomogeneity in the absence of grain boundaries, surfaces or other natural sources or sinks of vacancies. In this case, the vacancy concentration will exhibit transient evolution, but it will not lead to a net motion of the crystal in the infinite time limit. In essence, the vacancies will slosh back and forth, first as the original concentration gradient of the atomic species initially causes a preferential motion of vacancies, followed eventually by equilibration in the long-time limit. To examine this case, a quasi-one-dimensional simulation was conducted in a system of size \((L_x, L_y) = (a, 161a_y)\) where \(a\) is the lattice constant of the crystalline phase and \(a_y = \sqrt{3}a\). The initial configuration was produced using a one mode approximation for \(n\) at a uniform concentration difference of \(\psi = 0\) and average number density difference of \(\bar{n}/\bar{C} = 0\):

\[
n(x, y, t = 0) = \bar{n} + C(\cos(2q_y y)/2 - \cos(q_x x) \cos(q_y y)),
\]

where \(q_x = 2\pi/a\) and \(q_y = q_x/\sqrt{3}\). The amplitude \(C\) was initially set to \(1/2\) and Equations (3) and (4) were evolved until equilibrium was established at \(t = 10^4\), when the percent change in the total free energy, \(F\) given in Equation (1), per time step was less than \(10^{-14}\%\). The grid spacing for these simulations was \(\Delta x = 0.989634 = a/7\).

To study the Kirkendall effect, a concentration difference was introduced into the relaxed state such that \(\psi = 0.1\) for \(y = [-L_y/2, 0]\) and \(\psi = -0.1\) for \(y = [0, L_y/2]\). Equations (3) and (4) were then evolved to study the influence of different atomic mobilities. Results of a sample simulation are illustrated in Figure 1 for a mobility ratio of \(M_B/M_A = 0.1\).

As shown in Figure 1, the density is initially enhanced on the positive \(y\) side as the \(A\) atoms (the fast diffuser) diffuse from negative to positive \(y\) faster than the \(B\) atoms (the slow diffuser) diffuse from positive to negative \(y\). The enhancement of density in the crystalline region can be interpreted as depletion of vacancies; conversely, its reduction indicates a vacancy concentration larger than the equilibrium value. Atomistically, the \(A\) atoms exchange more often with vacancies than the \(B\) atoms, giving rise to a large net \(A\) flux where the concentration gradient is large. This flux is mainly compensated by the vacancy flux since the mobility of \(B\) is small. This results in net mass transport toward the \(B\)-rich side (or conversely, net vacancy transport toward the \(A\)-rich side). Thus, the PFC model clearly retains the features stemming from such atomistic processes. At very late times when the concentration field, \(\psi\), relaxes to equilibrium (i.e. \(\psi = 0\) everywhere), the density returns to a uniform state, in agreement with a simulation based on continuum-level diffusion equations [27]. Therefore, mass transport is only a transitory effect when there are no sources or sinks of vacancies.

To quantify mass transport in these simulations, it is useful to calculate the center of mass in the sample, which is defined in the usual manner, i.e.

\[
y_{cm} = \frac{\int d\vec{r} y (1 + n)}{\int d\vec{r} (1 + n)},
\]

since \(\rho = \rho(1 + n)\). In Figure 2a, \(y_{cm}\) is plotted as a function of the square root of time for a mobility ratio of \(M_B/M_A = 0.1\). As seen in this figure, the center of mass
Figure 1. Various fields are plotted at selected times for a one-dimensional diffusion couple with a mobility ratio of $M_B/M_A = 0.1$. Figures (i), (ii), (iii) and (iv) correspond to the number density difference ($n$), concentration difference ($\psi$) and the number density differences over their corresponding average values for $A$ ($n_A - \bar{n}_A$) and $B$ ($n_B - \bar{n}_B$) species, respectively.

Figure 2. (a) The center of mass as a function of the square root of time for the simulations shown in Figure 1. The arrows correspond to the selected times shown in Figure 1. The dots are the results of the numerical simulation, and the line is given by Equation (11) in the Appendix. (b) The effective diffusion constant, derived in the Appendix, is shown as a function of $R = (M_A - M_B)/(M_A + M_B)$. The dots are again from the simulation; the line is given by Equation (14) in the Appendix.
initially moves to positive $y$ and then slowly relaxes back to zero. Thus the vacancies slosh back and forth but do not permanently move the sample. The precise movement of $y_{cm}$ can be predicted, assuming that the density and concentration satisfy linear coupled diffusion equations, as discussed in the Appendix. These calculations show that for short times $y_{cm}^2 = 2D_{eff}t$, and $y_{cm} \sim e^{-t/\tau}$ at late times, where the effective early-time diffusion constant, $D_{eff}$, and the decay constant, $\tau$, are given in the Appendix. The analysis in the Appendix contains two adjustable parameters ($\alpha$ and $\beta$). These parameters in principle can be calculated from an amplitude expansion of the binary PFC model, but such an analysis is beyond the scope of the current manuscript. For $M_B/M_A = 0.1$, the motion of $y_{cm}$ can be fitted quite accurately with the choice ($\alpha$, $\beta$) = (1.11, 0.662), as shown in Figure 2a. To further verify these calculations, the effective early-time diffusion constant was numerically calculated for various $M_B/M_A$ ratios and compared to the analytic calculations in the Appendix using the same values of $\alpha$ and $\beta$ obtained for the $M_B/M_A = 0.1$ case. The numerical and analytic results are in excellent agreement as shown in Figure 2b, where the ratio $R$ is given by $R = (M_A - M_B)/(M_A + M_B)$.

3.2. Surfaces as sources and sinks of vacancies

As discussed in the previous section, the biased diffusion of one species over the other can lead to motion of the center of mass due to vacancy diffusion from one region to another. However, if there are no sinks or sources of vacancies, the center of mass will eventually return to its original position when equilibrium is reached. In reality, solids contain defects such as surfaces, grain boundaries, and dislocations that supply or absorb vacancies. In this section, we first examine the influence of the liquid–solid interface, which can serve as sources and sinks of vacancies, for two classical examples. In these examples, a small crystal is equilibrated with a liquid at zero concentration (i.e. even mixture of $A$ and $B$). Then a concentration inhomogeneity is introduced such that either the top half or central region of the crystal has a different concentration from the lower or outer part of the crystal, respectively. The results of the simulations are described in Sections 3.2.1 and 3.2.2.

3.2.1. Crystal motion

To simulate the crystal motion resulting from the Kirkendall effect, an initial condition was created by setting the concentration of the bottom (top) half of the crystal to 0.1 ($-0.1$) in a system of approximate size (148$a$, 148$a$). The mobility ratio was taken to be $M_B/M_A = 0.001$. A comparison of the initial crystal position with that at later times is shown in Figure 3. The time dependence of $y_{cm}$ for these simulations is shown in Figure 4a for two different values of $M_B/M_A$. The spatial dependences of $n$ and $\psi$ are shown in Figures 4b and c. The results indicate that the crystal has moved upward by melting atomic layers on the lower surfaces and nucleating new layers on the upper surfaces, implying that the top surfaces (surfaces rich in slow diffusers) provide sources of vacancies and the bottom surfaces (surfaces rich in fast diffusers) act as sinks for vacancies. The PFC model again captures the atomic-level processes. As $A$ atoms diffuse upwards, vacancies are depleted on the upper half, which then drives the vacancy flux from the liquid to
the solid, moving the upper interface upwards. Conversely, the vacancy concentration is enhanced on the bottom half, and thus there is a thermodynamic driving force for vacancies to be ejected from the solid. Indeed, the liquid concentration just outside of the solid is significantly below the equilibrium level (see the sharp drop in $n$ for $y < 20$ in Figure 4b). However, melting on this side appears to be a slower process than the growth on the initially slow-diffuser-rich side.

Since vacancies are injected at the top surfaces and ejected at the bottom surfaces, a permanent displacement of the crystal results, unlike the simulations presented in Section 3.1. For $M_B/M_A = 0.1$, some back diffusion of vacancies does occur but the sample equilibrates in a permanently shifted position. The corresponding magnified views of the top portion of the crystal show the growth of the crystal via nucleation of a new layer in the middle of the interface, away from the corners, which then grows outward toward the corners (see the bottom panels in Figure 3).
Another important consequence of the Kirkendall effect is the formation of pores when a solid consisting of the faster atoms is surrounded by a solid of the slower species. To examine this phenomenon a single crystal was equilibrated at $\psi = 0$, then the concentration in the central circular region of radius $\psi C_{\text{fast}}$ of the crystal was increased to $\psi = 0.2$ and lowered to $\psi = -0.2$ elsewhere in the solid. The initial concentration in the liquid was unaltered at $\psi = 0$. The mobility ratio was set to $M_B/M_A = 0.001$. The results of this simulation are shown in Figure 5. As the system evolves, the more mobile atoms in the central region diffuse into the surrounding slow-diffuser-rich region until the density locally reduces to such an extent that a liquid phase nucleates and grows. Note that nucleation of the liquid region occurs not at the center but near the diffusion interface on the initially fast-diffuser-rich side where the vacancy concentration is most enhanced, in agreement with the prediction from continuum-level simulations [27,45,46]. Furthermore, there exists a vacancy flux into the crystal on the outer liquid–solid interface, which causes the crystal to expand outward.

Since the current PFC model does not permit the formation of the vapor phase, our observations are limited to the formation of a liquid region instead. However, our results indicate that processes such as vacancy injection, ejection, and supersaturation, which would lead to pore formation, are observed naturally in the model. Given the development of a vapor-liquid–solid PFC model, we expect that pore formation can be properly simulated in this approach. This will be deferred to future work.

3.3. Grain boundaries and dislocations

In most crystals, dislocations and grain boundaries provide sources and sinks of vacancies. In this section, the interactions of small and large angle grain boundaries are examined. A small angle grain boundary is essentially an array of well separated dislocations, while a large angle grain boundary is essentially a continuous line of disordered region. The grain boundaries were created using the method described

![Figure 5. Formation of a liquid region due to the Kirkendall effect. The number density is shown at four times, $t = 0, 15,000, 200,000$ and $500,000$, in (a), (b), (c) and (d), respectively. The initial concentration is set such that it was 0.2 in the central region of radius 15.3$a$, $-0.2$ between the central region and dashed hexagon, and 0 elsewhere. In (d) the radius of the inner liquid region is approximately 13$a$.](image)
Briefly, this method consists of first establishing a configuration of two perfect crystals at different orientation separated by a small layer of supercooled liquid. Simulations were then run to allow the liquid layers to solidify and naturally form a grain boundary between the two crystals. Since the simulations were conducted in a periodic system, two grain boundaries within the computational domain are formed.

Two types of simulations were performed to examine the interaction of the grain boundaries with the concentration field and the density field. In the first set of simulations, a square wave concentration profile was introduced parallel to the grain boundary so that the diffusion interface was perpendicular to the grain boundary for a mobility ratio of $M_B/M_A = 0.01$. The simulations were conducted in a system of approximate size $(148a, 148a)$. An initial concentration profile has been established such that the system is rich in species $A$ on the left half ($\psi = 0.1$) and $B$ rich on the right side ($\psi = -0.1$). The evolution of the density field is shown in Figures 6a and b for the low and high angle grain boundaries, respectively. In the figures, a smoothed number density is shown; blue indicates low density, and red corresponds to high density. The smoothing consisted of six consecutive box averages over a box of size $(3\Delta x, 3\Delta x)$. As interdiffusion proceeds, a flux of the fast-diffusing $A$ species from left to right arises, and this flux is balanced by a counter-flux mostly consisting of vacancies (with a small amount of the slow diffuser, $B$). The net vacancy flux is manifest in a decreased density, as indicated by the expanding blue regions with increasing blue intensity; this is most strongly observed around the isolated dislocation cores in the low angle grain boundary case and along the grain boundary plane for the high angle case. In addition, a net mass flux is also evident on the right side of the simulation cell from an expansion of red regions and increasing red intensity, as well as the narrowing of the dislocation cores.

Figure 6 shows clearly that the vacancy concentration is enhanced (or conversely, the average density is reduced) along the grain boundaries, in agreement with the corresponding continuum-level simulations [28]. Experiments on a Cu/NiAl couple observed Kirkendall porosity around grain boundaries [49] which is consistent with an enhanced vacancy concentration along such boundaries. Both continuum-level simulations [28] and experiments on a Sn/Au thin-film couple [50] have further found that interdiffusion is enhanced along the grain boundary, which was only weakly observed in the PFC model. This difference stems from the simplified mobilities we have assumed for this study. As mentioned earlier, we defer consideration of the concentration-dependent mobility matrix with coupling terms to a future study.

A second set of the grain boundary simulations was performed with the diffusion interface coincident with the grain boundary in a system of approximate size $(1182a, 6a, y)$. As in the previous simulation, both a small and a large grain boundary misorientation were investigated. The initial configuration consisted of $\psi = 0.2$ ($-0.2$) above (below) the grain boundary. Sample snapshots of these configurations are shown in Figures 7a–e and f–j for high and low angle grain boundaries, respectively. As can be seen in these figures, the net vacancy flux results in the formation of a liquid region indicating that these cases may lead to Kirkendall void formation. Since the grain boundary in these cases coincides with the diffusion
interface, the grain boundary serves as a nucleation site. In the small angle boundary case, (a)–(e), the liquid region initially forms at the isolated dislocation core and expands over time along the direction of interdiffusion toward the fast-diffuser-rich side. In the high angle boundary case, a merging of the liquid regions can be observed at a later time and, as is evident from the small remaining crystal of different orientation in Figure 7j, the merging of the liquid region has occurred within the B-rich (bottom) crystal.

Figure 6. The smoothed average number density as a function of time for two different initial configurations. In both (a) and (b), the initial concentration profile is 0.1 (–0.1) on the left (right) half of the cell, and the dashed black line indicates the location of a symmetric tilt grain boundary separating the upper and lower portions of the cell. Blue corresponds to low density, and red indicates high density. The mismatch angle of the grain boundary is 3.1° and 32.2° for (a) and (b), respectively. In both (a) and (b), the figures (i), (ii), (iii) and (iv) correspond to t = 5000, 10 000, 15 000 and 21 000, respectively. Each panel depicts one quarter of this full simulation cell.

Figure 7. The number density n is depicted in (a)–(e) and (f)–(j) for a low-angle (θ = 4.8°) and high-angle (θ = 19.4°) grain boundary cases, respectively. (a)–(e) and (f)–(j) correspond to t = 10 000, 15 000, 25 000, 50 000 and 145 000, respectively. The black tick marks indicate the initial position of the grain boundary and compositional change. Each panel depicts a portion of size (42a, 6a.), where the total cell is size (1182a, 6a.).
4. Conclusions

In this paper, the binary phase field crystal model incorporating variable atomic mobilities of the two species was employed to study the Kirkendall effect, broadly defined here as phenomena resulting from net vacancy flux arising from unequal mobilities of atomic species. Three different aspects of the Kirkendall effect were investigated. In a perfect crystal with no sources or sinks of vacancies, net mass transport was shown to be a transitory effect that did not permanently translate the crystal, in agreement with existing continuum simulation results [27]. The transitory dynamics were shown to be consistent with the simple linear coupled diffusion equations for the density and concentration, and the detailed analysis was provided in the Appendix. In contrast, when surfaces were introduced, a net vacancy flux developed and a permanent shift of the crystal was observed with one side of the crystal growing by nucleating new crystalline layers due to supersaturation of atomic species and the other side melting due to undersaturation. A second simulation demonstrated that the binary phase field crystal model captures vacancy injection, ejection and supersaturation that can lead to the phenomenon of Kirkendall voiding. Small nanocrystals, with the interior initially enriched in the higher mobility species, showed melting in the interior region, indicating that, if a vapor phase is allowed to form, it can lead to the formation of pores during the interdiffusion process. Finally, diffusion across and parallel to small and large angle grain boundaries has been studied. It has been shown that grain boundaries in the phase field crystal model act as sinks and sources for vacancies and, in some cases, act as sites for the formation of Kirkendall voids.

Acknowledgements

K.R.E. acknowledges support from NSF under Grant No. DMR-0906676. K.T. is grateful for the financial support from NSF under Grant Nos. DMR-0502737 and DMR-0746424. J.J.H. was supported by a Natural Science and Engineering Reasearch Council (NSERC) of Canada Discovery grant.

References

Appendix. One-dimensional center of mass motion

To obtain an approximate analytical form for the motion of the center of mass in one dimension, it is convenient to consider the equations of motion for the number density $n$ and concentration $\psi$, which can be written as [33]

$$\frac{\partial n}{\partial t} = M_1 \nabla^2 \frac{\partial F}{\partial n} + M_2 \nabla^2 \frac{\partial F}{\partial \psi}$$
$$\frac{\partial \psi}{\partial t} = M_2 \nabla^2 \frac{\partial F}{\partial n} + M_1 \nabla^2 \frac{\partial F}{\partial \psi},$$

(6)

where $M_1 = M_A + M_B$ and $M_2 = M_A - M_B$. To estimate the diffusion of concentration and mass for an initial condition in which $\psi$ is a square wave and $n$ is a perfect crystal, it is useful to propose linearized equations of motion for $\psi$ and the locally averaged density $\bar{n}$ as

$$\frac{\partial \delta \bar{n}}{\partial t} = \alpha M_1 \nabla^2 \delta \bar{n} + \beta M_2 \nabla^2 \psi$$
$$\frac{\partial \psi}{\partial t} = \alpha M_2 \nabla^2 \delta \bar{n} + \beta M_1 \nabla^2 \psi,$$

(7)

where $\delta \bar{n}$ is the local average density deviation from the overall average density and the parameters $\alpha$ and $\beta$ are fitting parameters that, in principle, could be derived from Equations (3) and (4) using the amplitude expansion method discussed in [51]. Solving these in Fourier space for $\delta \bar{n}(k,t)$, subject to the boundary conditions, $\delta \bar{n}(k,0) = 0$ and $\psi(k,0) = \psi_{k,0}$, gives

$$\delta \bar{n}(k,t) = -\frac{2R\beta}{F} \hat{\psi}_{k,0} \exp \left( -\frac{(\beta + \alpha)M_1 k^2 t}{2} \right) \sinh \left( \frac{F M_1 k^2 t}{2} \right),$$

(8)

where $F \equiv \sqrt{\left( \beta - \alpha \right)^2 + 4\beta \alpha R^2}$, $R \equiv (M_A - M_B)/(M_A + M_B)$, $k \equiv n \pi/L$ and

$$\delta \bar{n}(k,0) = \frac{1}{L} \int_{-L}^{L} dy \sin(ky) \delta \bar{n}(y,t).$$

(9)

For a square wave initial condition for $\psi$ of amplitude $\psi_o$, $\hat{\psi}_{k,0} = -4\psi_o/(\pi n)$ for $n$ odd and zero otherwise, thus the solution for $\bar{n}$ is

$$\delta \bar{n}(y,t) = \frac{8R\beta\psi_o}{F\pi} \sum_{n=1,3,...} \frac{1}{n} \sin \left( \frac{n\pi y}{L} \right) \exp \left( -\frac{(\beta + \alpha)M_1 (n\pi)^2 t}{2L^2} \right) \sinh \left( \frac{F M_1 (n\pi)^2 t}{2L^2} \right).$$

(10)

The center mass can now be evaluated, i.e.

$$\gamma_{cm} = \frac{\int_{-L}^{L} dy \left( 1 + \bar{n}_o + \delta \bar{n} \right)}{\int_{-L}^{L} dy \left( 1 + \bar{n}_o + \delta \bar{n} \right)}$$
$$= \frac{8R\beta\psi_o L}{F\pi^2(1 + \bar{n}_o)} \left[ \sum_{n=1,3,...} \frac{1}{n^2} \exp \left( -\frac{(\beta + \alpha)M_1 (n\pi)^2 t}{2L^2} \right) \sinh \left( \frac{F M_1 (n\pi)^2 t}{2L^2} \right) \right].$$

(11)

In the late-time limit, the summation is dominated by $n=1$ and noting $F < \alpha + \beta$, Equation (11) yields

$$\gamma_{cm} \approx \frac{8R\beta\psi_o L}{F\pi^2(1 + \bar{n}_o)} \exp \left( -\frac{(\beta + \alpha - F)M_1 \pi^2 t}{2L^2} \right)$$

(12)

or $\gamma_{cm} \sim e^{-t/\tau}$. In the early-time limit, the summation over $n$ can be replaced by an integration to obtain

$$\gamma_{cm} \approx \frac{2R\beta\psi_o L}{F\pi^2(1 + \bar{n}_o)} \left[ \frac{\pi^3 M_1 t}{2L^2} \left( \sqrt{\alpha + \beta + F} - \sqrt{\alpha + \beta - F} \right) \right]$$
$$= \frac{2^{1/2} \beta \psi_o R M^{1/2}(\sqrt{\alpha + \beta + F} - \sqrt{\alpha + \beta - F})}{F(1 + \bar{n}_o)\pi^{1/2}} \sqrt{t}$$

(13)
or $y_{cm} \propto \sqrt{t}$. This result is reminiscent of simple diffusion where the mean square displacement $\langle x^2 \rangle = 2Dt$, which would imply an effective diffusion constant of

$$D_{\text{eff}} = \frac{\beta^2 \psi_o^2 R^2 M_1 (\sqrt{\alpha + \beta + \bar{F}} - \sqrt{\alpha + \beta - \bar{F}})^2}{F^2 (1 + \bar{n}_o)^2 \pi}.$$  \hfill (14)

In the small $R$ limit this becomes

$$D_{\text{eff}} \approx \frac{2\beta^2 \psi_o^2 (\sqrt{\alpha - \sqrt{\beta}})^2}{\pi (1 + \bar{n}_o)^2 (\alpha - \beta)^2} M_1 R^2 + O(R^4 + \cdots),$$  \hfill (15)

and when $R \approx 1$, it is

$$D_{\text{eff}} = \frac{2\beta^2 \psi_o^2 M_1}{(1 + \bar{n}_o)^{1/2} \pi^{1/2}} \left( \frac{\sqrt{8\beta\alpha}}{\alpha + \beta} \right) \left( 1 - R \right)^{1/2} + \cdots.$$  \hfill (16)

In summary, Equations (12) and (13) predict that the center of mass increases as the square of time at early times and then at late times exponentially decays back to zero.