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Computational Studies of Interfacial Structure, Chemistry, and Dynamics

by

Yitao Wang

Presented to the Graduate and Research Committee

of Lehigh University

in Candidacy for the Degree of

Doctor of Philosophy

in

Materials Science and Engineering

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Dissertation Signature Sheet

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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Computational Studies of Interfacial Structure, Chemistry, and Dynamics

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Dedication

To all who dare to dream and persevere

To my beloved parents and partner

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Abstract

Interfaces are ubiquitous in materials and they have a profound impact on the processing and properties of most engineering materials. In this dissertation, we address two projects using atomistic and mesoscale computational models to investigate how the structure, chemistry, and dynamics of solid-liquid (S-L) interfaces and grain boundaries (GBs) affect microstructure formation and evolution during processing treatments or under extreme operating conditions.

In one project, we examine solidification kinetics in multicomponent alloys. A mesoscale phase-field (PF) framework is developed to investigate planar front solidification rates in ternary alloys, used as a model multicomponent system, as a function of various mass transport processes and nonequilibrium conditions. With the aid of this framework, we explore the effects of off-diagonal diffusion coefficients on controlling the S-L interface velocity and solute partition coefficients.

In another project, we explore GB solute segregation under radiation conditions. Under irradiation of metallic alloys, the formation and evolution of point defects drive GB radiation-induced segregation (RIS). Using a combination of experiments, kinetic Monte Carlo (KMC) simulations, and mesoscale PF modeling, we investigate the impact of grain microstructure (i.e., grain size and grain size ratio) on RIS profiles in a model Fe-Cr alloy. PF simulation results reveal that RIS increases with grain size, in good agreement with experimental observations. Additionally, we examine the role

of GB and bulk sink strength in RIS profiles. Beyond these non-equilibrium processes, GB segregation also occurs under thermal equilibrium conditions, particularly in multi-principal element alloys (MPEAs). Owing to their far-from-dilute compositions, MPEAs exhibit remarkable combinations of engineering properties and show unique segregation behaviors. We employ atomistic simulations to generate a series of asymmetric tilt GBs in a model CoCrFeMnNi MPEA, and quantify GB segregation and its impact on local chemical ordering. Atomistic simulation results highlight the need to account for GB interactions with alloying elements when designing advanced MPEAs with novel chemistries.

Chapter 1

Introduction

Materials are fundamental to modern civilization, shaping nearly every aspect of our daily lives – from the nanoelectronics powering our devices to the infrastructure and transportation systems that connect our world. Throughout history, entire eras have been defined by the materials that enabled technological advancement, from the Stone Age to the Bronze and Iron Ages. Today, the progress of technology remains closely tied to our ability to design and produce materials with tailored properties for increasingly complex applications. At the heart of these advances lies the understanding and control of material interfaces, as many of the governing processes that dictate material properties and long-term performance originate at the interfaces between phases or crystalline grains.

Materials interface refers to the spatial region where two distinct bulk phases or differently oriented crystals meet. Of particular interest are the interfaces in crystalline materials, including solid-solid (S-S), solid-liquid (S-L), and solid-vapor (S-V) interfaces. Another important class of interfaces in polycrystalline materials is the grain boundary (GB), which separates adjacent crystals of the same phase but with different crystallographic orientations. All these interfaces play a critical role

in many material phenomena that are far from equilibrium, such as rapid solidification [1–4], sintering [5, 6], and grain growth under extreme environments [7–11]. As an example, Fig. 1.1 illustrates three experimental cases of the aforementioned phenomena. Specifically, Fig. 1.1(a) shows the evolution of solid dendrites during solidification [12], which is driven by the kinetics of S-L interfaces. Figure 1.1(b) depicts an example of grain growth in pure Pt observed in experiments [13], driven by the migration of GBs. Figure 1.1(c) shows the morphological evolution of the stainless 316L micro–nanopowder samples during sintering observed in experiments [14]. Another example by Huang et al. [15] showed that GBs in nanocrystalline metals are dynamic interfaces whose plasticity and mobility evolve under loading, with twinning serving as a self-assisted mechanism that instantaneously reconfigures GB geometry and enhances boundary kinetics. Xie et al. [16] highlighted that twin boundaries are dynamic interfaces whose migration kinetics depend strongly on deformation rate. Several experimental studies [17–19] demonstrated that austenite/ferrite interfaces are dynamic phase boundaries whose migration kinetics are activated under heating conditions. All the aforementioned studies demonstrate that these interfaces are dynamic entities that govern microstructural evolution under specific processing conditions and external stimuli, ultimately controlling material properties and performance.

The impact of interfaces spans a broad spectrum of material properties including mechanical [20], thermal [21], electrical [22], magnetic [23], optical [24], and electrochemical [25] behavior, and is governed by thermodynamic state variables such as temperature, pressure, and chemical potential, as well as by the interface geometry such as inclination and orientation [26].

Over the past several decades, foundational theories of interfaces have been proposed and developed [27–29], establishing the principles of interfacial thermodynamics

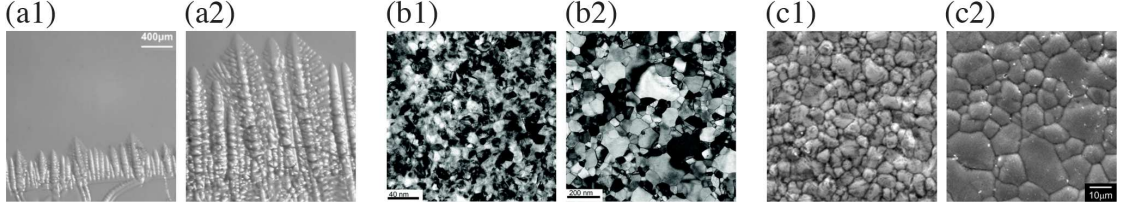


Figure 1.1: Interface-driven phenomena include (a) solidification, demonstrated by dendritic evolution of succinonitrile during the process [12], (b) grain growth, depicted by transmission electron microscopy (TEM) images of as-deposited Pt post-annealing at 500 °C [13], (c) sintering, illustrated by scanning electron microscope (SEM) micrograph of the sintered parts of stainless 316L micro-nanopowder at 1100 °C [14].

and kinetics and advancing our understanding of how interfaces control microstructural evolution. In recent years, the emergence and rapid development of additive manufacturing (AM) technologies have reignited interest in interfacial phenomena under far-from-equilibrium processing conditions. In AM, far-from-equilibrium processes such as rapid solidification during laser powder bed fusion and localized sintering in binder jetting create large thermal gradients, high cooling rates, and complex thermal histories. Under these conditions, the dynamics of S-L and S-S interfaces become critical in determining the final microstructure, including grain morphology, texture, and porosity distribution. As a result, understanding how interfaces form and evolve is essential for designing materials with tailored properties and performance.

This dissertation is organized into three major topics, each addressing distinct material interfaces and the role of their structure, chemistry, and dynamics in controlling microstructural evolution and material properties: (i) solidification kinetics in multicomponent alloys, (ii) GB segregation in multi-principal element alloys (MPEAs), and (iii) radiation-induced segregation (RIS) at GBs in metallic systems. The organization is as follows: Chapter 2 establishes the necessary background, introducing the fundamental concepts and theoretical frameworks relevant to interfaces. Chapter 3 presents the research motivation and reviews recent experimental and

computational studies that highlight current challenges and research gaps in interface science. Chapter 4 outlines the open scientific questions. Chapter 5 focuses on the solidification kinetics in multicomponent alloys under rapid solidification conditions. This work has been peer-reviewed and published in Computational Materials Science [4]: Y. Wang, D. Tournet, and F. Abdeljawad, “A computational study of solidification kinetics in multicomponent alloys”, Computational Materials Science 244 (2024): 113161. <https://doi.org/10.1016/j.commatsci.2024.113161>. Chapter 6 examines thermal segregation at GBs in MPEAs, highlighting the need to account for GB interactions with alloying elements when designing advanced MPEAs with novel chemistries. This study has been peer-reviewed and published in the Journal of Materials Science [30]: Y. Wang, J. Jeffries, R. Roumina, E. Martinez, S. Mathaudhu, E. Marquis, F. Abdeljawad, “Grain boundary segregation and chemical ordering in CoCrFeMnNi multi-principal element alloy”, Journal of Materials Science (2025): 1-15. <https://doi.org/10.1007/s10853-025-11420-5>. Chapter 7 addresses RIS at GBs in binary alloys, quantifying the interplay between RIS and microstructural evolution under irradiation conditions. This work is currently in preparation for submission.

Chapter 2

Background

2.1 Computational Materials Science

Over the past few decades, rapid advances in computing power have established modeling and simulation as indispensable tools in materials research. Today, computational methods enable detailed investigations of materials behavior across a wide range of length and time scales – from quantum-level interactions to continuum-scale responses – providing critical insights into the relationships between processing, structure, properties, and performance that govern materials systems.

Computational materials science and engineering is an inherently interdisciplinary field that draws on principles from materials science, physics, chemistry, and computer science to predict and interpret complex material behavior. A broad suite of computational techniques, i.e., density functional theory (DFT) [35], molecular dynamics (MD) [36], phase-field (PF) modeling [37, 38], kinetic Monte Carlo (KMC) [39], and continuum models [40], has been developed to capture materials phenomena from atomic-scale structures and microstructural evolution to macroscale properties and performance shown in Fig. 2.1.

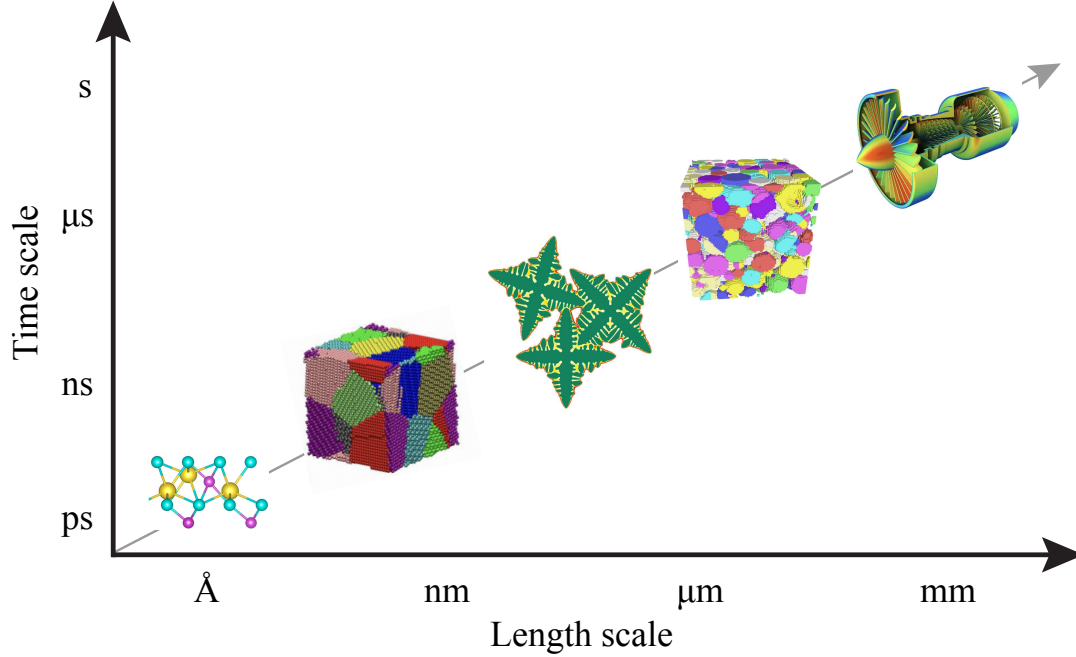


Figure 2.1: Computational methods in materials science and engineering across a wide range of length and time scales [31–34].

Within this broader domain, computational materials science focuses primarily on understanding fundamental mechanisms across length scales, while computational materials engineering applies this knowledge to the design, optimization, and validation of materials for specific engineering applications. Integrated computational materials engineering [41] extends this approach further by linking models across scales through combined bottom-up and top-down strategies, bridging atomistic mechanisms with macroscopic performance to accelerate materials innovation, see Fig. 2.1.

Defects – ranging from nanoscale features such as vacancies, interstitials, dislocations, and interfaces to larger-scale flaws like cracks and voids – play a critical role in determining a material’s overall properties. For example, atomistic simulations and PF models are widely used to examine how defects, including interfaces, influence the mechanical and thermal properties of materials. Advances in computational methods now make it possible to capture these effects with greater accuracy and to link

small-scale defect dynamics to macroscale material performance.

Despite challenges such as high computational cost, complex multiscale coupling, and the need for rigorous experimental validation, ongoing advances in areas such as multiscale frameworks, high-performance computing, and machine learning continue to broaden the scope of computational materials research. As a result, these computational tools offer powerful capabilities for designing, predicting, and optimizing materials in fields such as electronics, biomedicine, automotive, aerospace, and nuclear energy.

2.2 Solidification Kinetics in Metallic Systems

Solidification is the process by which a liquid transforms into a solid as atoms arrange into an ordered crystalline structure. In metallic systems, this transformation is mediated by the solid–liquid (S–L) interface, the moving boundary separating the solid and liquid phases. Atomic rearrangements at this interface drive the phase change, and its behavior critically influences microstructural evolution, solute distribution, and defect formation in the solid [42]. The morphology of the interface – ranging from planar to cellular to dendritic – is governed by factors such as thermal gradients, solute partitioning, and interface kinetics [43]. These characteristics ultimately control the properties and performance of the solidified material.

When dealing with phase transformations, i.e., solidification, it is essential to consider the thermodynamic driving forces that control the motion of the S–L interface. In particular, we are interested in the difference of free energy between the solid and liquid phases at temperatures that are not in equilibrium. For example, if a liquid metal is undercooled by $\Delta T = T_m - T_0 > 0$ below melting temperature T_m , solidification will be accompanied by a decrease in Gibbs free energy ΔG , as shown in

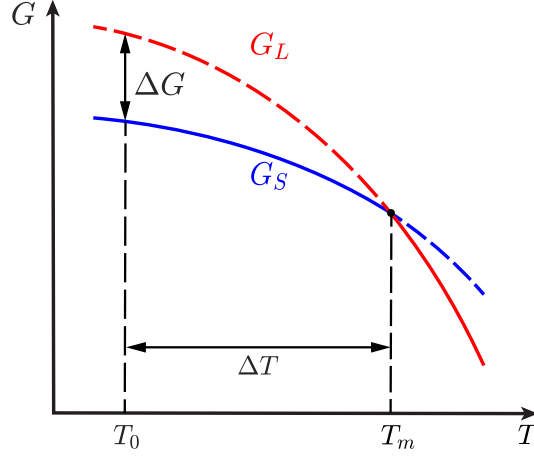


Figure 2.2: Difference in Gibbs free energy (ΔG) between solid and liquid phases with undercooling (ΔT).

Fig. 2.2. This difference in free energy between solid and liquid phases serves as the driving force for solidification. The free energies of the solid G_S and liquid G_L at a temperature T_0 are presented in the following [42]

$$G_S(T_0) = H_S(T_0) - T_0 S_S(T_0), \quad (2.1)$$

$$G_L(T_0) = H_L(T_0) - T_0 S_L(T_0), \quad (2.2)$$

where H_S and H_L are the enthalpies of solid and liquid phases, respectively, and S_S and S_L are the entropies of solid and liquid phases, respectively. We will define the free energy difference between liquid and solid at temperature T_0 and T_m as

$$\Delta G(T_0) \equiv G_L(T_0) - G_S(T_0) = \Delta H(T_0) - T_0 \Delta S(T_0), \quad (2.3)$$

$$\Delta G(T_m) = 0 = \Delta H(T_m) - T_m \Delta S(T_m). \quad (2.4)$$

Here,

$$\Delta H = H_L - H_S \quad \text{and} \quad \Delta S = S_L - S_S. \quad (2.5)$$

Rearranging Eq. 2.4, we have [42]

$$\Delta S(T_m) = \frac{\Delta H(T_m)}{T_m} = \frac{L_f}{T_m}. \quad (2.6)$$

Here, L_f is the latent heat of fusion. For large undercooling, there will be a contribution from the specific heats. Recall that the heat capacity at constant pressure C_P is defined as [44]

$$C_P = \left(\frac{\delta q}{\delta T} \right)_P = \left(\frac{\delta H}{\delta T} \right)_P, \quad (2.7)$$

which yields

$$dH = C_P dT. \quad (2.8)$$

After integrating both sides of Eq. 2.8 from T_m to T_0 , which gives

$$H(T_0) = H(T_m) + \int_{T_m}^{T_0} C_P dT. \quad (2.9)$$

Combining Eq. 2.6 and Eq. 2.8, which yields

$$dS = \frac{C_P dT}{T}. \quad (2.10)$$

After integrating both sides of Eq. 2.10 from T_m to T_0 , we can get the following

expression

$$S(T_0) = S(T_m) + \int_{T_m}^{T_0} \frac{C_P dT}{T}. \quad (2.11)$$

Plugging Eq. 2.9 and Eq. 2.11 into Eq. 2.5 for solid and liquid phases, respectively, which gives

$$\Delta H(T_0) = \Delta H(T_m) + \int_{T_m}^{T_0} (C_{P,L} - C_{P,S}) dT, \quad (2.12)$$

$$\Delta S(T_0) = \Delta S(T_m) + \int_{T_m}^{T_0} \left(\frac{C_{P,L}}{T} - \frac{C_{P,S}}{T} \right) dT. \quad (2.13)$$

Substitute Eq. 2.12 and Eq. 2.13 into Eq. 2.3, we can get the driving force for solidification with large undercooling [42]

$$\begin{aligned} \Delta G(T_0) = & \Delta H(T_m) + \int_{T_m}^{T_0} (C_{P,L} - C_{P,S}) dT \\ & - T_0 \left(\Delta S(T_m) + \int_{T_m}^{T_0} \left(\frac{C_{P,L}}{T} - \frac{C_{P,S}}{T} \right) dT \right). \end{aligned} \quad (2.14)$$

For small undercooling, the contribution from the specific heats and the integrals in Eq. 2.12 and Eq. 2.13 can be ignored, which means that $\Delta H(T_0) \approx \Delta H(T_m)$ and $\Delta S(T_0) \approx \Delta S(T_m)$. Substituting these relations into Eq. 2.3 gives

$$\Delta G(T_0) = \Delta H(T_m) - T_0 \Delta S(T_m). \quad (2.15)$$

Plugging Eq. 2.6 into Eq. 2.15, the free energy change with a small undercooling is given by [42]

$$\Delta G(T_0) = L_f - T_0 \frac{L_f}{T_m} = \frac{L_f(T_m - T_0)}{T_m} = \frac{L_f \Delta T}{T_m}, \quad (2.16)$$

where the undercooling $\Delta T = T_m - T_0 > 0$.

2.2.1 Energy Balance at the Solid-liquid Interface: The Stefan Condition

The evolution of the S-L interface during solidification is governed by a local energy balance, which requires that the latent heat released or absorbed due to phase transformation be balanced by the net heat conducted through the interface. This condition, known as the Stefan condition [45, 46], provides a fundamental relation that links thermal transport to interface motion.

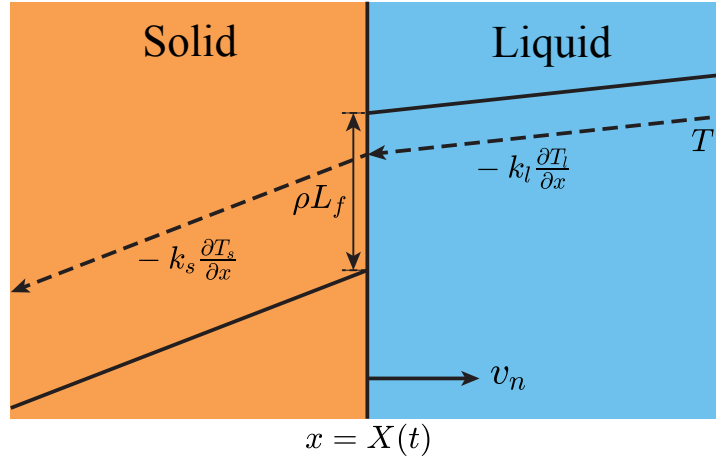


Figure 2.3: A schematic representation of the enthalpy and heat flow for the Stefan condition.

To derive the condition, consider a one-dimensional (1D) domain where the S-L interface is located at $x = X(t)$ and moves with velocity $v_n = dX/dt$, as shown in Fig. 2.3. As the liquid solidifies, latent heat is released at the interface at a rate per unit area given by [42]

$$q_{\text{latent}} = \rho L_f v_n, \quad (2.17)$$

where ρ is the density of solid phase and L_f is the latent heat of fusion. This energy

must be conducted away from the interface through the adjacent S-L interface. The conductive heat fluxes on either side of the S-L interface are described by Fourier's law [47]

$$q_s = -k_s \left. \frac{\partial T_s}{\partial x} \right|_{x=X^-}, \quad q_l = -k_l \left. \frac{\partial T_l}{\partial x} \right|_{x=X^+}, \quad (2.18)$$

where k_s and k_l are the thermal conductivities of the solid and liquid, respectively, and T_s and T_l are the temperature fields in the solid and liquid phases, respectively. The net heat flux into the interface is the difference between the incoming flux from the liquid and the outgoing flux into the solid, which is given by

$$q_{\text{net}} = q_l - q_s = -k_l \left. \frac{\partial T_l}{\partial x} \right|_{x=X^+} + k_s \left. \frac{\partial T_s}{\partial x} \right|_{x=X^-}. \quad (2.19)$$

Enforcing energy conservation at the interface by equating the latent heat release, Eq. 2.17, to the net heat flux, Eq. 2.19, yields the 1D Stefan condition [42]

$$\rho L_f v_n = k_s \left. \frac{\partial T_s}{\partial x} \right|_{x=X^-} - k_l \left. \frac{\partial T_l}{\partial x} \right|_{x=X^+}. \quad (2.20)$$

For a general three-dimensional (3D) interface with arbitrary orientation, the Stefan condition is expressed in vector form as [42]

$$\rho L_f v_n = \mathbf{n} \cdot (k_s \nabla T_s - k_l \nabla T_l), \quad (2.21)$$

where $\mathbf{n}$ is the unit normal vector pointing from the solid to the liquid, ∇T_l and ∇T_s are the temperature gradients evaluated at the interface on the liquid and solid sides, respectively. This relation serves as a critical boundary condition in solidification modeling and captures the essential coupling between temperature gradients and interface kinetics.

2.2.2 Scheil's Equation

In rapid solidification processes (i.e., casting and AM), diffusion in the solid phase is typically negligible, while the liquid is assumed to remain compositionally homogeneous due to sufficient convection or stirring. Under these conditions, the redistribution of solute during nonequilibrium solidification can be described using the Scheil's equation, which is a foundational model for predicting microsegregation in binary alloys [48].

To derive this relation, we start by equating the solute rejected into the liquid to the increase in solute concentration within the remaining liquid when a small increment of solid, df_s , forms. Assuming equal molar volumes for solid and liquid, this yields [48]

$$(c_l - c_s) df_s = (1 - f_s) dc_l. \quad (2.22)$$

Here, f_s is the solid fraction, and c_l and c_s are the solute concentrations in the liquid and solid, respectively. Assuming local equilibrium at the S-L interface, we use the partition coefficient defined as $k = c_s/c_l$ and substitute $c_s = kc_l$ into Eq. 2.22, which yields

$$\frac{df_s}{1 - f_s} = \frac{dc_l}{(1 - k)c_l}. \quad (2.23)$$

Integrating Eq. 2.23 both sides and applying the boundary condition $c_s = kc_0$ when $f_s = 0$ gives [48]

$$c_s = kc_0(1 - f_s)^{k-1}, \quad (2.24a)$$

$$c_l = c_0 f_l^{k-1}. \quad (2.24b)$$

Here, c_0 is the nominal concentration and f_l is the liquid fraction. The Eq. 2.24 is known as the non-equilibrium lever rule or the Scheil's equation [48], which can

predict progressive solute enrichment in the remaining liquid and increasing solute content in the solid as solidification proceeds. This model remains a valuable tool for estimating microsegregation in alloys solidified under nonequilibrium conditions.

2.2.3 Constitutional Undercooling

During the solidification of an alloy, solute rejected by the advancing S-L interface enriches the liquid ahead of it. This local solute buildup lowers the equilibrium liquidus temperature near the S-L interface. If the imposed temperature gradient is insufficient to counteract this effect, a region of liquid ahead of the interface becomes undercooled relative to its equilibrium liquidus temperature, a phenomenon known as constitutional undercooling [49, 50]. This undercooling is the driving force for morphological instability of the interface, leading to cellular or dendritic microstructures [50].

Consider a binary alloy where diffusion in the solid is negligible, and the only mode of solute transport in the liquid is diffusion. In the absence of convection or stirring, solute rejected by the solid accumulates in the liquid ahead of the moving interface, creating a solute boundary layer.

At steady state, the rate at which solute diffuses down the concentration gradient away from the interface is balanced by the rate at which solute is rejected from the solidifying liquid, which is given by [48]

$$-D_l \frac{\partial c_l}{\partial x} = v(c_l - c_0), \quad (2.25)$$

where D_l is the solute diffusivity in the liquid, c_l is the local solute concentration in the liquid, c_0 represents the nominal bulk alloy concentration, and v describes the S-L interface velocity.

Integrating Eq. 2.25 and applying boundary condition (at S-L interface, $c_l(x =$

0) = c_0/k), the solute concentration profile in the liquid is expressed as [48]

$$c_l(x) = c_0 + c_0 \left(\frac{1-k}{k} \right) \exp \left(- \frac{x}{(D_l/v)} \right), \quad (2.26)$$

where it describes how solute builds up in the liquid ahead of the moving S-L interface, forming a solute boundary layer of characteristic thickness D_l/v .

The equilibrium liquidus temperature at any point ahead of the interface is given by [48]

$$T_l(x) = T_m + m c_l(x) = T_m + m c_0 \left[1 + \left(\frac{1-k}{k} \right) \exp \left(- \frac{x}{(D_l/v)} \right) \right], \quad (2.27)$$

where T_m is the melting point of the pure solvent and m is the liquidus slope. The actual temperature field is assumed to vary linearly with distance according to the applied temperature gradient G , yielding $T(x) = T_{int} + Gx$, where T_{int} is the S-L interface temperature.

For the planar S-L interface to remain stable, the actual temperature must always remain above the local equilibrium liquidus temperature ahead of the S-L interface, which gives $T(x) > T_l(x)$. Equivalently, the applied temperature gradient must be steeper than the local liquidus gradient caused by the solute buildup in the liquid.

Differentiating Eq. 2.27 yields

$$\frac{dT_l}{dx} = m \frac{dc_l}{dx}. \quad (2.28)$$

At the interface ($x = 0$), the solute concentration gradient is expressed as

$$\left. \frac{dc_l}{dx} \right|_{x=0} = c_0 \left(\frac{1-k}{k} \right) \frac{v}{D_l}. \quad (2.29)$$

Plugging Eq. 2.29 into Eq. 2.28, the critical temperature gradient required to suppress constitutional undercooling can be obtained [42]

$$G_c = m c_0 \left(\frac{1-k}{k} \right) \frac{v}{D_l}. \quad (2.30)$$

Here, G_c is the critical temperature gradient. If $G < G_c$, a region ahead of the S-L interface becomes constitutionally undercooled, causing the planar front to become unstable and to break down into a cellular or dendritic morphology. This condition demonstrates how solute buildup and thermal conditions together control the transition from planar to cellular or dendritic solidification, highlighting the critical role of diffusion-controlled solute enrichment in determining the resulting microstructure.

2.3 Grain Boundaries in Polycrystalline Materials

Most functional and structural materials are polycrystals, consisting of differently oriented grains and internal solid-solid interfaces known as GBs. These GBs separate the individual grains, which can vary in size, shape, and orientation. In spite of the fact that GBs are crystallographic discontinuities with a few atomic distances in width, they play a significant role in various processes and properties of polycrystalline materials, including solute segregation [51–53], grain growth [54–56], creep [57], mechanical strength [58–60], cohesion and embrittlement [61, 62], corrosion [63, 64], wear [65, 66], and electrical and magnetic [67–69] properties.

2.3.1 Grain Boundary Degrees of Freedom

In general, a GB possesses eight degrees of freedom (DOF); five are macroscopic and the other three are microscopic [70]. For five macroscopic DOF, three of them

describe the GB misorientation and the other two define the direction of GB plane normal, or inclination. The three microscopic DOF specify the relative translations of the two abutting grains forming the GB parallel and perpendicular to the GB plane. The combination of these eight DOF determines the relative position and orientation of the adjoining crystals, which is crucial for understanding the characteristics and properties of the GB, such as energy, mobility, self-diffusion, as well as other phenomena related to GB, including defect nucleation from GBs and defect interactions with GBs.

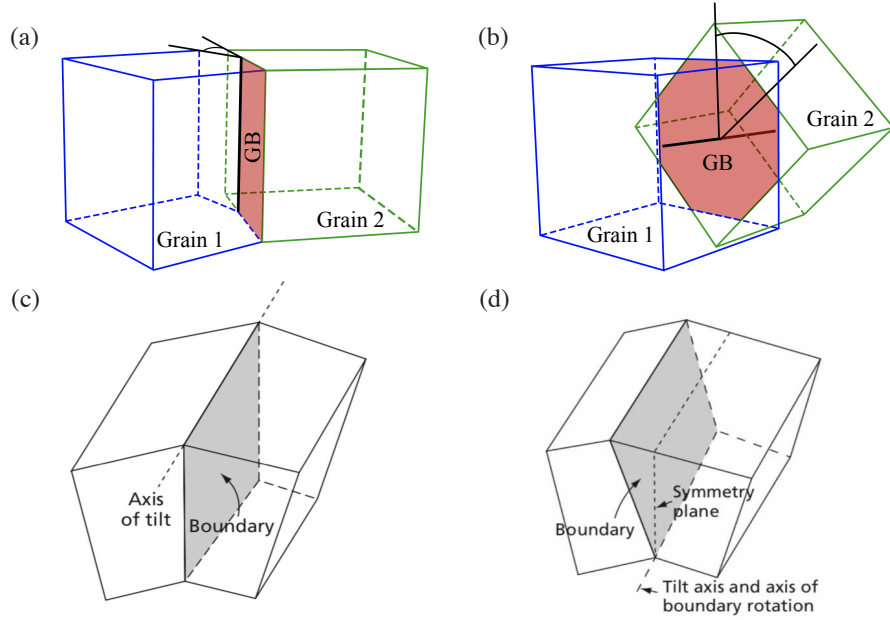


Figure 2.4: A schematic representation of (a) a tilt GB, (b) a twist GB [71], (c) symmetrical tilt GB, and (d) asymmetrical tilt GB [72].

GBs can be categorized into two types depending on the direction of the rotation axis with respect to the GB normal plane: tilt and twist GBs. The boundary is termed a tilt GB if the rotation axis is perpendicular to the normal, as shown in Fig. 2.4(a). On the other hand, a twist GB is identified by the rotation axis being parallel to the normal, as illustrated in Fig. 2.4(b). Based on the symmetry of the

GB plane, tilt GBs can be mainly categorized into symmetric and asymmetric tilt GBs that are presented in Figs. 2.4(c) and (d), respectively. In a symmetric tilt GB, the two adjoining grains are tilted by equal angles but in opposite direction about the boundary plane. This GB plane is parallel to the rotation axis, and the Miller indices of the plane are same in both grains, while the Miller indices of the plane are different in a bi-crystal with an asymmetrical tilt GB.

2.3.2 The Coincidence Site Lattice

The coincidence site lattice (CSL) model provides a fundamental framework for characterizing special GBs based on the geometric alignment of lattice sites across adjoining grains. When two crystals are joined with a specific misorientation, a subset of lattice points may coincide periodically, resulting in a superlattice that defines the CSL. These periodic coincidence sites reduce the structural mismatch at the boundary and are indicative of high-symmetry configurations that can significantly lower the GB energy.

The degree of lattice coincidence is described by the Σ value, which denotes the reciprocal density of coincidence sites. It can be expressed as follows [70]:

$$\frac{1}{\Sigma} = \frac{N_{\text{coincident}}}{N_{\text{total}}}, \quad (2.31)$$

where $N_{\text{coincident}}$ and N_{total} are the number of coincident sites and the total number of lattice sites in the CSL, respectively. Lower Σ values correspond to GBs with higher densities of coincidence sites and are generally associated with lower interfacial energies, due to reduced atomic-scale disruptions. The misorientation angle of CSLs

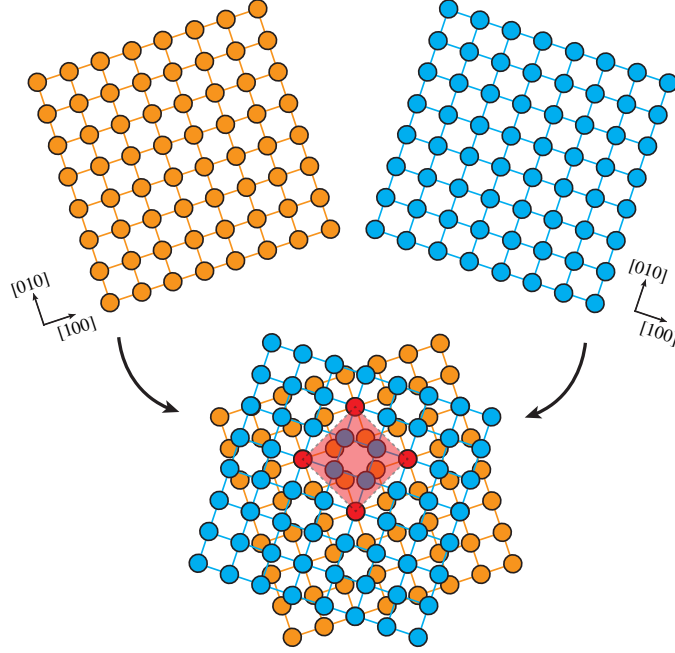


Figure 2.5: A schematic illustrating the construction of a CSL in a simple cubic lattice. A $\Sigma 5$ twist GB is generated by a rotation of 36.87° about the axis $[001]$.

with low Σ values can be determined as follows [73]:

$$\theta = 2 \tan^{-1} \left(\frac{a_2}{a_1 \sqrt{N}} \right), \quad (2.32)$$

where a_1 and a_2 are integers satisfying $a_2 < a_1$, $N = \sqrt{h^2 + k^2 + l^2}$, and $[hkl]$ denotes the rotation axis. The Σ value is determined by repeatedly dividing $a_1^2 + Na_2^2$ by 2 until the result is an odd number.

As an illustrative example shown in Fig. 2.5, consider a GB formed by rotating two identical cubic crystals by $\theta = \pm 18.44^\circ$ about the $[001]$ axis. This specific misorientation yields a configuration where one in every five lattice sites coincides, corresponding to a $\Sigma 5$ GB.

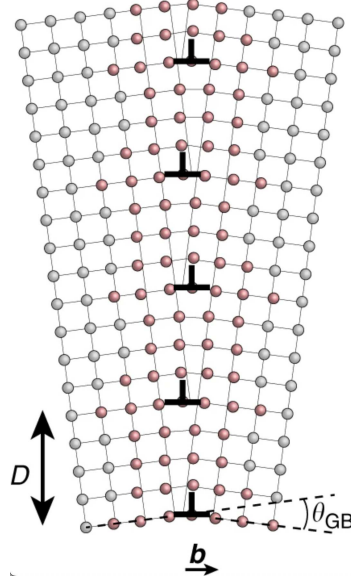


Figure 2.6: Low-angle GB illustrating a periodic array of dislocations, where D denotes the spacing between adjacent dislocations, and b describes the Burgers vector [74].

2.3.3 The Atomic Structure of Grain Boundaries

GBs can be further classified as low-angle or high-angle boundaries based on their misorientation angles [26]. In low-angle GBs, the boundary structure can be represented by a periodic array of dislocations, as shown in Fig. 2.6. According to basic geometric principles, the misorientation angle associated with such a configuration can be expressed as:

$$\theta = 2 \sin^{-1} \left(\frac{|b|}{2D} \right), \quad (2.33)$$

where D is the spacing between the dislocations, and b represents the Burgers vector. As the misorientation increases, the terminating lattice planes become increasingly inclined, contributing more to the boundary energy. One of the earliest and most widely used models for quantifying the energy of low-angle tilt GBs is the Read–Shockley model. This model assumes the GB is composed of a regular dislocation

array, and it expresses the GB energy as [75, 76]:

$$\gamma_{\text{gb}} = \frac{\mu b}{4\pi(1 - \nu)} \theta \ln \left(\frac{b}{\theta r} \right), \quad (2.34)$$

where μ is the shear modulus, b is the magnitude of the Burgers vector, ν is Poisson's ratio, θ is the misorientation angle, and r is the radial distance from the dislocation core. This equation highlights the logarithmic dependence of energy on misorientation, and it is valid in the small-angle regime where dislocation elasticity theory is applicable.

2.4 Grain Boundary Solute Segregation

GB solute segregation is the tendency of solute atoms to preferentially occupy GB regions rather than remaining uniformly distributed in the bulk. This behavior originates from the distinct structural and energetic environment of GBs, which often provide energetically favorable sites for solute accommodation. GB segregation plays a pivotal role in governing microstructural evolution and properties by influencing materials phenomena such as diffusion [53, 77], cohesion and fracture resistance [78, 79], activated sintering [80, 81], transport properties [82], electrical conductivity [83, 84] and radiation response [85, 86]. A quantitative description of segregation requires thermodynamic models that relate GB solute concentrations to bulk composition and temperature. In this section, classical approaches, i.e., the Gibbs adsorption isotherm, the Langmuir–McLean isotherm, and the Fowler–Guggenheim isotherm, are briefly introduced.

2.4.1 The Gibbs Adsorption Isotherm

The Gibbs adsorption isotherm provides a fundamental thermodynamic description of how the energy associated with an interface changes in response to variations in the concentration of a component in contact with that interface. In the context of binary alloys, this relationship is given by [87, 88]

$$\Gamma = - \left(\frac{\partial \gamma_{gb}}{\partial \mu} \right)_{T,p}, \quad (2.35)$$

where Γ represents the solute excess at the GB, γ_{gb} is the GB energy, and μ is the chemical potential of the solute species. Equation 2.35 states that, at constant temperature and pressure, the segregation of solute atoms to a GB generally reduces the GB energy.

Historically, Eq. 2.35 has been a valuable tool for estimating the degree of GB segregation by relating experimentally measured changes in GB energy to variations in bulk alloy composition [88]. For example, early experimental investigations into GB solute segregation applied Eq. 2.35 to quantitatively determine the enrichment of phosphorus [89] and tin [90, 91] in γ -iron, and silicon and sulfur [92] in δ -iron. These studies provided some of the first quantitative insights into the thermodynamic link between solute enrichment and interfacial energetics.

Despite its conceptual elegance, the practical application of Eq. 2.35 to real materials is challenged by difficulties in accurately measuring GB energy as a function of both temperature and solute concentration, particularly in complex alloys or at high solute levels. As a result, alternative models for quantifying GB segregation have been proposed, such as the Langmuir–McLean [93] and Fowler–Guggenheim isotherms [94].

2.4.2 The Langmuir–McLean Isotherm

Langmuir proposed another model for surface adsorption [95], later adapted by McLean [93, 96] to describe equilibrium GB segregation in polycrystalline materials under the assumptions of an ideal dilute solution, where solute–solute interactions are neglected. This model is based on the chemical equilibrium established between the solute atoms in the bulk and those segregated at the GB. Within this framework, the GB segregation energy, ΔH_{seg}^0 , is defined as the difference in the enthalpy of a solute atom at the GB compared to that in the bulk.

The Langmuir–McLean isotherm quantitatively relates the solute concentration at the GB, c_{gb} , to that in the bulk, c_b , for a dilute binary alloy system, which is given by [93, 97]

$$\frac{c_{gb}}{1 - c_{gb}} = \frac{c_b}{1 - c_b} \exp \left(- \frac{\Delta H_{seg}^0}{RT} \right), \quad (2.36)$$

where R is the universal gas constant and T is the absolute temperature, and $\Delta H_{seg}^0 = H_{gb}^{\text{solute}} - H_b^{\text{solute}}$ is the GB segregation energy. Equation 2.36 assumes that GB segregation sites are identical and independent, and that the bulk solution remains sufficiently dilute to neglect interactions between solute atoms.

2.4.3 The Fowler–Guggenheim Isotherm

In concentrated alloys, interactions between solute atoms become important and cannot be ignored. To incorporate these effects, Fowler and Guggenheim developed a regular solution isotherm that considers solute–solute interactions explicitly. The segregation enthalpy, which depends on the solute concentration at the GB, can be expressed as [88, 94]

$$\Delta H_{seg} = \Delta H_{seg}^0 + 2Z\omega_{ij}c_{gb}, \quad (2.37)$$

where Z denotes the number of nearest neighbors at the GB, ω_{ij} represents the interaction energy between solute i and solvent j atoms, defined by $\omega_{ij} = N_A(\epsilon_{ij} - (\epsilon_{ii} + \epsilon_{jj})/2)$. Here, N_A is Avogadro's number, and ϵ_{ij} , ϵ_{ii} , ϵ_{jj} are the bond energies between solute i and solvent j . By considering Eq. 2.37, Fowler–Guggenheim Isotherm expressed the GB concentration at equilibrium as follows [88,94]

$$\frac{c_{gb}}{1 - c_{gb}} = \frac{c_b}{1 - c_b} \exp \left(- \frac{\Delta H_{seg}^0 + 2Z\omega_{ij}c_{gb}}{RT} \right). \quad (2.38)$$

2.5 Radiation-induced Segregation

RIS is a common non-equilibrium phenomenon in irradiated materials, where the atomic species preferentially accumulate in defect sinks, i.e., dislocations, dislocation loops, and GBs, driven by mobile point defects (PDs) produced under irradiation [98, 99].

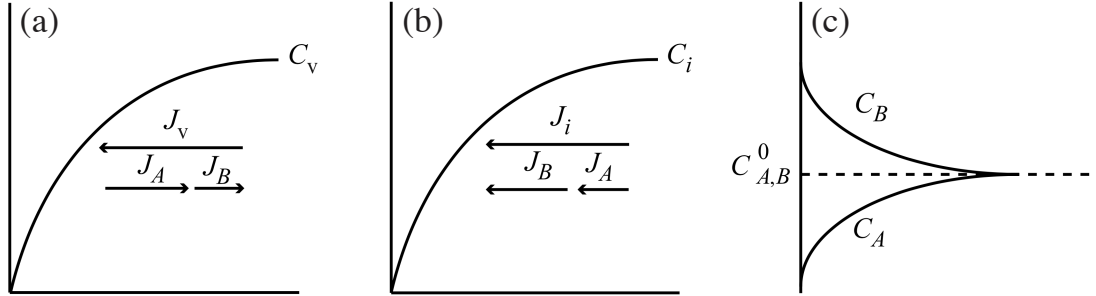


Figure 2.7: Schematic of RIS in a binary A-B system showing (a) the evolution of the vacancy concentration profile by the flux of vacancies to the GB balanced by an equal (unequal) and opposite fluxes of A and B atoms, (b) the evolution of the interstitial concentration profile by the flux of interstitials to the GB compensated by an equal (unequal) fluxes of A and B atoms migrating as interstitials, (c) the resulting concentration profiles of A and B atoms at steady state [100].

Considering a binary A-B alloy under high temperature and irradiation, Fig. 2.7 shows a schematic of the RIS process. Vacancies and interstitials generated during

irradiation migrate to the GB and form the concentration profiles in Fig. 2.7. For vacancies [Fig. 2.7(a)], the flux of vacancies to the GB is compensated by the fluxes of A and B atoms moving in the opposite direction ($J_V = -(J_A^V + J_B^V)$). If A atoms dominate the vacancy flux beyond their alloy fraction ($J_A^V > J_B^V$), more A atoms migrate away from the GB, leading to the depletion of A atoms and segregation of B atoms at the GB, and vice versa. On the other hand, for interstitials [Fig. 2.7(b)], their flux to the GB is balanced by the fluxes of A and B atoms in the same direction ($J_I = J_A^I + J_B^I$). If B atoms dominate the interstitial flux over their alloy fraction ($J_B^I > J_A^I$), B (A) atoms enrich (deplete) at the GB, and vice versa. Fluxes of both vacancies and interstitials to the GB can lead to the enrichment of one alloying element and the depletion of another. Naturally, RIS arises from the difference in partial fluxes of PDs. Finally, as shown in Fig. 2.7(c), the coupling between PDs and atomic species drives the concentration gradients of A and B to a steady state, when the fluxes of atomic species driven by PDs are balanced by the fluxes driven by diffusion-driven back fluxes [100].

Chapter 3

Motivation and Recent Studies

This dissertation is focused on interfacial dynamics in three materials problems: rapid solidification, GB segregation, and RIS. In this chapter, we provide the motivation and recent studies in each topic. Section 3.1 discusses rapid solidification and its implications for microstructural evolution. Section 3.2 introduces GB segregation in MPEAs. Finally, Section 3.3 reviews RIS.

3.1 Rapid Solidification

3.1.1 Motivation

AM, particularly laser powder bed fusion (LPBF), has emerged as a transformative technology for producing geometrically complex metallic components by selectively melting successive layers of metal powder to build three-dimensional objects [101,102]. LPBF enables high design flexibility and rapid production rates, making it highly attractive for aerospace, biomedical, and energy applications [103]. However, the process involves a complex interplay of thermal-fluid dynamics, solid mechanics, particle dynamics, and solid-state transformations, as shown in Fig. 3.1, all of which col-

lectively govern microstructural evolution and ultimately determine material properties [104–108]. Elucidating and optimizing these coupled processes is, therefore, essential for tailoring microstructure and achieving the desired properties in LPBF-fabricated alloys.

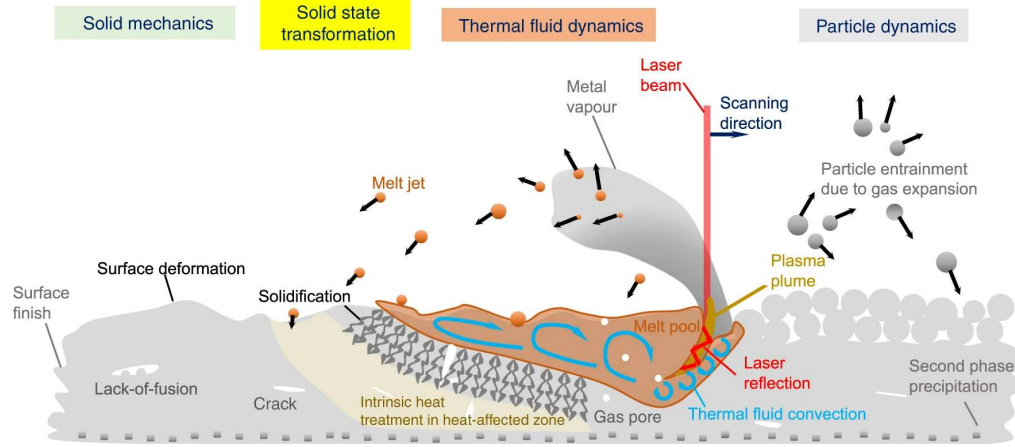


Figure 3.1: Different physical effects and associated physics involved in LPBF-AM [109].

Among the various mechanisms that shape AM microstructures, solidification is one of the most fundamental processes, governing the initial stages of microstructural formation and evolution in a broad spectrum of metallic systems. Owing to its critical role in advanced manufacturing technologies [106, 108], and its importance as a route for producing novel alloys [110–112], the physics of solidification has attracted significant attention. Grain morphology, size, and orientation during solidification arise from a complex interplay of thermodynamic driving forces and kinetic processes, including solute redistribution and latent heat transport across solid–liquid (S–L) interfaces [42, 113]. As a result, understanding and controlling solidification growth rates is considered a key aspect of microstructure control.

Rapid solidification can occur in a variety of materials processing techniques, such

as LPBF-AM [114], laser welding [115], melt spinning [116], and thermal spray coating [117]. These conditions are characterized by large undercooling, high solidification front velocities, and extreme cooling rates [118,119]. Under such circumstances, the rapid extraction of heat was shown to enhance solid solubility, promote the formation of nonequilibrium phases, and refine a host of microstructural features [117,120].

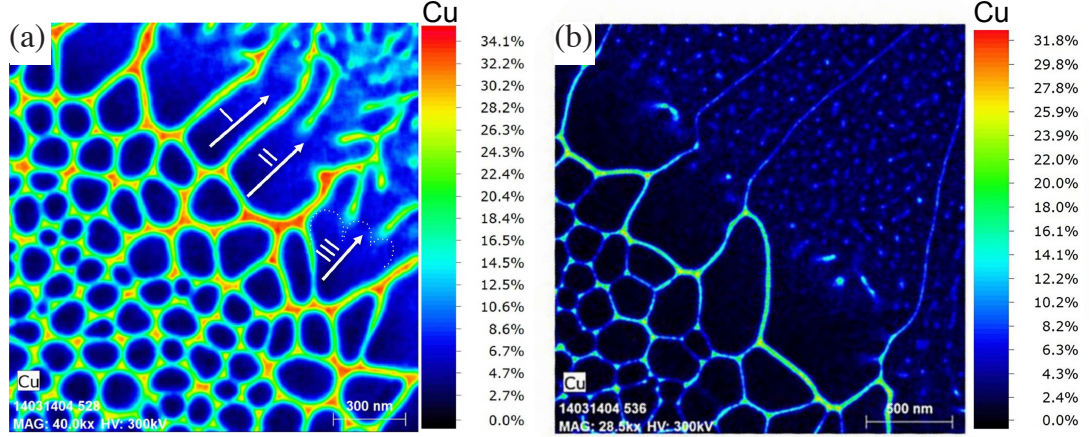


Figure 3.2: Experimental results on the effects of solute trapping. (a) Cu concentration map obtained by energy dispersive x-ray spectrometry (EDXS) in Al-Cu alloys [121]. (b) Cu concentration distribution from TEM-based EDXS in Al-Cu alloys [122].

3.1.2 Solute Trapping

Solute trapping is one of the significant effects that occurs during rapid solidification for metallic alloys. It refers to the incorporation of more solute into the solid phase than what is predicted by thermodynamic equilibrium. This phenomenon has a profound impact on microsegregation, solidification morphology, length scales of microstructure, and the consequent precipitation of secondary phases [123]. Figure 3.2 illustrates experimental Cu concentration maps in Al-Cu alloys, revealing the impact of solute trapping on morphological evolution and solute segregation behavior.

ior [121, 122].

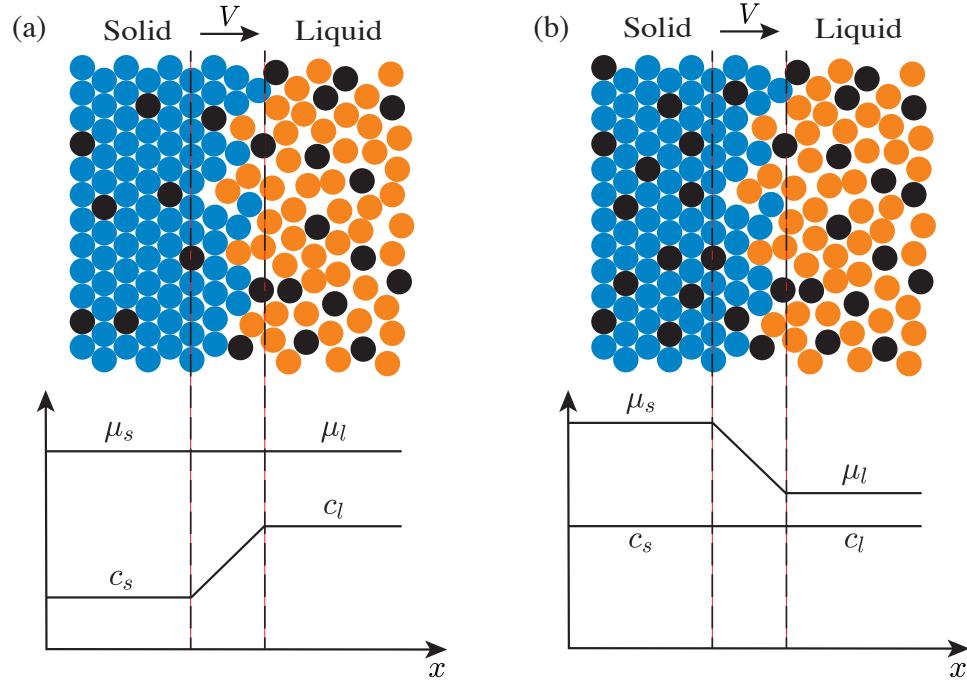


Figure 3.3: Schematics of local equilibrium and far-from-equilibrium S-L interfaces. (a) The S-L interface is in local equilibrium, corresponding to a slow interface velocity. (b) The S-L interface is far-from-equilibrium in rapid solidification, resulting in complete solute trapping.

As shown in Fig. 3.3(a), under the conditions of slow solidification velocity in binary alloys, where component 1 is the solute and component 2 is the solvent, the S-L interface is at local equilibrium. The atoms have sufficient time to diffuse locally away ahead of the interface. If the concentration in the liquid ahead of the moving interface is c_l , then in equilibrium the solid concentration after the passed interface has concentration $c_s = k_e c_l$, where k_e represents the equilibrium partition coefficients of component 1. As illustrated schematically in Fig. 3.3 (a), solute 1 (black) is being rejected from the solid (blue) into the liquid (orange) for $k_e < 1$. The local equilibrium interface ensures the same chemical potentials of solute in the solid and liquid phases, i.e., $\mu_s = \mu_l$.

Figure 3.3(b) shows the S-L interface is far-from-equilibrium in rapid solidification, where the time available for solute diffusion ahead of the advancing S-L interface becomes increasingly limited. Consequently, solute atoms are unable to diffuse away from the interface and become partially incorporated into the solid phase. In the limit of complete solute trapping, all solute atoms are captured by the solid, resulting in equal concentrations in both phases, i.e., $c_s = c_l$. Under such far-from-equilibrium conditions, the chemical potentials of the solute and solvent no longer satisfy equilibrium partitioning across the interface, i.e., $\mu_s \neq \mu_l$.

3.1.3 Recent Studies

A substantial body of theoretical studies has been devoted to understanding nonequilibrium rapid solidification. For example, Boettinger and Coriell [124] reported that interfacial nonequilibrium effects (i.e., deviation from the phase diagram, nonequal chemical potentials at the S-L interface) become significant at high solidification growth rates. Baker and Cahn [125] formulated general conditions for the interface temperature (i.e., kinetic undercooling) and composition (i.e., velocity-dependent partition coefficient) during solidification. In the limit of vanishing interface velocity, these expressions reduce to the equilibrium phase diagram liquidus and partition coefficient $k_e = c_s/c_l$, where c_s (c_l) denote the solid (liquid) solute concentration [124,125]. On the other hand, under rapid solidification conditions, solute trapping occurs, leading to a reduction of solute partitioning across the S-L interface [126]. To capture these deviations from chemical equilibrium at the S-L interface, several models introduced a velocity-dependent partition coefficient [126–131]. For example, the continuous growth model explicitly quantifies the dependence of the partition coefficient on S-L interface velocity, approaching unity at high solidification velocities [126], see

Fig. 3.4 [131]. Galenko and Sobolev [129] extended their model to account for local nonequilibrium conditions by employing a relaxational method for both the solute concentration and its flux, yielding hyperbolic dynamical equations for solute concentrations in contrast to the classical Fickian (parabolic) formulation.

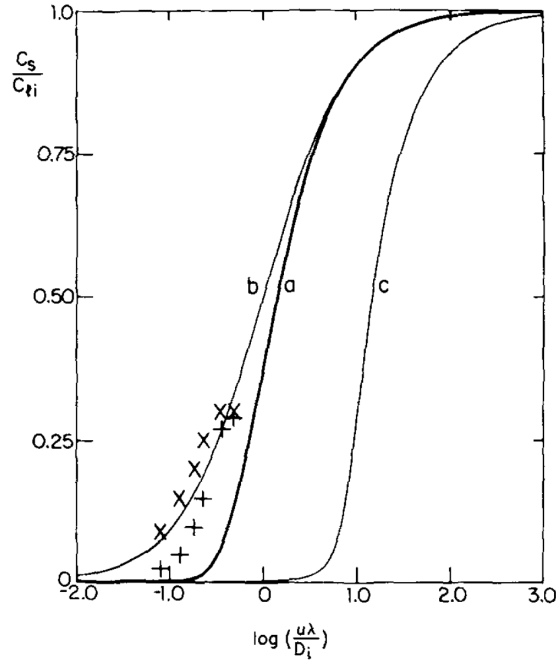


Figure 3.4: (a) Stepwise growth model [131], (b) continuous growth model [132], and (c) Baker model [125] describing the velocity-dependent partition coefficient as a function of the dimensionless solidification velocity [131].

In the domain of computational modeling, the PF method has become a widely utilized approach for predicting microstructural evolution during materials processing [37,38,134,135]. Numerous PF models have been applied to study rapid solidification phenomena [122,133,136–143]. Building upon the binary alloy PF model with an antitrapping current [144,145], Pinomaa and Provatas [122,133] introduced a tunable parameter that governs solute trapping during rapid solidification and demonstrated its influence on solidification morphologies in a Si-9at.%As binary alloy, see Fig. 3.5.

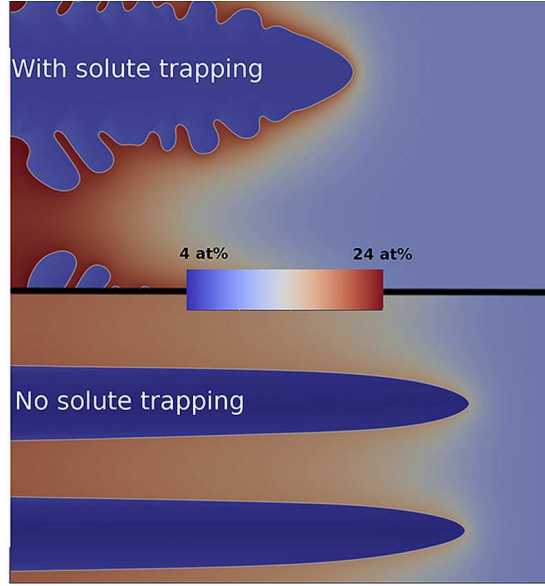


Figure 3.5: A PF study of the solute trapping effects on the solidification morphology in a Si-As binary alloy [133].

Their asymptotic analysis and numerical simulations established a quantitative relationship linking the solute trapping parameter to PF model coefficients. A similar approach was followed in other PF frameworks for dilute binary alloys during rapid solidification [139, 146]. More recently, Ji et al. [136] proposed a transport function that enhances solute diffusion within the diffuse S-L interface, enabling accurate reproduction of velocity-dependent partition coefficient and kinetic undercooling over multiple orders of magnitude in S-L interface velocity. Similarly, Steinbach, Zhang, and Plapp [140], along with Zhang and Steinbach [141], developed a multi-phase finite interface dissipation PF model for rapid solidification, introducing a kinetic parameter termed interface permeability to control the rate of solute redistribution across the S-L interface. Within this PF framework, the degree of solute trapping can be systematically controlled through the choice of interface permeability parameters during rapid solidification. Furthermore, a combined computational and experimental study

by Karayagiz et al. [147] applied the finite interface dissipation PF model to explore rapid solidification of Ni-Nb alloys during AM.

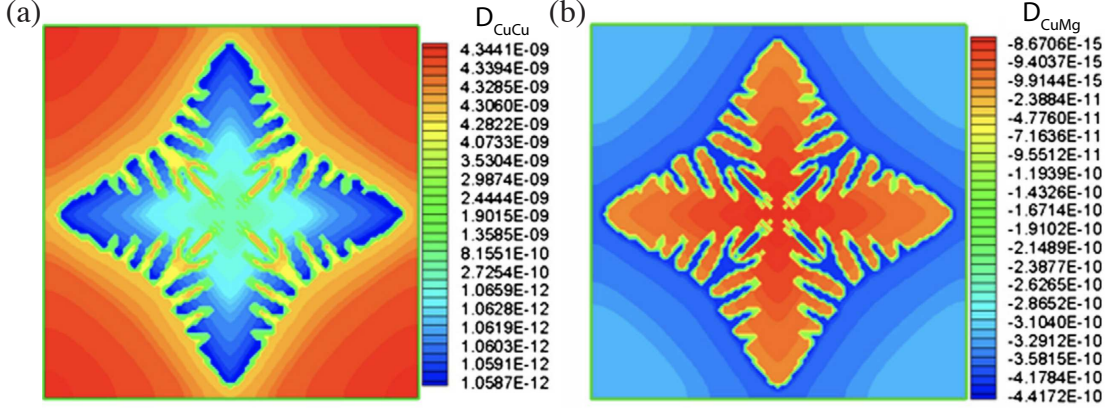


Figure 3.6: Diffusion matrix profiles in an Al-Cu-Mg ternary alloy. Concentration-dependent main (a) D_{CuCu} and (b) off-diagonal D_{CuMg} diffusion coefficients [148].

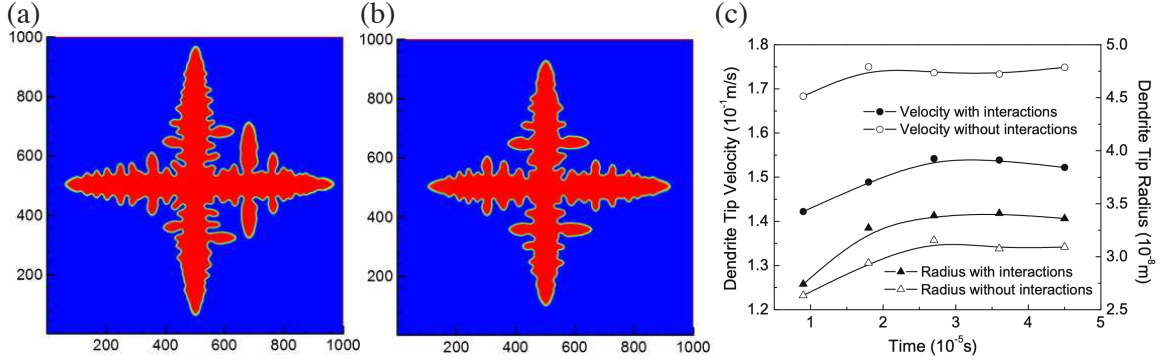


Figure 3.7: The effects of solute-solute interactions on solidification microstructure in an Al-Cu-Si ternary alloy. Dendrite morphologies during solidification (a) with solute interactions and (b) without solute interactions at the same time. (c) Quantitative comparison of dendrite tip velocity and tip radius for cases with and without solute interactions [149].

In the context of AM and alloy design, increasing attention has been directed toward multicomponent systems such as high-entropy alloys [111,150–155]. The complexity arises from the fact that rapid solidification in these alloys involves strongly

coupled transport phenomena and evolving morphologies over multiple length scales. A theoretical study by Altieri and Davis [156] reported that the addition of elemental species in a multicomponent alloy plays a destabilizing role, and that the relative values of the diffusion coefficients of different elemental species significantly affect the morphological stability of the S-L interface. More recently, models have also been proposed to capture planar front and dendrite tip dynamics in the high-velocity regime, explicitly incorporating the full diffusivity matrix in the liquid phase as well as partial solute drag effects, in conjunction with CalPhaD-based thermodynamic input [157, 158]. These results emphasized the cross-diffusion contributions can significantly affect alloy solidification, as demonstrated in systems such as Inconel 718 and stainless steel 316L [157]. The influence of the off-diagonal diffusion coefficients, however, has not yet been systematically investigated in more tractable and interpretable systems such as model ternary alloys. At the dendritic length scale, Chen et al. [159] applied a cellular automaton model to investigate dendritic solidification in a ternary Al-Si-Mg alloy, demonstrating that the solute-solute interactions influence interface undercooling and dendrite tip kinetics. Similarly, Zhang et al. [148] developed a cellular automaton model to simulate dendrite growth in multicomponent alloys, incorporating solute-solute interactions through coupled kinetic and thermodynamic calculations. They presented diffusion matrix profiles for an Al-Cu-Mn ternary system, as shown in Fig. 3.6, which reveal that the diffusion coefficients exhibit strong concentration dependence and that the off-diagonal terms can attain negative values, indicating the underlying solute-solute interactions [148]. Moreover, another study adopting PF framework coupled with thermodynamic and diffusion mobility database demonstrated the effects of solute-solute interactions on solidification microstructure in an Al-Cu-Si ternary alloy [149]. As shown in Fig. 3.7(a) and (b), the dendrite morphology, i.e., tip growth velocity and secondary arm spacing, is notably

influenced by solute–solute interactions. Furthermore, quantitative analysis of the dendrite tip velocity and radius [see Fig. 3.7(c)] demonstrates significant differences between cases with and without solute-solute interactions, highlighting their critical role in governing solidification microstructure [149].

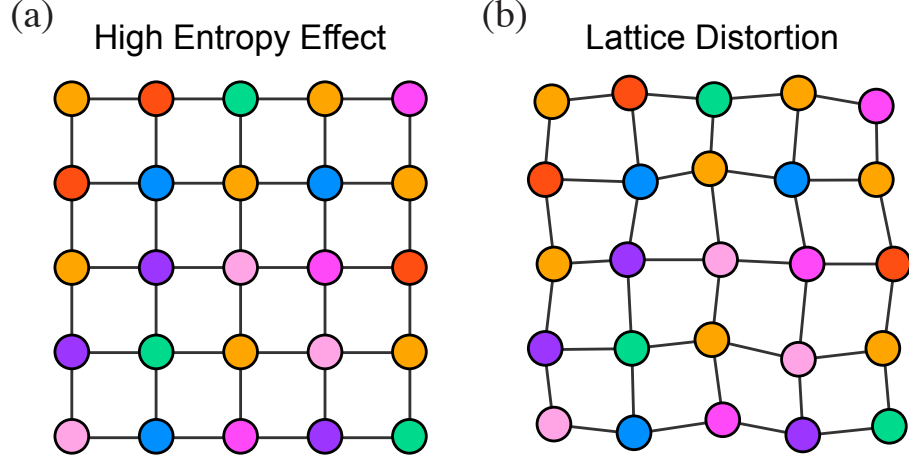


Figure 3.8: Schematic representation of (a) the high-entropy effect and (b) the lattice distortion effect governing the properties of MPEAs.

3.2 Grain Boundary Segregation in Multi-principal Element Alloys

3.2.1 Multi-principal Element Alloys

Unlike conventional alloys, which are composed of a host element and alloying species, MPEAs are a class of materials that consist of multiple principal elements in equiatomic or near equiatomic concentrations [160,161]. The use of multi-principal element compositions offers a new strategy by which the properties and functionalities of alloys can be tailored [162–166] due to effects such as high entropy and lattice distortion,

as shown in Fig. 3.8.

The two main effects are described as follows. First, the high-entropy effect originates from the large configurational entropy associated with multi-principal elements, which favors the formation of simple solid-solution phases. Second, the lattice distortion effect arises from atomic size mismatches and variations in interatomic bonding, leading to significant deviations from an ideal crystal lattice [167–169].

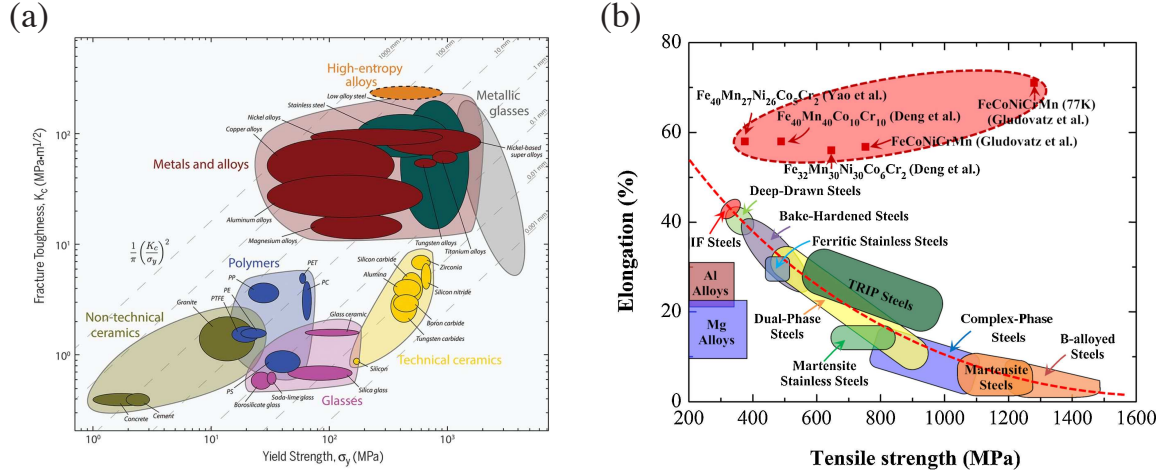


Figure 3.9: Excellent mechanical properties of MPEAs in comparison with various other material systems. (a) Ashby map depicting the relationship between fracture toughness and yield strength [170]. (b) A plot of tensile strength vs. ductility [171].

Indeed, MPEAs with unique combinations of properties, including simultaneous strength and ductility [172–174], high hardness [175, 176], and wear resistance [177–179], have been reported. For example, Fig. 3.9 shows the excellent mechanical properties of MPEAs, i.e., yield and tensile strength, toughness, and ductility, compared to other material systems. Several studies explored the use of MPEAs in applications involving extreme environments, such as elevated temperatures [180, 181], oxidation [182], and radiation [160, 183]. For example, exceptional radiation resistance and thermal stability have been reported in WTaCrV [184] and WTaCrVHf [185]

MPEAs.

3.2.2 Chemical Short-range Order

Owing to their far-from-dilute concentrations, solute-solute interactions in MPEAs provide a driving force for non-random distribution of elemental species and chemical short-range order (SRO) [186,187]. SRO in metallic alloys, particularly in MPEAs, refers to a deviation from a random atomic distribution, characterized by a preferential arrangement of distinct atomic species within a limited spatial range, typically encompassing the first and second nearest-neighbor coordination shells [188,189]. While the long-range crystallographic periodicity remains statistically disordered, SRO reflects local compositional correlations driven by differences in atomic size, electronegativity, and bonding energetics [190,191]. In other words, atomic pairs with energetically favorable interactions are more likely to occur as neighbors, while energetically unfavorable pairings are avoided, leading to a non-random local arrangement without long-range order.

Computational studies explored SRO in many MPEA systems [174,192–194]. For example, Fig. 3.10 depicts the atomic structures and chemical ordering in CoCuFeNiPd [Fig. 3.10(a)] and WTaCrVHf [Fig. 3.10(b)] MPEA systems. In Fig. 3.10(a), we can clearly see the formation of clusters or regions enriched in Cu, Co, and Ni at 300 K. It was shown that SRO-induced composite microstructures resulted in an enhancement of both mechanical strength and ductility in a CoCuFeNiPd alloy [174]. As shown in Fig. 3.10(b), it can be clearly seen that a CrV-rich precipitate with an attached CrHfTa phase forms, accompanied by additional ordering of the WTa pair at 10 K [195]. Computational studies explored SRO in the CoCrFeMnNi alloy system [196,197] and revealed strong Cr–Cr and Cr–Mn interactions and L1₂ type or-

dering [197, 198]. Woodgate et al. [196] examined the impact of magnetism on SRO in CoCrFeMnNi and highlighted Mn-Fe and Mn-Ni atomic correlations in the low-temperature regime. A recent experimental study employing atom probe tomography reported SRO in a ternary CoCrNi alloy, where anti-clustering was observed for Cr-Ni pairs [199]. Interestingly, a computational study by Ding et al. [200] highlighted the possibility of using SRO as a strategy to control stacking fault energies and, therefore, tailor the mechanical properties of MPEAs, which provides a novel pathway for the design of next-generation MPEAs with superior properties.

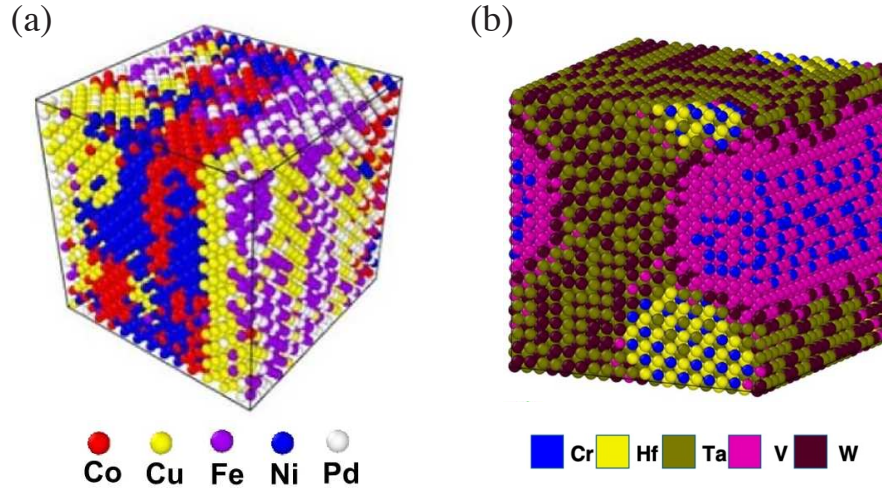


Figure 3.10: Atomic configurations and chemical ordering in (a) CoCuFeNiPd [174] and (b) WTaCrVHf [195] MPEA systems at given temperatures.

3.2.3 Experimental Observations

While the abovementioned studies in Sections 3.2.2 provide useful insights into phase stability and chemical redistribution in MPEAs, such investigations also demonstrated major challenges in quantitatively describing GB segregation, especially in MPEA systems where phase decomposition and heterogeneous nucleation at GBs are present. Using atom probe tomography, Li et al. [201] revealed the heterogeneous nature of

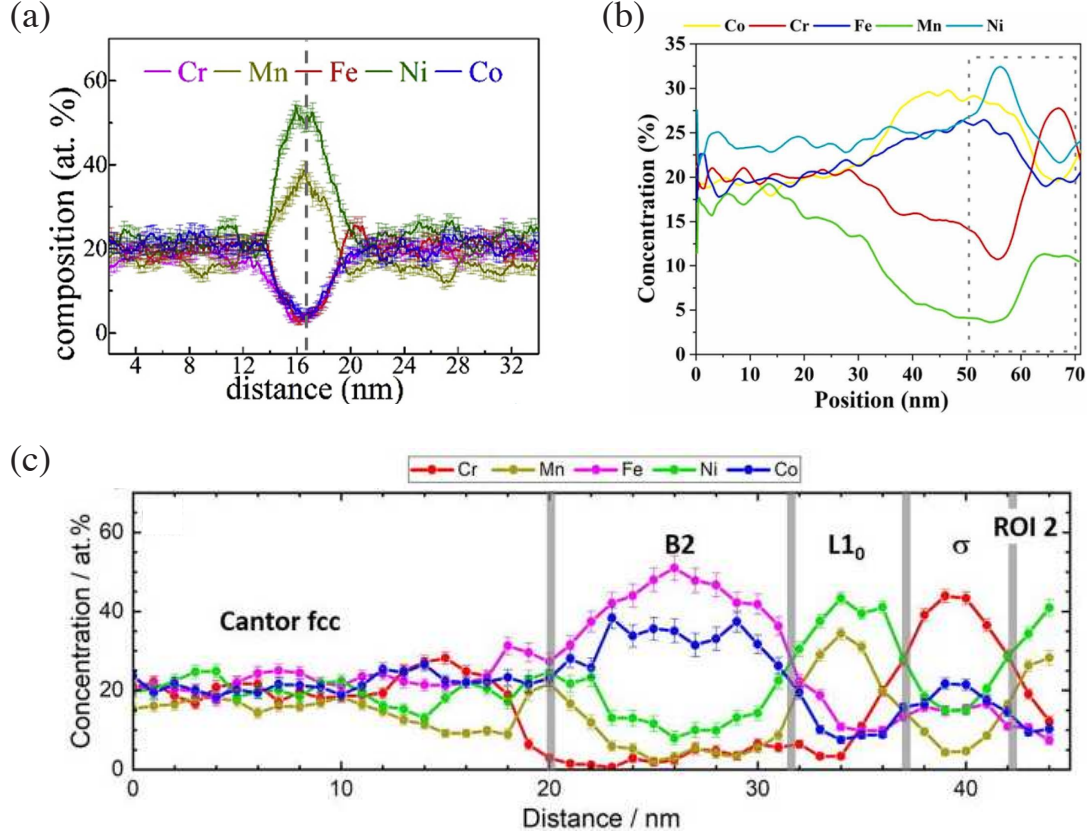


Figure 3.11: Concentration profiles across GBs in equiatomic CoCrFeMnNi MPEAs after annealing (a) at 450°C for 18 hrs [201], (b) at 550°C for 10 hrs [203], and (c) at 300°C for 1 hr [204].

GB segregation and spinodal-like decomposition at boundaries in equiatomic CoCr-FeMnNi MPEAs annealed at 723 K for up to 18 hrs. In Fig. 3.11(a), it can be clearly seen that Ni and Mn are highly enriched at the GB, while Cr, Fe, and Co exhibit depletion at the GB. Their study also revealed unintentional segregation of carbon and boron [201]; however, it is not clear if the segregation of carbon and boron impurities leads to interaction effects favoring Ni segregation. We note that Ni-C interactions have been found to be strong in bulk Ni and at Ni surfaces [202].

Other experimental studies examined concurrent phase decomposition and GB segregation of various elemental species in the CoCrFeMnNi alloy [203–207]. For

example, Fig. 3.11(b) depicts the concentration profile across the GB in equiatomic CoCrFeMnNi MPEAs after annealing at 550°C for 10 hrs [203]. It revealed the enrichment of Ni, Fe, and Co in the regions adjacent to the GB, while their concentrations decrease precisely at the GB, coinciding with the formation of a Cr-rich σ phase. This behavior further indicates the phase separation at the GB, leading to the emergence of Ni-rich and Cr-rich domains. Figure 3.11(c) illustrates the decomposed phases, namely Cr-rich (Cr-bcc and σ), NiMn-rich ($L1_0$), and FeCo-rich (B2) phases in equiatomic CoCrFeMnNi MPEAs after annealing at 300°C for 1 hr [204]. One experimental study on CoCrFeMnNi investigated GB diffusion in the temperature range of 673–1173 K and revealed no GB segregation [208]. A recent atomistic simulation study showed Cr segregation to (001) free surfaces and a near $\Sigma13$ twist GB at 1200 K in the CoCrFeMnNi system [209]. Another specific example deals with extreme environments of radiation and elevated temperatures, where irradiation-induced GB segregation has been reported in a wide range of MPEAs [86, 183, 210]. However, it is not clear in many of these alloys whether the observed GB segregation is due solely to irradiation-induced effects (i.e., force-flux coupling of solutes and PDs) or is it a combined effect of both irradiation conditions and equilibrium thermal segregation driven by solute-GB energetics.

3.3 Radiation-induced Segregation

3.3.1 Motivation

Nuclear fusion, the process of combining light atomic nuclei into heavier nuclei, offers a promising pathway toward sustainable and clean energy production. The containment materials used for the fusion reactor core, however, are subjected to extreme

operating environments, i.e., intense radiation damage and high temperature. Body-centered cubic (BCC) structured ferritic/martensitic steels have been recognized as a potential candidate for advanced nuclear reactors [211–215] due to their superior thermal conductivity, high corrosion resistance, and excellent radiation tolerance compared to austenitic steels [216–218]. Among these, Fe-Cr alloys with 9 at.% Cr have shown minimal shifts in the ductile-to-brittle transition temperature [219,220], leading to high mechanical stability under irradiation, and as a result, being considered as one of the most promising candidates for plasma-facing materials (PFMs).

Irradiation of crystalline materials creates a large number of PDs (i.e., vacancies and self-interstitials), which then diffuse and annihilate at structural defects that serve as PD sinks such as dislocations, voids/bubbles, and GBs. Driven by force-flux coupling, the net fluxes of PDs induce solute atoms to diffuse toward or away from PD sinks, resulting in the variation of alloy composition close to the PD sinks. This non-equilibrium phenomenon is known as RIS [99,221–223].

RIS can locally alter the alloy composition in the vicinity of defect sinks and drive the redistribution of solute species far from these sinks (i.e., the bulk), leading to the degradation of material properties [100,224,225]. For example, it was shown that the depletion of Cr at GBs lowers the stress corrosion cracking resistance in austenitic steels [224,226]. Miller et al. [227] reported that the enrichment of phosphorus at GBs leads to the embrittlement of materials. Allen et al. [228] revealed that void swelling resistance is closely related to changes in the lattice parameter caused by RIS. Further, RIS can be considered as a precursor for heterogeneous precipitation at defect sinks induced by radiation [99,229]. For example, a few experimental studies by Okamoto et al. [99] and Barbu et al. [230] provided direct evidence of the transition from RIS to precipitation, as demonstrated by the formation of the Ni_3Si ordered phase in austenitic steels.

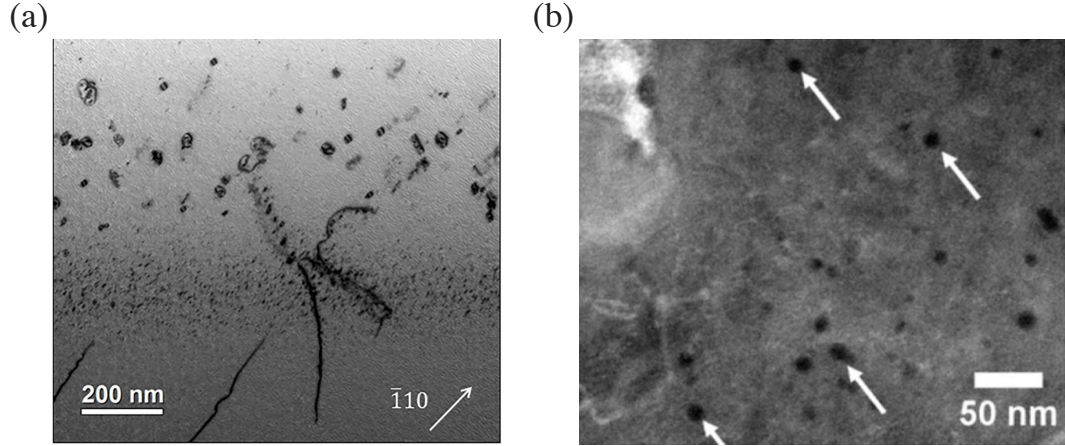


Figure 3.12: Experimental observations of radiation-induced defects. (a) Radiation-induced dislocation loops in Fe-Cr irradiated at 300° C with 5 MeV Fe^{2+} ions [231]. (b) Radiation-induced cavities in ferritic/martensitic steel alloy T91 subjected to dual-ion irradiation at 445° C to a dose of 16.6 dpa [232].

In addition to the degradation of material properties associated with RIS, the evolution of PDs into extended defect structures serves as another critical pathway for radiation-induced damage. The aggregation and clustering of PDs give rise to extended defect structures such as dislocation loops and voids, which in turn accelerate the deterioration of mechanical properties. For example, Vogel et al. [231] reported that excess interstitials preferentially cluster on crystallographic planes and form radiation-induced dislocation loops, see Fig. 3.12(a). Taller et al. [232] showed that vacancies aggregate into three-dimensional clusters that evolve into radiation-induced cavities or voids, see Fig. 3.12(b). These radiation-induced defects play a pivotal role in governing the degradation of structural materials under service conditions. Dislocation loops formed under irradiation act as strong obstacles to dislocation glide, leading to an increase in yield strength. However, this strengthening is accompanied by a loss of ductility, manifesting as radiation-induced hardening and embrittlement [233–235]. Cavities and voids, on the other hand, nucleate and grow under sustained irradiation, resulting in significant volumetric changes known as ir-

radiation swelling, which undermines dimensional stability [236, 237]. Furthermore, the accumulation of voids and bubbles along GBs can degrade cohesion, promoting intergranular embrittlement and fracture [238, 239].

Therefore, understanding RIS, radiation-induced defects, and their interactions is fundamental for predicting microstructural behavior under irradiation.

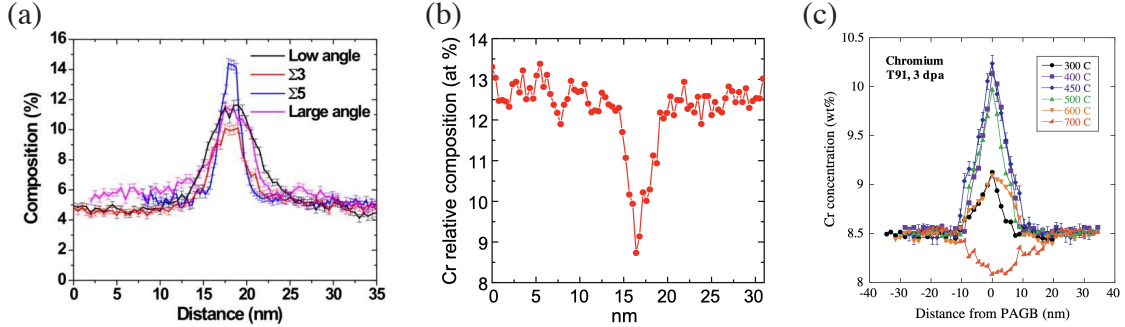


Figure 3.13: (a) Cr enrichment at various GBs in Fe-6 at.% Cr after neutron irradiation to 1.82 dpa at 290°C [240]. (b) Cr depletion across GB in oxide-dispersion strengthened Fe-12 wt.% Cr after ion implantation at 500°C [241]. (c) The dependence of RIS profiles of Cr on temperature in T91 with proton irradiation to 3 dpa [242].

3.3.2 Recent Studies

There have been numerous experimental studies focusing on the RIS behavior of Cr in ferritic/martensitic structural alloys. Some of them showed enrichment of Cr at GBs [243, 244], others reported depletion of Cr at GBs [245]. Takahashi et al. [245] showed Cr depletion at GBs in Fe-5 at.% Cr and Fe-13 at.% Cr after electron irradiation at 673 K to a dose of 3 dpa. Kato et al. [243] and Ohnuki et al. [244] revealed Cr enrichment in Fe-Cr model alloy by adding various solute additions at high dose rates. Recently, Lu et al. [246] reviewed 15 experimental studies and summarized that 8 studies indicated Cr enrichment, while 7 showed Cr depletion. For example, Fig. 3.13(a) shows the enrichment of Cr at various GBs in Fe-6 at.% Cr after neu-

tron irradiation to 1.82 dpa at 290°C [240]. In contrast, Fig. 3.13(b) depicts the depletion of Cr at GBs in a oxide-dispersion strengthened ferritic/martensitic steels under heavy-ion implantation at 500°C [241]. Furthermore, Wharry and Was [242] observed that in ferritic/martensitic steel T91, Cr generally enriches at GBs under most irradiation conditions below 700°C but becomes depleted at 700°C when all other factors remain constant, as shown in Fig. 3.13(c). Unfortunately, none of these studies were conducted using the same alloy, microstructure, temperature, dose, dose rate, or irradiating particle. These indecisive and, in some cases, conflicting experimental findings highlight the necessity for a systematic investigation of RIS in ferritic/martensitic alloys.

In conventional metals characterized by large grain size and low GB density, as shown in Fig. 3.14(a), radiation-induced interstitials migrate rapidly toward free surfaces, leading to swelling. Vacancies, on the other hand, accumulate more gradually and coalesce into stable voids that hinder dislocation motion, resulting in hardening and embrittlement [247]. GBs, however, act as effective sinks by rapidly trapping and eliminating radiation-induced PDs. As a result, nanocrystalline alloys, characterized by nanoscale grains and a high volume fraction of GBs, as illustrated in Fig. 3.14(b), exhibit superior radiation tolerance [248–252].

Existing computational studies have demonstrated grain size effects on RIS behavior. For example, Martinez et al. [253] examined the interplay between defect sinks and solute segregation in Fe-Cr alloys using a KMC framework based on an atomistic model, and found that Cr segregation decreases linearly with increasing interface density (i.e., decreasing grain size), but the study was confined to a small grain size regime, specifically around 20 nm. Hoffman et al. [254] investigated the effects of grain size, thermal segregation, and injected interstitials on RIS in Fe-Ni-Cr alloys using lattice-based atomic KMC simulations and reported that reducing grain

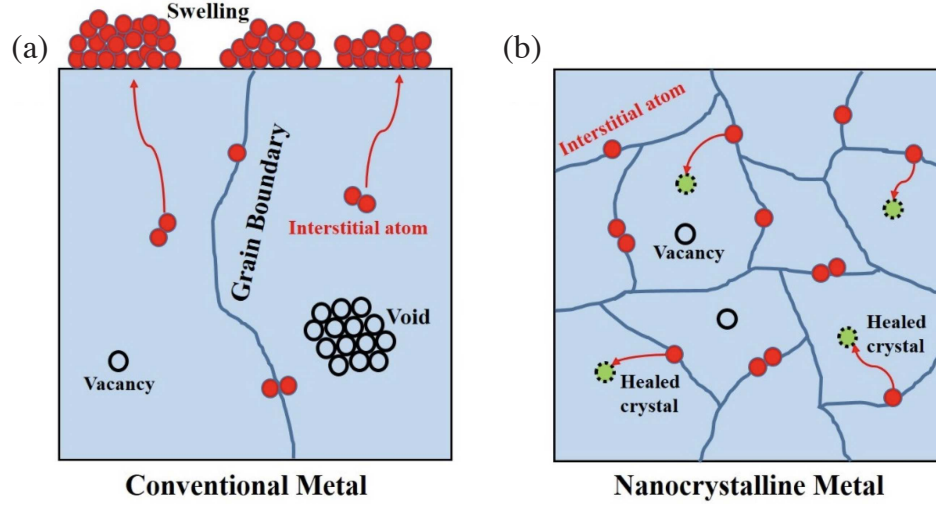


Figure 3.14: Schematic illustration of the evolution of radiation-induced self-interstitials and vacancies in (a) conventional materials and (b) nanocrystalline materials [247].

size leads to less RIS. Rezwan et al. [255] studied the effects of grain size and GB migration on RIS in Fe-Ni-Cr alloys using PF modeling and revealed that RIS increases linearly with grain size for grains exceeding 15 nm. However, for grain sizes below 15 nm, deviations from this linear behavior were observed, which can be attributed to the pronounced grain size dependence of solute concentration at the grain center in this regime. In addition, some experimental studies have reported the influence of grain size on RIS. For example, Etienne et al. [256] compared the irradiation response of ultrafine-grained 316 austenitic stainless steel (UFG-316-SS) with that of conventional 316 stainless steel under 10 dpa Fe ion irradiation at 350°C and indicated that UFG-316-SS exhibits enhanced radiation tolerance, as evidenced by a reduced density of solute clusters, lower solute segregation at dislocations, and suppressed RIS at GBs. Hoffman et al. [257] studied grain size effects on RIS and precipitation in 304L austenitic stainless steels manufactured using severe plastic deformation techniques and revealed that RIS is significantly suppressed in nanostructured steels due to decreased vacancy flux toward GBs. Rajan et al. [258] demonstrated that grain

refinement in 316-SS significantly reduces RIS with UFG samples showing minimal Cr depletion at GBs compared to coarse-grained counterparts.

In addition to the influence of grain size on RIS, the interactions of RIS with materials defects (i.e., GBs and dislocation loops) are equally important [259,260]. Several studies have explored interface sink strength effects on RIS. For example, Demkowicz et al. [261] emphasized that the steady-state radiation-induced defect concentrations are highly sensitive to the interface sink strength, and materials with high interface density but weak interface sink strength may exhibit poor radiation resistance unless both the density of interfaces and sink efficiency are optimized. Watanabe et al. [262] reported that GB sink strength, which varies with misorientation, plays a critical role in RIS, and indicated that applying the perfect sink assumption to non-random boundaries can lead to inaccurate assessments of GB RIS behavior. Recent experimental studies have shown that the GB character and the crystallographic structure of boundary planes, quantitatively represented by the sink strength parameter, strongly influence the distribution and magnitude of RIS concentration profiles [263–265]. Yet, existing computational studies always assume ideal GBs that can accommodate PDs instantaneously without a saturation limit, which could be a non-physical assumption due to the complexity of GB geometry.

Chapter 4

Open Questions

This chapter presents key open questions related to the three topics: rapid solidification in multicomponent alloys, thermal equilibrium GB segregation in MPEAs, and non-equilibrium GB RIS in metallic alloys.

4.1 Rapid Solidification

While the studies highlighted in Section 3.1.3 provide fundamental insights into rapid solidification, they have mainly been used to study binary alloys. Furthermore, even though several researchers have looked at rapid solidification in multicomponent alloys, their studies did not consider the off-diagonal diffusion coefficients of the various species. The impact of various mass transport mechanisms during rapid solidification of multicomponent alloys has not been systematically explored. Therefore, the goal of this research is to address the following questions:

1. What is the impact of the diffusivities of various species on solidification rates in a multicomponent alloy?

2. What role do off-diagonal diffusion coefficients play in controlling the partition coefficients and growth velocity?
3. What is the impact of various mass transport coefficients during rapid solidification conditions?

4.2 Grain Boundary Segregation

The experimental studies discussed in Section 3.2.3 highlight the need for a fundamental understanding of GB chemical states in MPEAs in order to quantify microstructure evolution pathways during processing treatments and predict the performance of these alloys under operating conditions [86]. This is precisely the goal of this work. Some relevant questions we seek to address are:

1. Can we quantify multi-element GB segregation in MPEAs and its dependence on temperature?
2. Does GB segregation influence local chemical ordering in the bulk?
3. How does GB segregation in MPEAs depend on boundary geometry?

4.3 Radiation-induced Segregation

The studies in Section 3.3.2 highlight the need for a fundamental understanding of RIS in metallic alloys in order to quantify microstructural evolution under irradiation. Although several computational studies have investigated grain size effects, they have primarily focused on fine grains (i.e., on the order of tens of nanometers). In addition, some studies have neglected critical factors such as recombination effects and bulk sink strength, both of which are essential for accurately capturing RIS behavior.

Furthermore, existing models commonly assume GBs to be perfect or ideal sinks—a non-physical simplification that will be relaxed in this work. Therefore, this study aims to address the following questions:

1. What role does irradiation conditions, i.e., GB and bulk sink strength, play in controlling GB chemical profiles?
2. What is the impact of the grain size (i.e., GB density) on RIS concentration profiles in metallic alloys?
3. What is the role of grain size ratio, i.e., a GB connecting two adjacent grains with different sizes, in RIS under given irradiation conditions?

Chapter 5

Solidification Kinetics in Multicomponent Alloys

In this chapter, we employ the finite interface dissipation PF model by Zhang and Steinbach [141] to examine solidification kinetics in ternary alloys. The rationale for choosing ternary alloys is that they represent a model system with multicomponent effects including cross-diffusion (off-diagonal diffusion coefficients), while offering computational tractability. While many PF formulations of binary alloys have been proposed to account for rapid solidification [133, 136, 139–142, 146], our goal here is not to benchmark these models against each other, but rather investigate various transport processes during equilibrium and rapid solidification of multicomponent alloys. The rest of the chapter is organized as follows: thermodynamics of ternary alloys and the PF model formulation are presented in Section 5.1. Simulation results and discussions are presented in Section 5.2. Finally, Section 5.3 provides concluding remarks and a summary of the work.

5.1 Theoretical and Computational Model

We start with a presentation of the thermodynamics of ternary alloys and the relevant transport coefficients. Then, we continue with an exposition of the finite interface dissipation PF model by Zhang and Steinbach [141] specific to ternary alloys.

5.1.1 Thermodynamics of Ternary Alloys

In this work, we consider a ternary alloy of solutes labeled 1 and 2 and a host labeled 3 that are characterized by the concentration fields c_1 , c_2 , and c_3 , respectively. Irreversible thermodynamics stipulates that driving forces arise due to gradients in chemical potentials and are written according to [266]

$$J_i = - \sum_{j=1}^3 L_{ij} \nabla \mu_j, \quad i = 1, 2, 3, \quad (5.1)$$

where J_i and μ_i are the flux vector and chemical potential of the i^{th} species, respectively. L_{ij} are the kinetic transport coefficients, which according to Onsager's reciprocity theorem $L_{ij} = L_{ji}$ [266]. Using the Gibbs-Duhem equation $c_3 d\mu_3 = -c_1 d\mu_1 - c_2 d\mu_2$ [see Appendix A], one can write the flux equation above as

$$J_i = -\tilde{L}_{i1} \nabla \tilde{\mu}_1 - \tilde{L}_{i2} \nabla \tilde{\mu}_2, \quad i = 1, 2, \quad (5.2)$$

where

$$\tilde{\mu}_i = \mu_i - \mu_3, \quad i = 1, 2, \quad (5.3)$$

is the chemical potential of the i^{th} species measured with respect to that of the host, i.e., the diffusion potential, and $\tilde{L}_{ij} = L_{ij} - c_j \sum_{k=1}^3 L_{ik}$. Therefore, only two flux

equations are needed to describe a ternary alloy. To obtain expressions for these diffusion potentials, we assume a free energy density function f of the form

$$f = \sum_{i=1}^3 G_i c_i + \frac{RT}{V_m} \sum_{i=1}^3 c_i \ln c_i, \quad (5.4)$$

where G_i is the free energy density of pure i , T is the temperature, V_m is the molar volume of the alloy, and R is the ideal gas constant. By using $\mu_i = \partial f / \partial c_i$ in conjunction with Eqs. 5.2 through 5.4, we obtain the diffusion potentials $\tilde{\mu}_i = G_i - G_3 + (RT/V_m) \ln (c_i/c_3)$. Then, the flux equation, Eq. 5.2, can be expressed in terms of concentration gradients using $\nabla \tilde{\mu}_i = \sum_{j=1}^2 (\partial \tilde{\mu}_i / \partial c_j) \nabla c_j$ leading after some algebra to [see Appendix A for details]

$$J_i = - \sum_{j=1}^2 D_{ij} \nabla c_j \quad \text{and} \quad D_{ij} = \frac{RT}{V_m} \left[\frac{L_{ij}}{c_j} - \frac{L_{i3}}{c_3} \right], i, j = 1, 2, \quad (5.5)$$

where $\partial \tilde{\mu}_i / \partial c_j$ is the thermodynamic factor [267–269] and D_{ij} are the relevant diffusion coefficients subject to [266]

$$D_{11} + D_{22} > 0, \quad (5.6a)$$

$$(D_{11} + D_{22})^2 \geq 4(D_{11}D_{22} - D_{12}D_{21}), \quad (5.6b)$$

$$(D_{11}D_{22} - D_{12}D_{21}) \geq 0. \quad (5.6c)$$

Here, it is important to emphasize that the off-diagonal diffusivities, D_{12} and D_{21} , can be negative. As a demonstration of the physical constraints given by Eq. 5.6 and using $D_{11} = 1$, Fig. 5.1 shows the permissible range of the off-diagonal diffusivities, D_{12} and D_{21} , using D_{22} values of 0.5 [Fig. 5.1(a)], 1 [Fig. 5.1(b)], and 1.5 [Fig. 5.1(c)].

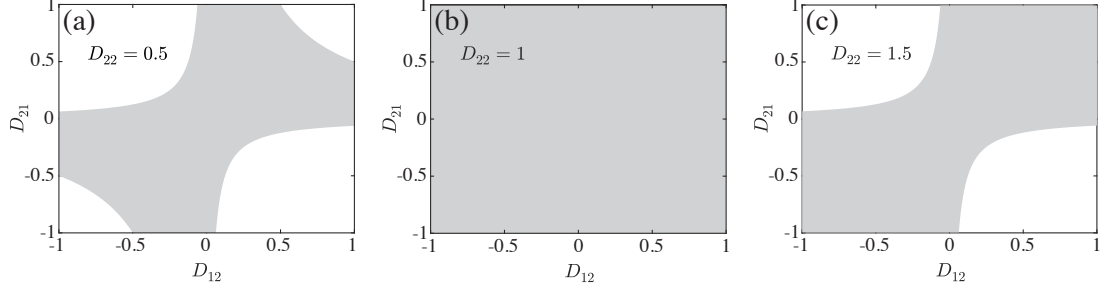


Figure 5.1: Using $D_{11} = 1.0$ as a reference diffusivity in a ternary alloy, the permissible range (regions shaded in gray) of the off-diagonal diffusion coefficients, D_{12} and D_{21} , using (a) $D_{22} = 0.5$, (b) $D_{22} = 1$, and (c) $D_{22} = 1.5$.

5.1.2 Phase Field Formulation

The PF model presented herein follows the one by Steinbach, Zhang, and Plapp [140] and Zhang and Steinbach [141], and the reader is referred to these references for more details. We first introduce scalar order parameters (OPs) ϕ_s and ϕ_l describing the phase fractions of the solid and liquid bulk phases, respectively, which are subject to $\phi_s + \phi_l = 1$. Motivated by Section 5.1.1 above, we will only track the concentration fields of solutes 1 and 2. We define c_i^s and c_i^l as the phase concentration fields of the solute i in the solid and liquid phases, respectively, and the total concentration of species i , c_i , is given by the mixture sum

$$c_i = \phi_s c_i^s + \phi_l c_i^l, \quad i = 1, 2. \quad (5.7)$$

With these definitions for the OPs and concentration fields, the total free energy functional $\mathcal{F}_{tot}$ of a two-phase, solid and liquid, ternary alloy system is given as [140,

$$\mathcal{F}_{tot} = \int [f_{chm} + f_{int}] d\mathbf{r}, \quad (5.8a)$$

$$f_{chm} = \phi_s f_s + \phi_l f_l + \sum_{i=1}^2 \lambda_i (c_i - \phi_s c_i^s - \phi_l c_i^l), \quad (5.8b)$$

$$f_{int} = \frac{4\sigma_{sl}}{\eta} \left(\phi_s \phi_l - \frac{\eta^2}{\pi^2} \nabla \phi_s \cdot \nabla \phi_l \right), \quad (5.8c)$$

where the total energy is additively decomposed into bulk f_{chm} and interfacial f_{int} components. The first two terms on the right-hand side (RHS) of Eq. 5.8b describe the bulk chemical free energies interpolated between the solid f_s and liquid f_l phases using the OPs. The last term on the RHS of Eq. 5.8b employs a Lagrange multiplier λ_i for each of the solutes in order to ensure mass conservation for all species between the solid and liquid phases. λ_i is determined by establishing equilibrium between the solid and liquid phases as detailed in Refs. [140, 141]. Equation 5.8c defines the S-L interfacial contribution, where σ_{sl} sets the S-L interface energy and η represents the numerical interfacial width.

For a system that is described by the field c and has a total energy functional $\mathcal{F}$, variational principles for non-conserved (model A) dynamics result in a governing equation of the form $\partial c / \partial t = -L \delta \mathcal{F} / \delta c$, where L is a kinetic coefficient. In their finite interface dissipation treatment, Zhang and Steinbach [141] employed non-conserved dynamics of concentration fields (mass conservation is ensured through the use of Lagrange multipliers) in multicomponent systems by defining a kinetic coefficient P_i for each elemental species i . The parameter P_i has the unit of $\text{m}^3/(\text{J}\cdot\text{s})$ and is termed the interface permeability parameter controlling the redistribution of species across the S-L interface. The resultant dynamical equations for the spatio-temporal

evolution of the concentration fields are written as [140, 141]

$$\phi_s \frac{\partial c_i^s}{\partial t} = \nabla \cdot \left(\phi_s \sum_{j=1}^2 D_{ij}^s \nabla c_j^s \right) + P_c \phi_s \phi_l (\tilde{\mu}_i^l - \tilde{\mu}_i^s) - \phi_s (c_i^l - c_i^s) \frac{\partial \phi_l}{\partial t}, \quad (5.9a)$$

$$\phi_l \frac{\partial c_i^l}{\partial t} = \nabla \cdot \left(\phi_l \sum_{j=1}^2 D_{ij}^l \nabla c_j^l \right) - P_c \phi_s \phi_l (\tilde{\mu}_i^l - \tilde{\mu}_i^s) + \phi_l (c_i^l - c_i^s) \frac{\partial \phi_s}{\partial t}, \quad (5.9b)$$

where we use $P_1 = P_2 = P_c$ for all results presented in this work. $\tilde{\mu}_i^l$ ($\tilde{\mu}_i^s$) defines the chemical potential of the i^{th} species with respect to that of the host element in the liquid (solid) phase.

Similarly, the evolution of the PF OPs follows non-conserved dynamics given by [140, 141]

$$\frac{\partial \phi_s}{\partial t} = K_{sl} \left[\sigma_{sl} \left\{ \nabla^2 \phi_s + \frac{\pi^2}{\eta^2} \left(\phi_s - \frac{1}{2} \right) \right\} + \frac{\pi^2}{8\eta} \Delta g_{sl} \right], \quad (5.10)$$

where

$$K_{sl} = \frac{8\eta \mu_{sl} P_c}{8\eta P_c + \mu_{sl} \pi^2 \sum_{i=1}^2 (c_i^s - c_i^l)^2} \quad (5.11)$$

is the PF kinetic coefficient and

$$\Delta g_{sl} = f_l - f_s - \sum_{i=1}^2 (\phi_s \tilde{\mu}_i^s + \phi_l \tilde{\mu}_i^l) (c_i^l - c_i^s) \quad (5.12)$$

is the chemical driving force for solidification. In Eqs. 5.9 and 5.10, we only track ϕ_s as $\phi_l = 1 - \phi_s$ and $\partial \phi_l / \partial t = -\partial \phi_s / \partial t$.

A close examination of Eq. 5.11 shows that in the limit of $P_c \rightarrow \infty$ indicating local equilibrium, the PF kinetic coefficient $K_{sl} \rightarrow \mu_{sl}$, where μ_{sl} is the intrinsic PF mobility describing S-L interface attachment kinetics. On the other hand, nonequilibrium

effects are captured for finite values of P_c and the limit $P_c \rightarrow 0$ leads to $K_{sl} \rightarrow 0$, i.e., the PF OPs cease to evolve.

The dynamical equations for the concentration, Eq. 5.9, and OP, Eq. 5.10, fields require functional forms for the liquid $f_l = f_l(\{c_i^l, i = 1, 2, 3\})$ and solid $f_s = f_s(\{c_i^s, i = 1, 2, 3\})$ free energy densities, which can be used to calculate chemical potential differences $\tilde{\mu}_i^s$ and $\tilde{\mu}_i^l$. In this work, we adopt the following forms for f_l and f_s

$$f_l = \frac{RT}{V_m} \sum_{i=1}^3 c_i^l \ln c_i^l, \quad (5.13a)$$

$$f_s = \frac{RT}{V_m} \sum_{i=1}^2 c_i^s \ln \left(\frac{c_i^s}{k_i^e} \right) + \frac{RT}{V_m} c_3^s \ln (c_3^s z(\theta)), \quad (5.13b)$$

where V_m and R are defined in Section 5.1.1 and

$$k_i^e = \frac{c_i^s}{c_i^l}, \quad i = 1, 2, \quad (5.14)$$

is the equilibrium partition coefficient for solute i . The function $z(\theta)$ given by

$$z(\theta) = \frac{1 + T_3 \theta \sum_{i=1}^2 \frac{1}{m_i^e}}{1 + T_3 \theta \sum_{i=1}^2 \frac{k_i^e}{m_i^e}} \quad (5.15)$$

defines the contribution due to the solvent, where T_3 is the melting temperature of the solvent and

$$\theta = \frac{T_3 - T}{T_3} \quad (5.16)$$

is the rescaled undercooling. The first term on the RHS of Eq. 5.13b accounts for temperature contributions of the alloying components using the equilibrium partition coefficients k_i^e . The second term on the RHS of Eq. 5.13b accounts for contributions

due to the solvent. This is achieved by enforcing mass balance of the solvent in the liquid and solid phases and assuming a linearized phase diagram with $T^l = T_3 + m_1^e c_1^l + m_2^e c_2^l$, where m_1^e and m_2^e are the slopes of the liquidus along the c_1 and c_2 directions, respectively. The interested reader is referred to Appendix B for more details on how the function $z(\theta)$ is derived. To illustrate the structure of the function $z(\theta)$, Fig. 5.2(a) shows plots of $z(\theta)$ as a function of the rescaled undercooling θ for a ternary alloy with $T_3 = 1500$ K, $m_1^e = m_2^e = -400$ K/at. fraction and various values of k_1^e and k_2^e . Using these parameters, Fig. 5.2(b) shows surface plots of the liquid f_l and solid f_s , with $\theta = 0.06$, free energy densities as a function of solute concentrations.

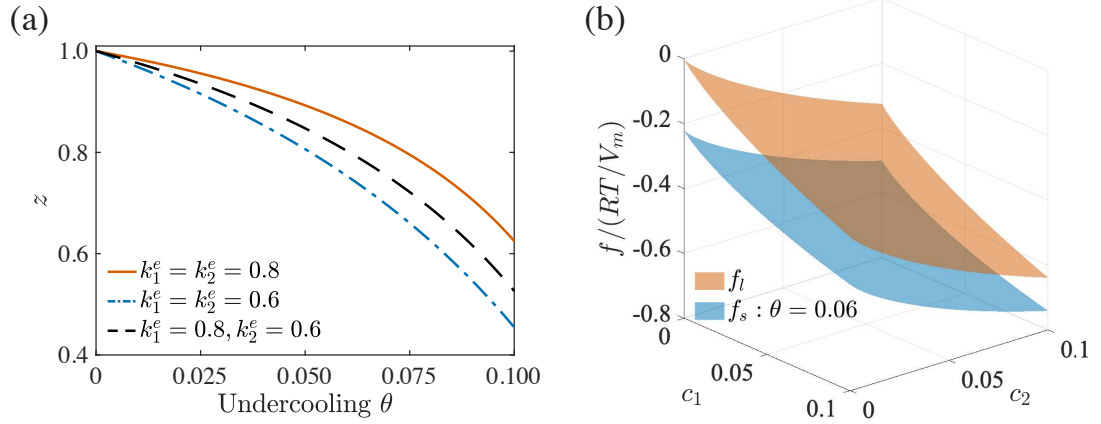


Figure 5.2: (a) A plot of $z(\theta)$ given by Eq. 5.15 as a function of the rescaled undercooling θ for various values of k_1^e and k_2^e using $T_3 = 1500$ K and $m_1^e = m_2^e = -400$ K/at. fraction. (b) Surface plots of the liquid f_l and solid f_s , with $\theta = 0.06$, free energy densities as a function of solute concentrations using $T_3 = 1500$ K, $m_1^e = m_2^e = -400$ K/at. fraction, $k_1^e = 0.8$, and $k_2^e = 0.6$.

With the definitions of the liquid and solid free energies given by Eq. 5.13, expressions for the chemical potential differences needed in the concentration and PF

dynamical equations are given by

$$\tilde{\mu}_i^l = \mu_i^l - \mu_3^l = \frac{RT}{V_m} \ln \left(\frac{c_i^l}{c_3^l} \right), \quad i = 1, 2, \quad (5.17a)$$

$$\tilde{\mu}_i^s = \mu_i^s - \mu_3^s = \frac{RT}{V_m} \left[\ln \left(\frac{c_i^s}{k_i^e} \right) - \ln (c_3^s z(\theta)) \right], \quad i = 1, 2. \quad (5.17b)$$

5.1.3 Non-dimensionalization and Model Implementation

The dynamical equations for the concentration, Eq. 5.9, and OP, Eq. 5.10, fields are made non-dimensional by introducing dimensionless space and time as $\bar{\mathbf{r}} = \mathbf{r}/d_o$ and $\bar{t} = t/\tau$, respectively, where τ and d_o represent reference time and length scale (pixel size), respectively. Also, the energy density is rescaled with respect to E_o/d_o^3 , where E_o is some reference energy. We introduce the following non-dimensional parameters: $\bar{\eta} = \eta/d_o$, $\bar{\sigma}_{sl} = \sigma_{sl}d_o^2/E_o$, $\bar{\mu}_{sl} = E_o\tau\mu_{sl}/d_o^4$, $\Delta\bar{g}_{sl} = d_o^3\Delta g_{sl}/E_o$, $\bar{f}_l = d_o^3f_l/E_o$ and $\bar{f}_s = d_o^3f_s/E_o$. Inserting these non-dimensional quantities into Eqs. 5.9 and 5.10 yields the following for the non-dimensional diffusion coefficients

$$\bar{D}_{ij}^s = \frac{D_{ij}^s\tau}{d_o^2} \quad \text{and} \quad \bar{D}_{ij}^l = \frac{D_{ij}^l\tau}{d_o^2}, \quad i, j = 1, 2, \quad (5.18)$$

and non-dimensional interface permeability and PF kinetic parameters

$$\bar{P}_c = \frac{E_o\tau}{d_o^3}P_c \quad \text{and} \quad \bar{K}_{sl} = \frac{E_o\tau}{d_o^4}K_{sl}. \quad (5.19)$$

The resulting non-dimensional governing equations for the concentration and OPs have the same form as their dimensional counterparts. For all simulation studies reported in this work, representative systems are discretized to produce a simulation box of $N_x \times N_y$ pixels, where the pixel size along the x and y directions is $\Delta x = \Delta y$. The S-L interfacial width $\bar{\eta}$ is resolved by ten pixels needed for both numerical

accuracy and computational tractability. The non-dimensional dynamical equations are numerically solved using the explicit Euler method for time derivatives and central finite differencing for spatial gradients. In all results presented in this work, we set $\Delta x = \Delta y = 1.0$ and use a numerical time step $\Delta t = 0.0001$.

5.1.4 Simulation Setup

The goal of this work is to investigate solidification rates in ternary alloys and their dependence on various mass transport processes including cross-diffusion. Further, we seek to quantify nonequilibrium solidification effects, controlled in this PF work by the interface permeability parameter $\bar{P}_c$. To explore these effects, planar front solidification studies are conducted using a two-dimensional (2D) simulation domain with $N_x = 780\Delta x$ and $N_y = 20\Delta y$ along the x and y directions, respectively. Periodic boundary conditions for all fields along the y -direction and no-flux conditions for all fields along the x -direction are employed. In the initial state, a region on the left-hand side of the simulation domain of width $50\Delta x$ is made solid ($\phi_s = 1$) and the rest of the simulation domain is liquid ($\phi_s = 0$). The simulation domain is subjected to a uniform undercooling θ , and the position of the S-L interface is tracked over time and used to calculate its steady-state velocity V . Figure 5.3(a) shows a schematic of the simulation domain and the boundary conditions used in all simulations reported in this work.

In this work, diffusion in the liquid is considered and the one in the solid phase is negligible, an assumption commonly used in PF models of solidification [133, 144, 270]. We set $\bar{D}_{ij}^s = 10^{-6}$ in the solid phase to ensure numerical convergence of the PF model. For the remainder of this paper, we drop the superscript l on the liquid phase diffusion coefficients $\bar{D}_{ij}^l$ for notational convenience. Another point is worth mentioning here.

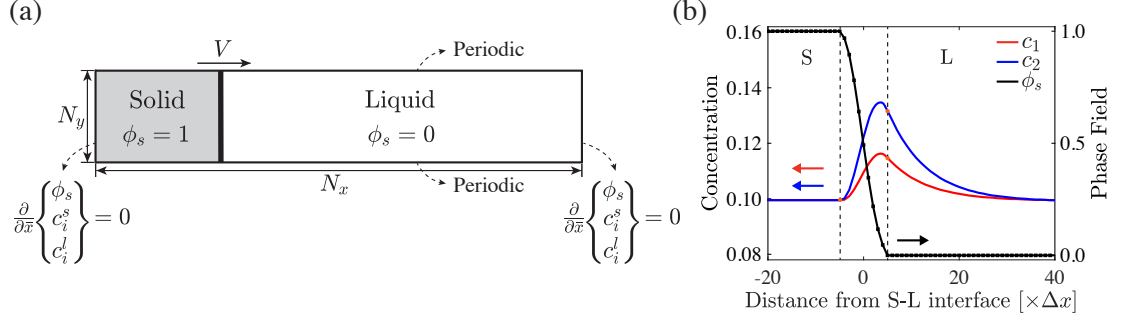


Figure 5.3: (a) The PF simulation domain used in this work, where no-flux conditions for all fields are used on the left and right ends of the domain and periodic boundary conditions are used along the top and bottom boundaries. (b) An example of a PF solidification simulation of a ternary alloy, where the solute concentrations at $\phi_s = 0.01$ and 0.99 (dashed vertical lines) are used to calculate the partition coefficients using Eq. 5.20.

The thermodynamic treatment of ternary alloys depicted in Section 5.1.1 shows that the diffusion coefficients are concentration- and temperature-dependent, see Eq. 5.5. However, due to the lack of data for the Onsager coefficients L_{ij} of ternary alloys with arbitrary compositions and our goal of systematically examining the impact of various mass transport processes on solidification rates, we assume the diffusion coefficients to be constant. In future studies, this assumption can be relaxed if the composition and temperature dependencies of the Onsager coefficients L_{ij} are obtained from atomistic simulation studies. For all simulations presented here, we use the simulation parameters for a model ternary alloy listed in Table 5.1.

Table 5.1: The PF and alloy model parameters used in this work.

Parameter	Value
Interface energy, $\bar{\sigma}_{sl}$	1.0
Interface mobility, $\bar{\mu}_{sl}$	1.0
Interface width, $\bar{\eta}$ [Δx]	10.0
Equilibrium partition coefficient, k_1^e	0.8
Equilibrium partition coefficient, k_2^e	0.6
Liquidus slope, m_1^e [K/at. fraction]	-400
Liquidus slope, m_2^e [K/at. fraction]	-400
Melting temperature of the solvent, T_3 [K]	1500

The velocity-dependent partition coefficients $k_1(V)$ and $k_2(V)$ are obtained numerically from the PF simulations using the definition given by [140, 271]

$$k_i(V) = \frac{c_i|_{\phi_s=0.99}}{c_i|_{\phi_s=0.01}}, \quad i = 1, 2. \quad (5.20)$$

Figure 5.3(b) shows an example of a PF simulation, where the dashed vertical lines are drawn at $\phi_s = 0.01$ and 0.99 , and the compositions at these PF values are used to calculate $k_i(V)$ for solute i .

5.2 Results and Discussion

5.2.1 Partition Coefficients without Cross-diffusion

We first start by examining the dependence of the solute partition coefficients on the interface permeability parameter $\bar{P}_c$. To this end, we examine alloys with $k_1^e = 0.8$, $k_2^e = 0.6$, $\bar{D}_{11} = \bar{D}_{22} = 1.0$ and $\bar{D}_{12} = \bar{D}_{21} = 0$ (i.e., no cross-diffusion), and explore cases with rescaled undercooling θ in the range of 0.05 and 0.1 . With the temperature scaling used here, Eq. 5.16 (i.e., with respect to the solvent melting temperature $T_3 = 1500$ K), this respectively corresponds to temperatures 75 K and 150 K below T_3 . Initially, the liquid portion of the simulation domain, see Fig. 5.3(a), has $c_1^l = c_2^l = 0.1$ and the solid one has $c_1^s = 0.08$ and $c_2^s = 0.06$. The position of the S-L interface is monitored and used to calculate the steady-state interface velocity V . Figure 5.4(a) and (b) shows plots of the velocity-dependent partition coefficients $k_1(V)$ and $k_2(V)$, respectively, for several values of the interface permeability parameter $\bar{P}_c$. Values of the partition coefficients increase with decreasing $\bar{P}_c$. In the small velocity limit, the partition coefficients approach their equilibrium values, i.e., $k_1^e = 0.8$, and $k_2^e = 0.6$. It can also be seen that $\bar{P}_c$ values of 1.0 and 10.0 yield similar trends for the

partition coefficients as a function of velocity, indicating that $\bar{P}_c \geq 1$ corresponds to solidification under equilibrium conditions, at least for the model parameters chosen here. According to Refs. [140, 141], the equilibrium condition is recovered, where the chemical potentials are equal at the interface, with large values of P_c . Similar trends for the dependence of the partition coefficient on the interface permeability parameter were observed in solidification studies of binary Ni-Nb alloys [147].

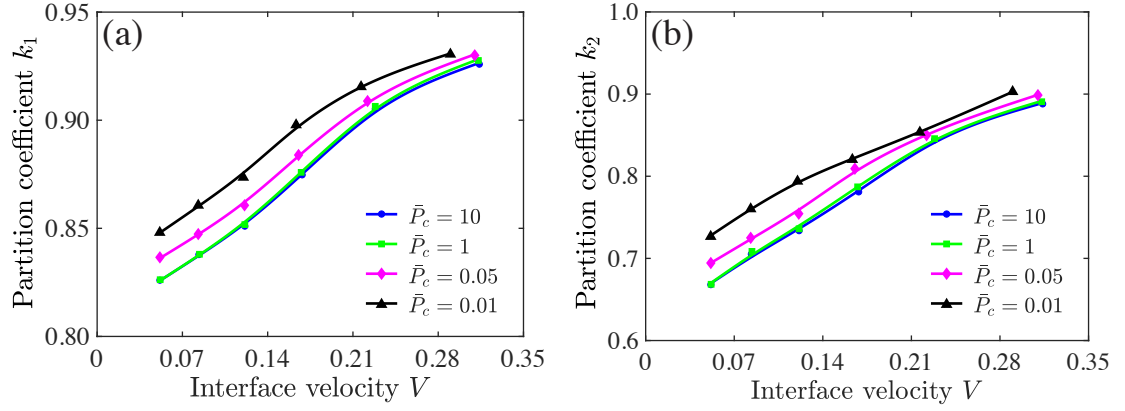


Figure 5.4: For a ternary alloy of solutes labeled 1 and 2, the velocity-dependent partition coefficients (a) $k_1(V)$ and (b) $k_2(V)$ for various values of the interface permeability parameter $\bar{P}_c$. In both panels, $k_1^e = 0.8$, $k_2^e = 0.6$, $\bar{D}_{22} = \bar{D}_{11} = 1$, $\bar{D}_{12} = \bar{D}_{21} = 0$. Refer to Table 5.1 for the PF model parameters.

5.2.2 Mass Transport Coefficients

We now direct our attention to the role of various mass transport processes in solidification kinetics. Specifically, we systematically investigate the impact of off-diagonal diffusion coefficients, $\bar{D}_{12}$ and $\bar{D}_{21}$, nominal concentration levels, and interface permeability $\bar{P}_c$ on growth rates. We employ the planar front geometry shown in Fig. 5.3(a) and use the PF model parameters in Table 5.1. We set $\bar{D}_{11} = 1$ as the reference diffusivity and consider ternary alloys with $c_1 = 0.1$ for solute 1 and explore cases with $c_2 = 0.025$ and 0.1 . Mathematically, we seek to explore the S-L interface velocity

hypersurface given by

$$V = V(\bar{D}_{12}, \bar{D}_{21}, \bar{D}_{22}, \bar{P}_c, c_2), \quad (5.21)$$

subject to the physical constraints on the diffusion coefficients given by Eq. 5.6.

Figure 5.5 shows contour slices of the S-L interface velocity V , where each panel

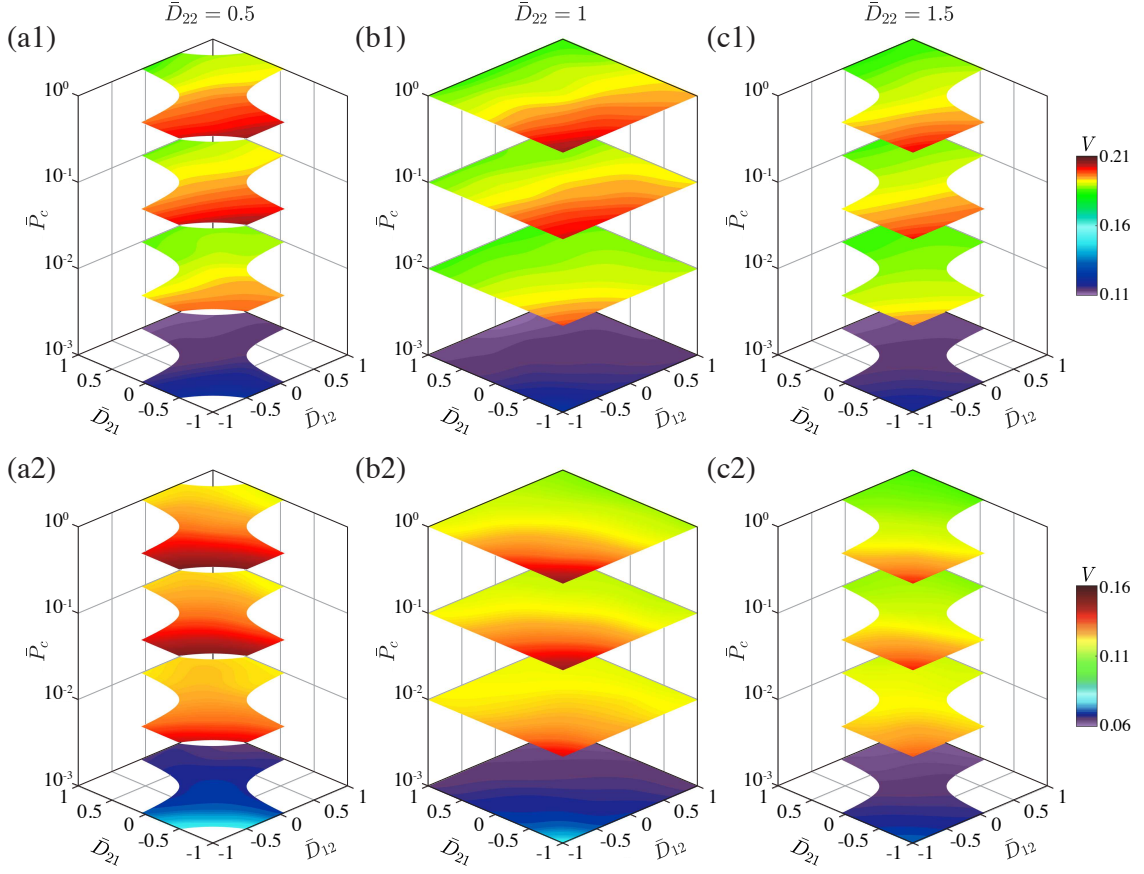


Figure 5.5: Contour slices of the S-L interface velocity V as a function of the off-diagonal diffusion coefficients, $\bar{D}_{12}$ and $\bar{D}_{21}$, and PF interface permeability parameter $\bar{P}_c$ for various values of $\bar{D}_{22}$ noting that $\bar{D}_{11} = 1.0$. The S-L interface velocity using [(a1), (b1), and (c1)] $c_2 = 0.025$ and [(a2), (b2), and (c2)] $c_2 = 0.1$. In all panels, $c_1 = 0.1$ and $\theta = 0.067$.

depicts the velocity as a function of the off-diagonal diffusion coefficients, $\bar{D}_{12}$ and $\bar{D}_{21}$, and interface permeability parameter $\bar{P}_c$. Results for two values of the concentration

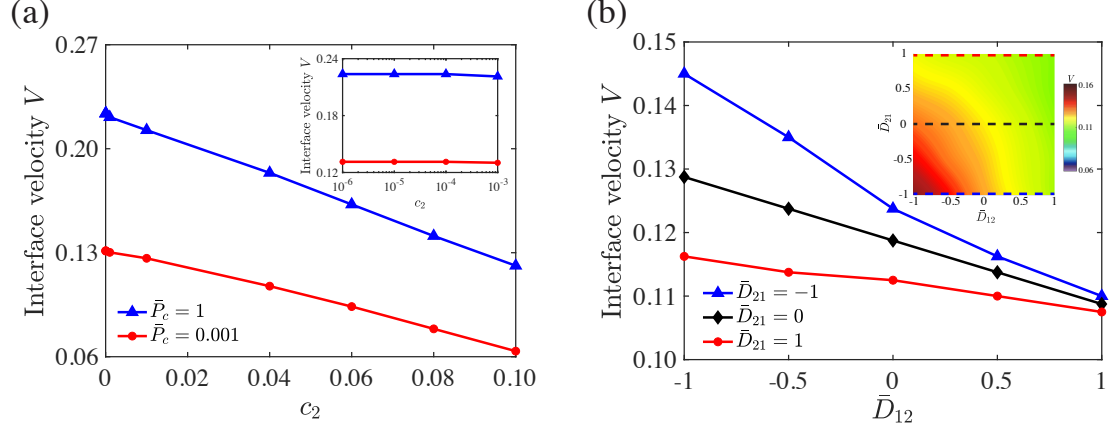


Figure 5.6: (a) The S-L interface velocity as a function of c_2 while setting $c_1 = 0.1$ (i.e., impact of ternary alloy additions) and using $\bar{P}_c = 1$ and 0.001 . (b) Using the slice from Fig. 5.5(b2) with $\bar{P}_c = 1.0$, line scans of the S-L interface velocity V as a function of $\bar{D}_{12}$ for various values of $\bar{D}_{21}$.

of solute 2, while fixing $c_1 = 0.1$, are shown: $c_2 = 0.025$ in the top row [Fig. 5.5(a1), (b1), and (c1)] and $c_2 = 0.1$ in the bottom row [Fig. 5.5(a2), (b2), and (c2)]. Also, Fig. 5.5 shows results using $\bar{D}_{22} = 0.5$ [Fig. 5.5(a1) and (a2)], $\bar{D}_{22} = 1.0$ [Fig. 5.5(b1) and (b2)], and $\bar{D}_{22} = 1.5$ [Fig. 5.5(c1) and (c2)]. The results depicted in Fig. 5.5 reveal a few general trends. First, the S-L interface velocity V increases with the interface permeability parameter $\bar{P}_c$. As indicated in Section 5.1.2, under local equilibrium conditions, where $\bar{P}_c \rightarrow \infty$, Eqs. 5.10 and 5.11 show that K_{sl} approaches the classical interface attachment kinetics parameter. On the other hand, in the limit $\bar{P}_c \rightarrow 0$, the PF kinetic parameter $K_{sl} \rightarrow 0$. Such limits can be seen in the velocity contour slices in Fig. 5.5.

Second, Fig. 5.5 shows results for two representative values for c_2 , while setting $c_1 = 0.1$, namely $c_2 = 0.025$ in the top panels [(a1), (b1), and (c1)] and $c_2 = 0.1$ in the bottom ones [(a2), (b2), and (c2)]. It can be seen that increasing c_2 from 0.025 [top panels] to 0.1 [bottom panels] while fixing all other parameters leads to a decrease in the S-L interface velocity V . To further demonstrate this effect, Fig. 5.6(a) shows

simulation results of the S-L interface velocity as a function of c_2 using $\bar{D}_{11} = \bar{D}_{22} = 1$, $\bar{D}_{12} = \bar{D}_{21} = 0$, and $c_1 = 0.1$. The inset in Fig. 5.6(a) shows a close-up view in the regime with $10^{-3} > c_2 > 10^{-6}$, where the binary alloy limit is recovered when $c_2 \rightarrow 0$. Ternary alloy effects (i.e., the impact of adding a third element) can be clearly seen, where increasing c_2 away from the binary alloy limit results in a decrease in the S-L interface velocity using $\bar{P}_c = 1$ and 0.001. Similar trends for the velocity as a function of solute concentration have been observed in binary alloys [124, 272].

A third trend, which can be observed in Fig. 5.5, deals with the impact of liquid phase off-diagonal diffusion coefficients, $\bar{D}_{12}$ and $\bar{D}_{21}$, on solidification velocity. It can be seen that negative values of $\bar{D}_{12}$ and $\bar{D}_{21}$ increase the S-L interface velocity, and that this trend holds for the various values of $\bar{D}_{22}$ used in this work [recall that $\bar{D}_{11} = 1$ is the reference value]. To further highlight this effect, a surface slice from Fig. 5.5(b2) with $\bar{P}_c = 1$ is taken as an example and is shown in Fig. 5.6(b), where line scans of the S-L interface velocity V as a function of $\bar{D}_{12}$ are depicted using $\bar{D}_{21} = -1, 0$, and 1. It can be clearly seen that V increases with decreasing $\bar{D}_{12}$ and $\bar{D}_{21}$ values. A negative value for $\bar{D}_{12}$ ($\bar{D}_{21}$) indicates diffusion of species 1 (2) up the concentration gradient of solute 2 (1). A solidification study of a Al-Cu-Mg alloy employing diffusion mobility databases revealed negative off-diagonal Cu-Mg, D_{CuMg} , and Mg-Cu, D_{MgCu} , diffusion coefficients [273].

While the results depicted in Figs. 5.5 through 5.7 highlight the role of various transport coefficients $\bar{D}_{ij}$ in solidification rates using the same values for the interface permeability parameters, i.e., $\bar{P}_1 = \bar{P}_2 = \bar{P}_c$, it is important to note that the finite interface dissipation PF model allows for an interface permeability parameter unique for each solute type. As a demonstration, Appendix C provides an example of ternary alloy solidification with different values for $\bar{P}_1$ and $\bar{P}_2$.

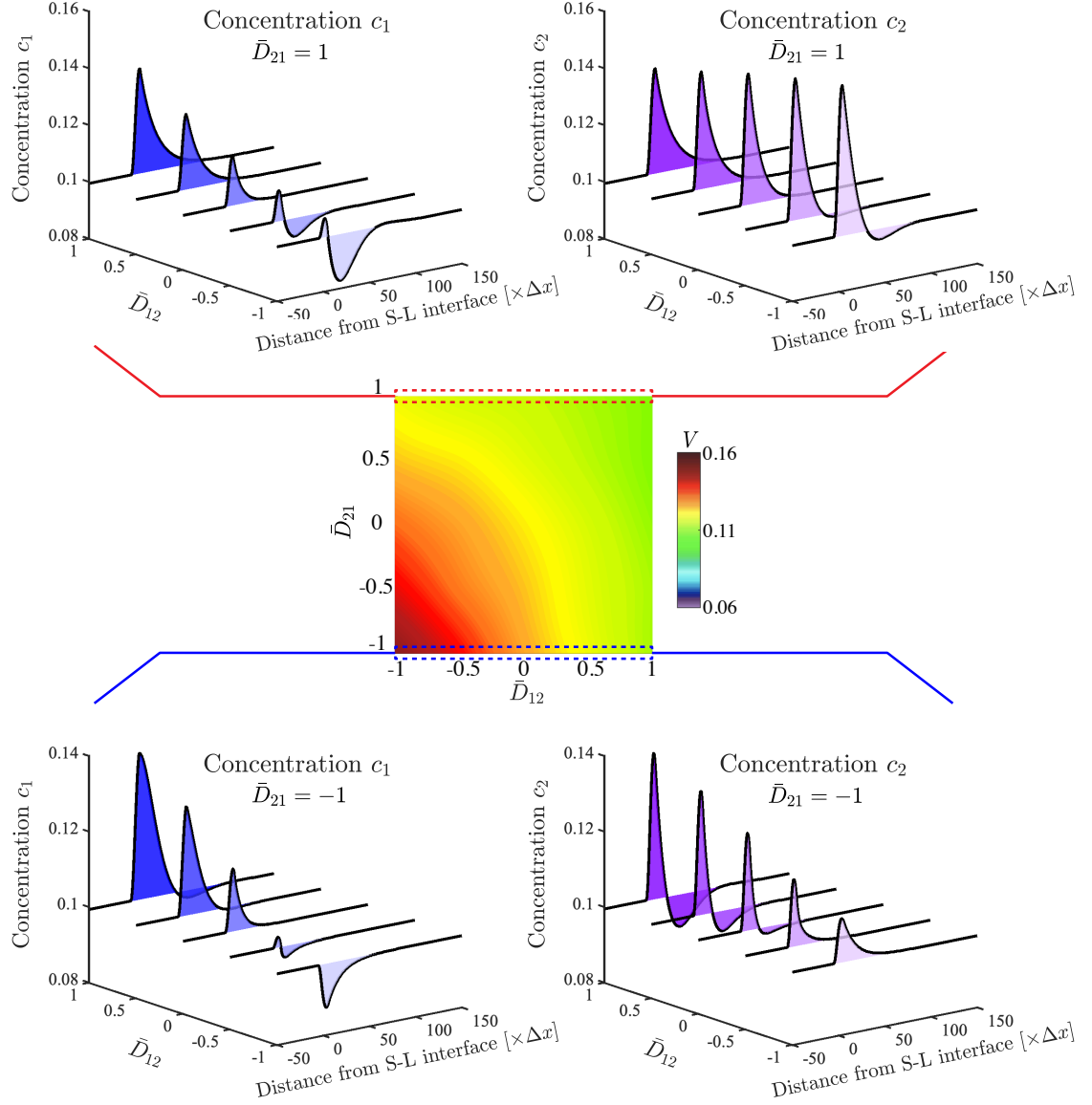


Figure 5.7: Using the slice from Fig. 5.5(b2) with $\bar{P}_c = 1.0$ and $\bar{D}_{22} = 1.0$, concentration profiles of solutes 1 and 2 in the vicinity of the S-L interface for various values of the off-diagonal diffusion coefficients, $\bar{D}_{12}$ and $\bar{D}_{21}$. The profiles of c_1 (c_2) are labeled in blue (purple).

5.2.3 Concentration Profiles

The trends observed in Fig. 5.5 for the dependence of the S-L interface velocity V on the off-diagonal diffusion coefficients, $\bar{D}_{12}$ and $\bar{D}_{21}$, can be understood by examining the concentration profiles in the vicinity of the S-L interface. As an example, we use a slice of the velocity surface in Fig. 5.5(b2) with $\bar{P}_c = 1$ and plot concentration profiles for several values of $\bar{D}_{12}$ in Fig. 5.7 using $\bar{D}_{21} = 1$ [top panels] and $\bar{D}_{21} = -1$ [bottom panels]. The concentration profiles of species 1 are in blue, while c_2 profiles are in purple. A close examination of the top panels in Fig. 5.7 with $\bar{D}_{21} = 1$ reveals that as $\bar{D}_{12}$ decreases the concentration c_1 at the S-L interface decreases. A similar observation can also be seen in the bottom panels of Fig. 5.7, where decreasing $\bar{D}_{12}$ leads to a decrease in both c_1 and c_2 at the S-L interface. The trends in Fig. 5.7 suggest that decreasing the off-diagonal diffusion coefficients while holding everything else fixed leads to less drag effects due to less solute pile-up at the S-L interface. The RHS of Eq. 5.9 reveals that several diffusional fluxes control the evolution of the concentration fields, e.g., for c_1 the two relevant fluxes are $-D_{11}\nabla c_1$ and $-D_{12}\nabla c_2$. As a result, the relative magnitude and sign of the off-diagonal diffusion coefficients impact the diffusional fluxes of solutes, which influence the concentration profiles ahead of the S-L interface and, as a result, the interface velocity.

Finally, the results depicted in Figs. 5.5 through 5.7 assume an undercooling $\theta = 0.067$, see Eqs. 5.15 and 5.16. Using systems with $\bar{P}_c = 1.0$, $\bar{D}_{11} = \bar{D}_{22} = 1.0$, $\bar{D}_{21} = -1$, $c_1 = c_2 = 0.1$, Fig. 5.8 depicts the impact of undercooling θ and off-diagonal diffusion coefficient $\bar{D}_{12}$ on the S-L interface velocity. It can be seen that decreasing $\bar{D}_{12}$ increases V across several values for the undercooling θ . Further, the interface velocity V shows a stronger dependence on θ than $\bar{D}_{12}$, at least for the model parameters used in this study.

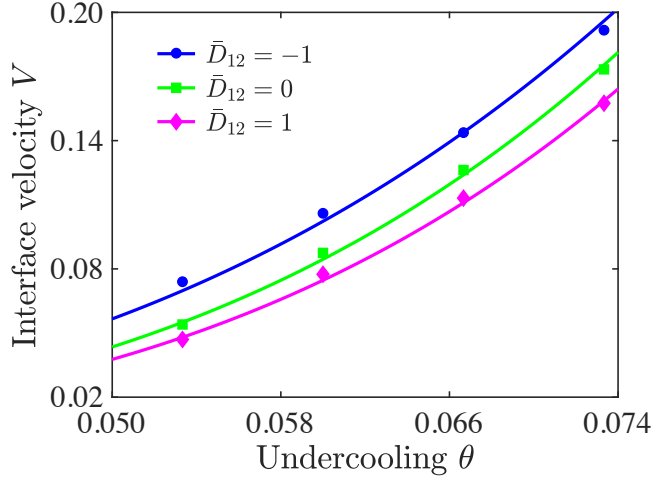


Figure 5.8: The S-L interface velocity V as a function of the undercooling θ [see Eq. 5.16] and off-diagonal diffusion coefficient $\bar{D}_{12}$. Other parameters are set to: $\bar{P}_c = 1.0$, $\bar{D}_{11} = \bar{D}_{22} = 1.0$, $\bar{D}_{21} = -1$, $c_1 = c_2 = 0.1$.

The results shown in Figs. 5.5 through 5.8 do not consider the temperature dependence of the transport coefficients. Accounting for such a dependence requires detailed calculations using, for example, atomistic calculations [274–276]. The interplay between undercooling and the various temperature- and concentration-dependent transport coefficients and their impact on solidification rates will be an interesting effect to investigate in a future study.

5.2.4 Partition Coefficients

We now direct our attention to the velocity-dependent partition coefficient of solute 1, k_1 , and that of solute 2, k_2 . These partition coefficients describe the relative affinity of solutes for the solid and liquid solvent phases. According to Eq. 5.20, for a given solute i the liquid phase in the vicinity of the S-L interface is enriched if $k_i < 1$ or depleted if $k_i > 1$ [277]. A knowledge of k values as a function of solidification conditions and alloy properties would enable the quantification of solute redistribution and trapping

during solidification.

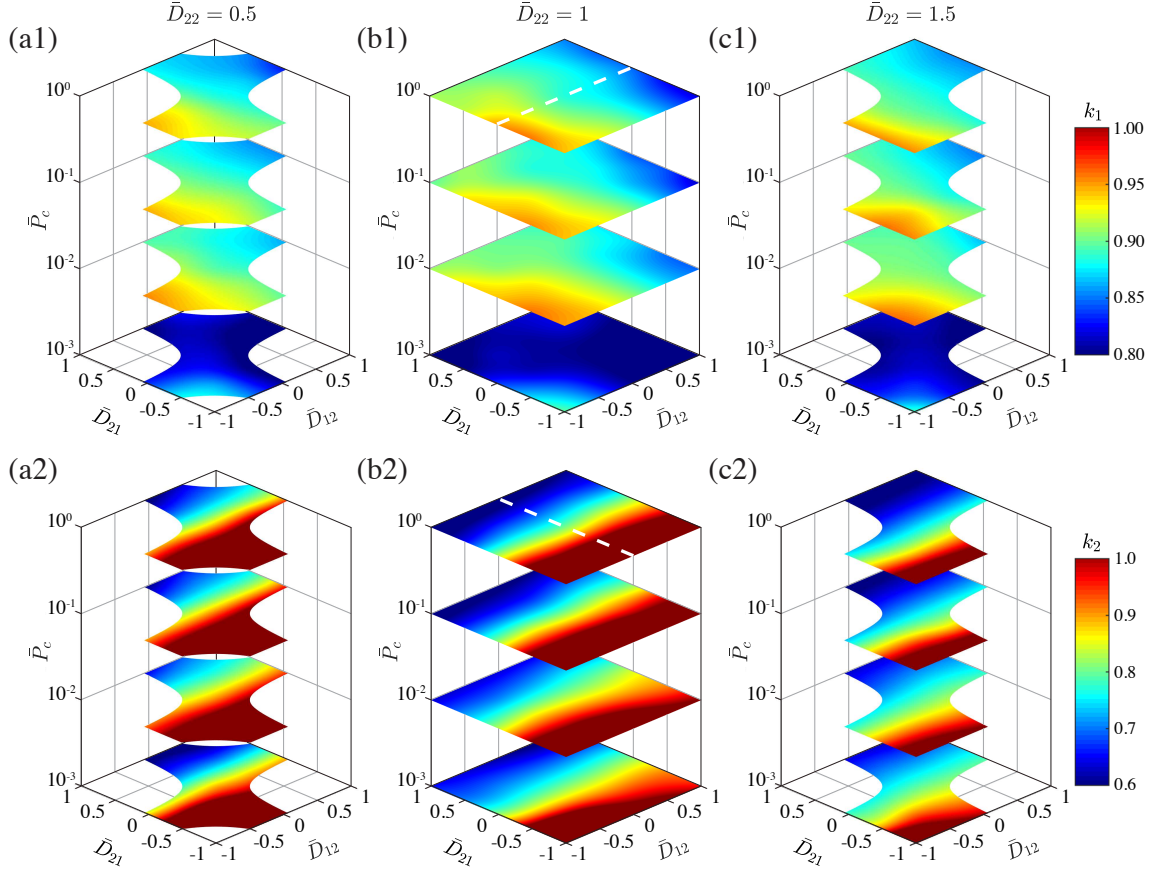


Figure 5.9: Contour slices of the velocity-dependent partition coefficient [(a1), (b1), and (c1)] k_1 and [(a2), (b2), and (c2)] k_2 as a function of the off-diagonal diffusion coefficients, $\bar{D}_{12}$ and $\bar{D}_{21}$, and interface permeability parameter $\bar{P}_c$ for various values of $\bar{D}_{22}$ noting that $\bar{D}_{11} = 1.0$. Here, we set $c_1 = 0.1$, $c_2 = 0.025$, and rescaled undercooling $\theta = 0.067$.

Using the PF model parameters and alloy properties listed in Table 5.1, Fig. 5.9 shows the velocity-dependent partition coefficient k_1 [Fig. 5.9(a1), (b1), and (c1)] and k_2 [Fig. 5.9(a2), (b2), and (c2)] for various values of the off-diagonal diffusion coefficients, $\bar{D}_{12}$ and $\bar{D}_{21}$, and interface permeability parameter, $\bar{P}_c$, using $c_1 = 0.1$, $c_2 = 0.025$, and $\theta = 0.067$. As discussed in Section 5.1.2, the parameter $\bar{P}_c$ in this PF formalism is used to capture nonequilibrium solidification conditions, where local

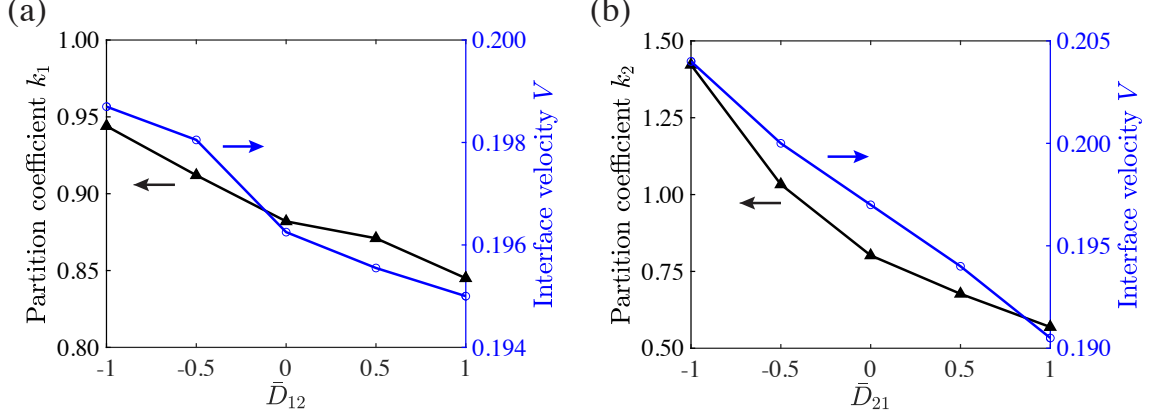


Figure 5.10: The partition coefficient (a) k_1 as a function of $\bar{D}_{12}$ with $\bar{D}_{21} = 0$ and (b) k_2 as a function of $\bar{D}_{21}$ with $\bar{D}_{12} = 0$. Included in both panels is the corresponding S-L interface velocity V . Other parameters are set to: $\bar{P}_c = 1.0$, $\bar{D}_{22} = 1.0$, $c_1 = 0.1$, and $c_2 = 0.025$.

equilibrium at the S-L interface is attained in the limit $P_c \rightarrow \infty$ leading to $K_{sl} \rightarrow \mu_{sl}$. In general, values of the partition coefficients increase with decreasing $\bar{D}_{12}$ and $\bar{D}_{21}$. As shown in Fig. 5.7, negative values for the off-diagonal diffusion coefficients, $\bar{D}_{12}$ and $\bar{D}_{21}$, lead to depletion of the solute concentrations ahead of the S-L interface, thereby increasing the values of the partition coefficients.

For the model parameters used in Fig. 5.9, it can be seen that values of k_1 are more sensitive to variations in $\bar{D}_{12}$ than in $\bar{D}_{21}$ [see Fig. 5.9(a1), (b1), and (c1)], while the opposite is true for k_2 , i.e., k_2 is more sensitive to variations in $\bar{D}_{21}$, refer to Fig. 5.9(a2), (b2), and (c2). For example, Fig. 5.10 shows line scans of the partition coefficients and interface velocity V as a function of off-diagonal diffusion coefficients using $\bar{P}_c = 1.0$, see dashed lines in Fig. 5.9(b1) and (b2) for the location of these line scans in parameter space. Plots of k_1 and V as a function of $\bar{D}_{12}$ are shown in Fig. 5.10(a) while Fig. 5.10(b) shows plots of k_2 and V as a function of $\bar{D}_{21}$. The strong dependence of k_1 and k_2 on the off-diagonal diffusion coefficients is evident. It is interesting to note that for the case depicted in Fig. 5.10(b), k_2 attain values

greater than one when $\bar{D}_{21} < 0$. For negative values of the off-diagonal diffusion coefficients, the concentration profile in the liquid phase ahead of the S-L interface is depleted [see Fig. 5.7], and according to Eq. 5.20 this leads to values of the partition coefficient that are greater than unity.

The results depicted in Fig. 5.5 for the S-L interface velocity V and Fig. 5.9 for the partition coefficients, k_1 and k_2 , highlight the important role that off-diagonal diffusion coefficients play in growth rates and solute redistribution during solidification processing. Further, within this PF framework the interface permeability parameter $\bar{P}_c$ influences solidification rates and solute profiles ahead of the S-L interface. While this study focused on providing a systematic exploration of the interplay of these kinetic processes on solidification rates in ternary alloys, it will be interesting, in a future study, to consider the concentration and temperature dependencies of these transport coefficients and their impact on solidification rates. This in turn requires detailed studies using, for example, atomistic simulations to quantify such dependencies.

5.3 Conclusions

Solidification physics has been the subject of active research recently for its relevance to a wide range of advanced processing technologies such as melt-based AM. The PF modeling framework is a powerful computational tool used to predict the formation and evolution of microstructure during solidification processing. However, most PF solidification studies focus on dilute binary alloys. In this work, we employed the multi-phase finite interface dissipation PF model by Zhang and Steinbach [141] to investigate the impact of various mass transport processes on solidification rates of multicomponent alloys. As a model system, we considered ternary alloys as they ex-

hibit multicomponent effects, yet the PF model is computationally tractable. With this PF modeling framework, a kinetic model parameter, termed interface permeability, was used to account for nonequilibrium interfacial effects that emerge during rapid solidification.

We performed a systematic computational study exploring the impact of various mass transport coefficients and nonequilibrium effects on planar front solidification rates. Simulation results revealed that the off-diagonal, or cross-diffusion, coefficients play a critical role in controlling the S-L interface velocity and solute partition coefficients. For the model parameters employed in this work, it was found that negative values for the off-diagonal diffusion coefficients increase the solute partition coefficients due to depletion of the liquid phase concentrations ahead of the S-L interface. Further, given an undercooling the S-L interface velocity was found to increase with decreasing the off-diagonal diffusion coefficients. Computational studies of nonequilibrium interfacial effects showed that decreasing the PF interface permeability parameter while holding all other parameters fixed resulted in both an increase in solute partition coefficients and a decrease in the S-L interface velocity. Also, computational studies revealed that large variations, i.e., several orders of magnitude, in the PF interface permeability parameter were needed to capture such nonequilibrium interfacial effects during rapid solidification. In broad terms, our work highlights the role of various mass transport processes and nonequilibrium effects on solidification rates of multicomponent alloys.

Chapter 6

Grain Boundary Segregation and Chemical Ordering in CoCrFeMnNi Multi-principal Element Alloy

In this chapter, we employ atomistic simulations to explore the interplay between chemical ordering and GB segregation of several $[001]$ asymmetric tilt GBs in the equiatomic CoCrFeMnNi, so-called Cantor alloy, chosen due to the emerging experimental literature on chemical ordering and GB chemistry in this system [86, 201, 205]. The remainder of this chapter is structured as follows. Section 6.1 details the computational methods, Section 6.2 presents the simulation results and discussion, and Section 6.3 provides a summary of the work along with concluding remarks.

6.1 Computational Methods

Atomistic simulations employing Molecular Statics (MS), Molecular Dynamics (MD), and Monte Carlo (MC) are used to investigate the interaction of elemental species with GBs and quantify SRO. All atomistic simulations reported in this work are performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package [278] and visualizations of atomistic structures are generated using OVITO [279]. The OVITO implementation of the common neighbor analysis (CNA) [280] and polyhedral template matching (PTM) algorithm [281] is used to identify crystal structures and GB regions. A series of CoCrFeMnNi alloy bi-crystals with [001] asymmetric tilt GBs are generated and studied using a second nearest-neighbor modified embedded atom method (2NN MEAM) interatomic potential fit to the energetics of the unary, binary, and ternary combinations of the CoCrFeMnNi system [282]. Furthermore, it was shown that this interatomic potential reproduces the observed mechanical properties and solid solution hardening effects in CoCrFeMnNi MPEAs at arbitrary compositions [282].

In this work, we explore a series of [001] asymmetric tilt GBs in equiatomic CoCrFeMnNi. A fully periodic atomistic system is created from two half-crystals, each of which is rotated such that the resulting GB has the specified geometry, described in this work by the misorientation angle θ and the Σ value, where $1/\Sigma$ represents the fraction of lattice points that are in coincidence [283]. Figure 6.1(a) shows a schematic of the bi-crystal geometry used in this work, where the crystal [100] and [010] directions of one of the half-crystals are aligned with the global x and y directions. The second half-crystal is then rotated to produce the desired GB misorientation angle θ . Table 6.1 lists the axes for the two half-crystals for each GB examined in this work and the resultant misorientation angle θ and Σ value. We recognize that the GB

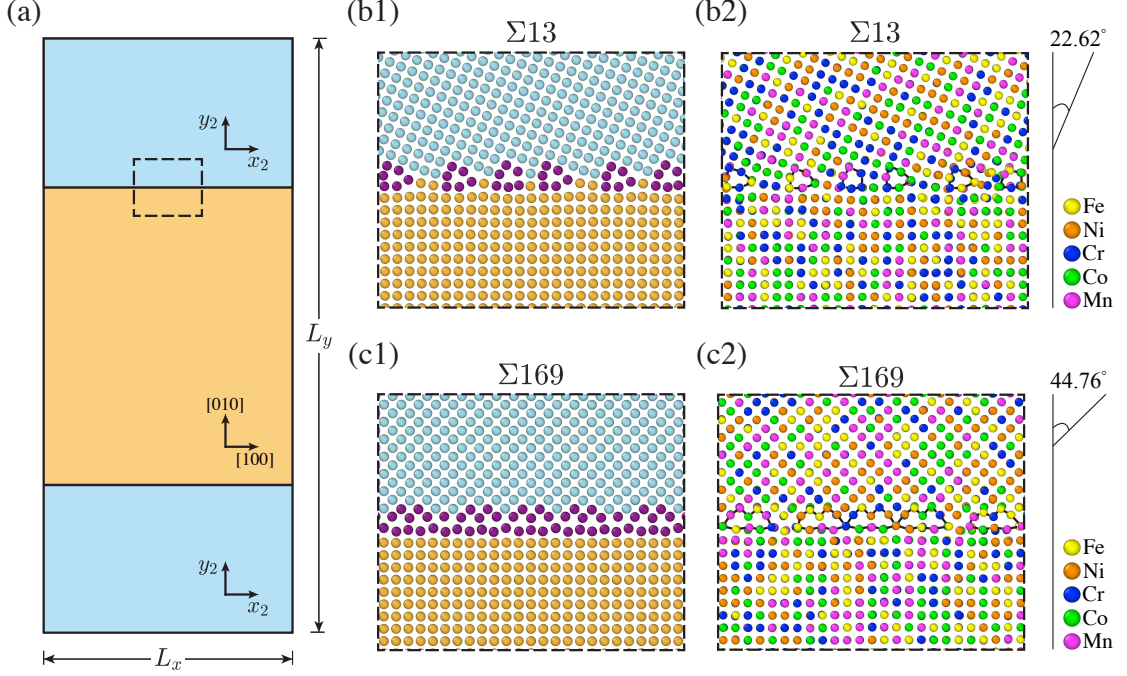


Figure 6.1: (a) The MPEA bi-crystal geometry employed in this work. (b) and (c) Atomic structures of the MPEA bi-crystals with (b1-b2) $\Sigma 13$ $(010)/(\bar{5} 12 0)$ and (c1-c2) $\Sigma 169$ $(010)/(\bar{1}19 120 0)$ asymmetric tilt GBs. Atomic structures are shown after: (b1 and c1) generation using the Ni component of the CoCrFeMnNi interatomic potential [282] and (b2 and c2) conversion to CoCrFeMnNi GBs and energy minimization.

geometry is described by five macroscopic degrees of freedom, three for misorientation and two for plane normal [283], and that the GBs explored in this work probe a small region in the higher-dimensional GB geometry space. In future work, it will be interesting to fully characterize multi-element GB segregation as a function of the boundary geometry.

To generate MPEA GBs, we first start by using the γ -surface method [284] to construct Ni GBs using the pure Ni component of the MPEA interatomic potential used in this work. A sequence of relative small displacements between the two half-crystals is used in conjunction with atom deletions and conjugate gradient energy minimizations to identify low energy GB configurations. The systems are allowed to expand or contract perpendicular to the GB plane. The dimension and number

of atoms for each bi-crystal geometry used in this study are listed in Table 6.1. As representative examples, Fig. 6.1(b1) and (c1) shows respectively the atomic structures of the $\Sigma 13$ (010)/($\bar{5}$ 12 0) and $\Sigma 169$ (010)/($1\bar{1}9$ 120 0) Ni GBs, where atoms colored in orange/blue (purple) denote FCC (non-FCC) ordering according to the common neighbor analysis [280]. Once the Ni GB structures are constructed, they are converted to equiatomic CoCrFeMnNi systems by randomly assigning Co, Cr, Fe, Mn, and Ni elements in the atomistic bi-crystal. Then, conjugate energy minimization is used while allowing the simulation box to expand or contract to maintain zero pressure. Figure 6.1(b2) and (c2) shows representative examples again of the $\Sigma 13$ (010)/($\bar{5}$ 12 0) and $\Sigma 169$ (010)/($1\bar{1}9$ 120 0) CoCrFeMnNi GBs, where each atom type is assigned a unique color.

Table 6.1: The crystallographic orientations of the half-crystals, GB misorientation angle θ , number of atoms, and system size for all MPEA bi-crystals used in this work. For one of the half-crystals, the $[100]$ and $[010]$ crystal directions are aligned with the global x and y directions and the second half-crystal is rotated to produce the desired GB misorientation angle. The out of plane $[001]$ crystal direction is common to both half-crystals.

Σ	$\mathbf{y}_1 / \mathbf{y}_2$	θ ($^\circ$)	Number of atoms	$L_x \times L_y$ (nm $\times$ nm)
25	$[0\ 1\ 0] / [\bar{7}\ 24\ 0]$	16.26	17,472	8.8×20.6
13	$[0\ 1\ 0] / [\bar{5}\ 12\ 0]$	22.62	18,192	9.2×20.6
17	$[0\ 1\ 0] / [\bar{8}\ 15\ 0]$	28.07	23,760	12.0×20.6
5	$[0\ 1\ 0] / [\bar{3}\ 4\ 0]$	36.87	17,520	8.8×20.6
169	$[0\ 1\ 0] / [1\bar{1}9\ 120\ 0]$	44.76	16,845	8.5×20.7

After the generation of MPEA GB structures, the hybrid MC-MD scheme [285, 286] is used to equilibrate the structural aspects and compositional degrees of freedom of the atomistic bi-crystals. With such an approach, an MC step is performed with conserved atomic swaps, in which two atoms are randomly selected and if they were

different chemical species, their chemical identities are swapped and accepted with a Boltzmann factor based on the energy change at the prescribed temperature. This MC simulation models a closed system with a fixed number of atoms for each elemental species. In this work, each MC-MD cycle includes 1000 MC steps followed by a 10 ps MD simulation at the desired temperature and zero pressure leading to a trajectory in phase space that is consistent with the canonical NPT ensemble. Temperatures in the range of 673–1200 K are explored in this work. The MC-MD cycle was repeated until the total simulation time was 8 ns. To ensure that the MPEA GB structures approach chemical equilibrium, we monitor the rescaled total energy of the system $\bar{E}_{sys}$ and the fraction of accepted swaps of each chemical pair $\bar{\phi}_{acc}$ which are given by

$$\bar{\phi}_{acc} = \frac{\phi_{acc}(t) - \phi_{acc}(t_f)}{\phi_{acc}(t_o) - \phi_{acc}(t_f)} \quad \text{and} \quad \bar{E}_{sys} = \frac{E_{sys}(t) - E_{sys}(t_f)}{E_{sys}(t_o) - E_{sys}(t_f)}, \quad (6.1)$$

where $t_o = 0$ and $t_f = 8$ ns define the initial and final simulation times (after 8 ns of MC-MD cycles). Here, E_{sys} is the total energy of a MPEA bi-crystal system and ϕ_{acc} is the fraction of accepted MC atomic swaps of each chemical pair. An asymptotic rescaled energy profile indicates an approach toward chemical equilibrium. Based on the definitions given by Eq. 6.1, as the system approaches equilibrium, the rescaled total energy $\bar{E}_{sys}$ and rescaled fraction of accepted MC swaps $\bar{\phi}_{acc}$ approach zero.

For example, Fig. 6.2(a) through (c) shows results for the $\Sigma 5$ (010)/($\bar{3}40$) asymmetric tilt GB, where Fig. 6.2(a) depicts the initial GB structure with gray (purple) denoting FCC (non-FCC) atoms. Figure 6.2(b) shows this MPEA GB after MC-MD simulations at $T = 1000$ K, where each element type is assigned a unique color. Figure 6.2(c) is a plot of the rescaled fraction of accepted MC atomic swaps $\bar{\phi}_{acc}$ for the various chemical pairs. At simulation times < 2 ns, transients exist for the fraction of accepted swaps due to the initial atomic positions of various alloying elements and

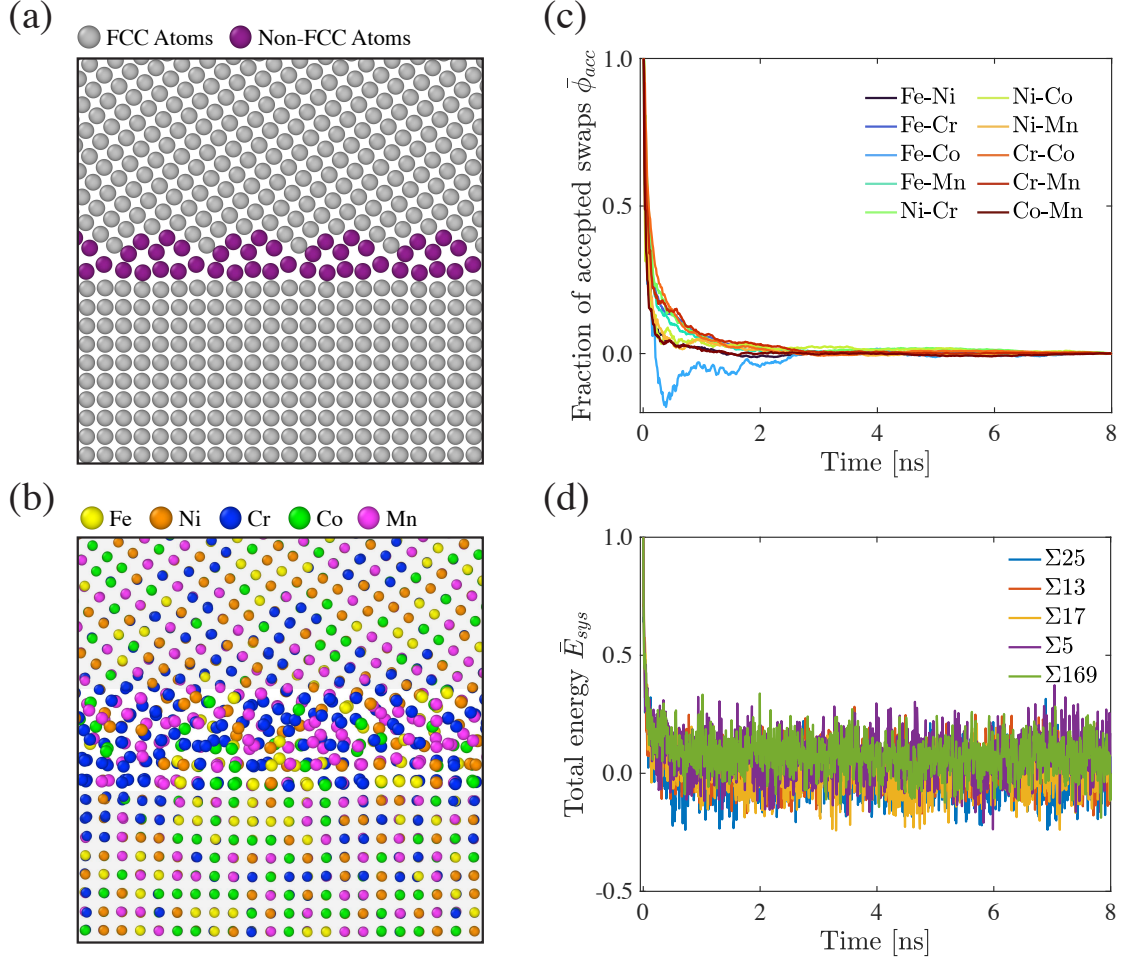


Figure 6.2: (a–c) For the $\Sigma 5$ (010)/ $(\bar{3}40)$ asymmetric tilt GB: (a) atomic structure of the GB before MC-MD simulations, (b) the GB structure after MC-MD simulations to equilibrate the structural and chemical degrees of freedom at $T = 1000$ K, and (c) a plot of the rescaled fraction of accepted atomic MC swaps of each chemical pair $\bar{\phi}_{acc}$, see Eq. 6.1, during MC-MD at $T = 1000$ K. (d) A plot of the rescaled total system energy $\bar{E}_{sys}$, see Eq. 6.1, for all GBs explored in this work during MC-MD at $T = 1000$ K.

effects combining elasticity and chemistry. However, it is important to note that $\bar{\phi}_{acc}$ for the various chemical pairs approaches zero rapidly, after ≈ 3 ns of MC-MD, indicating chemical and structural equilibrium. Figure 6.2(d) depicts the rescaled system energy $\bar{E}_{sys}$ at $T = 1000$ K for all GBs explored in this work, where it can be seen that the energy reaches an asymptote indicating chemical equilibrium. As our simulations are performed in the NPT ensemble, the energy fluctuations in Fig. 6.2(d) are because the system exchanges energy with a thermostat to maintain the desired temperature and adjusts its volume to maintain the prescribed zero pressure.

After equilibrating the compositional degrees of freedom of the MPEA bi-crystals, we quantify GB segregation by calculating the GB solute excess using Cahn’s determinant approach given by [287]

$$\Gamma_i = \frac{N_i^{gb} - N_{tot}^{gb}c_i}{A_{gb}}, \quad i = \text{Fe, Ni, Cr, Co, Mn}, \quad (6.2)$$

where Γ_i is the GB solute excess of element type i . N_{tot}^{gb} and N_i^{gb} are the total number of atoms and number of atoms of element type i in the GB layer, respectively, and A_{gb} is the GB area. c_i is the nominal composition of element type i . Positive values for Γ_i indicate segregation and negative ones indicate desegregation.

In addition to calculating GB excess of various elemental species, we quantify SRO in the MPEA bi-crystals using the Warren-Cowley parameters χ_{ij} given by [188, 288, 289]

$$\chi_{ij} = 1 - \frac{p_{ij}}{2c_i c_j}, \quad (6.3)$$

where p_{ij} is the probability of finding two element types i and j within a specific cutoff distance, c_i and c_j are the global concentrations of species i and j , respectively.

$\chi_{ij} < 0$ ($\chi_{ij} > 0$) indicates attractive (repulsive) interactions between species i and j [186]. To reveal the interplay between GB segregation and SRO, we calculate χ_{ij} in atomistic slabs of width ≈ 15 Å that are parallel to the GB plane. This approach of obtaining spatial profiles for χ_{ij} allows us to reveal how GB segregation influences bulk chemical profiles and SRO in the immediate vicinity of boundary regions.

We quantify solute-solute interactions, which give rise to non-random distribution of elemental species, in MPEAs by calculating the regular solution heat of mixing model parameter Ω_{ij} for each chemical pair i - j in equiatomic CoCrFeMnNi at $T = 0$ K. In regular solution thermodynamics, $\Omega_{ij} \propto \epsilon_{ij} - 0.5(\epsilon_{ii} + \epsilon_{jj})$, where ϵ_{ij} is the i - j bond energy. With this convention, zero energy is when the atoms are separated to infinity and ϵ_{ii} , ϵ_{jj} , and ϵ_{ij} are negative quantities [48]. We computed the best-fit 0 K Ω_{ij} from atomistic simulations as follows: First, the chemical potentials μ_i are calculated from LAMMPS using a substitution method, where atoms in a reference solid solution with energy E° are repeatedly replaced by atoms of the other alloying types giving [290]

$$\mu_i - \mu_j = \left\langle E_\sigma^{(i)} - E_\sigma^{(j)} \right\rangle, \quad (6.4)$$

where $E_\sigma^{(j)}$ denotes the energy of alloying type j occupying site σ , and $\langle \cdot \rangle$ denotes an average over lattice sites. Second, from these chemical potentials we recover the free energy per atom at 0 K, i.e. $g = \sum_i \mu_i x_i$, which is then fit, using the Moore-Penrose inverse in the fitting routine [291], to the regular solution model given by [48]

$$g = \sum_i \mu_i^\circ x_i + \sum_{i < j} \Omega_{ij} x_i x_j. \quad (6.5)$$

Here, μ_i° denotes the cohesive energy of a pure sample of i and x_i denotes the atomic

fraction of species i .

6.2 Results and Discussion

6.2.1 Grain Boundary Segregation

Serving as a baseline for our GB segregation study, we start by examining the impact of temperature on chemical redistribution in bulk CoCrFeMnNi MPEA. We consider a single crystal CoCrFeMnNi MPEA whose [100], [010], and [001] crystal directions are aligned with the x , y , and z directions, respectively, and perform MC-MD simulations at temperatures of 673 K, 800 K, 1000 K, and 1200 K. Figure 6.3(a) shows the atomic structures of this CoCrFeMnNi single crystal at various temperatures, where the formation of a Cr-rich phase (i.e., regions in blue in Fig. 6.3(a)) can be seen at $T = 673$ K. The formation of Cr-rich BCC and σ phases has been shown in several thermodynamic databases [292–294] and experimentally observed in equiatomic CoCrFeMnNi [206, 207, 295–297]. To quantify the results shown in Fig. 6.3(a), we calculate the concentration profiles of various elemental species along the crystal [010] direction averaged along the other two directions using atomic slabs of width ≈ 10 Å and the results are shown in Fig. 6.3(b) for $T = 673$ K and 1200 K. Regions with high Cr concentrations can be seen at $T = 673$ K indicating the formation of a Cr-rich phase. Furthermore, depletion of Fe and Co can be seen at Cr-rich domains. In contrast, the concentration profiles of various elemental species are uniform at 1200 K. Based on the results shown in Fig. 6.3, annealing at temperatures above 800 K results in more homogeneous distributions of the elemental species in the CoCrFeMnNi system.

Data for the regular solution heat of mixing model parameter Ω_{ij} for each chemical

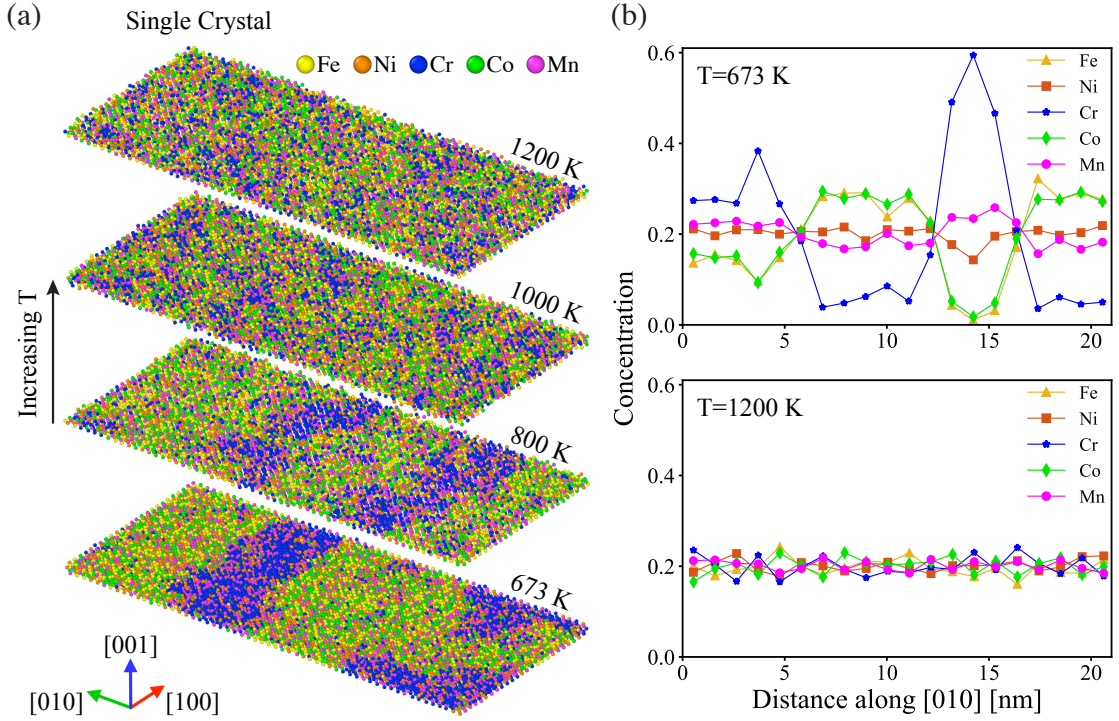


Figure 6.3: (a) Atomic structures of CoCrFeMnNi single crystals after MC-MD simulations at various temperatures. (b) For the CoCrFeMnNi single crystals in (a), concentration profiles along the crystal [010] direction at $T = 673$ K and $T = 1200$ K.

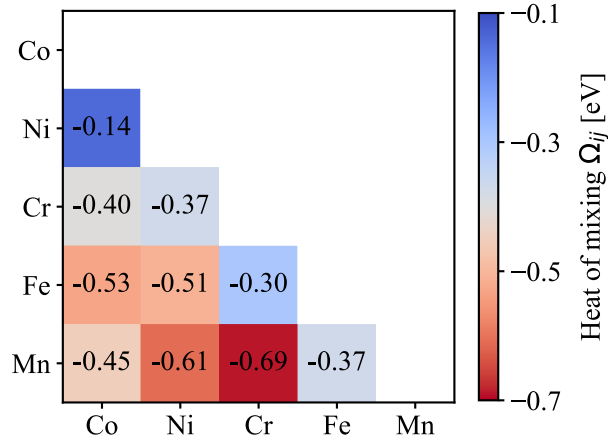


Figure 6.4: Regular solution heat of mixing model parameters Ω_{ij} for each i - j pair in equiatomic CoCrFeMnNi at $T = 0$ K. In regular solution thermodynamics, the alloy free energy is described using Eq. 6.5.

pair i - j in equiatomic CoCrFeMnNi at $T = 0$ K are shown in Fig. 6.4. In regular solution models, positive values for Ω_{ij} describe repulsive i - j interactions and negative values, where the i - j bond is more favorable than the i - i and j - j bonds, control the degree of ordering of the alloy [48]. It can be seen from Fig. 6.4 that the Cr-Mn, Ni-Mn, and Co-Fe pairs exhibit the most negative Ω_{ij} values indicating the favorable formation of these chemical pairs. Indeed, the concentration line scans shown in Fig. 6.3(b), albeit at $T = 673$ K, reveal the formation of domains rich in Cr and Mn and others with enhanced Co and Fe levels.

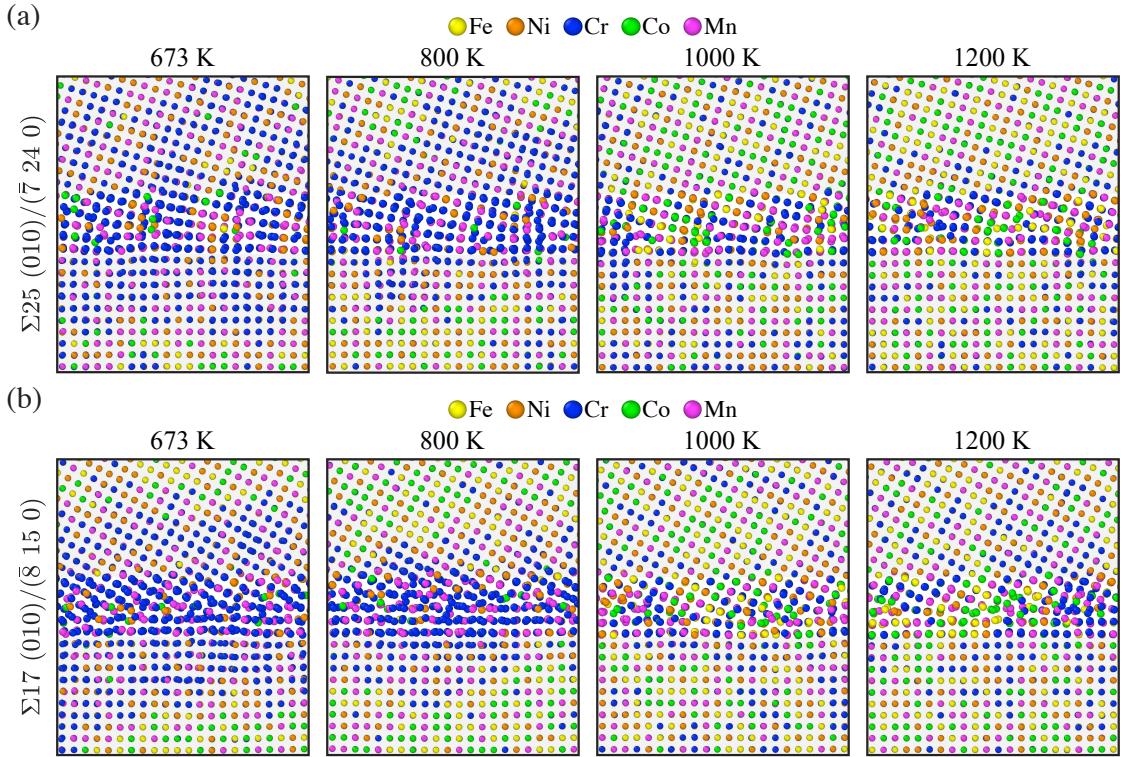


Figure 6.5: For (a) $\Sigma 25$ (010)/($\bar{7}$ 24 0) and (b) $\Sigma 17$ (010)/($\bar{8}$ 15 0) asymmetric tilt GBs, atomic structures after MC-MD simulations at various temperatures.

We next explore temperature effects using MPEA bi-crystal geometries. Figure 6.5 shows representative MC-MD results for the $\Sigma 25$ (010)/($\bar{7}$ 24 0) [Fig. 6.5(a)] and $\Sigma 17$ (010)/($\bar{8}$ 15 0) [Fig. 6.5(b)] asymmetric tilt CoCrFeMnNi GBs at several tempera-

tures. At $T = 673$ K and 800 K, formation of Cr-rich domains can be seen at the GBs, in which boundary regions serve as heterogeneous nucleation sites for such domains. It can also be seen that the spatial profiles of Cr-rich domains extend into the bulk crystals beyond the GB core (i.e., boundary structural units, see Fig. 6.1). At $T = 1000$ K and 1200 K, no phase formation is observed at the GBs and the boundary profiles qualitatively reveal enrichment of Cr (blue). These observations are consistent with atomistic simulation results by Wynblatt and Chatain [209], which revealed Cr segregation to (001) free surfaces and a near $\Sigma 13$ twist GB in CoCrFeMnNi MPEA. Based on the results shown in Fig. 6.5, we focus our segregation studies on temperatures above 1000 K in order to quantify GB segregation without the complexities associated with heterogeneous phase nucleation at GBs.

At $T = 1000$ K, Fig. 6.6 depicts the atomic structures of all GBs explored in this work after MC-MD simulations, where each element type is assigned a unique color. Enrichment of Cr (blue) and Mn (magenta) at all GBs can be seen. Local distortions are also observed at the GBs due to their heterogeneous chemical profiles and accompanying misfit strains (i.e., differing atomic radii of the constituent elements in CoCrFeMnNi [298]). To quantify the results depicted in Fig. 6.6, Fig. 6.7 reports the GB solute excess Γ_i of various element types as a function of the misorientation angle θ at $T = 1000$ K [Fig. 6.7(a)] and $T = 1200$ K [Fig. 6.7(b)]. The solute excess plots reveal several trends: First, it can be seen that both Cr and Mn segregate to all GBs explored in this work with Cr showing higher segregation levels than Mn. Furthermore, the segregation of Cr and Mn is accompanied by desegregation of Fe, Co, and Ni. At temperatures $T < 1000$ K, enrichment of Ni and Cr at CoCrFeMnNi GBs has been attributed to nucleation of Ni-rich and Cr-rich phases. For example, Otto et al. [207] performed prolonged anneals on the equiatomic CoCrFeMnNi and revealed the formation of $L1_0$ -NiMn, B2-FeCo and Cr-rich BCC phases at 773 K

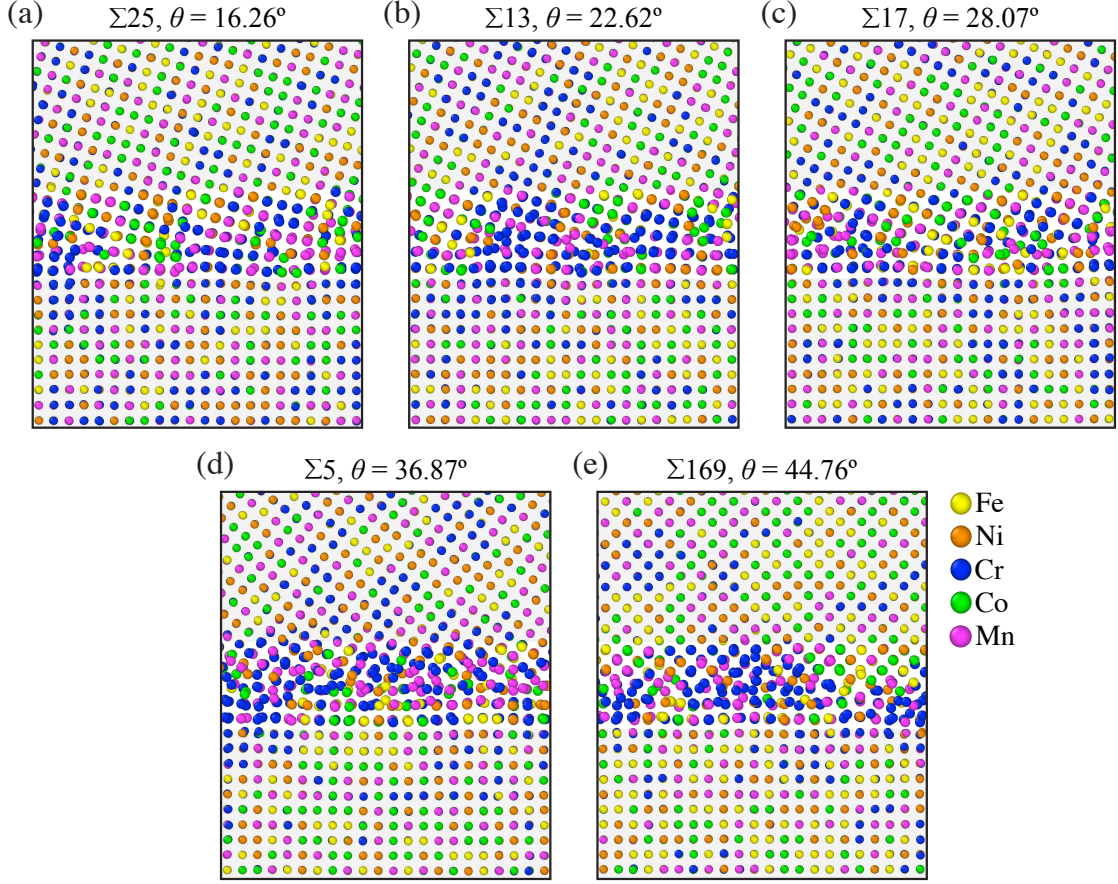


Figure 6.6: At $T = 1000$ K, atomic structures after MC-MD simulations of all GBs explored in this work, where each element type is assigned a unique color. (a) $\Sigma 25$ $(010)/(\bar{7} 24 0)$, (b) $\Sigma 13$ $(010)/(\bar{5} 12 0)$, (c) $\Sigma 17$ $(010)/(\bar{8} 15 0)$, (d) $\Sigma 5$ $(010)/(\bar{3} 4 0)$, and (e) $\Sigma 169$ $(010)/(\bar{1} 19 120 0)$.

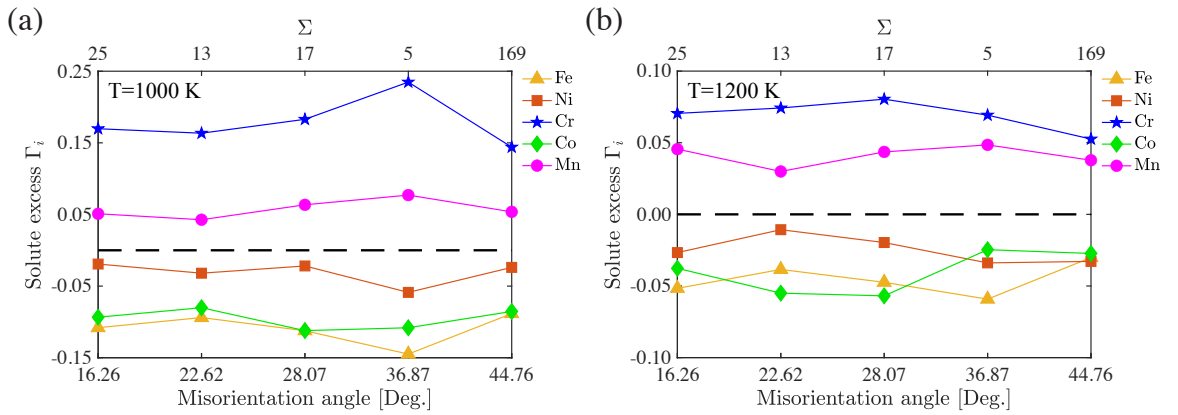


Figure 6.7: GB solute excess Γ_i of various element types as a function of misorientation angle θ at (a) $T = 1000$ K and (b) $T = 1200$ K.

and formation of a Cr-rich σ -phase at 973 K. They also showed that CoCrFeMnNi remains a single-phase solid solution at temperatures above 1000 K [207]. Second, GB solute excess decreases with the increase in temperature with the Cr showing the most sensitivity to temperature. For example, GB Cr excess decreases by half as the temperature increases from 1000 K to 1200 K. Third, for the GB geometries explored in this work, GB segregation does not show a strong dependency on the misorientation angle about the common [001] tilt axis. It would be interesting to investigate in future work whether this trend for multi-element GB segregation holds in the five-dimensional space describing GB geometry.

Next, we compare our GB segregation results depicted in Figs. 6.5 through 6.7 to experimental observations of GB chemical states in CoCrFeMnNi. An experimental study employing atom probe tomography and using CoCrFeMnNi samples that were heat treated at 723 K for 18 hrs reported GB segregation of Ni and Mn and revealed $\approx$ 10-20% variations in GB Mn and Ni content between high- and low-angle GBs [205]. It is important to note, however, that at such annealing temperatures the enrichment of Ni and Mn is due to precipitation of a NiMn phase at the GB as reported elsewhere [207]. In another study using atom probe tomography on CoCrFeMnNi samples aged at 723 K for up to 48 hrs, Li et al. [201] observed complex GB chemistry, where segregation of Ni and Mn occurred in some regions within a GB region, while segregation of Cr and depletion of Mn and Ni were observed in other regions within the same GB. The authors attributed this heterogeneous chemical distribution to a spinodal-like decomposition within the GB into Cr-rich domains and regions rich in Ni and Mn. At temperatures above 1000 K, where experimental studies revealed that CoCrFeMnNi exists in a single-phase solid solution state [207], our quantitative results of GB solute excess reveal Cr and Mn segregation with a weak dependence on the misorientation angle at least for the asymmetric tilt GBs explored in this work.

6.2.2 Chemical Short-range Ordering

Now, we direct our attention to the interplay between GB segregation and chemical ordering in CoCrFeMnNi. In alloy thermodynamics, solute-solute interactions provide a driving force for chemical ordering, and such interactions depend on the concentrations of various alloying elements and local atomic environments. Based on the observations in Fig. 6.7, the interaction of GBs with various alloying elements and subsequent segregation of some species and desegregation of others alters the local bulk chemical profiles and SRO in the vicinity of the GB region. To demonstrate this effect, Fig. 6.8(a) and (b) provides analysis of SRO using the Warren-Cowley order parameters χ_{ij} in the CoCrFeMnNi bi-crystal with a $\Sigma 5$ $[010]/[\bar{3} 4 0]$ asymmetric tilt GB at $T = 1000$ K, while Fig. 6.8(c) lists the bulk χ_{ij} values at $T = 1000$ K using the single crystal simulations in Fig. 6.3.

For the five-component CoCrFeMnNi alloy, we calculate a total of 15 χ_{ij} , $\{i, j = \text{Co, Cr, Fe, Mn, Ni}\}$ parameters, which are shown in Fig. 6.8(a) as a function of distance from the GB plane. The dashed line in red in Fig. 6.8(a) shows the bulk values for χ_{ij} , which are also depicted in Fig. 6.8(c). Recall that in order to reveal the spatial dependence of chemical ordering due to GB segregation effects, we calculate χ_{ij} in the bi-crystal systems using atomic slabs with width $\approx 15\text{\AA}$ that are parallel to the GB plane. The interested reader is referred to Figs. D.1 through D.4 in Appendix D for plots of all χ_{ij} SRO parameters for all GBs explored in this work. The spatial profiles of the χ_{ij} parameters shown in Fig. 6.8(a) demonstrate that GB regions exhibit unique χ_{ij} values and that χ_{ij} approach the bulk values [cf. Fig. 6.8(c)] far from the GB region. As an example, we show in Fig. 6.8(b) three representative χ_{ij} profiles, namely χ_{CrCr} , χ_{CrMn} , and χ_{FeCo} , as a function of distance from the $\Sigma 5$ $[010]/[\bar{3} 4 0]$ GB plane. Large negative values for χ_{CrCr} and χ_{CrMn} are observed within

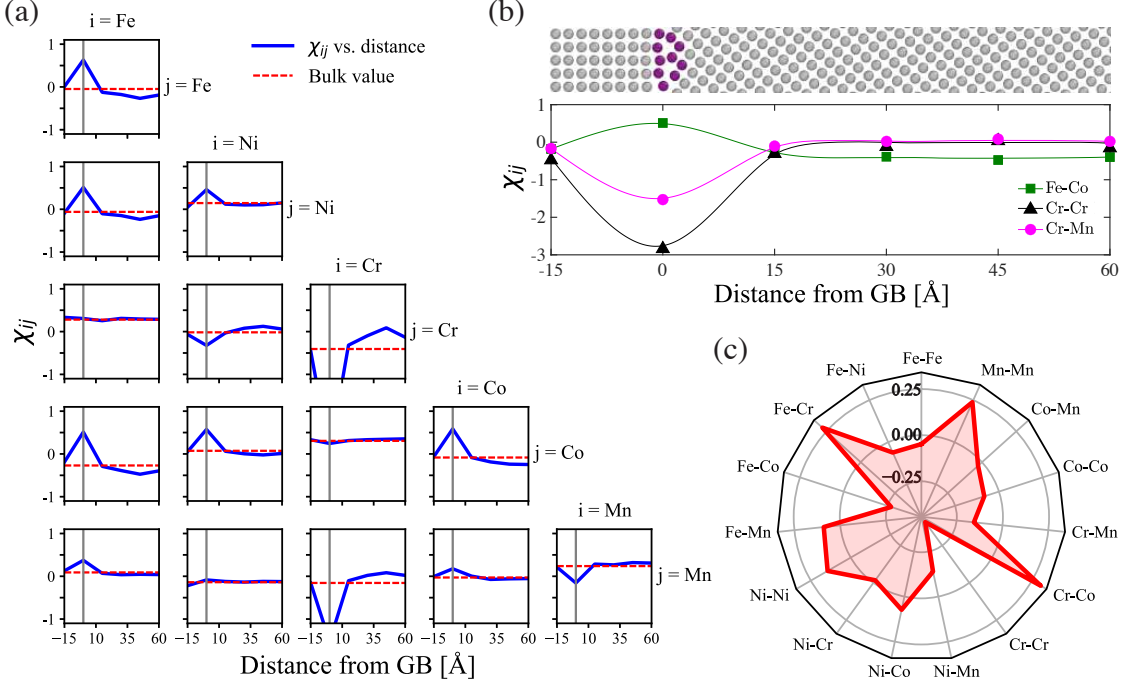


Figure 6.8: (a–b) For the $\Sigma 5$ (010/ $\bar{3}40$) GB after MC-MD simulations at $T = 1000$ K, (a) all χ_{ij} order parameters as a function of distance from the GB plane where the dashed lines in red represent the bulk values and (b) close-up view depicting χ_{FeCo} , χ_{CrCr} , and χ_{CrMn} parameters as a function of distance from the GB plane. (c) χ_{ij} parameters for bulk CoCrFeMnNi after MC-MD simulations at $T = 1000$ K.

the GB region indicating attractive Cr-Cr and Cr-Mn interactions; a trend that is consistent with the GB segregation data of Cr and Mn shown in Fig. 6.7. Furthermore, Fig. 6.8(b) and (c) shows that $\chi_{\text{FeCo}} \approx 0.5$ within the GB region and reaches $\chi_{\text{FeCo}} \approx -0.4$ in the bulk far from the boundary. This profile of χ_{FeCo} reveals a contrasting behavior, in which repulsive Fe-Co interactions (i.e., $\chi_{\text{FeCo}} > 0$) exist within the GB and attractive Fe-Co interactions (i.e., $\chi_{\text{FeCo}} < 0$) are observed in the bulk. While most studies of chemical ordering in MPEAs report bulk values for χ_{ij} [174, 196, 197], the results depicted in Fig. 6.8 reveal solute-solute interactions and χ_{ij} parameters within the GB region that are distinct from those in the bulk region. This highlights the need to account for materials defects, such as GBs, in treatments of chemical

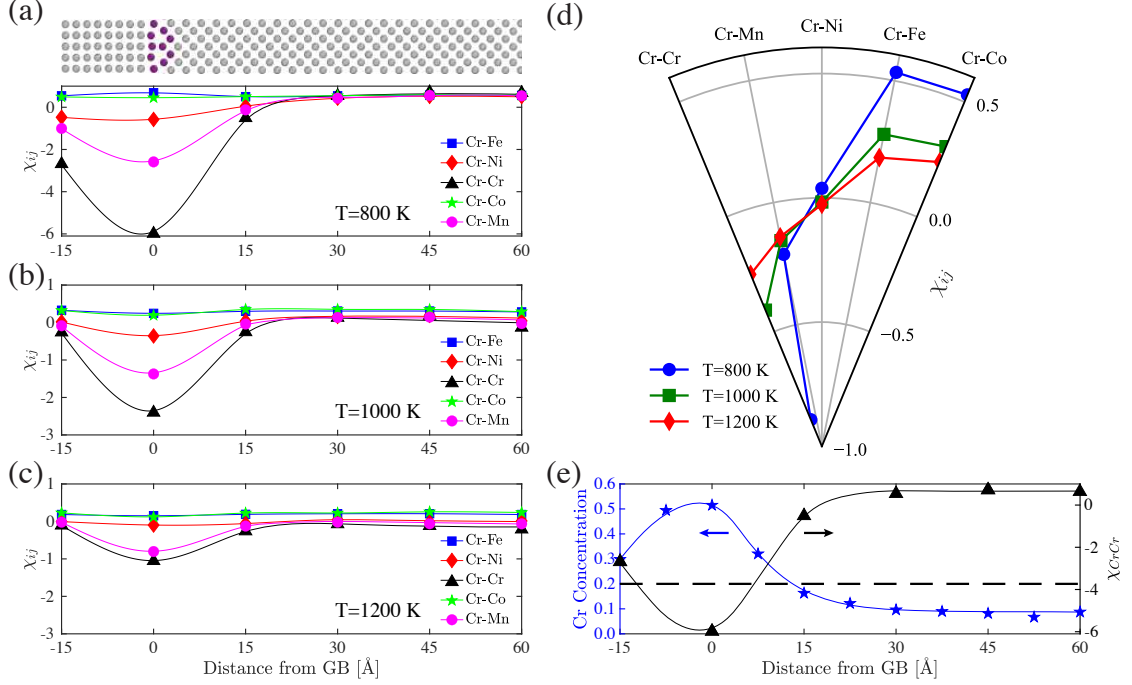


Figure 6.9: (a-c) For the $\Sigma 169$ (010)/($\bar{1}19$ 120 0) asymmetric tilt GB, χ_{Crj} , $\{j = \text{Co, Cr, Fe, Mn, Ni}\}$ SRO parameters as a function of the distance from the GB plane after MC-MD simulations at (a) 800 K, (b) 1000 K, and (c) 1200 K. (d) Values of χ_{Crj} , $\{j = \text{Co, Cr, Fe, Mn, Ni}\}$ for bulk CoCrFeMnNi after MC-MD simulations at 800 K, 1000 K, and 1200 K. (e) At $T = 800$ K, a plot of Cr concentration and χ_{CrCr} SRO parameter as a function of distance from the GB. The dashed line indicates the nominal bulk Cr concentration.

ordering and chemistry-property relationships in MPEAs.

Finally, we investigate SRO in MPEA bi-crystals as a function of temperature. Herein, we focus our analysis on Cr interactions as Fig. 6.7 reveals enrichment of Cr at the GBs (see Appendix D for plots of all SRO parameters for all GBs explored in this work). For the CoCrFeMnNi bi-crystal with a $\Sigma 169$ (010)/($\bar{1}19$ 120 0) asymmetric tilt GB used as a representative example, Fig. 6.9(a) through (c) shows results for Warren-Cowley order parameters χ_{Crj} $\{j = \text{Co, Cr, Fe, Mn, Ni}\}$ at $T = 800$ K [Fig. 6.9(a)], 1000 K [Fig. 6.9(b)], and 1200 K [Fig. 6.9(c)]. Using the single crystal MPEA systems, the bulk values for χ_{Crj} $\{j = \text{Co, Cr, Fe, Mn, Ni}\}$ at $T = 800$ K, 1000 K, and 1200 K

are shown in Fig. 6.9(d). Panels (a) through (c) of Fig. 6.9 show that the SRO parameters attain distinct values within the GB region and change rapidly away from the boundaries. Furthermore, large negative values for χ_{CrCr} and χ_{CrMn} are observed within the GB region indicating attractive interactions for the Cr-Cr and Cr-Mn pairs. In terms of their magnitudes within the GB, $\chi_{\text{CrCr}} < \chi_{\text{CrMn}} < \chi_{\text{CrNi}} < 0$ for temperatures in the range of 800-1200 K, which indicates stronger attractive Cr-Cr GB interactions than those for Cr-Ni. These trends are consistent with the results in Fig. 6.7, which reveal segregation of Cr and Mn to the GBs. It can also be seen from Fig. 6.9(a)–(c) that χ_{CrCo} and χ_{CrFe} are greater than zero within the GB indicating repulsive pair interactions, and that these boundary values are similar in magnitude to those in the bulk region. Also, a close examination of Fig. 6.9(a) reveals that χ_{CrCr} far from the GB region does not approach the bulk value shown in Fig. 6.9(d), which is obtained using simulations on single crystal MPEAs. This can be explained using Fig. 6.9(e), which is a plot of Cr concentration and χ_{CrCr} across the $\Sigma 169$ (010)/(1 $\bar{1}$ 9 120 0) GB at 800 K. The MPEA bi-crystals used in our simulations are closed systems, and, as a result, chemical redistribution resulting in Cr enrichment at the GB leads to Cr depletion in the bulk region below the nominal Cr concentration of 0.2. Since solute-solute interaction energies depend on solute concentration levels, lowering the bulk Cr concentration due to GB segregation changes bulk SRO values. The results depicted in Fig. 6.9 highlight the need to account for materials defects, such as GBs, and their interactions with elemental species when describing SRO in MPEAs. Figure 6.9 also shows that SRO descriptors, such as the Warren-Cowley order parameters, vary spatially due to the interaction of elemental species with materials defects. Investigating the impact of grain size and GB density on boundary segregation and the spatial profiles of SRO will be an interesting effect to explore in a future study.

6.3 Conclusions

The primary aims of this work are to investigate the interaction of GBs with various alloying elements in MPEAs, quantify the resultant GB segregation as a function of temperature, and understand how GB-solute interactions influence chemical ordering in MPEAs. To achieve this, we employed classical atomistic simulations to generate MPEA bi-crystal geometries with a series of [001] asymmetric tilt GBs and performed hybrid Monte Carlo-molecular dynamics simulations to investigate GB segregation and SRO at different temperatures. The equiatomic CoCrFeMnNi, so-called Cantor alloy, was used as a model MPEA system. At temperatures in the range of 673 K – 800 K, formation of domains rich in Cr was observed in agreement with experimental observations. At temperatures above 800 K, our atomistic simulations revealed segregation of Cr and Mn to GBs and desegregation of Fe, Co, and Ni. Quantitative analysis revealed a weak dependence of GB solute excess of various alloying elements on boundary geometry, at least for the asymmetric tilt GBs explored in this work. Furthermore, simulation results showed that GB solute excess decreases rapidly with the increase in temperature in the range of 1000 K – 1200 K. We then employed the Warren-Cowley order parameters to quantify SRO and investigate the interplay between GB segregation and chemical ordering. Our analysis revealed that GB regions exhibit SRO characteristics that are distinct from the bulk. For example, our SRO analysis revealed that some pair interactions (e.g., Fe-Co) in CoCrFeMnNi are repulsive within the GB region but are attractive in the bulk crystal. Such results highlight the complex nature of multi-element GB-solute interactions in MPEAs. It was also found that the negative Warren-Cowley order parameters (i.e., attractive pair interactions) within the GB region increase rapidly with temperature. Such trends for the SRO parameters within the GB region are consistent with GB solute excess results,

in which GB segregation levels decrease with the increase in temperature. In broad terms, our results highlight the need to consider GB interactions with various alloying elements in efforts aimed at establishing chemistry-structure-property relationships in MPEAs. For example, while recent studies showed that SRO can influence the properties of MPEAs, our analysis suggests GB segregation as a strategy to locally modify SRO characteristics and, as a result, tailor the engineering properties of MPEAs.

Chapter 7

Experimental and Computational Studies of the Impact of Grain Microstructure on Radiation-induced Segregation

In this chapter, we present a collaborative study conducted with experimental researchers at the Colorado School of Mines and computational experts at Clemson University. By combining experimental studies, KMC simulations, and mesoscale PF modeling, we investigate the influence of grain microstructure on RIS in a model Fe–Cr alloy. The grain microstructure is characterized by the grain size and grain size ratio and their impact on steady-state concentration profiles of Cr, interstitials, and vacancies are systematically explored. The rest of the chapter is organized as follows: materials system and experimental studies are presented in Section 7.1. Section 7.2 outlines the theoretical and computational framework, including the thermodynamics of multicomponent and binary systems with PDs, the PF model formulation, and

KMC simulations. The experimental and simulation results are presented and discussed in Section 7.3. Finally, Section 7.4 provides concluding remarks and a summary of the work.

7.1 Materials System and Experimental Studies

A Fe-9.6 at.%Cr model alloy (9.6 at.%Cr, 0.039 at.%C, 0.004 at.%N) was vacuum induction melted, cast and hot isostatically pressed at 1185°C and 103 MPa for 4 hours. Ultrafine-grained (UFG) materials were fabricated via high-pressure torsion (HPT). Disks of 10 mm in diameter were processed under 5 GPa at room temperature and 1 rpm for 10 turns. The average as-HPT grain size is about 230 μm . Annealing at 500°C for 2.5h and 4h was conducted to increase the grain size to about 450 nm and 1 μm respectively. Bright field (BF) STEM images of the pre-irradiation microstructures are shown in Fig. 7.1. Ion irradiation was conducted at the Michigan Ion Beam Laboratory. The samples were irradiated with 9 MeV Fe^{3+} ions at 400°C using a defocused beam in a high vacuum environment (pressure below 10^{-7} torr). Irradiation damage was calculated with SRIM software package using the quick Kinchin-Pease mode [299] and a displacement energy of 40 eV [300]. The nominal dose rate was about 2×10^{-4} dpa/s and the samples were irradiated to 5 dpa at a depth of 1200 nm. Precession electron diffraction (PED) was employed to identify random high-angle GBs. TEM specimens were prepared using dual-beam focused ion-beam (FIB) on a FEI Helios Nanolab 600i SEM. GB chemistry was quantified by STEM-EDS on a FEI Talos F200X S/TEM operated at 200 kV. Elemental maps of 10nm-height were collected and averaged vertically to produce a line profile using the Velox software.

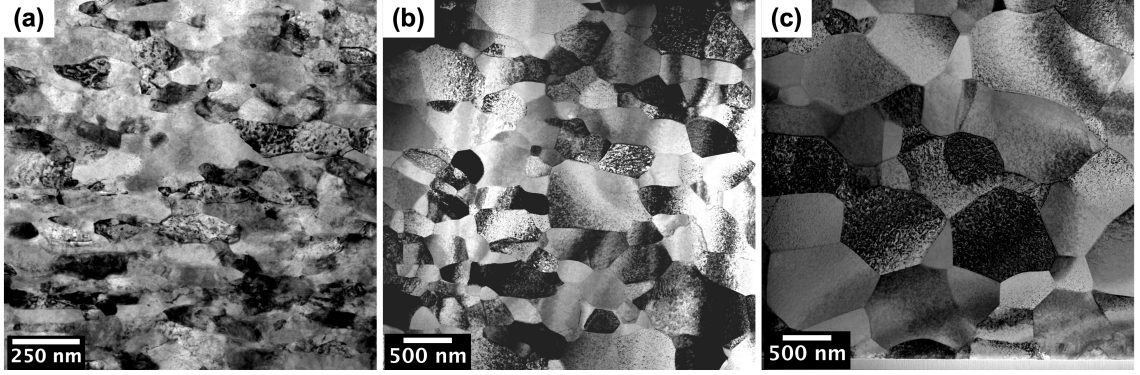


Figure 7.1: STEM-BF images of the ultrafine-grained (UFG) Fe-9.6 at.%Cr materials: (a) as-HPT, (b) HPT+500°C/2.5h, and (c) HPT+500°C/4h.

7.2 Theoretical and Computational Model

7.2.1 Thermodynamics of Multicomponent Alloys with Point Defects

We start with a general theoretical treatment of RIS in multicomponent alloys. We consider an n -component alloy with $i = 1, 2, \dots, n$ atomic species in addition to interstitials and vacancies. The elemental species are described using concentration fields $c_1, c_2, \dots, c_n$, where $1, 2, \dots, n-1$ are the labels used for the solutes and n is the one for the host. In addition, interstitials and vacancies are characterized by the concentration fields c_I and c_V , respectively. In accordance with irreversible thermodynamics [301], in an n -component alloy, fluxes of species i arise due to gradients in the chemical potentials and are given by $J_i = -\sum_{j=1}^n L_{ij} \nabla \tilde{\mu}_j$, where $\tilde{\mu}_j$ is the chemical potential of species j and L_{ij} are the Onsager transport coefficients. In the context of irradiation of metallic alloys, the fluxes are due to chemical potential gradients of atomic species $\{\nabla \tilde{\mu}_i, i = 1, 2, \dots, n\}$ and those of the interstitials $\nabla \tilde{\mu}_I$ and vacancies $\nabla \tilde{\mu}_V$. Furthermore, following the treatment detailed in Ref. [302] it is assumed that atomic and PD fluxes are expressed in terms of fluxes of atoms that are mediated

by PDs, each of which has distinct Onsager transport coefficients. As a result, the atomic fluxes J_i and those of the interstitials J_I and vacancies J_V are written as

$$J_i = - \sum_{j=1}^n [L_{ij}^I(\nabla \tilde{\mu}_j + \nabla \tilde{\mu}_I) + L_{ij}^V(\nabla \tilde{\mu}_j - \nabla \tilde{\mu}_V)], \quad i = 1, \dots, n, \quad (7.1a)$$

$$J_I = - \sum_{i=1}^n \sum_{j=1}^n L_{ij}^I(\nabla \tilde{\mu}_j + \nabla \tilde{\mu}_I), \quad (7.1b)$$

$$J_V = - \sum_{i=1}^n \sum_{j=1}^n L_{ij}^V(-\nabla \tilde{\mu}_j + \nabla \tilde{\mu}_V). \quad (7.1c)$$

Here, L_{ij}^I and L_{ij}^V define the Onsager transport coefficients for interstitial and vacancy mediated diffusion, respectively. Figure 7.2 shows schematics describing these diffusion mechanisms, where Fig. 7.2(a) describes vacancy mediated transport L_{ij}^V , in which an atomic species hops from an equilibrium lattice site to a neighboring vacant site. Figure 7.2(b) depicts an interstitial transport, L_{ij}^I , wherein an atomic species in a dumbbell hops to neighboring interstitial site.

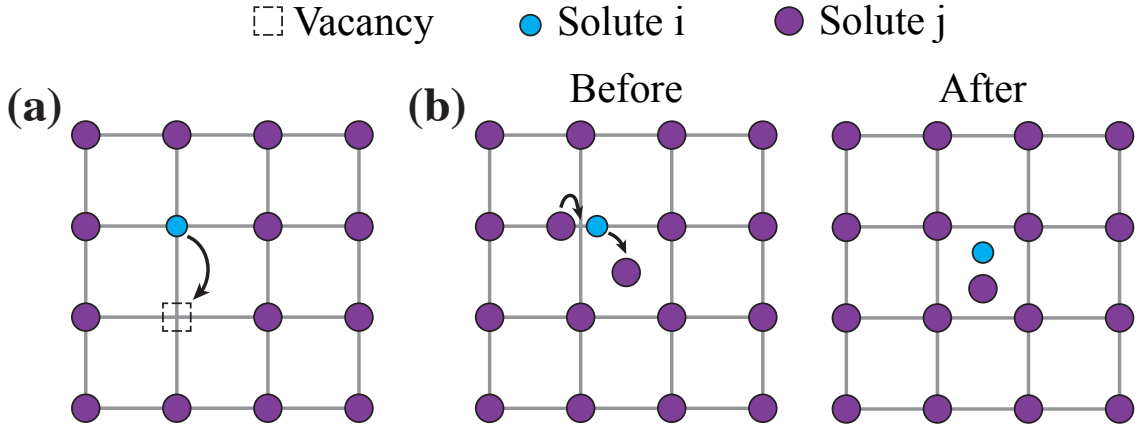


Figure 7.2: A schematic depicting (a) vacancy mediated transport coefficients, L_{ij}^V , and (b) interstitial mediated transport coefficients, L_{ij}^I .

With the aid of the Gibbs-Duhem relation and using the chemical potential of the host $\tilde{\mu}_n$ as a reference [see Appendix E], one can write Eq. 7.1 for the fluxes in

terms of differences in the chemical potential of atoms or PDs and that of the host, so-called diffusion potential, expressed as

$$\mu_i = \tilde{\mu}_i - \tilde{\mu}_n, \quad i = 1, 2, \dots, n-1, \quad (7.2a)$$

$$\mu_I = \tilde{\mu}_I - \tilde{\mu}_n \quad \text{and} \quad \mu_V = \tilde{\mu}_V - \tilde{\mu}_n. \quad (7.2b)$$

The resulting flux equations are written as

$$J_i = - \sum_{j=1}^{n-1} L_{ij}^* \nabla \mu_j - \sum_{p=1}^n L_{ip}^I \nabla \mu_I + \sum_{q=1}^n L_{iq}^V \nabla \mu_V, \quad i = 1, 2, \dots, n-1, \quad (7.3a)$$

$$J_I = - \sum_{j=1}^{n-1} \left(\sum_{k=1}^n L_{kj}^I - 2c_j \sum_{p=1}^n \sum_{q=1}^n L_{pq}^I \right) \nabla \mu_j - \sum_{m=1}^n \sum_{l=1}^n L_{ml}^I \nabla \mu_I, \quad (7.3b)$$

$$J_V = \sum_{j=1}^{n-1} \sum_{k=1}^n L_{kj}^V \nabla \mu_j - \sum_{p=1}^n \sum_{q=1}^n L_{pq}^V \nabla \mu_V, \quad (7.3c)$$

where

$$L_{ij}^* = L_{ij}^I + L_{ij}^V - 2c_j \sum_{k=1}^n L_{ik}^I. \quad (7.4)$$

With the description given by Eq. 7.3, only $n+1$ independent flux equations are needed to describe an n -component alloy with PDs, i.e., interstitials and vacancies.

7.2.2 Binary alloys with point defects

Since this work deals with the impact of microstructure (grain size, grain size ratio, GB sink strength) on RIS in binary alloys, we consider a substitutional binary alloy of solute (labeled 1) and host (labeled 2) in addition to interstitials and vacancies.

For the case of binary alloys, the flux expressions given by Eq. 7.3 reduce to

$$\begin{bmatrix} J_1 \\ J_I \\ J_V \end{bmatrix} = -[Z_{\alpha\beta}] \begin{bmatrix} \nabla\mu_1 \\ \nabla\mu_I \\ \nabla\mu_V \end{bmatrix}. \quad (7.5)$$

Here $[Z_{\alpha\beta}]$ is the matrix of the Onsager transport coefficients given by

$$[Z_{\alpha\beta}] = \begin{bmatrix} L_{11}^I + L_{11}^V - 2c_1(L_{11}^I + L_{12}^I) & L_{11}^I + L_{12}^I & -(L_{11}^V + L_{12}^V) \\ L_{11}^I + L_{12}^I - 2c_1L^I & L^I & 0 \\ -(L_{11}^V + L_{12}^V) & 0 & L^V \end{bmatrix}, \quad (7.6)$$

where

$$L^I = \sum_{i,j} L_{ij}^I = L_{11}^I + L_{12}^I + L_{21}^I + L_{22}^I, \quad (7.7a)$$

$$L^V = \sum_{i,j} L_{ij}^V = L_{11}^V + L_{12}^V + L_{21}^V + L_{22}^V \quad (7.7b)$$

describe the sum of all Onsager matrix elements for interstitials (L^I) and vacancies (L^V). Here, it is important to note that the Onsager transport coefficients for interstitials L_{ij}^I and vacancies L_{ij}^V are, in general, solute concentration and temperature dependent.

7.2.3 Phase field formulation

In Sections 7.2.1 and 7.2.2, mass fluxes are expressed in terms of gradients of the chemical potentials of various species and PDs. The next step is to obtain expressions for these chemical potentials. To this end, we employ a PF modeling framework that captures relevant microstructural features (i.e., grains, GBs) and alloy free energies,

which are then used to obtain the chemical potentials. For binary alloys, we use a solute concentration field, $c_1(\mathbf{r}, t) = c(\mathbf{r}, t)$, and also introduce concentration fields of interstitials, $c_I(\mathbf{r}, t)$, and vacancies, $c_V(\mathbf{r}, t)$. In addition, we introduce a structural order parameter (OP), $\phi(\mathbf{r}, t)$, used to resolve the grain microstructure of a metallic alloy. In this work, ϕ attains constant values in bulk crystalline grains and changes smoothly, yet sharply across a GB region. Using the concentration and OP fields, a total free energy functional $\mathcal{F}_{tot}$ is proposed and used to derive dynamical equations for the evolution of concentration and PF fields. Since our study is mainly concentrated with the impact of grain size and GB sink strength in RIS without considering GB migration, our OP fields will be static and are only used to locate GB regions. For our RIS study, the total free energy $\mathcal{F}_{tot}$ is written as

$$\mathcal{F}_{tot} = \int d\mathbf{r} \left[f_{hom}(c, c_I, c_V, \phi, T) + \frac{\epsilon^2}{2} |\nabla c|^2 \right], \quad (7.8)$$

where f_{hom} is the local binary alloy free energy density accounting for PDs. The second term on the right hand side of Eq. 7.8 is the classic PF gradient energy term, where ϵ controls the interfacial energy associated with compositional domains. In this work, we focus on binary alloys, where the regular solution approximation is used for the free energy density, f_{hom} , and is written as [302, 303]

$$\begin{aligned} f_{hom} = & G_1 c + G_2 (1 - c) + \frac{k_B T}{v_{at}} \left[c \ln c + (1 - c) \ln(1 - c) \right. \\ & \left. + c_I \ln \left(\frac{c_I}{c_I^{eq}} \right) + c_V \ln \left(\frac{c_V}{c_V^{eq}} \right) \right] + \Omega c (1 - c), \end{aligned} \quad (7.9)$$

where G_1 and G_2 are the free energy of pure solute and solvent states, respectively. The third term on the right-hand side of Eq. 7.9 describes the configurational entropy of a binary alloy accounting for PDs, where k_B is Boltzmann constant, T is absolute

temperature, v_{at} is the atomic volume, and c_I^{eq} (c_V^{eq}) is the equilibrium concentration of interstitials (vacancies) in the alloy. The last term on the right-hand side of Eq. 7.9 describes the heat of mixing of the binary alloy, where Ω is the regular solution model parameter.

Using Eqs. 7.8 and 7.9, the diffusion potentials (i.e., chemical potential with respect to that of the host) for the solutes $\mu_1 = v_{at}(\delta\mathcal{F}_{tot}/\delta c_1 - \delta\mathcal{F}_{tot}/\delta c_2)$, interstitials $\mu_I = v_{at}(\delta\mathcal{F}_{tot}/\delta c_I - \delta\mathcal{F}_{tot}/\delta c_2)$, and vacancies $\mu_V = v_{at}(\delta\mathcal{F}_{tot}/\delta c_V - \delta\mathcal{F}_{tot}/\delta c_2)$ are given by

$$\mu_1 = k_B T \ln \left(\frac{c}{1-c} \right) + v_{at} [G_1 - G_2 + \Omega(1-2c)], \quad (7.10a)$$

$$\mu_I = k_B T \ln \left(\frac{c_I}{c_I^{eq}(1-c)} \right) - v_{at}(G_2 + \Omega c), \quad (7.10b)$$

$$\mu_V = k_B T \ln \left(\frac{c_V}{c_V^{eq}(1-c)} \right) - v_{at}(G_2 + \Omega c). \quad (7.10c)$$

The governing equations describing RIS in a binary alloy follow reaction-diffusion dynamics and are given by

$$\frac{\partial}{\partial t} \begin{pmatrix} c \\ c_I \\ c_V \end{pmatrix} = -v_{at} \nabla \cdot \begin{pmatrix} J_1 \\ J_I \\ J_V \end{pmatrix} + \begin{pmatrix} 0 \\ g_I \\ g_V \end{pmatrix}. \quad (7.11)$$

Here, g_I and g_V are the RIS source, reaction and annihilation terms for interstitials and vacancies, respectively, and are given by [255, 302, 303]

$$g_I = K_o - P(\phi)K_{gb}(c_I - c_I^s) - K_b(1 - P(\phi))c_I - K_R c_I c_V, \quad (7.12a)$$

$$g_V = K_o - P(\phi)K_{gb}(c_V - c_V^s) - K_b(1 - P(\phi))c_V - K_R c_I c_V. \quad (7.12b)$$

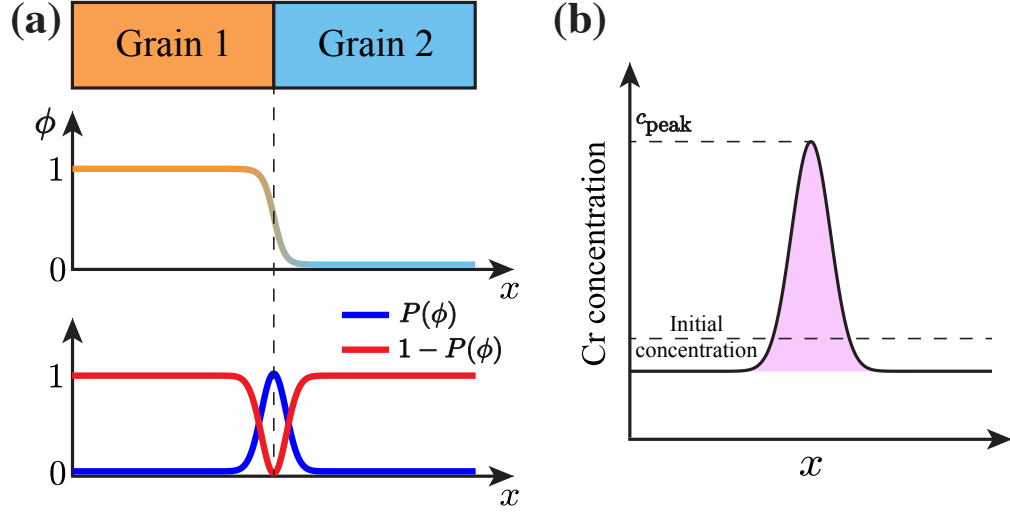


Figure 7.3: (a) Schematic representation of the PF OP ϕ across a GB. Using ϕ , the function $P(\phi)$ is used to locate the GB and the function $1 - P(\phi)$ identifies bulk crystals. (b) Solute concentration profile across a GB. RIS is quantified by reporting the peak GB concentration c_{peak} and solute excess, shaded region, defined as the area under the concentration profile.

Here, K_o is the dose rate, assumed to be constant. The second term on the right-hand side of Eq. 7.12a defines the PD absorption rate at GBs with a sink efficiency described by the parameter K_{gb} and GB saturation limits of c_I^s (c_V^s) for interstitials (vacancies). The parameter K_{gb} [units of 1/s] describes the time scale associated with the absorption of PDs at GBs during RIS. The function $P(\phi)$ is expressed in terms of the PF OP, which is used to locate the GB. Here, $P(\phi) = 0$ in the bulk and it rapidly peaks to 1 at the center of the GB region, the reader is referred to Fig. 7.3 for the shape of the function $P(\phi)$. In addition to absorption of PDs at GBs, other defects in the bulk can serve as sinks for PDs, and this effect is captured by the third term on the right-hand side of Eq. 7.12a, where K_b [units 1/s] is the sink efficiency of bulk defects. The last term on the right-hand side of Eq. 7.12a describes the recombination rate between vacancies and interstitials, where K_R [units of 1/s] is a parameter describing the time scales associated with such a recombination event

and is described in terms of PD diffusion coefficients and effective capture distance between the PDs [224].

With the above description for solute and PD fluxes described by Eq. 7.5, diffusion potentials given by Eq. 7.10, and dynamical equations, see Eq. 7.11, for the evolution of solute and PD concentration fields, we now have a complete modeling framework of RIS in binary alloys accounting for GB sink strength, bulk sinks, and PD recombination.

7.2.4 Non-dimensionalization and model implementation

The dynamical equations for the solute and PD concentration fields, Eq. 7.11, are made non-dimensional by introducing dimensionless space and time as $\bar{\mathbf{r}} = \mathbf{r}/d_o$ and $\bar{t} = t/\tau$, respectively, where τ and d_o represent reference time and length scale. We also use the thermal energy, $k_B T$, as the reference energy scale. Next, we introduce the following non-dimensional parameters: $\bar{\mu}_1 = \mu_1/k_B T$, $\bar{\mu}_I = \mu_I/k_B T$, $\bar{\mu}_V = \mu_V/k_B T$, $\bar{L}_{ij}^I = V_{at} k_B T L_{ij}^I \tau / d_o^2$, $\bar{L}_{ij}^V = V_{at} k_B T L_{ij}^V \tau / d_o^2$, $\bar{K}_o = K_o \tau$, $\bar{K}_{gb} = K_{gb} \tau$, $\bar{K}_R = K_R \tau$, $\bar{K}_b = K_b \tau$. Inserting these non-dimensional quantities into Eqs. 7.5, 7.6, 7.10, and 7.11 yields non-dimensional governing equations for the concentration fields of solute and PDs that have the same form as their dimensional counterparts.

For all simulation studies reported in this work, representative systems are discretized to produce a simulation box of $N_x \times N_y$ pixels, where the pixel size along the x and y directions is $\Delta x = \Delta y$. The non-dimensional dynamical equations are numerically solved using the explicit Euler method for time derivatives and central finite differencing for spatial gradients. In all results presented in this work, we set $\Delta x = \Delta y = d_o$. Here, it is important to note that the Onsager transport coefficients L_{ij}^I and L_{ij}^V are in general solute concentration dependent as will be shown in Sec-

tion 7.2.6. As a result, we use a finite difference scheme for the resulting “sandwich” diffusion operators [134] centering all terms including L_{ij}^I and L_{ij}^V appropriately [304].

7.2.5 Key model assumptions

Before we proceed to investigate the interplay between microstructures and RIS, we first highlight the key assumptions adopted in deriving our PF modeling framework: (i) PD concentrations, c_I and c_V , are assumed to be negligible so that interactions between PDs are neglected. (ii) In this study, we neglect the elastic interactions between PDs and defect sinks and focus solely on quantifying RIS behavior at neutral defect sinks. In addition, our model does not incorporate elasticity arising from the atomic size mismatch between solute and host atoms. This elastic contribution, however, can be incorporated by adding an additional elastic energy term to the total free energy, which depends on the alloy’s elastic constants and the dilatational strains arising from atomic size mismatch [259,305]. (iii) We assume the ideal solution without solute-solute interactions by using the heat of mixing $\Omega = 0$; this assumption can be relaxed in future studies. (iv) For this parametric study, we assume that the dose rate $\bar{K}_o$, GB sink strength parameter $\bar{K}_{gb}$, bulk sink strength parameter $\bar{K}_b$, and recombination rate between PDs $\bar{K}_R$ remain constant.

7.2.6 Kinetic Monte Carlo modeling

A KMC model previously developed for the Fe-Cr system [253,306] has been used to compute the transport coefficients. The model accounts for vacancy and interstitial diffusion, computing the rate for their hops following transitions state theory, $\Gamma = \nu \exp(-\Delta G/k_B T)$. The activation free energy is computed through a broken bond model with pair interactions depending on local concentration, and including

entropic effects [307]. Self-interstitials are assumed to remain in a $\langle 110 \rangle$ dumbbell configuration, possibly exchanging with the four nearest neighbors laying on the same $\{110\}$ plane as the dumbbell. The transport coefficients are computed following a generalized Einstein expression [308]:

$$L_{ij}^d = \frac{1}{V_{tot}k_B T} \lim_{t \rightarrow \infty} \frac{\langle R_i^d \cdot R_j^d \rangle}{2nt}, \quad (7.13)$$

where d represents the defect $\{V, I\}$ and $\{i, j\}$ are the elemental species, n is the dimensionality, t is the time, and V_{tot} is the volume. In the KMC model, the concentration of defects in the system is much larger than the equilibrium concentration, although the transport coefficients are defined at equilibrium. Therefore, the values obtained in the simulations need to be multiplied by the equilibrium concentration of defects, which is computed on-the-fly during the KMC runs following the method described in Ref. [309]. We computed the transport coefficients in the whole concentration range for temperatures between 500 and 900 K.

7.2.7 Simulation setup

The goal of this work is to investigate the impact of grain size and size ratio on RIS in binary alloys. To this end, we employ two-dimensional bi-crystal geometry shown in Fig. 7.4. The simulation domain consists of an internal grain of size W_g^{in} and outer grain, which crosses the periodic boundary, of size W_g^{out} . The number of pixels along the x (y) direction is N_x (N_y) with pixel size of $\Delta x = \Delta y = d_o = 1$ nm.

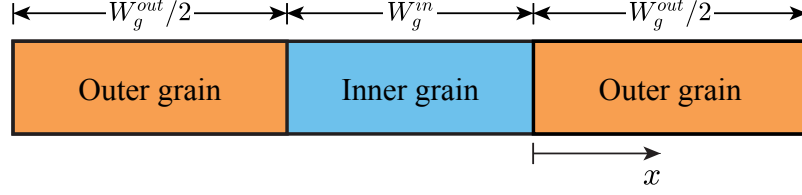


Figure 7.4: An illustration of the periodic bi-crystal geometry used in the PF simulations to examine the impact of grain size and grain size ratio on RIS profiles. The size of the inner grain is W_g^{in} and that for the outer grain is W_g^{out} .

7.3 Results and Discussion

7.3.1 Experimental results

We begin with the experimental studies of RIS as a function of grain size. As discussed in Section 7.1, Fig. 7.1 shows STEM-BF images depicting the grain structures of systems in the as-HPT, HPT followed with 500°C/2.5h, and HPT followed with 500°C/4h. These processing routes enabled the fabrication of Fe-9.6 at.%Cr alloys with a wide range of grain sizes.

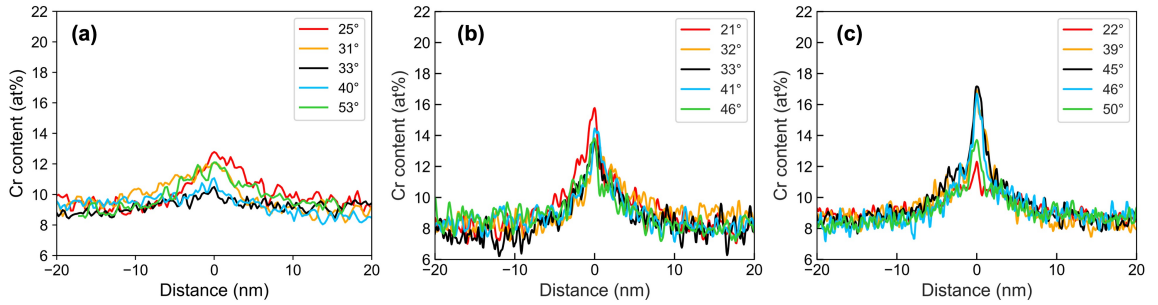


Figure 7.5: Post-irradiation GB concentration profiles for the Fe-9.6Cr alloy: (a) as-HPT, (b) HPT+500°C/2.5h, and (c) HPT+500°C/4h. For each sample, five GBs misorientations are characterized.

For each sample explored in this work, five GBs are analyzed and their Cr concentration profiles are shown in Fig. 7.5 along with their misorientation angles. The rationale for characterizing several GB misorientations is to get representative RIS

profiles and avoid reporting ones corresponding to special GB geometries. For the as-HPT alloy with the smallest average grain size, Fig. 7.5(a) reveals RIS at GBs with a peak boundary Cr concentration of ≈ 12 at.%. On the other hand, Figs. 7.5(b) and (c) show respectively GB concentration profiles for the samples with HPT followed with $500^\circ\text{C}/2.5\text{h}$ and HPT followed with $500^\circ\text{C}/4\text{h}$, where more pronounced RIS profiles are observed compared to the sample with a smaller grain size in Fig. 7.5(a). It is also interesting to note from Fig. 7.5 that variations in RIS profiles as a function of grain size are larger than those as a function of GB geometry. We acknowledge that the GB geometry is described by a five-dimensional space and probing RIS at only five data points is not sufficient to characterize the anisotropy in RIS due to GB geometry.

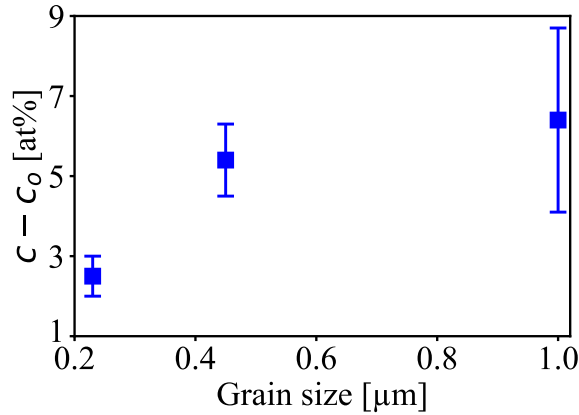


Figure 7.6: Relative GB Cr segregation, $c - c_o$, as a function of grain size for the irradiated Fe-9.6 at.%Cr alloy.

Next, we quantify RIS as a function of grain size. This is achieved by reporting the relative GB Cr concentration using the data in Fig. 7.5 as a function of the average grain size of the corresponding samples, and the results are shown in Fig. 7.6. The error bars in the plot correspond to the standard deviation of the measured solute excess, with values of 2.5 ± 0.5 , 5.4 ± 0.9 , and 6.4 ± 2.3 at.% corresponding to the

as-HPT, HPT followed with 500°C/2.5h, and HPT followed with 500°C/4h systems, respectively. It can be seen from Fig. 7.6 that the relative GB concentration $c - c_o$, i.e., RIS level, increases with grain size, at least for the ultrafine-grained materials explored in this work.

7.3.2 Transport coefficients

Motivated by the above experimental observations of RIS in UFG materials, we now shift our attention to computational studies of RIS and its dependence on grain microstructure in a Fe-9 at.%Cr binary alloy at 700 K. Again, in this work we explore two features related to the grain microstructure, namely the grain size and grain size ratio. As discussed in Section 7.2.3, the PF modeling framework formulated for the Fe-Cr binary alloy requires the transport coefficients L_{CrCr}^I , L_{FeFe}^I , L_{FeCr}^I , L_{CrCr}^V , L_{FeFe}^V , and L_{FeCr}^V and their composition dependence at 700 K, obtained using our KMC modeling and discussed in this section.

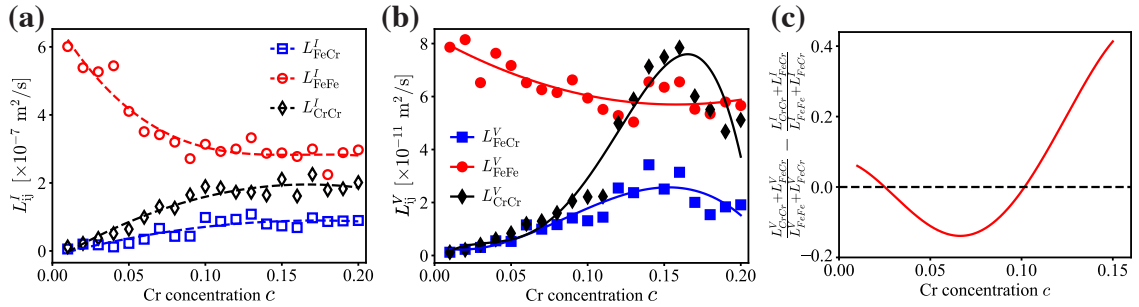


Figure 7.7: For the binary Fe-9 at.%Cr alloy at 700 K, KMC simulations of (a) Interstitial L_{ij}^I and (b) vacancy L_{ij}^V mediated Onsager transport coefficients as a function of Cr concentration. Markers represent KMC data and the lines are polynomial fits used in PF simulations. (c) The relative magnitude of $(L_{CrCr}^V + L_{FeCr}^V)/(L_{FeFe}^V + L_{FeCr}^V)$ and $(L_{CrCr}^I + L_{FeCr}^I)/(L_{FeFe}^I + L_{FeCr}^I)$ ratios obtained from fitted functions in (a) and (b) as a function of Cr concentration at 700 K.

Figure 7.7(a) and (b) shows respectively KMC modeling results of L_{ij}^I and L_{ij}^V $\{i,j = \text{Fe, Cr}\}$ as a function of Cr concentration c . The discrete data points are obtained

from the KMC simulations and the lines correspond to fitted functions, described below, used in our PF model. It can be seen that the transport coefficients show a strong nonlinearity in the dilute Cr concentration regime. It can also be seen that the interstitial mediated transport coefficients L_{ij}^I $\{i,j = \text{Fe, Cr}\}$ are much larger in magnitude than the corresponding vacancy mediated transport coefficients L_{ij}^V . Since our PF model requires transport functions that are differentiable, see Eq. 7.11, we use the KMC data to construct polynomial fits, up to fourth order, of L_{ij}^I and L_{ij}^V $\{i,j = \text{Fe, Cr}\}$ as a function of Cr concentration. The fitting procedure is detailed in Appendix F and the functional forms of these fits are given by Eq. F.1.

In a study by Piochaud et al. [302], the authors analytically showed that the tendency for solute segregation or depletion at GBs during irradiation of binary alloys is controlled by the ratio of the transport coefficients given by a parameter, which we denote α , as

$$\alpha = \frac{L_{CrCr}^V + L_{FeCr}^V}{L_{FeFe}^V + L_{FeCr}^V} - \frac{L_{CrCr}^I + L_{FeCr}^I}{L_{FeFe}^I + L_{FeCr}^I}. \quad (7.14)$$

When $\alpha < 0$, a binary alloy experiences enrichment of solutes at a GB, while $\alpha > 0$ leads to solute depletion. Using the functional fits, see Eq. F.1, for L_{ij}^I and L_{ij}^V , Figure 7.7(c) shows the calculated parameter α as a function of Cr concentration. Negative values for α indicating RIS can be seen in the composition range of $\approx 3\text{-}11$ at.%. The trend shown in Fig. 7.7(c) for the ratio of the transport coefficients, i.e., the parameter α , is in agreement with the one observed in Ref. [302]. For all PF simulations presented in this work, we will use the functional fits, see Eq. F.1, for the L_{ij}^I and L_{ij}^V $\{i,j = \text{Fe, Cr}\}$ transport coefficients.

7.3.3 Grain boundary and bulk sink strength

In this section, we investigate the impact of PD accommodation rates in both the GB and bulk regions on RIS profiles. This is achieved by performing systematic studies varying the GB, $\bar{K}_{gb}$, and bulk, $\bar{K}_b$, sink strength model parameters. While several expressions have been used to estimate values of the GB $\bar{K}_{gb}$ and bulk $\bar{K}_b$ sink strength parameters [224,310], these expressions are sensitively dependent on several material parameters and microstructural features whose experimental determination can be challenging.

To systematically investigate the impact of GB PD absorption rates on RIS profiles, we consider a Fe-Cr binary alloy bi-crystal with a grain size of $W_g^{in} = W_g^{out} = W_g = 60$ nm and transport coefficients at 700 K shown in Fig. 7.7. We also set the dose rate $\bar{K}_o = 7.5 \times 10^{-5}$ and use a PD recombination rate $\bar{K}_R = 10^3$. For this study, we set the bulk sink strength $\bar{K}_b = 10$. RIS profiles are characterized by reporting the peak GB concentration, c_{peak} , and solute excess [see Fig. 7.3(b) for details] as a function of GB sink strengths. Figure 7.8 shows results for the impact of GB $\bar{K}_{gb}$ sink strength parameters on RIS.

Figures 7.8(a)-(c) depict the concentration profiles of Cr [Fig. 7.8(a)], interstitials [Fig. 7.8(b)], and vacancies [Fig. 7.8(c)] across the GB as a function of GB sink strength parameter, $\bar{K}_{gb}$. The peak GB concentration, c_{peak} , is further quantified in Fig. 7.8(d). It can be clearly seen that the peak GB concentration, c_{peak} , increases with GB sink strength parameter, $\bar{K}_{gb}$, and follows a sigmoidal trend as illustrated by the dashed line. Panels (a) through (c) of Fig. 7.8 reveal that an increase in the GB sink strength parameter, $\bar{K}_{gb}$, results in an increase in Cr concentration and a decrease in interstitial and vacancy concentrations. Recall that increasing $\bar{K}_{gb}$ indicates that GBs absorb irradiation-induced PDs, interstitials and vacancies,

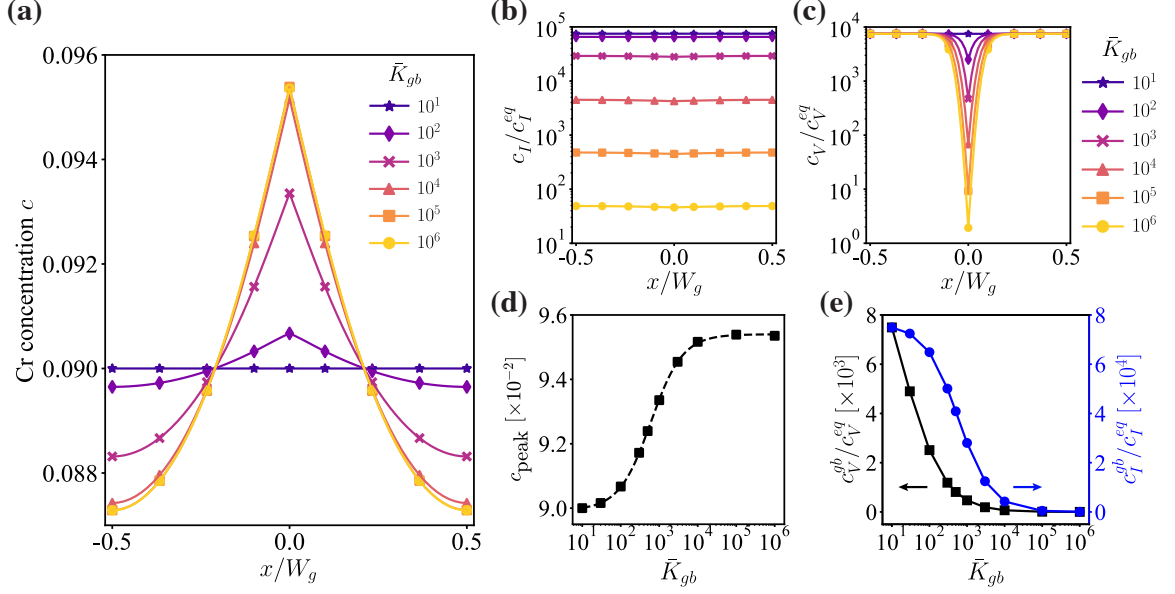


Figure 7.8: The impact of GB sink strength described by parameter $\bar{K}_{gb}$ on RIS profiles. Concentration profiles of (a) Cr c , (b) interstitial c_I , and (c) vacancy c_V across the GB for the bi-crystal with $W_g^{in} = W_g^{out} = W_g = 60$ nm as a function of $\bar{K}_{gb}$. The impact of $\bar{K}_{gb}$ on GB (d) peak Cr concentration c_{peak} and (e) interstitial and vacancy concentrations. In this work, ideal GB sink strength is approached with $\bar{K}_{gb} > 10^4$.

at a faster rate, i.e., time scale proportional to $1/K_{gb}$. It can also be seen from Fig. 7.8(b) and (c) that the GB vacancy concentration, c_V/c_V^{eq} , shows considerable variation with $\bar{K}_{gb}$ compared to that of the interstitial one c_I/c_I^{eq} . This is due to the fact that interstitial mediated transport coefficients L_{ij}^I $\{i,j = \text{Fe, Cr}\}$ are much larger in magnitude compared to the corresponding vacancy mediated ones, L_{ij}^V [see Fig. 7.7]. To demonstrate this effect, Fig. 7.8(e) shows a plot of the GB vacancy and interstitial concentrations normalized by their equilibrium values, i.e., c_V^{gb}/c_V^{eq} and c_I^{gb}/c_I^{eq} , as a function of the GB sink strength parameter $\bar{K}_{gb}$. Recall that time scale associated with defect accommodation at GBs is proportional to $1/\bar{K}_{gb}$. As a result, as $\bar{K}_{gb}$ increases (i.e., shorter defect accommodation time), the GB vacancy and interstitial concentrations asymptotically approach their equilibrium values. The GB interstitial concentration approaches its equilibrium value using larger values of

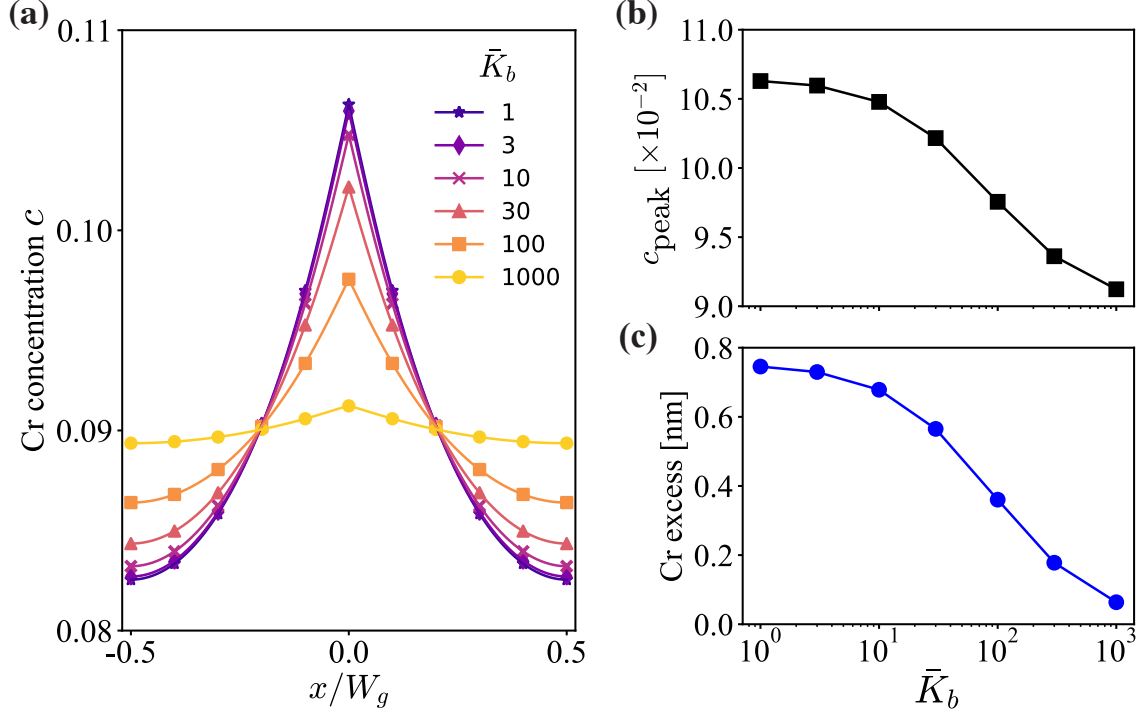


Figure 7.9: The impact of bulk sink strength described by the parameter $\bar{K}_b$ on RIS profiles. (a) Cr concentration across the GB for the bi-crystal with $W_g^{\text{in}} = W_g^{\text{out}} = W_g = 100$ nm as a function of $\bar{K}_b$. The impact of $\bar{K}_b$ on (b) GB peak Cr concentration c_{peak} and (c) GB Cr excess.

$\bar{K}_{gb}$ (i.e., shorter GB accommodation time) compared to that for the GB vacancy concentration.

Next, we investigate the impact of the bulk sink strength, characterized by the parameter $\bar{K}_b$, on RIS concentration profiles. For this study, we set the grain size $W_g^{\text{in}} = W_g^{\text{out}} = W_g = 100$ nm and employ the transport coefficients at 700 K given in Fig. 7.7. We also set the dose rate $\bar{K}_o = 7.5 \times 10^{-5}$ and use a PD recombination rate $\bar{K}_R = 10^3$. We also set the GB sink strength $\bar{K}_{gb} = 10^4$. Figure 7.9 shows results for the impact of bulk $\bar{K}_b$ sink strength parameters on RIS.

Figure 7.9(a) presents Cr concentration profiles across the GB for several values of $\bar{K}_b$. Again, the spatial distance across the GB is normalized by the grain size W_g . It can be seen that the extent of RIS at the GB decreases with increasing bulk sink

strength. Here, large (small) values of $\bar{K}_b$ describe bulk grains with large (small) density of defects (e.g., dislocations) that act as annihilation sites for irradiation-induced PDs [311,312]. To quantify the results depicted in Fig. 7.9(a) for the GB Cr concentration, Fig. 7.9(b) and (c) show respectively the peak GB concentration, c_{peak} , and Cr solute excess as a function of the bulk sink strength parameter, $\bar{K}_b$. A nonlinear behavior for c_{peak} and solute excess is observed, where the largest peak concentration and solute excess are observed in the regime with small values for $\bar{K}_b$. For the simulation parameters employed in this study, the peak concentration and solute excess approach their asymptotic values for $\bar{K}_b > 100$.

7.3.4 The role of grain microstructure in RIS

We now direct our attention to the influence of grain microstructure on RIS profiles. In polycrystalline materials, the grain microstructure is characterized using several metrics such as the average grain size, grain size distribution, and grain network topology. In this work, we explore the dependence of RIS profiles on two metrics describing the grain microstructure, namely the grain size and grain size ratio.

The impact of grain size on RIS

For this study, we consider the bi-crystal geometry shown in Fig. 7.4 and let the two half-crystals have the same size, $W_g^{in} = W_g^{out} = W_g$. We employ the transport coefficients for Fe-9 at.%Cr at 700 K shown in Fig. 7.7. We also set the dose rate $\bar{K}_o = 7.5 \times 10^{-5}$ and PD recombination rate $\bar{K}_R = 10^3$, and use GB and bulk sink strength parameters $\bar{K}_{gb} = 10^4$ and $\bar{K}_b = 10$, respectively. We perform systematic studies by varying the grain size, W_g , and quantify RIS profiles by reporting the peak GB concentration, c_{peak} , and solute excess. Figure 7.10 shows steady-state

concentration profiles of Cr [Fig. 7.10(a)], interstitials [Fig. 7.10(b)], and vacancies [Fig. 7.10(c)] across the GB for various grain sizes. For each simulation, the spatial distance across the GB is expressed in terms of the grain size W_g . Figure 7.10(a) shows that the GB Cr concentration increases with the grain size W_g , where the inset shows a close-up view in the regime with grain size $W_g = 6, 14, 30$ nm. On the other hand, the interstitial [Fig. 7.10(b)] and vacancy [Fig. 7.10(c)] concentrations (expressed with respect to their equilibrium values) decrease with decreasing the grain size.

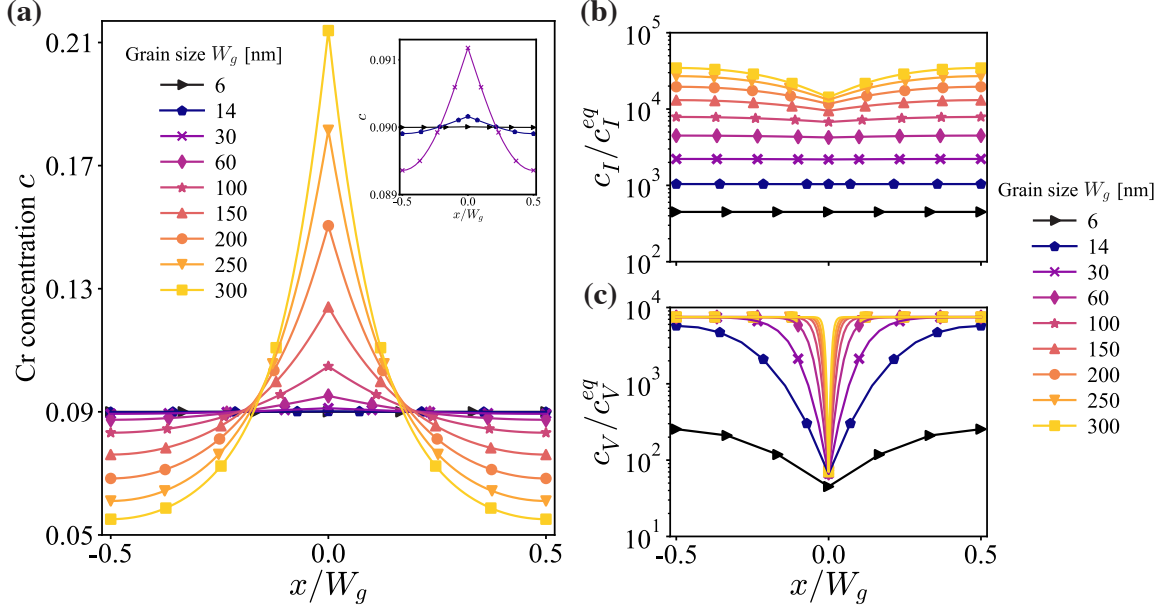


Figure 7.10: For the bi-crystal geometry with $W_g^{in} = W_g^{out} = W_g$, the impact of grain size W_g on RIS profiles. Concentration profiles of (a) Cr, (b) interstitial, and (c) vacancy across the GB for various grain sizes. Interstitial and vacancy concentrations are rescaled by their equilibrium values.

To further quantify the impact of grain size on RIS, we use the data from Fig. 7.10 to obtain the GB peak concentration and calculate solute excess as a function of grain size, W_g , and the results are shown in Fig. 7.11. Here, we note that our simulations span nearly two orders of magnitude in grain size ranging from 6 nm to 300 nm. The insets in Fig. 7.11 highlight the RIS behavior in the small grain size regime (i.e., W_g

$= 6, 14, 30$ nm), where RIS vanishes when $W_g \rightarrow 0$. For the simulation parameters used in this study, it can be seen that the peak GB concentration, c_{peak} , [Fig. 7.11(a)] and solute excess [Fig. 7.11(b)] show a non-linear trend across the whole grain size range explored in this work. However, Fig. 7.11 shows that for grain sizes $W_g > 100$ nm a near linear relationship for the peak GB concentration and solute excess as a function of W_g is observed.

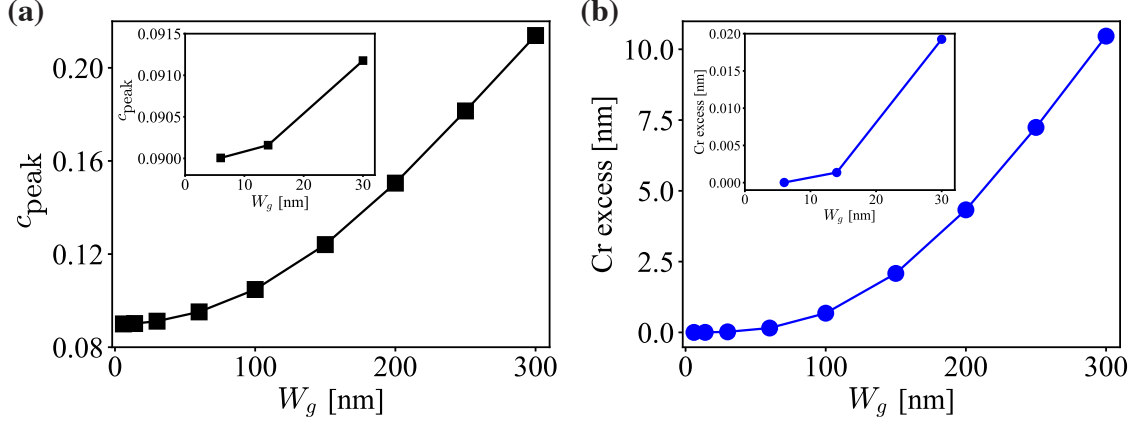


Figure 7.11: For the bi-crystal geometry with $W_g^{\text{in}} = W_g^{\text{out}} = W_g$, the impact of grain size W_g on GB (a) peak Cr concentration c_{peak} and (b) Cr solute excess. The insets are close-up views of the trends in the small grain size limit.

Our simulations exploring the impact of grain size on RIS employed a near-ideal sink strength with $\bar{K}_{gb} = 10^4$. Recall that $1/K_{gb}$ describes the time scale associated with the accommodation and annihilation of irradiation-induced PDs at GBs. In this context, perfect, or ideal, GB sinks are ones with $K_{gb} \rightarrow \infty$ indicating instantaneous accommodation of PDs. However, there is no physical reason as to why all GBs should be treated as ideal sinks. Herein, we perform simulations exploring the impact of both grain size W_g and non-ideality in GB sink strength $\bar{K}_{gb}$ on RIS and the results are shown in Fig. 7.12. The interstitial and vacancy concentrations at the GB are shown in Fig. 7.12(a) and (b), respectively, as a function of grain size W_g for various values of the GB sink strength parameter $\bar{K}_{gb}$. The limit $\bar{K}_{gb} \rightarrow \infty$ corresponds to an

ideal regime where GBs annihilate PDs instantaneously and attain their equilibrium values. It can be seen that the GB interstitial and vacancy concentrations increase with decreasing $\bar{K}_{gb}$. A decrease in the GB sink strength parameter indicates an increase in the time scale associated with the annihilation of PDs at the GB. As a result, the continuous generation of PDs due to irradiation and the long time scale, i.e., small values of $\bar{K}_{gb}$, associated with the annihilation of these defects at GBs results in an increase in the GB concentration of these PDs. It is also interesting to note that the GB concentrations of interstitials and vacancies show a stronger dependence on grain size W_g only in the small grain size regime. This is attributed to the fact that for a given value of GB sink strength, $\bar{K}_{gb}$, decreasing the grain size while keeping the same amount of GBs results in lower content of PDs generated due to irradiation.

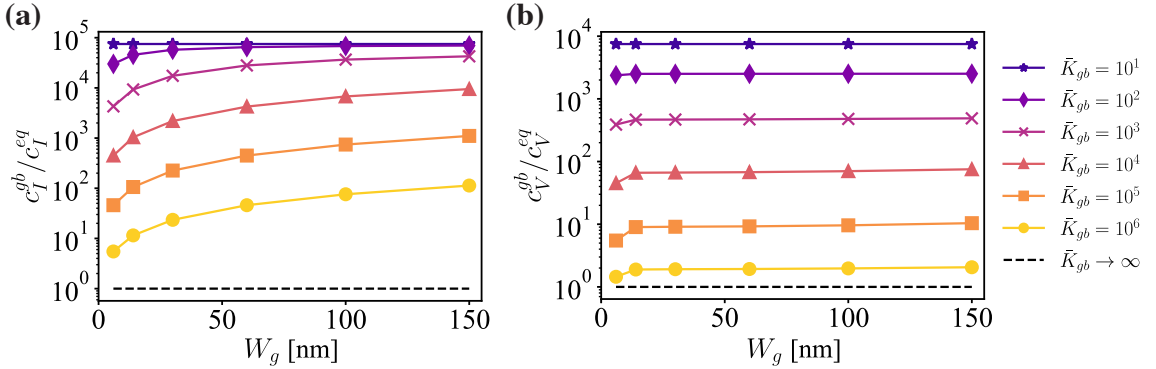


Figure 7.12: For the bi-crystal geometry with $W_g^{in} = W_g^{out} = W_g$, the interplay between grain size W_g and GB sink strength $\bar{K}_{gb}$ on RIS. Concentration profiles of (a) interstitials c_I and (b) vacancies c_V across the GB. Interstitial and vacancy concentrations are rescaled by their equilibrium values.

The impact of grain size ratio on RIS

We now consider another metric that characterizes a grain microstructure in metallic alloys, namely grain size ratio, and explore its impact on RIS profiles. To this end,

we consider the bi-crystal geometry shown in Fig. 7.4 with the inner and outer grains having sizes W_g^{in} and W_g^{out} , respectively. We define the grain size ratio R_g as

$$R_g = \frac{W_g^{out}}{W_g^{in}}. \quad (7.15)$$

In a polycrystalline metallic alloy, when two adjacent crystalline grains with different grain sizes experience the same radiation conditions, the total content of PDs in each grain will be different. This leads to asymmetry in PD fluxes which in turn influences RIS behavior at the GB separating these two grains. To explore such effects, we set the inner grain size to $W_g^{in} = 20$ nm and vary the outer grain size, W_g^{out} , resulting in variations in the grain size ratio, R_g . The limit of $R_g = 1$ corresponds to a bi-crystal with equal grain sizes. For this study, we use the transport coefficients for Fe-9 at.%Cr at 700 K shown in Fig. 7.7. Furthermore, we set the dose rate $\bar{K}_o = 7.5 \times 10^{-5}$ and PD recombination rate $\bar{K}_R = 10^3$. We also use GB and bulk sink strength parameters of $\bar{K}_{gb} = 10^4$ and $\bar{K}_b = 10$, respectively. We then perform systematic studies varying the grain size ratio, R_g , by varying the outer grain size, W_g^{out} , while keeping inner grain size $W_g^{in} = 20$ nm, and the results are shown in Figure 7.13.

Figure 7.13(a), (c), and (d) shows respectively profiles of the Cr, interstitial, and vacancy concentrations as a function of distance from the GB for various values of the grain size ratio R_g . Figure 7.13(b) is a magnified view of Cr concentration in Fig. 7.13(a). It can be seen from Fig. 7.13(a) that the GB peak Cr concentration increases with the grain size ratio, R_g . On the other hand, Fig. 7.13(d) shows that the dependence of GB vacancy concentration on grain size ratio, R_g , is not pronounced compared to that of interstitial or Cr concentrations. Furthermore, the Cr and interstitial concentration profiles are highly asymmetric about the GB plane compared to those in a system with an equal grain size, i.e., $R_g = 1$. Simulation results depicted

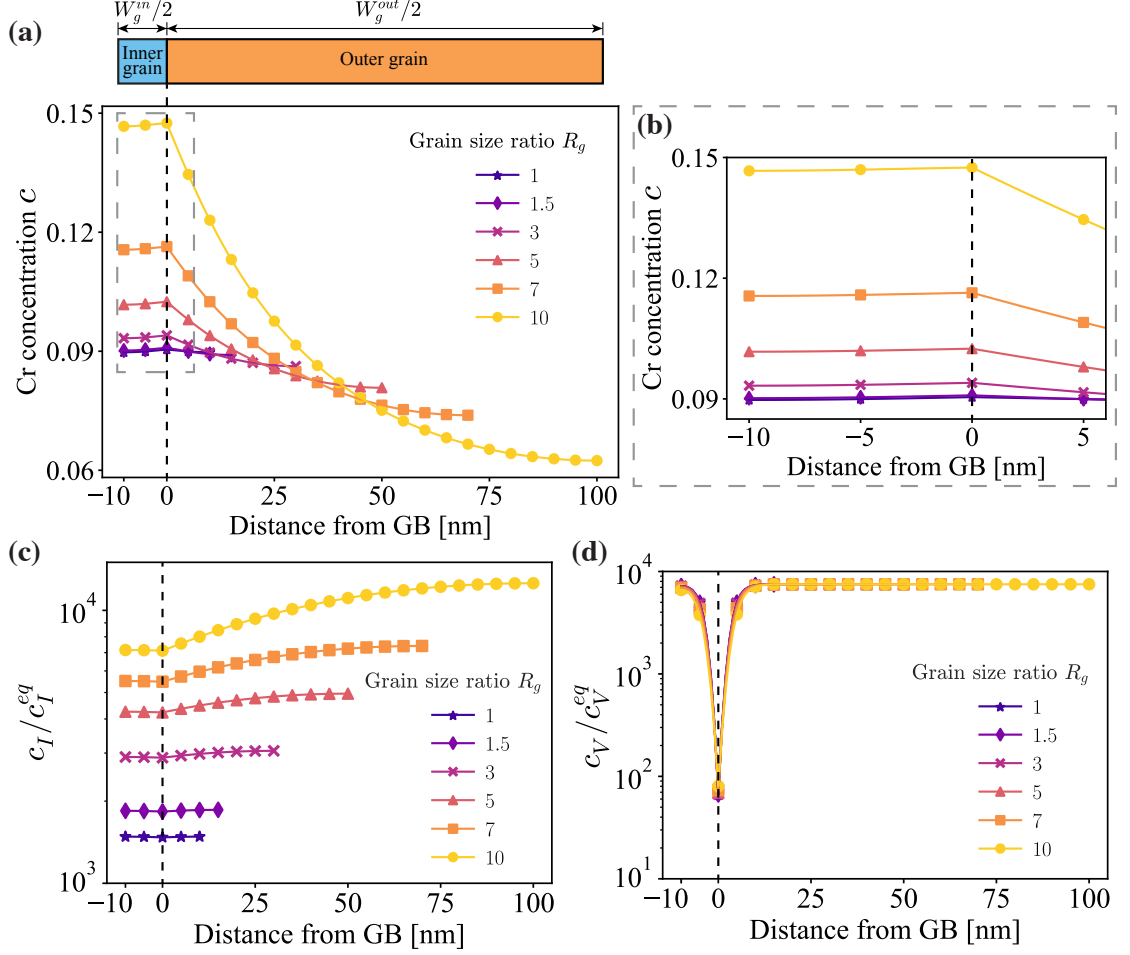


Figure 7.13: For the bi-crystal geometry with inner (outer) grain sizes W_g^{in} (W_g^{out}), the impact of grain size ratio $R_g = W_g^{out}/W_g^{in}$ on the GB concentration profiles of (a) Cr, (b) magnified view of Cr in (a), (c) interstitial c_I , and (d) vacancies c_V .

in Fig. 7.13 clearly show that metrics describing the grain microstructure beyond the average grain size influence RIS profiles.

We quantify the dependence of RIS on grain size ratio R_g by use the data from Fig. 7.13 to obtain the GB peak Cr concentration, c_{peak} . We also quantify the asymmetry in Cr concentration profiles [see Fig. 7.13(a)] about the GB by calculating the magnitude of the Cr concentration gradient in the outer, $|\nabla c|_{out}$, and inner, $|\nabla c|_{in}$, grains evaluated at the GB. Figure 7.14(a) is a plot of the GB peak Cr concentration

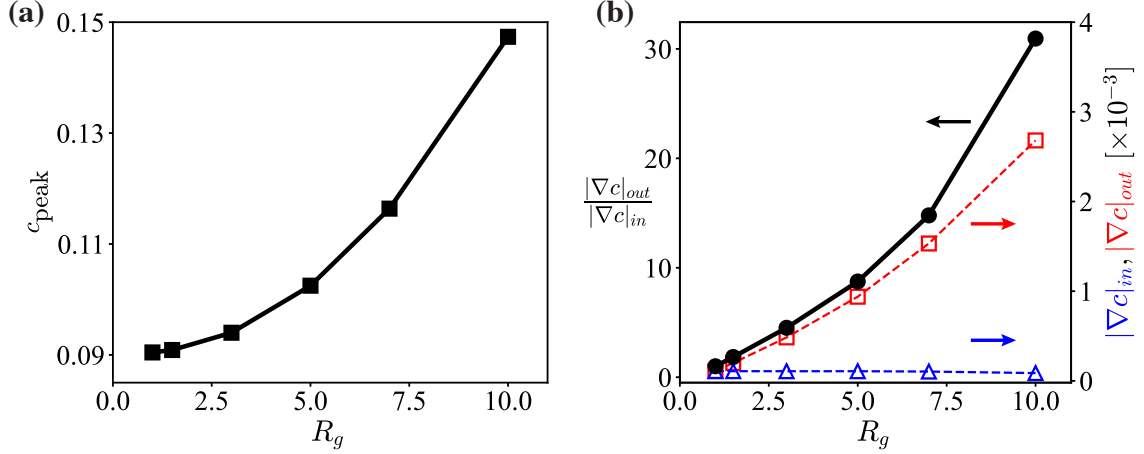


Figure 7.14: For the bi-crystal geometry with inner (outer) grain sizes W_g^{in} (W_g^{out}), the impact of grain size ratio $R_g = W_g^{\text{out}}/W_g^{\text{in}}$ on (a) GB peak concentration c_{peak} (b) concentration gradients on either side of the GB. The ratio of the concentration gradients $|\nabla c|_{\text{out}}/|\nabla c|_{\text{in}}$ is used as a measure of concentration asymmetry across the GB.

as a function of grain size ratio R_g clearly showing an increase in c_{peak} with R_g . As for the asymmetry in Cr concentration about the GB plane, Fig. 7.14(b) show a plot of $|\nabla c|_{\text{out}} / |\nabla c|_{\text{in}}$, which is the ratio of the magnitude of concentration gradient in the outer grain to the inner one, as a function of the grain size ratio R_g . Also included in Fig. 7.14(b) are plots of $|\nabla c|_{\text{out}}$ (dashed red line) and $|\nabla c|_{\text{in}}$ (dashed blue line). It can be seen that the degree of asymmetry on Cr concentration about the GB increases drastically with the grain size ratio R_g . A close examination of the plots of $|\nabla c|_{\text{out}}$ and $|\nabla c|_{\text{in}}$ shows that this asymmetry in Cr concentration profile is mainly due to the concentration profiles in the outer grain which show sharp gradients compared to those in the inner grain.

The results depicted in Figs. 7.10 through 7.14 clearly reveal a strong coupling between GB RIS profiles and the microstructure of metallic alloys, characterized in this work by the grain size and grain size ratio. For example, Fig. 7.11 reveals an increase in GB Cr concentration due to RIS with grain size W_g . These simulation

results for the dependence of RIS on grain size are in qualitative agreement with the experimental results shown in Fig. 7.6. Furthermore, our results reveal a strong dependence of RIS on the GB sink strength, or the degree of ideality in how GBs accommodate and annihilate irradiation-induced PDs. For example, the results depicted in Fig. 7.8 show that decreasing the GB sink strength parameter $\bar{K}_{gb}$ (i.e., increasing the time scale associated with the annihilation of PDs at GBs) results in an increase in interstitial and vacancy concentrations, as GBs do not serve as efficient sinks for these PDs.

7.4 Conclusions

In this work, combined experimental studies, KMC modeling, and PF simulations were performed to investigate the impact of grain microstructure on RIS behavior in a model Fe-Cr alloy. The grain microstructure was characterized by the grain size and grain size ratio and their impact on steady-state concentration profiles of Cr, interstitials, and vacancies were systematically explored. Experimental Fe-9.6 at.%Cr samples were prepared with average grain sizes in the range of 0.2–1.0 μm . Irradiation studies at 400°C were performed and the chemical profiles of several GB geometries were quantified. For an Fe-9.6 at.%Cr alloy, experimental results revealed that RIS increases with grain size. To quantitatively model the impact of grain microstructure on RIS profiles, KMC modeling was performed to calculate all relevant transport coefficients and their concentration dependencies. These transport coefficients were used as direct inputs to our PF model of RIS. PF computational studies revealed that RIS increases with grain size in agreement with experimental findings. Furthermore, our PF modeling results highlighted the dependence of RIS profiles on the GB sink strength, which describes the efficiency of a GB in accommodating and annihilating

irradiation-induced PDs. In addition to grain size, we performed computational studies exploring the impact of grain size ratio, i.e., a GB connecting two adjacent grains with different sizes, on RIS. In a model Fe-9 at.%Cr alloy, PF computational studies revealed asymmetric Cr profiles across the GB, the degree of which increases with increasing the grain size ratio. These results highlighted the need to consider more detailed metrics of the grain microstructure beyond the average grain size in order to quantitatively describe RIS profiles in metallic alloys. Furthermore, our results revealed that RIS is sensitively dependent on how efficient GBs serve as sinks for irradiation-induced PDs, and they put into question the commonly used assumption of treating GBs as perfect sinks.

Chapter 8

Summary and Future Work

8.1 Summary

In this dissertation, we employed computational methods to examine how interfacial structure, chemistry, and dynamics, specifically at S-L interfaces and GBs, govern microstructural evolution in diverse material systems.

For the solidification problem, we leveraged mesoscale PF modeling to investigate the role of various mass transport coefficients in controlling the solidification velocity and partition coefficients in multicomponent alloys during rapid solidification conditions. Simulation results demonstrate that the off-diagonal, or cross-diffusion, coefficients play a significant role in governing both the S-L interface velocity and the solute partition coefficients. For the model parameters used in this study, negative off-diagonal diffusion coefficients were found to enhance the solute partition coefficients by promoting solute depletion in the liquid phase ahead of the S-L interface. In addition, given an undercooling the S-L interface velocity was found to increase with decreasing the off-diagonal diffusion coefficients. Computational analyses of nonequilibrium interfacial effects further revealed that reducing the PF interface permeability

parameter, while keeping all other parameters constant, led to higher solute partition coefficients and lower S–L interface velocities. Furthermore, computational studies revealed that large variations, i.e., several orders of magnitude, in the PF interface permeability parameter were needed to capture such nonequilibrium interfacial effects during rapid solidification. In broad terms, this work elucidates the influence of coupled mass transport phenomena and nonequilibrium interfacial effects on the solidification kinetics of multicomponent alloys.

For the problem of GB segregation, we employed classical atomistic simulations to generate MPEA bi-crystal geometries with a series of [001] asymmetric tilt GBs and performed hybrid MC-MD simulations to investigate GB segregation and SRO at different temperatures. The equiatomic CoCrFeMnNi, so-called Cantor alloy, was used as a model MPEA system. In the temperature range of 673 – 800 K, the formation of Cr-enriched domains was observed, consistent with experimental findings. At temperatures above 800 K, atomistic simulations indicated the segregation of Cr and Mn to GBs, accompanied by the desegregation of Fe, Co, and Ni. Quantitative analysis further revealed that the GB solute excess of the constituent elements exhibited a weak dependence on boundary geometry, at least for the asymmetric tilt GBs investigated in this study. Furthermore, simulation results indicated that the GB solute excess decreases sharply with increasing temperature in the range of 1000 – 1200 K. To further elucidate the underlying chemical correlations, the Warren–Cowley SRO parameters were employed to quantify local chemical ordering and examine its interplay with GB segregation. The analysis revealed that GB regions exhibit SRO characteristics distinct from those of the bulk. For example, certain atomic pairs (e.g., Fe–Co) in CoCrFeMnNi display repulsive interactions within the GB region but attractive interactions in the bulk crystal. These findings highlight the complex nature of multi-element GB–solute interactions in MPEAs. Moreover,

it was observed that negative Warren–Cowley order parameters (i.e., attractive pair interactions) within the GB region increase rapidly with temperature. This trend in the SRO behavior is consistent with the GB segregation results, wherein the extent of GB segregation decreases as temperature increases. In broad terms, our results underscore the importance of accounting for GB interactions with multiple alloying elements when establishing chemistry–structure–property relationships in MPEAs.

Lastly, for the RIS problem, we conducted an integrated study combining experimental characterization, KMC modeling, and PF simulations to examine the influence of grain microstructure on RIS behavior in a model Fe–Cr alloy. The grain microstructure was characterized in terms of both average grain size and grain size ratio, and their effects on the steady-state concentration profiles of Cr, interstitials, and vacancies were systematically investigated. Experimental Fe-9.6 at%Cr samples were fabricated with average grain sizes ranging from 0.2–1.0 μm . Irradiation experiments were performed at 400°C and the resulting chemical profiles across various GB geometries were quantified. For an Fe-9.6 at%Cr alloy, experimental observations indicated that RIS increases with grain size. To quantitatively model the impact of grain microstructure on RIS profiles, KMC modeling was performed to calculate all relevant transport coefficients and their concentration dependencies. These computed transport coefficients were subsequently incorporated as direct inputs into the PF model for RIS. PF computational studies demonstrated that RIS increases with grain size, consistent with experimental observations. Moreover, PF modeling results revealed a strong dependence of RIS profiles on the GB sink strength, which describes the efficiency of a GB in absorbing and annihilating irradiation-induced PDs. Beyond grain size effects, we performed computational studies exploring the impact of grain size ratio, i.e., a GB connecting two adjacent grains with different sizes, on RIS. In a model Fe-9 at%Cr alloy, PF simulations revealed asymmetric Cr

concentration profiles across the GB, the degree of which increases with increasing the grain size ratio. These findings highlighted the importance of considering detailed microstructural descriptors beyond average grain size when quantitatively modeling RIS in metallic alloys. Furthermore, our results demonstrated that RIS is highly sensitive to the efficiency of GBs as sinks for irradiation-induced PDs, challenging the commonly adopted assumption that GBs act as perfect sinks.

8.2 Future Work

The present study outlines potential pathways for continued research which are highlighted below.

For the solidification problem, we can extend the PF model to include temperature gradient effects, anisotropic S–L interface properties, curvature-induced interface effects, and their influence on morphological instabilities such as cellular and dendritic growth. In addition, it is interesting to explore the coupled effects of undercooling and temperature- and concentration-dependent transport coefficients on solidification kinetics. Finally, coupling the PF model with data-driven or machine learning-based approaches may enable accelerated simulations and improved predictive capability, ultimately bridging the gap between mesoscale modeling and experimental observations.

For the problem of GB segregation, future studies should examine the influence of grain size (i.e., GB density) on GB segregation behavior and spatial SRO distributions. Further, GB segregation in MPEAs could be systematically explored across the full five-dimensional GB crystallographic space. Such a study would provide a comprehensive mapping of segregation trends as a function of misorientation, boundary plane inclination, and GB character. This could be pursued using large-scale

atomistic simulations combined with machine-learning models to interpolate across the high-dimensional space. Ultimately, such a systematic investigation would enable the development of predictive frameworks for tailoring GB chemistry and properties in MPEAs.

For the RIS problem, the RIS analysis in binary Fe–Cr alloys can be extended to multicomponent systems, i.e., Fe–Ni–Cr ternary alloys. In addition, incorporating polycrystalline models with explicit crystallographic orientations and triple junctions would enable more realistic microstructural representations. Such models would capture the collective behavior of GB networks, including the influence of GB connectivity and the unique role of triple junctions as sinks for solute atoms and PDs. Finally, the interaction between GB migration and RIS behavior remains an important aspect for future investigation. Developing models that couple GB migration kinetics with RIS would offer a more complete description of alloy stability under extreme environments, and could guide the design of nanocrystalline and metallic systems with enhanced radiation tolerance.

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Appendices

Appendix A

Generalized Flux Equations for Ternary Alloys

We start with a ternary alloy of solutes labeled 1 and 2 and a host labeled 3, where the concentrations of these elements are related through

$$c_1 + c_2 + c_3 = 1. \quad (\text{A.1})$$

Using the Gibbs-Duhem equation $c_1 d\mu_1 + c_2 d\mu_2 + c_3 d\mu_3 = 0$ along with Eq. A.1 yields

$$\nabla\mu_3 = -c_1\nabla\tilde{\mu}_1 - c_2\nabla\tilde{\mu}_2, \quad (\text{A.2})$$

where $\nabla\tilde{\mu}_1 = \nabla(\mu_1 - \mu_3)$ and $\nabla\tilde{\mu}_2 = \nabla(\mu_2 - \mu_3)$. Starting with Eq. 5.1, the flux equations for species 1 and 2 are

$$\mathbf{J}_1 = -\tilde{L}_{11}\nabla\tilde{\mu}_1 - \tilde{L}_{12}\nabla\tilde{\mu}_2, \quad (\text{A.3})$$

$$\mathbf{J}_2 = -\tilde{L}_{21}\nabla\tilde{\mu}_1 - \tilde{L}_{22}\nabla\tilde{\mu}_2, \quad (\text{A.4})$$

where $\tilde{L}_{11} = L_{11} - c_1(L_{11} + L_{12} + L_{13})$, $\tilde{L}_{12} = L_{12} - c_2(L_{11} + L_{12} + L_{13})$, $\tilde{L}_{21} = L_{21} - c_1(L_{21} + L_{22} + L_{23})$, $\tilde{L}_{22} = L_{22} - c_2(L_{21} + L_{22} + L_{23})$.

Next, we use the chain rule for the gradients of the chemical potential differences as follows

$$\nabla \tilde{\mu}_1 = \frac{\partial \tilde{\mu}_1}{\partial c_1} \nabla c_1 + \frac{\partial \tilde{\mu}_1}{\partial c_2} \nabla c_2, \quad (\text{A.5})$$

$$\nabla \tilde{\mu}_2 = \frac{\partial \tilde{\mu}_2}{\partial c_1} \nabla c_1 + \frac{\partial \tilde{\mu}_2}{\partial c_2} \nabla c_2, \quad (\text{A.6})$$

and substitute Eqs. A.5 and A.6 into Eqs. A.3 and A.4 to get

$$J_1 = - \left[\tilde{L}_{11} \frac{\partial \tilde{\mu}_1}{\partial c_1} + \tilde{L}_{12} \frac{\partial \tilde{\mu}_2}{\partial c_1} \right] \nabla c_1 - \left[\tilde{L}_{11} \frac{\partial \tilde{\mu}_1}{\partial c_2} + \tilde{L}_{12} \frac{\partial \tilde{\mu}_2}{\partial c_2} \right] \nabla c_2, \quad (\text{A.7})$$

$$J_2 = - \left[\tilde{L}_{21} \frac{\partial \tilde{\mu}_1}{\partial c_1} + \tilde{L}_{22} \frac{\partial \tilde{\mu}_2}{\partial c_1} \right] \nabla c_1 - \left[\tilde{L}_{21} \frac{\partial \tilde{\mu}_1}{\partial c_2} + \tilde{L}_{22} \frac{\partial \tilde{\mu}_2}{\partial c_2} \right] \nabla c_2. \quad (\text{A.8})$$

Now, we assume the following form for the chemical free energy of a ternary alloy

$$f = G_1 c_1 + G_2 c_2 + G_3 c_3 + \frac{RT}{V_m} [c_1 \ln c_1 + c_2 \ln c_2 + c_3 \ln c_3]. \quad (\text{A.9})$$

Then, the chemical potentials of solutes are given by

$$\mu_1 = G_1 + \frac{RT}{V_m} (1 + \ln c_1), \quad (\text{A.10})$$

$$\mu_2 = G_2 + \frac{RT}{V_m} (1 + \ln c_2), \quad (\text{A.11})$$

$$\mu_3 = G_3 + \frac{RT}{V_m} (1 + \ln c_3). \quad (\text{A.12})$$

Using Eqs. A.10 through A.12, the diffusion potentials are given by

$$\tilde{\mu}_1 = \mu_1 - \mu_3 = G_1 - G_3 + \frac{RT}{V_m} \ln \frac{c_1}{c_3}, \quad (\text{A.13})$$

$$\tilde{\mu}_2 = \mu_2 - \mu_3 = G_2 - G_3 + \frac{RT}{V_m} \ln \frac{c_2}{c_3}, \quad (\text{A.14})$$

which can be used to calculate the thermodynamic factors as: $\partial\tilde{\mu}_1/\partial c_1 = (1-c_2)RT/(V_m c_1 c_3)$, $\partial\tilde{\mu}_1/\partial c_2 = RT/(V_m c_3)$, $\partial\tilde{\mu}_2/\partial c_1 = RT/(V_m c_3)$, and $\partial\tilde{\mu}_2/\partial c_2 = (1-c_1)RT/(V_m c_2 c_3)$. Substituting the expressions for these thermodynamic factors into Eqs. A.7 and A.8 yields the following for the fluxes

$$J_1 = -\frac{RT}{V_m c_3} \left[\frac{1-c_2}{c_1} \tilde{L}_{11} + \tilde{L}_{12} \right] \nabla c_1 - \frac{RT}{V_m c_3} \left[\tilde{L}_{11} + \frac{1-c_1}{c_2} \tilde{L}_{12} \right] \nabla c_2, \quad (\text{A.15})$$

$$J_2 = -\frac{RT}{V_m c_3} \left[\frac{1-c_2}{c_1} \tilde{L}_{21} + \tilde{L}_{22} \right] \nabla c_1 - \frac{RT}{V_m c_3} \left[\tilde{L}_{21} + \frac{1-c_1}{c_2} \tilde{L}_{22} \right] \nabla c_2. \quad (\text{A.16})$$

The prefactors describing the transport coefficients can be written in simplified form as

$$\left(\frac{1-c_2}{c_1} \right) \tilde{L}_{11} + \tilde{L}_{12} = \frac{c_3}{c_1} L_{11} - L_{13}, \quad (\text{A.17})$$

$$\tilde{L}_{11} + \left(\frac{1-c_1}{c_2} \right) \tilde{L}_{12} = \frac{c_3}{c_2} L_{12} - L_{13}, \quad (\text{A.18})$$

$$\left(\frac{1-c_2}{c_1} \right) \tilde{L}_{21} + \tilde{L}_{22} = \frac{c_3}{c_1} L_{21} - L_{23}, \quad (\text{A.19})$$

$$\tilde{L}_{21} + \left(\frac{1-c_1}{c_2} \right) \tilde{L}_{22} = \frac{c_3}{c_2} L_{22} - L_{23}, \quad (\text{A.20})$$

which are used in Eqs. A.15 and A.16 to yield the following for the fluxes of species

1 and 2

$$J_1 = -\frac{RT}{V_m} \left[\frac{L_{11}}{c_1} - \frac{L_{13}}{c_3} \right] \nabla c_1 - \frac{RT}{V_m} \left[\frac{L_{12}}{c_2} - \frac{L_{13}}{c_3} \right] \nabla c_2, \quad (\text{A.21})$$

$$J_2 = -\frac{RT}{V_m} \left[\frac{L_{21}}{c_1} - \frac{L_{23}}{c_3} \right] \nabla c_1 - \frac{RT}{V_m} \left[\frac{L_{22}}{c_2} - \frac{L_{23}}{c_3} \right] \nabla c_2. \quad (\text{A.22})$$

Appendix B

Free Energy Functions for Ternary Alloys

The treatment herein follows the one described in Ref. [141] and is included for completeness. Starting with the liquid and solid free energies given by Eqs. 5.13a and 5.13b, the chemical potential for component i in these phases is given by

$$\mu_i^l = \frac{RT}{V_m} [1 + \ln c_i^l], \quad i = 1, 2, \quad (\text{B.1a})$$

$$\mu_i^s = \frac{RT}{V_m} \left[1 + \ln \left(\frac{c_i^s}{k_i^e} \right) \right], \quad i = 1, 2. \quad (\text{B.1b})$$

Equality of the chemical potential, Eq. B.1, for each component in the solid and liquid phases yields the expected equilibrium partition coefficients $k_i^e = c_i^s/c_i^l$.

Now for the solvent element, labeled 3, the chemical potentials are given by

$$\mu_3^l = \frac{RT}{V_m} [1 + \ln c_3^l], \quad (\text{B.2a})$$

$$\mu_3^s = \frac{RT}{V_m} [1 + \ln (c_3^s z(\theta))]. \quad (\text{B.2b})$$

Equating the chemical potential of the solvent in both the solid and liquid phases yields

$$z(\theta) = \frac{c_3^l}{c_3^s} = \frac{1 - c_1^l - c_2^l}{1 - c_1^s - c_2^s}. \quad (\text{B.3})$$

In this work, we assume a linearized phase diagram with

$$c_1^l = \frac{T - T_3}{m_1^e} \quad \text{and} \quad c_2^l = \frac{T - T_3}{m_2^e}, \quad (\text{B.4})$$

Inserting Eq. B.4 in Eq. B.3 with $k_i^e = c_i^s/c_i^l$ leads to

$$z(\theta) = \frac{1 - \frac{T - T_3}{m_1^e} - \frac{T - T_3}{m_2^e}}{1 - k_1^e \frac{T - T_3}{m_1^e} - k_2^e \frac{T - T_3}{m_2^e}} = \frac{1 + (T_3 - T) \sum_{i=1}^2 \frac{1}{m_i^e}}{1 + (T_3 - T) \sum_{i=1}^2 \frac{k_i^e}{m_i^e}}, \quad (\text{B.5})$$

and using $\theta = (T_3 - T)/T_3$, we get

$$z(\theta) = \frac{1 + T_3 \theta \sum_{i=1}^2 \frac{1}{m_i^e}}{1 + T_3 \theta \sum_{i=1}^2 \frac{k_i^e}{m_i^e}}. \quad (\text{B.6})$$

Appendix C

Solidification Velocity as a Function of Interface Permeability Parameters

To demonstrate the capability of the finite interface dissipation PF model to capture solidification in multicomponent alloys with different interface permeability parameters for the various components, i.e., P_i for the i th component, here we show a computational example of a ternary alloy solidification. The model parameters for this alloy case are the same as the ones used in the system depicted in Figs. 5.5(a2)–(c2). Namely, we use transport coefficients of $\bar{D}_{22} = \bar{D}_{11} = 1.0$, $\bar{D}_{12} = \bar{D}_{21} = 0$, alloy compositions of $c_1 = c_2 = 0.1$, and an undercooling $\theta = 0.067$. Other model parameters are listed in Table 5.1. We simulate cases with various values for the interface permeability parameters, where the dynamical equations for the evolution of concentration fields, Eq. 5.9, employ $\bar{P}_1$ for component 1 and $\bar{P}_2$ for component 2. Further, for the PF kinetic parameter, K_{sl} , we employ the general form for alloys with different values for their interface permeability parameters, which is given

by [140, 141]

$$K_{sl} = \frac{8\eta\mu_{sl}}{8\eta + \mu_{sl}\pi^2 \sum_{i=1}^2 \frac{(c_i^s - c_i^l)^2}{P_i}}. \quad (\text{C.1})$$

Figure C.1 is a contour plot of the S-L interface velocity V as a function of the interface permeability parameters $\bar{P}_1$ and $\bar{P}_2$, where it can be seen that the specific values of $\bar{P}_i$ greatly influence the solidification velocity.

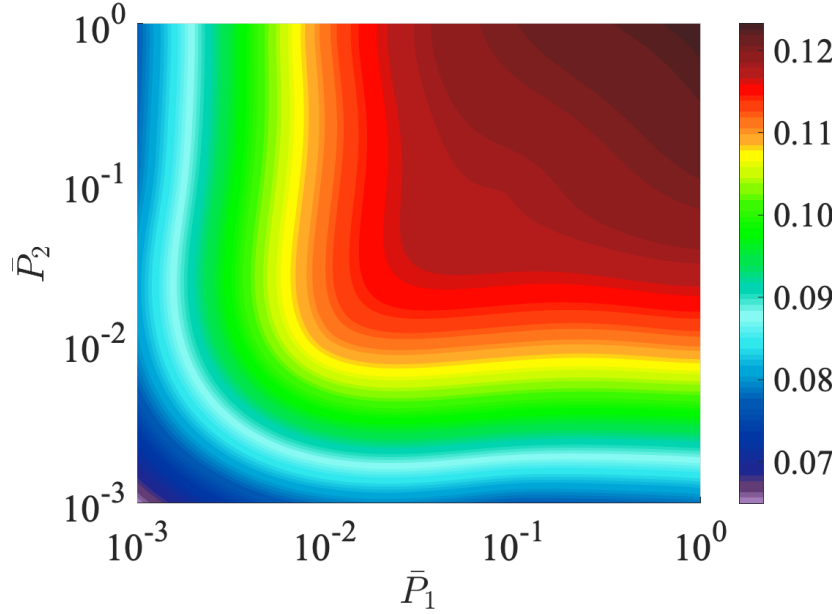


Figure C.1: A contour plot of the S-L interface velocity V as a function of the interface permeability parameters $\bar{P}_1$ and $\bar{P}_2$. A ternary alloy with $c_1 = c_2 = 0.1$, $\bar{D}_{22} = \bar{D}_{11} = 1.0$, $\bar{D}_{12} = \bar{D}_{21} = 0$, and $\theta = 0.067$ is used.

Appendix D

Warren-Cowley Order Parameters in MPEA Bi-crystals

The Figures below show the Warren-Cowley order parameters χ_{ij} , $\{i, j = \text{Co, Cr, Fe, Mn, Ni}\}$ at $T = 1000 \text{ K}$ for all MPEA GBs explored in this work. The SRO parameters for the $\Sigma 25 (0\ 1\ 0)/(\bar{7}\ 24\ 0)$, $\Sigma 13 (0\ 1\ 0)/(\bar{5}\ 12\ 0)$, $\Sigma 17 (0\ 1\ 0)/(\bar{8}\ 15\ 0)$, and $\Sigma 169 (0\ 1\ 0)/(1\bar{1}9\ 120\ 0)$ asymmetric GBs are shown respectively in Figs. D.1, D.2, D.3, and D.4.

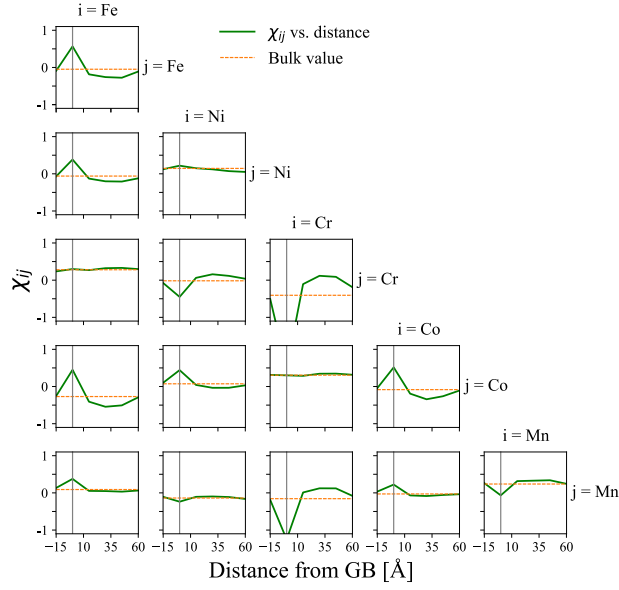


Figure D.1: For the $\Sigma 25 (0\ 1\ 0)/(\bar{7}\ 24\ 0)$ GB after MC-MD simulations at 1000 K, Warren-Cowley order parameters χ_{ij} $\{i, j = \text{Co}, \text{Cr}, \text{Fe}, \text{Mn}, \text{Ni}\}$ as a function of distance from the GB plane. The dashed lines represent values of the order parameters in the bulk.

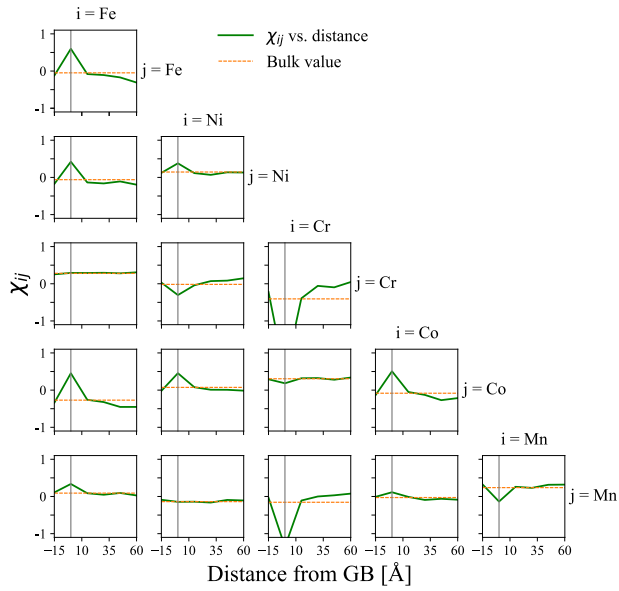


Figure D.2: For the $\Sigma 13 (0\ 1\ 0)/(\bar{5}\ 12\ 0)$ GB after MC-MD simulations at 1000 K, Warren-Cowley order parameters χ_{ij} $\{i, j = \text{Co}, \text{Cr}, \text{Fe}, \text{Mn}, \text{Ni}\}$ as a function of distance from the GB plane. The dashed lines represent values of the order parameters in the bulk.

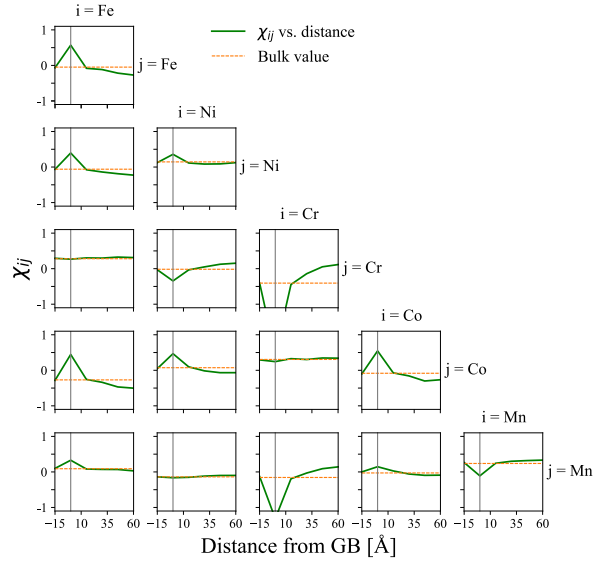


Figure D.3: For the $\Sigma 17 (0\ 1\ 0)/(\bar{8}\ 15\ 0)$ GB after MC-MD simulations at 1000 K, Warren-Cowley order parameters χ_{ij} $\{i, j = \text{Co}, \text{Cr}, \text{Fe}, \text{Mn}, \text{Ni}\}$ as a function of distance from the GB plane. The dashed lines represent values of the order parameters in the bulk.

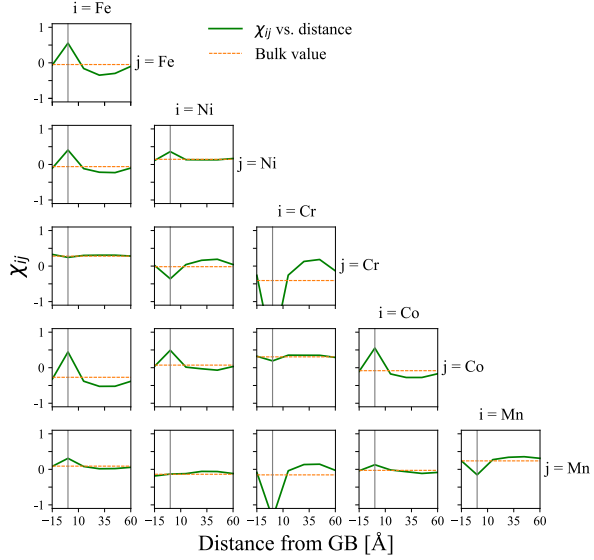


Figure D.4: For the $\Sigma 169 (0\ 1\ 0)/(\bar{1}19\ 120\ 0)$ GB after MC-MD simulations at 1000 K, Warren-Cowley order parameters χ_{ij} $\{i, j = \text{Co}, \text{Cr}, \text{Fe}, \text{Mn}, \text{Ni}\}$ as a function of distance from the GB plane. The dashed lines represent values of the order parameters in the bulk.

Appendix E

Generalized Flux Equations of Atomic Species and Point Defects

We start from a general multicomponent alloy system with $i = 1, 2, \dots, n$ atomic species and PDs, i.e., interstitials and vacancies. The solutes labeled $1, 2, \dots, n - 1$ and the host labeled n are represented by the concentration fields $c_1, c_2, \dots, c_n$, while the interstitials and vacancies are characterized by the concentration fields c_I and c_V , respectively. We assume that $c_I \ll 1$ and $c_V \ll 1$, and concentrations of atomic species are related through

$$\sum_{i=1}^n c_i = 1. \quad (\text{E.1})$$

Using the Gibbs-Duhem equation $\sum_{i=1}^n c_i d\tilde{\mu}_i = 0$ along with Eq. E.1 yields

$$\nabla \tilde{\mu}_n = - \sum_{i=1}^{n-1} c_i \nabla \mu_i = - \sum_{i=1}^{n-1} c_i \nabla (\tilde{\mu}_i - \tilde{\mu}_n). \quad (\text{E.2})$$

After expanding Eq. 7.1 and factoring out $\nabla \tilde{\mu}_j$, $\nabla \tilde{\mu}_I$, and $\nabla \tilde{\mu}_V$, the flux equations

for species i , interstitial, and vacancy are

$$J_i = - \left[\left\{ \sum_{j=1}^n (L_{ij}^I + L_{ij}^V) \nabla \tilde{\mu}_j \right\} + \sum_{p=1}^n L_{ip}^I \nabla \tilde{\mu}_I - \sum_{q=1}^n L_{iq}^V \nabla \tilde{\mu}_V \right], \quad i = 1, \dots, n, \quad (\text{E.3a})$$

$$J_I = - \left[\sum_{i=1}^n \sum_{j=1}^n L_{ij}^I \nabla \tilde{\mu}_j + \sum_{i=1}^n \sum_{j=1}^n L_{ij}^I \nabla \tilde{\mu}_I \right], \quad (\text{E.3b})$$

$$J_V = - \left[- \sum_{i=1}^n \sum_{j=1}^n L_{ij}^V \nabla \tilde{\mu}_j + \sum_{i=1}^n \sum_{j=1}^n L_{ij}^V \nabla \tilde{\mu}_V \right]. \quad (\text{E.3c})$$

We can reconstruct Eq. E.3a by adding and subtracting terms $(L_{ij}^I + L_{ij}^V) \nabla \tilde{\mu}_n$, $\sum_{p=1}^n L_{ip}^I \nabla \tilde{\mu}_n$, and $\sum_{q=1}^n L_{iq}^V \nabla \tilde{\mu}_n$. Similarly, Eq. E.3b can be reformulated through the addition and subtraction terms $\sum_{i=1}^n \sum_{j=1}^{n-1} L_{ij}^I \nabla \tilde{\mu}_n$ and $\sum_{i=1}^n \sum_{j=1}^n L_{ij}^I \nabla \tilde{\mu}_n$. Also, Eq. E.3c can be rearranged by introducing and eliminating terms $\sum_{i=1}^n \sum_{j=1}^{n-1} L_{ij}^V \nabla \tilde{\mu}_n$ and $\sum_{i=1}^n \sum_{j=1}^n L_{ij}^V \nabla \tilde{\mu}_n$. They can be simplified as follows

$$J_i = - \left[\left\{ \sum_{j=1}^{n-1} (L_{ij}^I + L_{ij}^V) \nabla (\tilde{\mu}_j - \tilde{\mu}_n) \right\} + \sum_{p=1}^n L_{ip}^I \nabla (\tilde{\mu}_I - \tilde{\mu}_n) - \sum_{q=1}^n L_{iq}^V \nabla (\tilde{\mu}_V - \tilde{\mu}_n) + 2 \sum_{k=1}^n L_{ik}^I \nabla \tilde{\mu}_n \right], \quad i = 1, \dots, n, \quad (\text{E.4a})$$

$$J_I = - \left[\sum_{j=1}^{n-1} \sum_{k=1}^n L_{kj}^I \nabla (\tilde{\mu}_j - \tilde{\mu}_n) + 2 \sum_{p=1}^n \sum_{q=1}^n L_{pq}^I \nabla \tilde{\mu}_n + \sum_{m=1}^n \sum_{l=1}^n L_{ml}^I \nabla (\tilde{\mu}_I - \tilde{\mu}_n) \right], \quad (\text{E.4b})$$

$$J_V = - \left[- \sum_{j=1}^{n-1} \sum_{k=1}^n L_{kj}^V \nabla (\tilde{\mu}_j - \tilde{\mu}_n) + \sum_{p=1}^n \sum_{q=1}^n L_{pq}^V \nabla (\tilde{\mu}_V - \tilde{\mu}_n) \right]. \quad (\text{E.4c})$$

Substituting Eq. E.2 into Eq. E.4 yields the following for the fluxes of species i ,

interstitial, and vacancy

$$J_i = - \sum_{j=1}^{n-1} L_{ij}^* \nabla \mu_j - \sum_{p=1}^n L_{ip}^I \nabla \mu_I + \sum_{q=1}^n L_{iq}^V \nabla \mu_V, \quad i = 1, 2, \dots, n-1, \quad (\text{E.5a})$$

$$J_I = - \sum_{j=1}^{n-1} \left(\sum_{k=1}^n L_{kj}^I - 2c_j \sum_{p=1}^n \sum_{q=1}^n L_{pq}^I \right) \nabla \mu_j - \sum_{m=1}^n \sum_{l=1}^n L_{ml}^I \nabla \mu_I, \quad (\text{E.5b})$$

$$J_V = \sum_{j=1}^{n-1} \sum_{k=1}^n L_{kj}^V \nabla \mu_j - \sum_{p=1}^n \sum_{q=1}^n L_{pq}^V \nabla \mu_V, \quad (\text{E.5c})$$

where

$$L_{ij}^* = L_{ij}^I + L_{ij}^V - 2c_j \sum_{k=1}^n L_{ik}^I. \quad (\text{E.6})$$

Appendix F

Polynomial Fits for the Onsager Transport Coefficients

The fitted functions for PDs mediated transport coefficients shown in Fig. 7.7 are listed below:

$$\begin{pmatrix} L_{\text{FeCr}}^I \\ L_{\text{FeFe}}^I \\ L_{\text{CrCr}}^I \\ L_{\text{FeCr}}^V \\ L_{\text{FeFe}}^V \\ L_{\text{CrCr}}^V \end{pmatrix} = \begin{bmatrix} -0.025 & 2.006 & -5.796 & 0 & 0 \\ 1.153 & -12.618 & 77.355 & -157.026 & 0 \\ -0.0490 & 4.483 & -13.426 & 0 & 0 \\ 5.73 \times 10^{-6} & -0.00025 & 0.008 & -0.0314 & 0 \\ 0.00014 & -0.00054 & 0.0017 & 0 & 0 \\ -4.02 \times 10^{-6} & 0.00091 & -0.0269 & 0.340 & -1.10 \end{bmatrix} \begin{pmatrix} 1 \\ c \\ c^2 \\ c^3 \\ c^4 \end{pmatrix}. \quad (\text{F.1})$$

Vita

Yitao Wang was born and raised in Shanghai, China. He received his Bachelor of Engineering in Marine Engineering from Dalian Maritime University in June 2019. He earned his Master of Science in Mechanical Engineering under the supervision of Professor Zhaoxu Meng at Clemson University in May 2021. Immediately after graduation, he began his doctoral studies in Mechanical Engineering at Clemson University with Professor Fadi Abdeljawad and later transferred to Lehigh University in August 2023 to continue his Ph.D. in Materials Science and Engineering under Professor Abdeljawad's mentorship. After graduating with his PhD in the fall of 2025, Yitao Wang is excited to begin working in an R&D position at the Lenovo Research Institute.