Phase Field Crystal Study of Kirkendall Effect-Induced Void Formation and Evolution at Phase Boundaries (Postprint)

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Abstract

The formation and expansion processes of voids at phase boundaries induced by the Kirkendall effect were investigated using a binary crystal phase-field model. Simulation results demonstrate that for phase boundaries with small misorientation angles, voids migrate toward the side with higher atomic mobility (the α phase), with void shapes evolving from an initial parallelogram to a hexagonal configuration. The atomic annihilation rate around the voids exceeds the generation rate, leading to void expansion, which is accompanied by phase boundary migration as well as concurrent phase growth and shrinkage. For phase boundaries with large misorientation angles, voids additionally expand along the phase boundary direction, resulting in void coalescence that splits apart the phase boundary, with the separated boundaries on both sides exhibiting a serrated morphology. During the diffusion process, the free energy of the system gradually decreases. For phase boundaries with small misorientation angles, increasing the difference in atomic mobility yields no significant difference in the free energy decrease. Conversely, for phase boundaries with large misorientation angles, a greater difference in atomic mobility leads to a faster rate of free energy reduction. As the misorientation angle of the phase boundary increases, the rate of free energy decrease progressively accelerates. The simulation results for phase boundary voids are consistent with experimental observations.

Full Text

Preamble

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Phase Field Crystal Study on the Formation and Evolution of Phase Boundary Void Induced by the Kirkendall Effect

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Abstract

The mechanical properties of materials are related to the integrity of interfaces (phase and grain boundaries). For substitutional alloys, Kirkendall voids tend to form more easily at phase boundaries or grain boundaries when the atomic mobilities of different species are unequal, which degrades the bonding quality of interfaces. So far, there have been many experimental studies on the evolution of Kirkendall voids and their formation mechanism. However, considering the rapid process from formation to evolution of Kirkendall voids, it is hard to capture such processes under real experimental conditions. Therefore, the formation and evolution mechanism of Kirkendall voids needs to be studied.

A binary phase field crystal model was used to simulate the process of void formation and expansion at phase boundaries induced by the Kirkendall effect. Simulated results show that for low misorientation phase boundaries (PB), the void moves toward the side with larger atomic mobility (α phase) and the void shape evolves from an initial parallelogram to a hexagon. The atomic annihilation rate around a void is faster than the growth rate, which results in void expansion. Phase boundary migration, phase growth, and shrinkage can also be observed during void expansion. For large misorientation PBs, voids can also expand along the PB direction, resulting in the connection of voids; consequently, the PB is separated and presents a zigzag shape. In the interdiffusion system, the free energy decreases. The descending speed of free energy is almost equal for low misorientation PBs, while it increases for large misorientation PBs when the atomic mobility difference becomes larger. The descending speed of free energy is proportional to PB misorientations. The PB void predicted from our computer simulation is consistent with experimental observations.

Keywords: binary phase field crystal model, Kirkendall effect, phase boundary, vacancy, Kirkendall void

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1. Model and Methods

1.1 Binary Phase Field Crystal Model

The binary phase field crystal model based on density functional theory was proposed by Elder et al. This model uses two field variables to express the free energy functional: the atomic density field n and the atomic concentration field (where represents the atomic densities of A atoms, B atoms, and the reference liquid phase, respectively). Under the condition of ignoring atomic scale differences, the dimensionless form of the free energy functional for substitutional binary phase field crystal models is expressed as follows:

[Equation for free energy functional would appear here]

where F represents the dimensionless free energy; Λ_0 denotes the dimensionless undercooling; B is the dimensionless liquid bulk modulus; B relates to the elastic constants of the solid crystal; B is the second-order coefficient in the Taylor expansion of the liquid bulk modulus, determining how the liquid bulk modulus varies with the atomic concentration field; K characterizes the gradient energy coefficient of the concentration field; ω determines the tendency for liquid-solid phase transformation; u, K, and ω together determine the phase separation scale; t, v, and γ are model parameters.

To simplify calculations without losing the fundamental physical characteristics of the binary phase field crystal model, the density field evolution equations for the two atom types A and B in this work are as follows:

[Equations (2) and (3) would appear here]

According to the relationship between atomic density and concentration fields, the kinetic evolution equations for the density field n and concentration field can be derived:

[Equations (4) and (5) would appear here]

where M and M are the atomic mobilities of A and B atoms, respectively. Based on the dimensionless time formulation, to simplify calculations, the mobility of A atoms is set to 1 (i.e., $M = 1$, with $M > M$). The Euler method is used for temporal discretization, while a semi-implicit Fourier spectral method is employed for spatial discretization. After discretization, the system evolves to obtain the atomic density and concentration fields.

1.2 Simulation Parameters and Initial Setup

The parameters for the binary phase field crystal model in this work follow those of Elder et al. The model parameters are selected as: [parameter list]. The equilibrium lattice constant is a q = 6.927. The computational domain is L = 1024Δx, L = 1024Δy, with periodic boundary conditions. The spatial and temporal step sizes are Δx = 0.1 and Δt = 0.1, respectively. The initial concentration field setup is shown in [Figure 1: see original paper].

[Figure 1: see original paper] Initial setup schematic of phase boundary void induced by the Kirkendall effect (x and y indicate the two directions of the simulated area. , PB, J , J , and J indicate the atomic concentration field, the position of the phase boundary, the A atomic flux from α phase to β phase, the B atomic flux from β phase to α phase, and the net vacancy flux from β phase to α phase, respectively)

2. Results and Discussion

In the simulation of phase boundary void formation and expansion, the computational domain consists of two phase regions with different misorientation angles. The upper α phase is set with an initial concentration = -0.15 (A-atom-rich region), while the lower β phase is set with an initial concentration = 0.15 (B-atom-rich region). At the beginning of the simulation, the mobilities of both atom types are set to $M = M = 1$, and a thin undercooled liquid phase is introduced between the two phases with different orientations to induce solidification, resulting in a phase boundary at the middle of the computational domain (shown as black dashed lines in [Figure 2: see original paper] and [Figure 3: see original paper]). Subsequently, the atomic mobilities are adjusted to $M = 100M$ to enable interdiffusion. To exclude the influence of another phase boundary created by periodic boundary conditions, only a portion of the computational domain (L = 512Δx, L = 100Δy) is selected for analysis.

2.1 Voids at Low Misorientation Phase Boundaries

[Figure 2: see original paper] shows the formation and evolution of voids at a low misorientation phase boundary ($q = 2°$). At evolution time $t = 1 \times 10^5$Δt, a void forms near the α phase side (higher atomic mobility region) with a parallelogram shape. During subsequent expansion (Figures 2b–e), the void moves toward the α phase side and continuously grows, with its shape evolving from a parallelogram to a hexagon. During void movement, the phase boundary also shifts toward the α phase side, resulting in β phase growth and α phase shrinkage.

The Kirkendall effect occurs during atomic diffusion in substitutional alloys, where atoms diffuse by exchanging positions with vacancies. Due to differences in atomic mobilities, vacancies preferentially exchange with atoms having higher mobility, resulting in net atomic flux and net vacancy flux throughout the diffusion process. Based on the vacancy mechanism, the diffusion process satisfies $J = J$ and $J = J$ (where J is the A atomic flux from α phase to β phase; J is the vacancy flux opposite to J ; J is the B atomic flux from β phase to α phase; J is the vacancy flux opposite to J).

In this case, a low misorientation phase boundary can be considered as composed of a set of dislocation cores with relatively large spacing. As shown in [Figure 2: see original paper]a, the selected analysis region contains only one dislocation core, which can serve as a vacancy annihilation source. During diffusion, since vacancies preferentially exchange with A atoms having higher mobility, there exists a net atomic diffusion flux $\Delta J = J - J$ from α phase to β phase, and a net vacancy diffusion flux $\Delta J = J - J$ from β phase to α phase. Vacancies diffuse to the upper region of the void and recombine with surrounding atoms, causing atomic positions to disappear and the void to expand. Atoms diffuse to the lower region of the void and accumulate, eventually precipitating and causing void annihilation at the lower region. Since the vacancy annihilation (recombination) rate is faster than the atomic precipitation rate, the void moves toward the α phase side and continuously expands based on the dislocation core. This also leads to β phase growth and α phase shrinkage. Additionally, the transformation of void shape from parallelogram to hexagon is related to the model, which simulates a hexagonal phase, so larger voids also tend to become hexagonal.

2.2 Voids at Large Misorientation Phase Boundaries

[Figure 3: see original paper] shows the formation and evolution of voids at a large misorientation phase boundary ($q = 12°$). At evolution time $t = 8 \times 10^3\Delta$t, two side-by-side voids form near the α phase side (higher atomic mobility region) with parallelogram shapes. During subsequent expansion (Figures 3a–j), the voids move toward the α phase side and continuously grow, with shapes also evolving from parallelogram to hexagon. Unlike the low misorientation case, voids also connect with each other. As observed in [Figure 3: see original paper]h, at $t = 1.4 \times 10^5\Delta$t, the connection of voids separates the phase boundary, and the separated phase boundaries on both sides present a zigzag shape. The phase boundary also moves similarly to the low misorientation case, and the results of void expansion, connection, and phase boundary movement cause β phase growth and α phase shrinkage.

Before connection, the void shape, movement, and expansion at large misorientation phase boundaries are similar to those at low misorientation boundaries. The lateral expansion and connection of voids can be explained as follows: large misorientation phase boundaries can be considered as composed of dislocation cores with relatively small spacing (reaching the critical value for inter-void diffusion). During void evolution, due to vacancy concentration differences between different voids, atoms and vacancies between voids undergo recombination reactions (excess vacancy annihilation), gradually leading to void connection.

2.3 Relationship Between Free Energy, Atomic Mobility, and Phase Boundary Misorientation

To characterize the effects of phase boundary misorientation and atomic mobility on system free energy during void formation, this study investigates different phase boundary misorientations ($q = 2°$, 7.6°, 12°, and 24°) and atomic mobility ratios ($M = M$, $M = 10M$, $M = 50M$, and $M = 100M$).

[Figure 4: see original paper] shows the free energy evolution curves over time for diffusion processes at low misorientation ($q = 2°$) and large misorientation ($q = 12°$) phase boundaries under different atomic mobilities. The results show that during diffusion, the free energy of both low and large misorientation systems exhibits the same decreasing trend, consistent with the requirement of free energy reduction in closed interdiffusion systems. However, comparing Figures 4a and 4b reveals that in low misorientation diffusion systems, the free energy descent rate is significantly faster when $M = M$ than when $M \neq M$, and it first reaches a relatively stable state with lower free energy. For large misorientation diffusion systems, the free energy descent rate corresponding to $M = M$ is faster than that of $M \neq M$ in the early diffusion stage, and at T 3 $\times 10^5\Delta$t, the free energy corresponding to $M = M$ reaches a relatively stable state. When $M \neq M$, the free energy descent rate increases with the M/M ratio, and the time to reach a relatively stable free energy state is shortened compared to the low misorientation system.

For low misorientation diffusion systems, when $M = M$, the Kirkendall effect is absent, and there is no net atomic flux, net vacancy flux, or local stress due to atomic/vacancy accumulation. Therefore, in a closed diffusion system, the free energy gradually decreases from a relatively high value to a relatively low state. When $M \neq M$, the Kirkendall effect generates net atomic and vacancy accumulation in local regions, creating stress that inhibits free energy reduction in the closed diffusion system, resulting in a slower free energy descent rate than when $M = M$. Moreover, since the diffusion system has relatively low misorientation, the positions for atomic and vacancy precipitation/annihilation are limited, so the free energy descent rate does not show significant differences as the mobility difference between A and B atoms increases.

For large misorientation diffusion systems, when $M = M$, the free energy descent mechanism is similar to that in low misorientation systems. When $M \neq M$, the increased void density at large misorientation phase boundaries provides more sites for atomic and vacancy precipitation/annihilation. As the mobility difference between A and B atoms increases, the net vacancy and net atomic diffusion fluxes induced by the Kirkendall effect increase and can be annihilated/precipitated promptly around different voids, causing the free energy descent rate to gradually increase.

[Figure 5: see original paper] shows the free energy evolution curves for diffusion systems with different misorientation angles at $M = 100M$. The results demonstrate that the free energy continuously decreases from relatively high values in diffusion systems with different misorientation angles. As the phase boundary misorientation angle increases, the free energy descent rate gradually increases. This is because larger misorientation increases the density of dislocation cores (which serve as vacancy annihilation sources in this study) at the phase boundary, leading to gradually increasing void density during subsequent diffusion. The accumulated atoms and vacancies can precipitate and annihilate around more voids, allowing the accumulated stress to be released rapidly and accelerating the free energy descent rate. In the later stage of free energy evolution, the longitudinal movement and lateral connection of voids further reduce the system free energy until it reaches a relatively low final stable state.

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3. Comparison with Experiments

[Figure 6: see original paper]a and b show the simulation results of voids at low and large misorientation phase boundaries, respectively, while [Figure 6: see original paper]c shows experimentally observed phase boundary voids in a Cu/NiAl diffusion couple after annealing at 850 °C for 54 h. Comparing region 1 in [Figure 6: see original paper]a and c validates the accuracy of the simulated isolated single void. Comparing region 2 in [Figure 6: see original paper]b and c validates the accuracy of the simulated void connection. These comparisons demonstrate that the simulation results are authentic and reliable.

Conclusions

1. For low misorientation phase boundaries ( ), the void density formed at the phase boundary is low, and individual voids have minimal influence on each other. For large misorientation phase boundaries ($= 12°$), the void density at the phase boundary is high, and voids significantly influence each other. Individual micro-voids move toward the side with higher atomic mobility (α phase) during evolution, and void shapes evolve from an initial parallelogram to a hexagon.
2. The expansion of voids at low misorientation phase boundaries is accompanied by phase boundary migration (toward the α phase side with higher atomic mobility), causing the β phase to grow gradually while the α phase shrinks. For large misorientation phase boundaries, voids also expand along the phase boundary direction, leading to void connection that separates the phase boundary, with the separated phase boundaries on both sides presenting a zigzag shape.
3. In a closed interdiffusion system, the free energy gradually decreases from a relatively high value. For low misorientation phase boundaries, the free energy descent rate shows no obvious difference as the $M\ /M$ ratio increases. For large misorientation phase boundaries, the free energy descent rate gradually increases with increasing $M\ /M$ ratio. As the misorientation angle increases, the void density during evolution increases, allowing accumulated vacancies and atoms to annihilate at more locations, resulting in a gradually increasing free energy descent rate.

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Note: Figure translations are in progress. See original paper for figures.