Atomistically informed phase field simulations for grain growth and phase transformation

by

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Atomistically informed phase field simulations for grain growth and phase transformation

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Abstract

The mechanical properties of metals and alloys are extremely sensitive to the microstructure. Different metallurgical processes, such as recrystallization, grain growth, and phase transformations, may modify the microstructure, where each process proceeds by the migration of interfaces that may be strongly affected by the presence of solutes and/or impurities due to solute drag. Quantifying the solute drag requires expensive and time-consuming experimental trials, which are further limited due to the vastly different length scales of solute segregation (few nm) and microstructural features such as grain sizes (few μ m). This study presents a computational approach that integrates the microstructure evolution model, i.e., here the phase field method, with atomistic simulations, i.e., density functional theory simulations (DFT), to identify the role of solutes on microstructural processes.

First, the experimental migration rates of a single well-defined grain boundary (GB) in Au during recrystallization heat treatments are rationalized using DFT calculations in combination with a continuum solute drag model. Here, an approach to determine the effective segregation energy from atomistic calculations is proposed, suggesting strong solute drag due to 2 ppm Bi impurities in the Au sample. In the microstructural scale, different grain boundaries exist with variability in GB properties, such as GB mobility and solute drag. A phase field model with a friction pressure is used to simulate solute drag on individual GBs. The simulations considering the variability in GB properties indicate that a representative GB can be defined that mimics the average grain size evolution in the presence and absence of solutes. Using the solute binding energies for five solutes

in nine different grain boundaries in FCC-Fe, the anisotropic phase field simulations suggest a minor role of segregation anisotropy on austenite grain growth, and as a result, the $\Sigma 5(310)[001]$ GB is considered as the representative GB. A solute trend parameter is proposed to identify solutes that promote grain refinement in agreement with experimental observations. Finally, the atomistically informed approach is extended to phase transformation in binary alloys. Here, phase field simulations that explicitly considered solute segregation in nanocrystalline materials agree with the steady-state solute drag model.

Lay Summary

Steel production contributes significantly to carbon-dioxide emissions, and using steel scrap instead of iron ore is proposed as a sustainable alternative to reduce emissions. Scrap, however, contains impurities such as Cu, Sn, Sb, etc., that may modify the microstructure and affect the final steel properties. Here, microstructure refers to the structure visible under a microscope. The impurities accumulate at specific places in the microstructure, such as the boundaries between crystals, and in response, the boundaries move slowly, resulting in different microstructures. In this study, a fundamental approach that considers atomic interactions in the nanoscale is presented to determine the boundary migration rates. A variability in boundary migration rates is considered, and impurities are classified based on their potential to modify the microstructure under different processing conditions. In practice, these results will help to determine the content of impurities that can be safely processed during steel production without affecting the properties.

Preface

The research presented in this thesis is conducted by the author, Ayush Suhane, under the supervision of Prof. Matthias Militzer. Most of the simulations and analysis were performed by the author in the Department of Material Engineering at the University of British Columbia (UBC) except for the atomistic simulations listed in detail below.

The grain boundary structure in Chapter 5 for the $\Sigma 13(134)[111]$ grain boundary in Au, and the binding energy of Fe and Bi in this grain boundary were calculated by Dr. Daniel Scheiber. The activation energies for the diffusion of Bi in Au in the vicinity of the grain boundary were provided by Dr. Maxim Popov. Dr. Vsevolod I. Razumovskiy and Prof. Lorenz Romaner assisted in the interpretation of the results presented in Chapter 5. Dr. Scheiber and Dr. Razumovskiy were involved in the discussion and assisted in the interpretation of results presented in Chapter 7. Dr. Hocine Lebbad helped with the phase field model formulation for interfacial segregation presented in Chapter 8.

Fig. 2.1, Fig. 2.2, Fig. 2.3, Fig. 2.5, Fig. 2.6, Fig. 2.7b, Fig. 2.8, Fig. 2.9, Fig. 2.10, and Fig. 2.11 have been taken with permission from the cited sources.

The results of Chapter 5 have been published under the title, Solute drag assessment of grain boundary migration in Au, *Acta Materialia* **224** (2022) 117473, authored by A. Suhane, D. Scheiber, M. Popov, V. I. Razumovskiy, L. Romaner, and M. Militzer. Portion of this work was also presented in the following conferences: THERMEC, Online (2021), EUROMAT, Online (2021); Alloying elements and migrating interfaces (ALEMI), Online (2021). The results of Chapter 6 have been published under the title, Representative grain boundaries during anisotropic grain growth, *Computational Materials Science* **220** (2023) 112048, authored by A. Suhane and M. Militzer. Part of this work was presented by the author at the Canadian Materials Science Conference (CMSC), Toronto, Canada (2022).

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Some of the results of Chapter 8 have been presented in the 8th International Conference on Solid \rightarrow Solid Phase Transformations in Inorganic Materials (PTM), Online (2022).

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List of Symbols

A	Grain boundary area in a unit cell
a,b	Solute drag fit parameters
A_c	Area of shrinking circle
a_r, b_r	Fit parameters for recrystallization
A_{tot}	Grain boundary area in atomistic calculations
B_i, T_i	Fit parameters for free energy of phases
С	Composition
<i>c</i> ₀	Bulk composition
c_C	Carbon concentration
Cgb	Grain boundary composition
$c_{gb,0}$	Site-saturation at the grain boundary
c_{eq}^i	Equilibrium solute composition in phase <i>i</i>
c^i_{GB}	Solute occupancy at site <i>i</i>
$c^{oldsymbol{lpha}},c^{oldsymbol{eta}}$	Composition in α and β phase at a grid point
$c^{oldsymbol{lpha}/eta}$	Interfacial solute composition from the α phase
$c^{eta/lpha}$	Interfacial solute composition from the β phase
\overline{D}	Average grain diameter
D	Trans-grain boundary diffusion
D_0	Pre-exponential factor for solute diffusion
D_b	Bulk diffusivity
D_{max}	Maximum diffusivity in the system
$D^{lpha}, D^{eta}, D^{int}$	Solute diffusion in α , β and at the interface

E	Effective segregation energy			
E_a	Diffusion activation energy from atomistic calculations			
$E_{avg,gb}$	Mean segregation energies for all grain boundaries			
E_b	Solute vacancy binding energy			
E_f	Vacancy formation energy			
E_{FS}	Total energy of slab without grain boundary			
E_{GB}	Total energy of slab with grain boundary			
E^i_{seg}	Binding energy at site <i>i</i>			
E_m	Migration barrier			
E_{avg}, E_{rep}	Average and representative segregation energy			
E_{max}, E_{min}	Maximum and minimum segregation energy			
E_{ref}^X	Reference energy of alloying element in bulk			
f_e	Fraction of low-segregation energy grain boundaries			
f_s	Fraction of low-mobility grain boundaries			
G	Gibbs free energy			
$g(\pmb{\phi})$	Double well function			
G_{chem}	Chemical free energy density			
G_d	Internal free energy density			
g_i	Orientation matrix for grain <i>i</i>			
G_{int}	Free energy density for the interface			
$G_{i,0}^p$	Standard state free energy of component i in phase p			
G_{seg}	Segregation free energy density			
G^lpha,G^eta	Bulk free energy density for α and β phase			
$h(oldsymbol{\phi}), p(oldsymbol{\phi})$	Interpolation functions			
h',p',g'	Derivative of interpolation function with respect to ϕ			
J	Diffusional Flux			
K	Fit parameter for grain growth			
k_1, k_2, k_3, k	Geometrical constants for grain growth model			
$k_{\scriptscriptstyle B}$	Boltzmann constant			
k_t	Adjustable parameter for time step			

L	Phase field mobility
l_{gb}	Length of grain boundary segment
L_{GBP}	Grain boundary resolution
M, M_{eff}	Effective mobility
M_0	Pre-exponential factor for mobility
M_c	Diffusion mobility
m_G	Phase field model parameter
M _{int}	Intrinsic mobility
M_{avg}, M_{rep}	Average and representative mobility
M_{max}, M_{min}	Maximum and minimum mobility
$M_{n,i}, M_{b,i}$	Normalized and averaged mobility of a bin
N	Total number of atoms in atomistic calculations
N_g	Number of occupied bins
N_{GB}	Total number of grain boundary sites in a unit cell
N_t	Number of measurements from phase field simulations
$N_{ u}$	Number of atoms per unit volume
O ₄₃₂	Symmetry operator for cubic materials
Q_d	Activation energy for solute diffusion
Q_m	Activation energy for mobility
\overline{R}	Average grain radius/size
r	Mobility ratio
R	Gas Constant
\overline{R}_0	Initial average grain size
$\overline{R}_{i}^{PF}, \overline{R}_{i}^{GG}$	Average size from phase field and grain growth model
T	Absolute temperature
T_0	Temperature for equal free energies of phases for the al-
	loy composition
T_m	Melting temperature
t _{ref}	Time for onset of recrystallization in reference alloy
t _{sim}	Simulation time

t_X	Time for onset of recrystallization in a given alloy
U	Chemical potential well
v	Velocity
V_m	Molar volume
x	Distance
X	Substitutional alloying element
X_r	Recrystallization fraction
${\boldsymbol lpha}, {\boldsymbol eta}$	Phases
$lpha_{\scriptscriptstyle SD},eta_{\scriptscriptstyle SD}$	Solute drag coefficients
$\pmb{lpha}_w, \pmb{eta}_w$	Weibull fit parameters
γ	Interface energy
Γ_0	Grain boundary surface density
Γ_{CLS}	Solute excess from solute drag model
Γ_{DFT}	Solute excess from atomistic calculations
Γ_{GB},Γ	Solute excess at the grain boundary
$\gamma_{max}, \gamma_{min}, \gamma_{rep}$	Maximum, minimum, and representative GB energy
ΔE	Segregation anisotropy
ΔE_P	Difference in free energies of product and parent phases
Δf	Difference in α phase fraction from the initial fraction
ΔG	Driving pressure
$\Delta G_{chem,int}$	Chemical driving pressure over the interface
$\Delta G_{chem,pf}$	Chemical driving pressure in phase field simulations
ΔG_{diff}	Dissipation due to diffusion
ΔG_{eff}	Effective driving pressure
ΔG_{ij}	Friction pressure between grain i and j
Δg_{ij}	Rotation matrix
ΔG_m	Intrinsic friction pressure
ΔG_{SD}	Solute drag pressure
$\Delta G_{SD,HS}$	Solute drag pressure from Hillert-Sundman model
$\Delta G_{SD,PB}$	Solute drag pressure from Purdy-Brechet model

$\Delta G_{SD,rep}$	Representative solute drag pressure		
ΔG_{seg}	Gibbs free energy of segregation		
ΔG_t	Total driving pressure		
ΔG_{tr}	Critical driving pressure for transition from high to low-		
	velocity limit		
ΔS	Vibration entropy		
ΔS_{ex}	Segregation entropy excluding configurational entropy		
Δt	Timestep		
Δx	Gridspacing		
$\Delta heta$	Disorientation angle		
$\Delta \theta_{12}, \Delta \theta_{23}, \Delta \theta_{34}$	Critical disorientation parameters		
$\Delta heta_c$	Critical disorientation angle		
δ	Half-interface width in phase field model		
δ_{SD}	Physical half-interface width in solute drag model		
ε	Relative average deviation		
$\varepsilon_P, \omega_P, L_P$	Phase field model parameters for phase transformation		
η_{ij}	Auxiliary variable to interpolate internal energy densities		
$\overline{\kappa}_{R}$	Average curvature in microstructure		
λ	Time exponent for grain growth		
$\lambda_{G,i},\kappa_G$	Phase field model parameters		
μ_0	Chemical potential of solute in bulk		
μ_i	Chemical potential of component <i>i</i>		
$\widetilde{\mu}$	Chemical potential difference with respect to the solvent		
Σ	Coincidence Site Lattice value		
$\boldsymbol{\sigma}, \Delta \boldsymbol{\theta}_g$	Parameters for Gaussian distribution		
${oldsymbol{\phi}}$	Phase field parameter		
$\Psi_1, heta_1, \Psi_2$	Euler angles		
ω_{Mn-C}	Solute interaction coefficient between Mn and C		

List of Abbreviations

BCC	Body	Centred	Cubic

- CLS Cahn-Lücke-Stüwe
- **DFT** Density Functional Theory
- FCC Face Centred Cubic
- GB Grain Boundary
- HS Hillert-Sundman
- KKS Kim-Kim-Suzuki
- MD Molecular Dynamics
- PB Purdy-Brechet
- **PFM** Phase Field Method
- **SRP** Solute Retardation Parameter
- WBM Wheeler-Boettinger-McFadden

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Chapter 1

Introduction

Metals and alloys, particularly steel, have been pivotal in addressing complex engineering challenges, resulting in advancements in the energy, transportation, and construction sectors. The rising demand for high-performance steels in these sectors, however, contributes significantly to carbon-dioxide emissions, as steel production alone accounts for approximately 40% of the total industrial emissions globally [1]. To limit the steel industry's impact on climate change, using steel scrap in electric arc furnace steelmaking is proposed as a sustainable alternative that results in a >70% reduction in CO₂ emissions compared to conventional steelmaking that utilizes iron ore in a blast furnace. Steel scrap, however, contains a variety of residual impurities such as Sb, Sn, Cu, Pb, etc., that may affect the properties of the final product [2, 3], e.g., >0.1 wt.% Cu in flat steel products leads to surface cracks during fabrication or service conditions and has significant implications on the durability of the steel [4].

It has been long recognized that the material properties depend on its microstructure. Here, the microstructure corresponds to the structural features such as grain size, phase fractions, dislocations, precipitates, interfaces, and their spatial arrangements. The relatively high impurity content in scrap may strongly influence the microstructure evolution during downstream thermo-mechanical processes in steel production, where grain growth, recrystallization, and phase transformation are key metallurgical processes that modify the microstructure. As a result, it is critical to quantify the role of impurities on these metallurgical processes.

In this regard, microstructure engineering seeks to develop knowledge-based process models that link processing parameters with material properties by controlling the microstructure. While empirical models like Johnson-Mehl-Avrami-Kolmogrov [5–7] and power law [8–10] have been used as process models, their predictive capabilities for different impurities are extremely limited [11, 12]. In addition, determining the empirical fit parameters through experimental trial and error is labour-intensive and prohibitively expensive. These models also ignore the morphology of the microstructure and do not account for the structure dependence or anisotropy in interface properties [13, 14]. Thus, advanced process models that account for a broader range of impurities and consider anisotropy in the microstructure are needed to design robust scrap-based production lines resulting in optimized steel properties.

In addition to evaluating the role of impurities, these process models are also valuable for designing new alloys through microstructure control using different strategies, e.g., rare earth microalloying additions. Such new high strength steels are sought-after for their ability to achieve light-weighting in automotive applications and other industrial sectors [15].

A significant challenge in developing the above-mentioned process models is due to the solutes and/or impurities that may accumulate at grain boundaries and/or interfaces and impede their migration rates at elevated temperatures due to solute drag [16–18]. The presence of solutes on interfaces, which occur at the atomic scale, and microstructure evolution, which can involve length scales up to a few micrometers in technical alloys, presents an additional challenge in characterizing the effect of solute drag on microstructure evolution. However, advances in computational materials science over the past decade have enabled the development of modeling approaches that can simulate across different length and time scales [19]. Atomistic simulations, such as Density Functional Theory, can provide quantitative insights into solute segregation, while mesoscale microstructure evolution models, including Phase field, Monte Carlo, and Cellular Automata, can account for solute drag. Integrating these approaches that are operative at different length scales can provide a more comprehensive insight into the microstructure evolution in the presence of solutes and/or impurities.

As a result, this study aims to develop an atomistically-informed phase field model capable of considering the effects of solute segregation and drag on microstructure evolution during phase transformation and grain growth. The remainder of this thesis is structured as follows: Chapter 2 provides a review of the experimental and theoretical advancements in solute effects on interface migration during phase transformation and grain growth. Chapter 3 summarizes the objectives, and Chapter 4 outlines the research methodology used in the present work. Chapter 5 investigates the movement of a single grain boundary in the presence of impurities using Density Functional Theory in combination with a conventional solute drag model. Chapter 6 employs a phase field model to analyze the effect of anisotropic grain boundary migration rates on the grain growth kinetics in the presence and absence of solutes. Chapter 7 utilizes the atomistically-informed model to examine the solute trends that promote grain refinement in austenite based on the available solute segregation data in FCC-Fe from atomistic calculations. Chapter 8 extends the proposed approach to phase transformation in a binary alloy. Finally, Chapter 9 summarizes the primary findings of this study and provides recommendations for future research.

Chapter 2

Literature Review

2.1 Introduction

Recrystallization, grain growth and phase transformation in metals and alloys involve migration of grain boundaries (GB) and/or interfaces under different driving pressures (ΔG), e.g. capillary pressure during curvature driven grain growth, difference in stored energy during recrystallization, and chemical potential gradient across the interface during phase transformation, respectively. The overall rate of these kinetic processes depends on the migration mechanisms of interfaces and how fast or slow these boundaries move in the material.

Despite extensive experimental investigations, very little is known about interface migration mechanisms. Nearly all theoretical attempts consider shuffling of thermally activated atoms across the interface [20]. For small driving pressures, i.e. $\Delta G \ll k_B T$, where k_B is the Boltzmann constant, and T is the absolute temperature, the interface is assumed to move perpendicular to the boundary plane and the velocity (ν) is proportional to the driving pressure across the boundary as,

$$v = M\Delta G \tag{2.1}$$

where, M is the interface mobility. Most studies consider M as a thermally acti-

vated parameter following an Arrhenius relationship, i.e., $M = M_0 \exp(-Q_m/RT)$, with M_0 and Q_m as pre-exponential factor and activation energy for interface migration, respectively. It should be noted that other mechanisms, e.g. disconnection mediated migration [21], may also be operative and the concept of thermally activated interface mobility may not hold for certain conditions. At sufficiently high temperatures, i.e. $T > 0.6 T_m$, where T_m is the melting temperature, atomic shuffling is the most dominant mechanism for GB migration in metals and alloys [22].

The interface mobility varies with interface structure [23] and temperatures, that may lead to structural transformations at the interface [24]. In cubic materials, the interface structure is completely described using five independent macroscopic parameters, i.e., three related to the orientation relationship between the grains (phases) and two to the boundary plane orientation. Consequently, interface mobility or energy vary in this five-dimensional space. Most experimental and theoretical studies, however, neglect the plane inclination dependence, and reduce the remaining three parameters to a single disorientation [25].

The interface mobility is also sensitive to the alloy chemistry [14]. In this regard, every technical material contains at least trace amount of impurities, and as a result, the mobilities determined from experimental observations are typically interpreted as effective mobilities, and their sensitivity to impurity content indicates strong solute-interface interactions. Solutes and/or impurities are either present in the form of precipitates or remain dissolved in solution. The precipitates can pin the grain boundaries and its effect on grain growth and recrystallization have been discussed in detail by Manohar et al. [26]. The solutes, that are dissolved in solution, segregate to the interfaces and reduce their migration rates (or mobility), a phenomenon which is commonly known as solute drag. It is important to separate the solute effects from the interface mobility by explicitly accounting for the solute drag. The next section reviews the developments in solute segregation and their effect on migrating interfaces.

2.2 Solute-interface interactions

2.2.1 Solute segregation

Lattice disorder and quantum-mechanical interactions between the solute and the solvent atoms at the interface promotes the accumulation of solutes at the interface resulting in solute segregation. Segregation can impact interface properties such as interface energy [27], mobility [23], or strength [28], with both positive and negative impacts on material properties. For example, small amounts of Bi in Cu, or lead in silver can weaken grain boundaries and may lead to intergranular brittle fracture instead of transgranular ductile fracture in pure Cu and Ag, respectively [29]. On the other hand, segregation can have beneficial effects such as Nb in ferrite leads to grain refinement [30], Nb or Zr addition to Cu stabilizes the nanocrystalline structure [31, 32], and Nd doping in Alumina improves its creep resistance [33].

The quantification of interfacial segregation is made possible by early experimental techniques such as Auger Electron Spectroscopy and Secondary Ion Mass Spectroscopy. These methods are confined to systems where the interfaces can be revealed through intergranular brittle fracture. Alternatively, 3D Atom Probe Tomography has emerged as a powerful tool for measuring solute content in the vicinity of the interfaces without the need for fracture. As a result, it has been widely used to study grain boundary segregation, including Nb and Mo in ferritic Fe [34], Bi in Cu [35], and Re in W [36], as well as interfacial segregation, such as Mn and Mo in austenite-ferrite interfaces [16].

These experiments facilitated the measurement of interfacial excess by determining the cumulative number of excess solute atoms across the boundary [37]. Interfacial excess is established as a thermodynamic parameter that shows minimal sensitivity to interfacial thickness and is less susceptible to local magnification effects [34]. In addition, the grain boundary segregation measurements are rationalized using the enrichment ratio which is determined by evaluating solute concentration at the grain boundary relative to the bulk. Seah and Hondros [27] demonstrated a linear correlation between the enrichment ratio and the inverse of solute solubility across a broad range of systems with varying solid solubility.

Variations in solute segregation are also dependent on the interface structure. Seah and Hondros [27] measured tin segregation in Fe and found a scatter of 15% in GB concentration between 500-850 °C at crystallographically unspecified grain boundaries. Conversely, Bi additions in Cu grain boundaries resulted in either entirely pure or fully decorated GBs suggesting strong variability in Bi segregation [38]. Further analysis of the structure dependence was conducted by measuring segregation in bicrystals with well-defined grain boundaries [39]. This analysis revealed a significant misorientation dependence in the enthalpy of segregation for C, P, and Si in Fe-3.5 Si at.%, as demonstrated in Fig. 2.1. These find-



Figure 2.1: Misorientation dependence of segregation enthalpy for C, P and Si in <100> symmetrical tilt GBs in Fe-3.5 Si at. % [39].

ings suggest that a few GBs with a coincidence relationship exhibit lower segregation levels, whereas other "general" GBs display higher segregation. However, a similar trend is not observed for Si segregation in austenitic steel, indicating a lack of correlation between solute segregation and the GB structure [40].
2.2.2 Segregation models

Owing to the importance of characterizing interfacial segregation, several phenomenological models are developed to describe the equilibrium segregation using thermodynamic parameters such as the segregation energy that varies with the interface structure, solute composition in bulk, temperature and pressure [17]. McLean [41] proposed a seminal model that considered statistical distribution of solutes at the grain boundary and in the bulk. Assuming that all the GB sites are substitutional, and remain available for segregation with identical Gibbs free energy of segregation (ΔG_{seg}), a relationship between the bulk composition, c_0 , and grain boundary concentration, c_{gb} , can be derived as,

$$\frac{c_{gb}}{1 - c_{gb}} = \frac{c_0}{1 - c_0} \exp\left(-\frac{\Delta G_{seg}}{k_B T}\right)$$
(2.2)

that is also known as the Langmuir-McLean segregation isotherm. The model considered all the grain boundary sites to be identical and quantified the segregation energy from experimental observations. Despite restrictive assumptions of the model, it has been successfully applied to describe the equilibrium GB concentration variation with temperature and bulk solute content in dilute alloys, e.g. P, Sn, S segregation in BCC Fe [39, 42] and In in Ni [43]. In some cases, only a fraction of the GB sites may be available for segregation. Consequently, Hondros and Seah [44] proposed replacing 1 in the left hand side of the Eq. (2.2) with a site saturation term, $c_{gb,0}$ that has been used to successfully describe the segregation of Sb in BCC Fe with $c_{gb,0}$ =0.27 [45].

However, there are disparities between the experimental results and the predictions made by the Langmuir-McLean model for other materials [17]. These discrepancies may stem from several factors, e.g. multiple segregation sites at the interface with different segregation/binding energies, solute-solute interactions, competition among interfacial sites, and/or non-equilibrium segregation of elements during non-equilibrium processing. To address these limitations, Seah and Hondros [27], followed by White and Coghlan [46], extended the LangmuirMcLean model by incorporating the site-specific binding energy of solutes at the grain boundary. In this refined approach, the occupation probability at each grain boundary site is calculated using Eq. (2.2) which considers distinct binding energies, and then these are averaged over all grain boundary sites to obtain the grain boundary concentration. The Langmuir-McLean model considers ideal interactions between the solute and the solvent atoms and as a result, its applications are limited to dilute binary, and in some cases, to multicomponent alloys where the solute-solute interactions can be considered negligible. The energetic interactions, however, become important for high solute concentrations at the grain boundaries, and in alloys where multiple solutes are competing for GB sites. A revised isotherm that included site-competition effects successfully demonstrated that P, a strong segregant that embrittles low carbon steels, can be replaced with boron at the grain boundary improving the ductility of grain boundaries [47]. Fowler and Guggenheim [17] considered a regular solution model and proposed solute interaction coefficients that can capture both attractive and repulsive solute interactions. Guttmann [48] expanded this approach to include co-segregating species in multicomponent alloys which has been used to explain the experimental GB segregation by considering the mutual interactions between the solute elements [17].

While these models are sufficiently complex to describe the physical phenomenon of GB segregation and the equilibrium composition of various elements at the interfaces, the interaction coefficients and the segregation energies remain largely unknown, and as a result, extensive efforts are underway to determine these parameters using both experimental and theoretical approaches.

2.2.3 Solute drag theory

During microstructure evolution, interfaces with segregated solutes migrate under a driving force, and their migration rates strongly depend on the solute content. Lücke and Detert [49] developed the first quantitative model to describe the strong reduction in recrystallization rates due to the addition of 0.01 % Mn or Fe in high purity Al. They considered a retarding force imposed by the segregated solutes on the migrating GB that decreases the GB migration rates and leads to an overall reduction in recrystallization rates. Cahn [50], and later, Lücke and Stüwe [51] further developed this force based approach that is now commonly known as the Cahn-Lücke-Stüwe (CLS) solute drag model and is summarized below.

The model assumes a lower chemical potential at the grain boundary due to the segregating solute that can be represented by a potential well, U(x), where x is the distance from the centre of the grain boundary. Further, the solute diffusivity across the GB, also referred as the trans-GB diffusivity, is defined by D(x). For a grain boundary moving with a steady state velocity v, the composition profile, c(x), is determined using Fick's diffusion equation [50], which depends on the choice of U(x) and D(x), neither of which are known with certainty. Cahn [50] assumed a triangular interaction potential, with E as the segregation parameter as shown in Fig. 2.2, and constant diffusivity in the grain boundary that is different from the one in the bulk [50]. The concentration profile at v = 0 recovers the



Figure 2.2: (a) Chemical potential and (b) concentration profile for different normalized velocities where $V_a < V_b < V_c < V_d < V_e$ (c) Solute drag pressure variation with velocity normalized with GB width and solute diffusivity in bulk [50, 51].

Langmuir-Mclean model in the dilute limit at each GB position. The retarding

'force' is considered to be proportional to -dU/dx, and the total drag pressure due to the solute atmosphere is determined by,

$$\Delta G_{SD} = -N_{\nu} \int_{-\delta_{SD}}^{\delta_{SD}} (c - c_0) \frac{dU}{dx} dx = 4N_{\nu} c_0 \nu k_B T \int_{-\delta_{SD}}^{\delta_{SD}} \frac{\sinh^2 \left[U(x)/2k_B T \right]}{D(x)} dx$$
(2.3)

Here, N_{v} is the number of atoms per unit volume at the grain boundary, $2\delta_{SD}$ is the GB width, and ΔG_{SD} is the solute drag pressure. For static grain boundaries, the pressure is equal and opposite from both sides of the grain boundary such that the net pressure sums to zero. For non-zero velocities, the steady state composition profiles and the resultant non-monotonic solute drag pressure is determined as shown in Fig. 2.2. The solute drag pressure can be rationalized by analyzing the limits of the model. In the low-velocity regime, the solute cloud moves with the grain boundary due to its tendency to stay within the grain boundary. Here, the boundary velocity makes it difficult for the solutes to follow the interface and results in an asymmetric composition profile. The migrating grain boundary provides an additional attractive pressure to solute atmosphere to move along with the GB, and consequently, an equivalent retarding pressure is exerted on the moving grain boundary that is referred to as the solute drag pressure. For high velocities, the interface breaks away from the solute atmosphere resulting in a decrease in the drag pressure. In this 'force' based approach, the solutes effectively reduce the driving pressure, i.e., $\Delta G_{eff} = \Delta G - \Delta G_{SD}$, such that a velocity-driving pressure relationship, $v = M\Delta G_{eff}$, or equivalently $v = M_{eff}\Delta G$ can be determined for different assumptions of U(x) and D(x).

In this formulation, both continuous and discontinuous transitions from high velocity to low velocity limit are possible depending on the driving pressure and bulk solute concentration as shown in Fig. 2.3. Depending on the impurity concentration, a decrease in the driving pressure, e.g. during curvature driven grain growth, may lead to a strong decrease in the GB migration rates where a "free" GB with no solute segregation in the high velocity limit can get trapped by the solute atmosphere at lower driving pressures. Note that an opposite transition, i.e., an increase in the GB migration rates due to an increase in the driving pressure



Figure 2.3: Velocity as a function of driving pressure for different bulk solute concentrations [52].

may also occur for different microstructural processes.

Lücke and Stüwe [51] revised the solute drag model to include site-saturation at discrete grain boundary sites. The authors highlighted that such a pseudoatomistic description of a planar interface yielded similar qualitative results to the continuum solute drag treatment described earlier. Molodov et al. [53] extended the model by incorporating solute-solute interactions using a regular solution model that recovered the Fowler-Guggenheim segregation isotherm for zero velocities. While the former model resulted in identical solute drag pressure for both segregating and anti-segregating solutes, the latter approach broke this symmetry such that the segregating solutes with attractive solute interaction resulted in higher drag in comparison to anti-segregating solutes.

Hillert and Sundman [54] proposed an alternative energy based "dissipation" approach that considered that the total available driving pressure (ΔG) is dissipated due to the structural changes, also known as intrinsic friction (ΔG_m), and due to solute diffusion (ΔG_{diff}). In other words, the dissipation due to diffusion at the interface consumes a portion of local chemical driving pressure and is the source of the solute drag effect. The intrinsic friction is given by the ratio between

the velocity and the GB mobility, whereas the dissipation due to solute diffusion is determined from the composition profile across the GB as,

$$\Delta G_{diff} = -N_{\nu} \int_{-\infty}^{\infty} (c(x) - c_0) \frac{d\widetilde{\mu}}{dx} dx \qquad (2.4)$$

here, $\tilde{\mu}$ is the chemical potential difference between the solute and the solvent species. For finite velocities, the dissipation due to diffusion increases due to deviation from equilibrium composition profile at the interface and reduces to zero at high velocities. Note that the integration limits in this approach are different than the force based approach, see Eq. (2.3), i.e., it includes the interface region and the region ahead of the interface, also referred to as spike. This is in contrast with the CLS model, where the force originates only from within the interface. However, Hillert and Sundman [54] showed that both approaches produce identical results in the dilute limit for the same assumptions of U(x) and D(x). In comparison to the CLS model, the energy dissipation approach is also applicable to non-dilute alloys.

Both the 'force' and 'energy dissipation' approaches are further developed to determine the solute effects during phase transformations. Purdy and Brechet [55] were the first to extend the CLS approach to model ferrite growth in Fe-C-X alloys where X is the substitutional element with negligible solute diffusivity in comparison to carbon. They assumed an asymmetric wedge shaped potential well, and determined the solute drag pressure from the composition profile using Eq. (2.3). However, Hillert and Odqvist [56] criticized this approach due to the non-negligible solute drag pressure at zero-velocities which is compared to the driving pressure over the interface instead of the total driving pressure for phase transformation. In fact, Hillert and Odqvist [56] have shown that the non-zero solute drag pressure at low velocities in the Purdy and Brechet's treatment [55] is equivalent to the energy dissipated due to the spike ahead of the interface. Chen and van der Zwaag [57] revised the Purdy-Brechet's model accordingly that now agrees with the energy dissipation approach.

Quantitative application of these continuum solute drag models is dependent on the interaction potential and trans-interface diffusivity of solutes. These parameters are, therefore, key to quantify the effect of solutes on microstructural processes that are driven by interface migration. In practice, experimental approaches are used to determine the effective mobility using $v = M_{eff}\Delta G$ where the solute drag effects are encapsulated in the effective mobility. The kinetic coefficients of the effective mobility such as the pre-exponential factor and the activation energy are, therefore, useful in providing more insights into the interpretation of the solute drag effect due to different solutes.

2.3 Experimental observations of interface migration

2.3.1 Grain boundary migration in bicrystals

The GB mobilities are typically determined using either bicrystal or polycrystal samples. Bicrystals are preferable over polycrystalline samples as the latter only provides information about GB mobilities averaged over multiple grain boundaries. The former geometry, while difficult to manufacture, enables systematic determination of kinetic properties of individual grain boundaries and/or interfaces.

Migration rates and GB mobilities have been investigated with both planar and curved GBs by monitoring GB displacement by either continuous or discontinuous measurements. A variety of driving forces such as magnetic field [58], elastic energy [59], and stored energy [60] that create a free energy differential across the grain boundary have been used to drive a planar grain boundary. However, these experiments depend on the material anisotropy and may not be equally applicable for other material systems. In contrast, curved grain boundaries migrate under the capillary pressure such that the net driving pressure remains constant or changes in a well-defined way, thereby, providing better control over experiments for a

range of temperatures with good reproducibility. One drawback, however, is that different segments of the curved grain boundaries differ in inclination angle. As a result, these experiments report reduced mobility, defined as the product of the absolute mobility and the grain boundary stiffness, that is averaged over all the GB inclinations in the curved boundary. As highlighted in [14], such an averaging yields physical values for reduced mobility from different experiments that is in contrast to the statistical averaging of grain boundary mobilities determined from experiments in polycrystals.

The reduced mobility of a $40^{\circ} < 111$ > tilt grain boundary in Aluminum is found to decrease from 7.4×10⁻⁸ m²/s to 1×10⁻⁹ m²/s, when the impurity content increased from 0.4 ppm to 1 ppm [61]. This is attributed to the strongly segregating impurities in Al such as Fe, Si and Ce [53]. Grünwald and Haessner [60] deformed a single crystal of Au which polygonized quickly into a stable structure and observed the migration of a single 30°[111] grain boundary during recrystallization heat treatments by monitoring GB displacement for different temperatures. As shown in Fig. 2.4, they found that the GB migration varied as a function of temperature such that the activation energy remained constant at 85 kJ/mol for higher temperatures, and transitioned smoothly to 123 kJ/mol at lower temperatures. This transition is attributed to the solute drag of Fe that is present in the highest concentration, i.e. 20 ppm, in comparison to other impurities. A similar transition in the activation energy is also observed in 30°<1010> in Zn [62], and 38°<111> tilt grain boundaries in Al [63].

Further studies that quantified the activation energy of reduced GB mobilities for a variety of grain boundaries have found a strong misorientation dependence for different materials, e.g. Pb [64, 65], Al [66–68], and Fe [69]. A nonmonotonous variation with distinct maxima and minima are observed for the activation energy of GB migration for <100>, <111> and <110> tilt grain boundaries in Al [70]. Such observations may suggest a structure dependence of intrinsic mobility that corresponds to the mobility of grain boundaries in pure material. However, the variability in activation energy is found to decrease with an increase



Figure 2.4: Migration rate of 30°[111] GB in gold with temperature [60].

in temperature that is attributed to the anisotropy in solute drag. Further evidence of segregation anisotropy is shown in Fig. 2.5a which shows the activation energy for GB migration in <100> tilt GBs in Al with 0.5 ppm, 2 ppm and 200 ppm impurity content [67]. Here, the activation energy is independent of the misorientation angle for a high-purity sample, and further increasing the impurity content leads to a profound misorientation dependence that eventually stabilizes at a higher activation energy for even-larger impurity content. Grain boundaries with a close to coincidence relationship are found to be less sensitive to the impurity concentration for the alloy with 2 ppm impurities. In this case, the impurities are interpreted to selectively segregate to certain GBs at intermediate concentrations, resulting in a non-uniformity of reduced mobilities. For higher impurity content, all GBs may saturate with impurities, reducing the variability in GB migration.

The seminal work of Aust and Rutter [64] who measured the migration rates of different grain boundaries in Sn-doped Pb is shown in Fig. 2.5b. These observations provided further evidence in favour of segregation anisotropy as opposed



Figure 2.5: (a) Migration activation energy for <100> tilt GBs in Al with different purity [67] (□: 0.5 ppm, ▲: 2 ppm, O: 200 ppm impurities) (b) GB velocities from zone-refined Sn-doped Pb for different concentrations of Sn [64].

to the misorientation dependence of intrinsic GB mobilities. While they reported a decrease in the migration rates for all grain boundaries due to the addition of Sn, a few grain boundaries with misorientations close to a coincidence relationship (referred to as special boundaries) were less affected by the addition of tin in comparison to the other grain boundaries. In other words, migration rates or effective mobility of so-called "special" boundaries decreased more slowly than the rest of the grain boundaries with increasing Sn concentration. The extrapolation of migration rates to pure-lead showed a minor effect of GB structure on mobility. Thus, it is concluded from experimental observations that solute drag and segregation anisotropy have a greater impact on GB migration rates in comparison to the influence of GB structure on intrinsic mobility.

2.3.2 Recrystallization and grain growth

Grain growth and recrystallization both involve migration of a network of grain boundaries. Empirical approaches such as Johnson-Mehl-Avrami-Kolmogorov that relates the recrystallization fraction (X_r) with time (t), i.e., $X_r = 1 - \exp(-a_r t^{b_r})$ is used to rationalize the recrystallization kinetics with fit parameters (a_r, b_r) that vary with the thermal treatment and alloy chemistry. Similarly, grain growth kinetics is interpreted using a power law $\overline{D} = Kt^{\lambda}$, where K is the thermally activated rate constant, and \overline{D} is the average grain diameter, to quantify the grain growth rates [8, 9, 71]. Here, $\lambda = 0.5$ corresponds to ideal grain growth where the grain size distribution normalized with the average grain size follows a scaling distribution. However, $\lambda < 0.5$ is determined for a number of material systems that is attributed to the presence of impurities [52]. To determine the fit parameters, K and λ , however, requires extensive experimental trials for different alloy chemistries and therefore, this approach has limited predictive capabilities.

This led to the development of physical models that explicitly consider solute drag due to impurities and/or alloying additions and, therefore, remain applicable to model grain growth for a wide range of alloy compositions and temperatures [30, 72]. A qualitative agreement between the solute drag theory and the experimental measurements is obtained for grain growth in Al with Cu and Mg additions [51]. In this study, the average grain growth rate in Al decreased rapidly above a critical concentration, e.g. 10 at. ppm for Cu and 100 at. ppm for Mg. Sinclair et al. [30] considered the CLS solute drag model to quantitatively describe the retardation in ferrite grain growth in Fe-0.095 Nb wt.% in comparison to pure Fe between 700-900 °C as shown in Fig. 2.6. Fu et al. [73] described austenite grain growth rates in Fe-0.09 C wt.% steels with 0.049 and 0.09 wt.% Nb between 950-1300 °C using a model that considered the combined effect of precipitation and solute drag. Using a similar model, Furumai et al. [74] systematically varied the Nb concentration between 0 to 0.06 wt.% and quantified the decrease in grain growth rates in Fe-0.09 C-1 Mn wt.% steels between 1100-1400 °C. In these studies, the solute drag parameters, i.e. effective segregation energy (E) and trans-GB solute diffusivity (D), were determined by fitting the physical model with the experimental measurements. Table 2.1 summarizes the variability in these fit parameters for different solutes from recrystallization and grain growth studies where the trans-GB diffusivity is assumed to follow an Arrhenius relationship with D_0 and



Figure 2.6: Experimental and model predictions for ferrite grain size as a function of temperature [30].

Table 2.1:	Effective se	egregation ene	ergy and t	rans-GB	diffusivity	for different
solut	es from recr	ystallization a	and grain	growth s	studies.	

Solute	Matrix	E (kJ/mol)	$D_0 (\mathrm{cm}^2/\mathrm{s})$	Q_d (kJ/mol)
V	Fe	2.5 [75], 10 [76]	2.4 [75], 4.8 [76]	260 [75, 76]
Nb	Fe	20 [72, 74], 25 [77]	8.3 [72], 0.83 [72]	266.5 [72, 74], 248 [30]
		29 [30], 47 [78]	1.7 [74]	344 [78]
Mo	Fe	18 [79], 40 [80]	6×10^{-3} [79]	166 [79], 270 [81]
		43 [81], 30 [82]	0.482 [81]	
Ti	Fe	14 [76]	0.14 [76]	240 [76]
Mg	Al	16-52 [51], 5 [83]	32-177 [51], 0.4 [83]	94-125 [51], 60 [83]
Cu	Al	26-55 [51], 3 [84]	550-3200 [51]	90-113 [51], 125 [84]
Pb	Sn	10 [85]	1 [85]	67 [85]

 Q_d as pre-exponential factor and activation energy, respectively.

As established previously, GBs may have different migration rates depending on their structure and solute content, only averaged estimates of the kinetic parameters may be inferred from these experiments. Anisotropic migration of grain boundaries may, in some cases, lead to distinctly different behaviour during grain growth and recrystallization. Here, a few grains with high mobile grain boundaries may consume neighbouring grains resulting in the development of a bimodal grain size distribution that is indicative of abnormal grain growth [86]. Preferential high mobility grain boundaries may be present due to high intrinsic mobility anisotropy, selective solute segregation at few grain boundaries, and/or due to non-uniform density of precipitates resulting in reduced pinning pressure for selective grain boundaries [87, 88]. Similarly, solute segregation at specific grain boundaries, e.g. Y in Mg [89], hinders their migration and as a result, influences the texture development during recrystallization. In particular, Y in Mg randomizes the texture that improves its ductility significantly. As a result, it is desirable to consider the effect of structure dependent grain boundary properties on grain growth and recrystallization.

2.3.3 Phase transformation

Solutes have been known to strongly influence the phase transformation kinetics, e.g. Mo in Ti [90], microalloying elements such as Nb, Ti, Mo in steels [91]. Phase transformation proceeds by nucleation and growth where the growth of the product phase can be strongly influenced due to solute drag. On an industrial scale, empirical models like Johnson-Mehl-Avrami-Kolmogrov are used to assess the transformation kinetics during continuous cooling conditions, e.g. ferrite and bainite formation from austenite in steels [91]. However, a large number of experiments are required to correlate the empirical model parameters with the alloy chemistry. A more fundamental approach, which considers the role of diffusing species in interface migration, requires fewer empirical parameters and provides deeper insight into phase transformation kinetics.

Interface migration during austenite decomposition involves two processes (1) structural rearrangement from FCC \rightarrow BCC, and (2) redistribution of solute elements across the interface and in the bulk, where each process consumes a portion of the total driving force across the interface [54]. On the one hand, the former process can be considered infinitely fast, e.g. fast diffusion of C in Fe-

C, and the kinetics is solely determined by the long range diffusion of carbon. This is also known as diffusion controlled transformation where a local equilibrium assumption is invoked such that the equilibrium conditions are established locally at the interface. Crusius et al. [92] and later, Beche et al. [93] demonstrated that these conditions are met for low-carbon steels for smaller undercoolings with an excellent agreement between theory and experiments. For larger undercoolings, however, the deviation was rationalized by considering finite free energy dissipation due to structural rearrangement or interface friction given by $\Delta G_m = v/M_{int}$. Here, M_{int} is the intrinsic interface mobility that is independent of the alloy chemistry. Naturally, there exists another extreme where redistribution of solute consumes negligible energy and the total driving pressure is consumed by internal friction. One such case is when ferrite grows massively into austenite without the redistribution of solutes that is also known as interface controlled transformation [94]. Thus, mixed mode approaches that consider both processes at the interface are capable of describing the transformations ranging from local equilibrium at low undercoolings to partitionless (massive) transformation at very high undercoolings [95].

The success of the mixed-mode models depends on the determination of interface mobility. Several researchers have utilized the interface controlled transformations in Fe-X systems (X=Mn, Ni, Nb), that are most suitable to extract the mobility, and reported surprisingly different values for the mobility of $\alpha - \gamma$ interface that varies within several orders of magnitude [96–100]. For instance, Hillert and Höglund [96] suggested an Arrhenius relationship, $M = 0.035 \exp(-17681/T) \text{ m}^4/\text{Js}$, whereas Gamsjäger et al. [100] reported the interface mobility as $1.7 \times 10^{-5} \exp(-16838/T) \text{ m}^4/\text{Js}$. In particular, the activation energy is consistent, but the pre-exponential term varies significantly in these studies. These values are, therefore, considered as effective mobilities that are dependent on the impurities and/or other alloying elements present in the steel samples. Thermodynamically, massive transformation is possible below a so called T_0 temperature where the free energy of parent and product phase are equal for the

alloy composition. However, a lower transformation temperature is observed in experimental measurements, for instance, in Fe-Ni [99, 101] and Fe-Mn [7, 97] alloys. These studies considered solute buildup at the interface and solute drag to rationalize the delay by considering solute interaction parameters as fit parameters. Recently, Zhu et al. [102] investigated massive transformation in Fe alloys with Ni, Mn and Co as solute additions using a solute drag model and derived the intrinsic mobility as $2.7 \times 10^{-6} \exp(-17440/T)$ m⁴/Js that is independent of the solute species. The determined mobility can also successfully reproduce the transformation kinetics in Fe-C alloys considering the mixed mode approach [103]. The effect of other alloying elements on the delay in transformation temperature is still not well quantified and requires further attention.

Industrial steels include at least one substitutional solute (X) along with carbon, and it is desirable to extend the mixed-mode approach to determine the phase transformation kinetics in ternary or higher order steels. Early extensions for ternary systems did not implicitly consider diffusion of the substitutional element, instead, they introduced effective mobilities as mathematical functions of substitutional solute in a binary mixed-mode model [104, 105]. However, the effective mobilities are sensitive to the cooling rate, chemistry and the direction of transformation. In considering ternary Fe-C-X alloys, complications arise due to extremely different diffusivities of carbon and substitutional solute. Two purely thermodynamic conditions, Local-Equilibrium and Para-Equilibrium as shown in Fig. 2.7a, have been explored to describe the transformation kinetics. Further details about these models can be found in a recent review article [106]. Local equilibrium assumes the equality of chemical potential for each species at the interface. In this case, the phase diagram is separated into two regimes, Partitioning Local Equilibrium and No Partition Local Equilibrium. In the former, transformation is controlled by the long range diffusion of X that results in sluggish transformation rates. The latter, on the other hand, corresponds to no long range diffusion of X but considers a thin spike of the substitutional element that is pushed in front of the migrating interface. The other condition, Para-Equilibrium, assumes that



Figure 2.7: (a) Schematic for Local Equilibrium No Partitioning (LENP) and Para Equilibrium (PE) conditions. (b) Ferrite growth kinetics in decarburization experiment for Fe-0.74C-0.86Si at 850 °C [106]. The model corresponds to the three-jump solute drag model [107] based on the energy dissipation approach.

the substitutional atoms are immobile and the transformation kinetics is solely determined by the bulk diffusion of carbon. Indeed, No Partitioning Local Equilibrium and Para-Equilibrium represent limits for a non-partitioned growth, and can not describe the observed phase transformation rates of ternary steels such as Fe-C-Cr, Fe-C-Si [108] shown in Fig. 2.7b for Fe-0.74C-0.86Si (wt.%) at 850 °C.

A general mixed-mode model that considered solute drag during interface migration is developed by Chen and van der Zwaag [57], commonly referred as the Gibbs Energy Balance approach. This model evaluates the interfacial composition and interface velocity by balancing the total chemical energy with the total energy dissipated due to other processes. The model captures a number of remarkable features such as the transition between non-partitioning growth conditions, predicts the incomplete transformation during the formation of bainitic ferrite, and suggests that the transformation might not necessarily start from Para-Equilibrium interfacial conditions. Alternatively, Zurob et al. [107] rationalized the ferrite growth during decarburization experiments in ternary iron alloys using a discrete three-jump solute drag model that considered dissipation due to solute diffusion based on the Hillert-Sundman [54] approach. They derived the effective segregation energy of solutes, such as - 2.5 kJ/mol for Mn, -15 kJ/mol for Mo, -1.5 kJ/mol for Cr, and -9 kJ/mol for Si for randomly oriented interfaces by fitting the experimental kinetics to the solute drag model [107, 108]. One such application of the model is shown in Fig. 2.7b. It should be noted that the transformation kinetics does not follow Para-Equilibrium and No Partitioning Local Equilibrium kinetics, and instead, these thermodynamic conditions correspond to limiting cases in the solute drag model.

These solute drag models have several limitations, (1) they utilize solute drag parameters that are not known a priori, (2) do not consider the crystallography of the interfaces and anisotropic mobility, (3) are limited to one-dimensional modeling of interface migration, and (4) ignore the morphology of the product and parent phase. These assumptions may be reasonable for interpreting decarburization experiments where a planar interface migrates and consumes a large number of austenite grains with different crystallographic orientation, thereby, averaging the effect of crystallography [109]. However, it is not the case for ferrite precipitation from austenite where specific orientation relationships are favourable for ferrite growth that becomes even more pronounced for bainitic or Widmanstätten growth from austenite [106]. For instance, Dong et al. [110] demonstrated that the semicoherent interfaces of Widmanstätten ferrite have lower mobility than the incoherent ferrite interfaces. Fang et al. [111] extended the Gibbs Energy Balance model to 3D microstructures by considering both nucleation and growth of ferrite grains as well as the effect of prior austenite grain size distribution on the final microstructure. As a result, modeling developments can benefit from approaches that can consider morphological and crystallographic effects of solutes during austenite to ferrite transformation. On the other hand, accurate information on effective segregation energy of solutes is also of significant interest. Atomistic calculations may help to quantify, or at least provide more information about the solute-interface interactions or the solute drag parameters.

2.4 Atomistic Simulations

2.4.1 Solute segregation

Several atomistic approaches, in particular Density Functional Theory (DFT), can quantify the solute-interface interactions. In this regard, research on determining the binding energy of solutes at different grain boundary sites has seen a significant increase in the past decade [112–116]. The binding energy, here, refers to the energy change that occurs when a solute is brought from the interior of a bulk material to a grain boundary site at T = 0 K. A decrease in energy indicates a favourable solute segregation to the GB site. In particular for steels, Jin et al. [112] investigated the binding energy profiles of common alloying elements such as Nb, Ti, Mo, V, Si, Cr, Mn, Co, Ni, Cu at the $\Sigma 5(013)$ [100] GB in BCC Fe. The structure of the grain boundary and the binding energy profiles are shown in Fig. 2.8. Solutes that are larger than Fe have a correlation between the atomic size and the average segregation energy that is determined from the White-Coghlan model [46]. Ito and Sawada [117] investigated the binding energies of these so-



Figure 2.8: (a) $\Sigma 5(013)[100]$ grain boundary in BCC Fe with labeled unique GB sites. (b) Binding energy of different solutes at GB sites [112].

lutes in FCC Fe for nine different [001] symmetric tilt grain boundaries for which the tilt angle varied between 18.9° to 77.3°. Solutes such as Nb, Mo and Ti show an increasing tendency to segregate in both BCC and FCC Fe GBs with a significant variability in site-specific binding energies. Jin et al. [112] also investigated the solute-solute interactions when the same solutes occupy different GB position as well as when one site is occupied by Nb and the other site with a different solute. They found that the Nb-Nb interactions reduce the effective segregation energies by more than 30% whereas interactions with different solutes is significant for Mo, Ti, Mn but not for Cu and Si. Wicaksono et al. [118] investigated segregation in the Fe-C-Mn system for the $\Sigma 3(111)[1\overline{10}]$ GB in BCC Fe and suggested a favourable segregation of Mn in the presence of carbon. In another study, Scheiber et al. [113, 119] demonstrated that the effective segregation energies for substitutional solutes in BCC-Fe as well as the solute enrichment of Re in W derived from the DFT segregation profiles are in close agreement with the experimentally determined segregation data for either systems. Jin et al. [120] extended the approach to study the solute binding of Ni, Mo, Nb, Cr, Si, Mn in a FCC-BCC interface. These simulations considered a Kurdjumov-Sachs orientation relationship between the FCC and BCC phase. Using the Langmuir-McLean type models for segregation, effective binding energies determined for solutes such as Mo and Mn were found to be in the same range of values determined from fitting the solute drag model with decarburization experiments [107]. However, it should be noted that this specific orientation relationship, while frequently observed in austeniteferrite transformations, is different than that of incoherent interfaces that migrate during decarburization experiments.

DFT simulations are, however, limited by (1) T = 0 K calculations, and (2) the size of the system, such that only a few hundred atoms can be simulated which strongly limits the applicability of DFT simulations to non-coincident grain boundaries or general grain boundaries. Atomistic Monte Carlo [121], and/or Molecular Dynamics (MD) [122, 123] methods can relax these limitations and simulate much larger systems ($\approx 10^6$ atoms). However, these simulations are limited by the accuracy and the availability of interatomic potentials for different alloy systems, and often report binding energies that differ from those determined from DFT calculations [124]. Recently, a Quantum Mechanical/Molecular Me-

chanics approach has been proposed that preserves the accuracy of Quantum Mechanical calculations and has the capability to determine binding energies in less coincident or general grain boundaries [125]. Here, a small region including the grain boundary and solute atom that considers quantum interactions is embedded in a larger region that considers atomic interactions. Huber et al. [125] demonstrated the strength of this approach by determining the binding energies of Mg and Pb in a general grain boundary in Al.

2.4.2 Solute diffusion

Diffusion of substitutional solutes across the interface is an important parameter for solute drag calculations. In the bulk, substitutional solutes diffuse primarily via vacancy mechanism. As a result, the activation energy for diffusion can be separated into three parts, vacancy formation, vacancy-migration and vacancysolute interactions [126]. Further, the pre-exponential factor is dependent on the jump frequency and the lattice parameter. Huang et al. [127], and later Versteylen et al. [128] used DFT calculations with the Nudged Elastic Band approach, that determines the minimum energy path for vacancy migration, to determine the diffusion coefficent of impurities in bulk BCC Fe. A reasonable agreement between the predicted impurity diffusivities and the experimental diffusivities has been found for BCC Fe [128], Mg [129], Co [130], and Al [131] as host materials.

Determining trans-GB diffusion, however, is more challenging due to the multiplicity of GB sites where the activation energy depends on the GB position. Kinetic Monte Carlo simulations that consider probability of individual solute jumps, where individual probabilities are determined from DFT simulations, can overcome these limitations [132–134]. Suzuki et al. [132] determined the self diffusion of Cu across the grain boundary for several grain boundaries using hybrid Monte Carlo/Molecular Dynamics simulations, and suggested that the effective activation energy for trans-GB diffusion is close to the minimum activation energy among multiple GB sites.

2.4.3 Interface migration

MD simulations with a variety of techniques such as artificial driving force [135, 136], capillarity technique [137, 138], elastic strain [139, 140], and random walk [141, 142] approaches have been used to determine the temperature dependence of GB mobilities in pure materials. Using Ni, Mendelev et al. [143] demonstrated that either of the methods that consider planar GBs produce identical GB mobilities. Wicaksono et al. [138] investigated coherent and incoherent curved GBs in BCC Fe and determined the migration activation energy as 10 and 12 kJ/mol, respectively, which are an order of magnitude smaller than the experimentally determined activation energies. The discrepancy is attributed to the presence of impurities in experimental samples [143]. MD simulations have been used to determine the crystallographic dependence of GB mobility in pure materials that is not accessible to experiments. Olmsted et al. [136] utilized the artificial driving force technique to sample the GB mobility of 388 GBs in Ni that is shown in Fig. 2.9. Surprisingly, no correlation was found between the disorientation angle,



Figure 2.9: Mobilities of 388 GBs in Ni at 1400 K [136].

inclination angle, coincidence relationship characterized by the Σ value of grain boundaries and their mobilities. Furthermore, the absolute GB mobility varied by more that 2 orders of magnitude for the investigated grain boundaries. In contrast with the theory of GB migration, only a few grain boundaries (57% of 388 (GBs) demonstrated thermally activated migration whereas other GBs showed antithermal (mobility decreases with temperature), and athermal (mobility remains constant with temperature) migration with temperature [136, 144]. Hoyt [145], however, have suggested to interpret these mobilities with caution due to the use of artificially high driving forces that is different than the expected driving pressures during grain growth and recrystallization. MD simulations have also been used to determine the mobility of a semi-coherent interface between FCC and BCC phases in pure Fe. Bos et al. [146], and later Song and Hoyt [147], considered different interatomic potentials, both of which indicate BCC phase as the most stable phase at all temperatures. The chemical energy difference between the FCC and the BCC phase, therefore, serves as the driving force for interface migration. In the former simulations, the migration rates varied between 200-700 m/s indicating a martensitic transformation [146]. The latter considered a different interface that was 4.04° rotated from the Kurdjumov-Sachs relationship [147]. In this case, the interface velocities are slower than those of Bos et al. [146] and the activation energy is determined as 16 kJ/mol that is an order of magnitude less than the activation energy determined from experiments [100, 147]. In general, the interface mobility also depends on the crystallography and a semi-coherent interface may not reflect the averaged interface mobility observed in experiments.

MD simulations are, however, severely restrictive in their length and time scales to determine the grain boundary and/or interface migration in the presence of solutes. The migration rates in these cases are mainly determined by the diffusion of solute species which is too slow to be detected in typical MD timescales. Further, the migration rates determined from MD simulations are unrealistically high, e.g. $\gg 0.01$ m/s [148], than the few µm/s typically observed in grain growth and recrystallization experiments. In addition, the simulation cell should be sufficiently large to develop a steady-state profile of the segregating solute to compare with the conventional solute drag models. These limitations are further exagger-

ated due to the unavailability of interatomic potentials for different alloy systems. Few studies have, however, used MD simulations to determine the change in GB mobility in the presence of solutes in the limit of low-driving pressures. For instance, Mendelev et al. [149] used MD simulations to parameterize the CLS solute drag model for an asymmetric $\Sigma 5$ tilt GB in Al with Fe impurities. They found a qualitative agreement between the simulations and the experimental GB mobilities as a function of temperature and Fe concentration. Sun and Deng [150] considered a Σ 5 grain boundary in Al with Ni, Ti, and Pb as impurities, and determined the GB mobilities using the random walk method in close agreement with the CLS solute drag model. Other atomistic techniques that can access atomistic length scale and diffusive time scales such as Phase Field Crystal [151] and atomistic Kinetic Monte Carlo [152] have been used to assess the solute effects on GB migration rates. While the former showed a structural pinning barrier, i.e. a threshold driving pressure for GB migration and the latter showed a significant effect of solute diffusivity on the solute drag pressure due to the atomic nature of the grain boundaries, both the approaches are in semi-quantitative agreement with the CLS solute drag model. In this regard, the CLS model can, at least qualitatively, describe the solute effects on GB migration in dilute alloys and an appropriate determination of continuum solute drag parameters such as effective segregation energy and trans-GB diffusivity from atomistic simulations remains a key challenge in the prediction of GB migration rates.

2.5 Mesoscale modeling

2.5.1 Overview of numerical methods

Several techniques have been used to simulate microstructure evolution during phase transformation, grain growth and recrystallization. These approaches include Monte Carlo Potts model [153–155], Phase field method [156, 157], Cellular Automata [158], Vertex models [159, 160] (or front tracking approach), and level-set method [161, 162] each with their own advantages and disadvantages.

As shown in Fig. 2.10, Monte Carlo Potts model and Cellular Automata discretize the microstructure domain into smaller cells, and modify the state of the cell based on predefined rules. One of the main strength of these methods is their



Figure 2.10: Schematic of (a) Vertex method, (b) Cellular Automata and/or Monte Carlo, and (c) Phase field method [163].

relative ease of implementation for both 2D and 3D simulations, and as a result, they have been extensively used to study the role of anisotropic GB properties on grain growth [155], texture evolution during recrystallization [154] and diffusional transformations including the solute drag effect [164]. These methods, however, are limited due to several factors. For Monte Carlo methods, it is challenging to relate the simulation time with the realistic time scale whereas it is not straightforward to accurately compute the grain boundary curvature in the latter which is a necessary driving force for grain growth.

The vertex method is a sharp-interface approach where the grain boundaries in a microstructure are considered to be composed of a network of vertices or nodes that are connected by straight lines. During GB migration, individual nodes move due to an applied driving force, followed by the reconnection with the network of nodes according to the pre-defined topological rules. As a result, large scale microstructures can be simulated with limited resources, however, their extension to 3D is relatively challenging due to the large number of topological changes which increases with the heterogeneity in the GB properties [165].

The phase field method (PFM), on the other hand, is a diffuse interface approach that considers a finite width of the grain boundary. The microstructure, in this case, is described using a set of phase field parameters that are continuous functions of space and time. The total free energy is described as a function of phase field parameters which includes at least two competing energy density terms, i.e., a gradient energy density and a barrier potential [157]. The microstructure evolves in order to minimize the total free energy. There is no need to explicitly track the interfaces and as a result, the phase-field method can easily handle complex microstructural features in two and three dimensions. During grain growth, for instance, grain boundary curvature is naturally included in its formulation and, as a result, no further approximations are required for curvature-driven grain growth. In contrast to the other approaches, the phase field method can incorporate additional physics such as solute diffusion, effect of strain, segregation etc. in a single framework by modifying the total free energy. These benefits have led to several developments in high performance computing, that have enabled realistic microstructure evolution using large scale simulations [166, 167]. These simulations, however, are prone to numerical instabilities, e.g. for highly anisotropic GB energies [168, 169]. Other limitations may arise when considering artificially wide interfaces, e.g. solute trapping during solidification, that may need additional corrections to reproduce experimental interface kinetics [170].

Level-set is a more recent approach, where structural GBs are represented by iso-contours of level set functions each of which describes a grain using signed distance metric. Here, each level-set function takes a positive distance value inside the grain and negative value outside the grain. The use of level-sets eliminates the need for diffuse interfaces, and the evolution of these sharp-interfaces correctly captures the topological changes during grain growth. A disadvantage, however, is that level-set functions require a re-initialization at each time step to maintain the signed distance characteristics that is a time-consuming process.

While these approaches have been utilized to characterize the role of anisotropic GBs on grain growth, Cellular Automata and Phase field method are more common to study phase transformation, whereas Level-set has also been recently extended to simulate austenite decomposition [171]. Among these methods, phase field is the most suitable approach to simulate complex morphological evolution during metallurgical processes, and as a result, is the method of choice.

2.5.2 Phase field modeling of grain growth

Different phase field models that can simulate grain growth have been proposed in the literature. A common theme among them is that the microstructure is described using non-conserved fields that represent the local structure and/or orientation of the grains. One of the two popular phase field frameworks, also known as continuum phase field approach, was developed by Chen and Yang [172], and Fan and Chen [156]. In this approach, the phase field parameter is considered to vary independently of other grains. In contrast, the multi-phase field approach proposed by Steinbach and Pezzolla [173] considers the phase field variables as the volume fraction of grains and, as a result, sum up to 1 at each point in the system. In the former case, the free energy has multiple degenerate minima, each corresponding to the bulk grain whereas one additional minima, where each phase field is zero, exists for the latter case. The volume fraction constraint forces one of the fields to be equal to 1 inside the bulk grains. These different free energy definitions lead to different microstructural evolution in detail, e.g. different equilibrium profiles or different shapes of grains, but produce nearly identical average grain size evolution and grain size distribution for equivalent model parameters [174].

Phase field modeling has been used to simulate microstructure evolution in 2D and in 3D to characterize the grain growth phenomena in ideal conditions (uniform GB mobility and energy in the absence of solutes/impurities). All the numerical simulations including the sharp interface approaches suggest a parabolic grain growth relationship for the average grain size [153, 154, 175]. The kinetic rate constant, however, depends on the dimensionality of the simulations [174]. The simulations also suggest a scaling or time-invariant size distribution for ideal grain growth. The quantitative grain size distribution, however, differs significantly

among different numerical simulations. While Anderson et al. [176] reported lognormal distribution, Kim et al. [177] indicated Hillert distribution, and Miyoshi et al. [166] and Kamachali et al. [178] demonstrated deviation from the Hillert's distribution [179]. It should be highlighted that the grain size distributions in experiments typically follow log-normal distributions and do not, in general, satisfy the parabolic grain growth relationship.

The phase field models have been extended to include the anisotropy in grain boundary properties such as mobility and energy [25, 175, 180, 181]. Kazaryan et al. [175] considered misorientation and inclination dependence of both mobility and energy, and later, Upmanyu et al. [25] determined these properties from atomistic simulations to simulate anisotropic grain growth. The simulations revealed that the GB mobility anisotropy results in a marginal change in grain evolution (except the grain growth rate is different), whereas a variability in grain boundary energy modifies the topology resulting in a deviation from the parabolic grain growth relationship. However, a recent phase field study highlighted that the GB mobilities that vary by more than two orders of magnitude show an increased probability for the initiation of abnormal grain growth conditions [182]. While these simulations consider grain growth in random textured microstructure, simulations with dual texture with different GB properties can also lead to extremely inhomogeneous microstructures [182–184]. In fact, Holm et al. [185] demonstrated that a microstructure with a few immobile grain boundaries can lead to grain growth stagnation. As a result, quantitative insights into the grain growth rates due to grain boundary anisotropy for a given thermal treatment and alloy chemistry requires more attention.

Solute segregation and solute drag have also been quantitatively incorporated in the phase field methodology [186–189]. Grönhagen and Ågren [186] considered a concentration dependent barrier in the bulk free energy that leads to solute segregation. A decrease in the GB migration rates is used to determine the solute drag pressure in agreement with the CLS solute drag model. Fan et al. [190] simulated grain growth in the presence of impurities by considering concentration dependent gradient energy. Kim et al. [187] adopted Grönhagen's approach and combined the solute drag model with the multi-phase field model for grain growth. In this study, they demonstrated that an isotropic solute segregation may promote abnormal grain growth under specific conditions, i.e., when the driving pressure due to the average grain size is close to the transition between "free" and "soluteloaded" grain boundaries. Since solute segregation is limited to the grain boundaries, these simulations are limited to smaller length scales and require excessive resources to simulate grain growth in mesoscale. In the microstructure scale, two different approaches have been used. Considering isotropic segregation, Strandlund et al. [191] determined an effective mobility as a function of driving pressure that is then used to simulate boundary migration without explicitly resolving the solute segregation at the grain boundaries. Shahandeh et al. [192], on the other



Figure 2.11: (a) Square of average grain size as a function of time for different solute drag parameter, *b* and fixed *a*, where the solute drag pressure is given as $av/(1+bv^2)$. (b) Grain growth exponent (λ) as a function of solute drag parameter, *b*, where the simulation fits the relationship $R^{1/\lambda} - R_0^{1/\lambda} = Kt$ and *K* is the kinetic coefficient. [192]

hand, considered a velocity dependent friction pressure that retards the migration of individual grain boundaries equivalent to the solute drag pressure proposed by the CLS solute drag model. Using this approach, Shahandeh et al. [192] demonstrated, as shown in Fig. 2.11, a deviation from the parabolic grain growth relationship for different solute drag parameters. These models, however, considered isotropic segregation at the GBs in contrast with the experimental observations. As a result, the effect of anisotropic segregation energy, that may also increase the mobility anisotropy, and its effect on grain growth warrants further attention.

2.5.3 Phase field modeling of phase transformation

In a binary system involving phase transformations, a conserved parameter, i.e., concentration is introduced at each point in the system. Further, an additional local free energy density representing the chemical free energy due to each phase is added to the total free energy functional that is different than the gradient energy density and the barrier potential. Appropriate interpolation schemes are utilized to define the chemical free energy at the interface [193]. The interface is considered as a mixture of two hypothetical phases, and their interpolation determines the local concentration at any position. In this regard, two types of modeling strategies are most common for studying phase transformation. The first approach was proposed by Wheeler, Boettinger and McFadden (WBM) that considers both the hypothetical phases at the interface to have identical concentration [194]. The other approach, initially proposed by Kim-Kim-Suzuki (KKS) [170] and later extended by Eiken et al. [195, 196], considers the ratio between the concentration of hypothetical phases is given by the equilibrium partition coefficient between the two phases.

While both the approaches have been used to simulate phase transformations, e.g. austenite decomposition [105, 197–199], the KKS approach quantitatively captures the transformation kinetics in mesoscale and can be coupled with the thermodynamic databases [195]. Solute segregation and its influence on the interface migration rates have been primarily studied using indirect measurements. These studies consider Para Equilibrium as the thermodynamic condition for ternary alloys, and introduce an effective interface mobility as a fitting parameter that varies with the heat treatment, e.g. cooling rates, and alloy chemistry indicating a role of solute drag [105, 200]. This approach requires a large number

of trials to quantitatively determine the effective mobility with limited applications to other alloy chemistries. A few studies, have however, incorporated the solute segregation explicitly by modifying the free energy functional.

Wheeler et al. [194] suggested introducing a concentration dependent potential that facilitates solute segregation at the interface. Using this approach, Zhang et al. [201] discussed the experimental growth rates of ferrite and its temperature dependence by considering Mo segregation in Fe-Mo alloys. In contrast, it is not possible to include a concentration dependent potential directly in the KKS model [202]. Recently, Kadambi et al. [202] considered the interface as a separate phase and proposed an extension to the KKS approach which interpolates the chemical free energy density between the bulk and the interface phase. However, disparate length scales of solute segregation and microstructural evolution makes it challenging to incorporate these methodologies to simulate phase transformation in technical alloys. Similar to grain growth, Zhu et al. [199] used a multi-phase field model and considered an adhoc velocity-dependent solute drag pressure as a friction pressure to simulate ferrite formation in an Fe-Mn-C alloy under Para Equilibrium conditions. Considering an effective segregation energy of Mn as -9.9 kJ/mol, they showed a transition to No Partitioning Local Equilibrium interfacial conditions. This approach, that can also simulate the morphological evolution of phases, is promising for ternary alloys during phase transformations. For such methods to be successful, it is necessary to (1) quantitatively determine the velocity dependence of the adhoc solute drag pressure considering solute segregation and, (2) identify the accurate solute drag parameters for different solutes.

2.6 Coupling approaches

Several attempts have been made to couple atomistic information with mesoscale microstructural models. Vaithyanathan et al. [203] proposed a multiscale method, where the components of the phase-field model like the free energy of phases, interface energy of coherent and semi-coherent interfaces, and lattice strains are evaluated using first principles, cluster expansion method and Monte-Carlo sim-

ulations. Bishop and Carter [204] proposed an upscaling strategy by utilizing molecular simulations. A Voronoi tessellation of each atom, followed by a local averaging was shown to yield a structural parameter which has similar characteristics to a phase field parameter across a grain boundary. More recently, attempts to couple MD with the phase field simulations have also been made. Berghoff and Nestler [205] used upscaling and symmetry arguments to increase the size of the growing structure in MD without changing the size of the domain. Miyoshi et al. [206] performed a one to one comparison of multi-phase field model and MD simulations of grain growth. Discrepancies in the quantitative comparison of grain growth kinetics are attributed to the anisotropic interfacial properties. Kim et al. [207] utilized anisotropic grain boundary segregation and energy reduction due to segregation from atomistic simulations and demonstrated a change in texture due to P additions in BCC Fe using phase field simulations. In this respect, it is encouraging to utilize various averaging techniques at the atomic scale to identify relevant mesoscale parameters to determine realistic microstructure evolution for different metallurgical processes.

2.7 Summary

A network of grain boundaries and/or interfaces migrate during grain growth, recrystallization, and phase transformation. Their migration rates vary with the interface structure, and are extremely sensitive to the solutes and/or impurities present in the sample. Solutes and/or impurities interact with the moving interface on the atomistic scale, and reduce their migration rates due to solute drag. Conventional process models utilize either empirical models, or utilize phenomenological mean-field approaches with effective interface properties to fit the experimental observations. These approaches, however, require large number of time-consuming trials to determine the effective properties and have limited transferability to other alloy chemistries.

The CLS solute drag model has gained widespread attention to describe experimental GB migration rates semi-quantitatively, and also agrees qualitatively with the atomistic simulations. The CLS model utilizes solute segregation energy and trans-GB diffusivity as fit parameters, and it is not obvious how to determine these effective GB parameters from atomistic simulations. Phase field models have been developed that can resolve solute segregation during GB migration, but their application to microstructural length scale requires expensive computational resources. To circumvent this issue, a friction pressure approach, that applies a retarding pressure on migrating GB equivalent to the CLS solute drag pressure, is utilized for grain growth simulations. Further challenges in describing grain growth arises due to the anisotropic nature of grain boundaries. In this regard, mesoscale modeling techniques have considered the role of anisotropic mobility in pure materials, but have ignored the effect of segregation anisotropy during grain growth.

Similar challenges, in terms of the effective interface parameters, exist in quantifying the phase transformation kinetics using the solute drag models with an added complexity of long-range diffusion of solutes. Conventional solute drag models are either one-dimensional or use an analytical relationship for solute drag pressure in mesoscale simulations. The solute-drag description in phase transformation can be verified with the phase field model, that can be further used for mesoscale simulations. While the state-of-the-art solute drag approaches have been used to fit the experimental observations, a better understanding of solute effects on metallurgical processes may benefit from the development of approaches that can introduce atomistically informed parameters to mesoscale simulations. Such simulations may facilitate exploring various alloy design strategies to obtain a microstructure with desired properties.

Chapter 3

Scope and Objectives

The goal of this work is to develop an atomistically informed phase field method that can determine the effect of solute segregation on the microstructure evolution during grain growth and phase transformation. In particular to grain growth, an approach that can relate the atomistic binding energy profiles to the effective solute drag parameters is needed to quantify the grain boundary migration rates in the presence of solutes and/or impurities. During microstructure evolution, an additional challenge lies due to the grain boundary network such that the individual GB segments can have anisotropic migration rates due to anisotropic mobility or solute drag. In these cases, determination of a representative grain boundary that is also accessible to DFT calculation can be useful to guide the grain growth studies for alloy design. Phase transformations, are more complex since the solutes, in addition to interfacial segregation, can also partition across the interface. An appropriate solute drag pressure, similar to grain growth, needs to be integrated with the phase field simulations where different solute drag models are available in the literature.

With the aim of achieving the overall goal, four specific objectives are identified as follows:

• Develop an approach to quantify the migration rates of a single grain boundary from density functional theory calculations in combination with the solute drag model.

- Determine the effect of anisotropy in grain boundary properties such as mobility, energy and solute drag on the grain growth evolution in mesoscale.
- Define a representative grain boundary to classify solutes according to their potential on retarding grain growth rates.
- Extend the atomistically informed approach to phase transformation in binary alloys and compare the predictions from the phase field simulations with a classical solute drag model.

Chapter 4

Methodology

4.1 Overview

This chapter outlines the methodology to couple atomistic simulations with the phase field method to simulate microstructure evolution during grain growth and phase transformation in binary alloys. Sec. 4.2 provides a brief overview of Density Functional Theory calculations for determination of binding energy at different grain boundary (GB) sites and solute diffusion in the vicinity of grain boundaries. It should be emphasized that all the atomistic simulations shown here, are performed by Dr. Daniel Scheiber and Dr. Maxim Popov at the Materials Center Leoben, and as a result, the details of the atomistic calculations reported in the present work are summarized in Appendix A. A specific grain boundary in Au is investigated in the present work for which the experimental migration rates are available. An approach to determine the effective segregation energy from the atomistic solute-interface interactions is presented in Sec. 4.3 and Sec. 4.4. The continuum solute drag model that utilizes the effective segregation energy to determine the migration rates of grain boundaries and interfaces is described in Sec. 4.5. In the microstructure scale, a network of grain boundaries and/or interfaces migrate at different rates due to anisotropy in solute segregation and GB mobility. Sec. 4.6 summarizes the phase field model for grain growth that considers anisotropy in GB properties such as GB mobilities and solute drag where the latter is simulated using a friction pressure approach. Further, an overview of a single-phase field model that explicitly accounts for segregation at phase interfaces, and an equivalent friction pressure model that can simulate phase transformation in mesoscale without resolving solute segregation, are presented along with the implementation details and numerical benchmarks. Finally, a mean-field model for grain growth is outlined in Sec. 4.7.

4.2 Atomistic simulations

Density Functional Theory (DFT) considers that the total energy of a many-body interacting system can be uniquely defined by the electron charge density such that its minimum corresponds to the ground state density. The total energy includes contributions from kinetic interactions between non-interacting electrons, nucleinuclei, and electron-nuclei Coulombic interactions, and an additional Exchange-Correlation energy which includes contributions from electron-electron interactions. Several different Exchange-Correlation functions, such as Local Density approximation and Generalized Gradient approximations exist in the literature where the latter provides a more accurate description of the ground state, e.g., lattice parameters are obtained in agreement with experimental observations [208]. Using an appropriate minimization scheme, e.g. conjugate gradient [209], the ground state structure for a system, e.g. a grain boundary or bulk crystal, is determined by structure and force relaxations until the energy and its gradient between two consecutive iterations are smaller than a threshold value. Note that the ground state structure is determined at T = 0 K which has been shown to produce reliable and accurate results of the solute binding energies [210].

With respect to the present work, Grünwald and Haessner [60] measured the migration rates of the $30^{\circ} < 111>$ grain boundary in Au which contained multiple impurities, particularly Fe and Bi in 20 ppm and 2 ppm respectively. As a result, the experimental grain boundary is approximated for the DFT calculations as a $\Sigma 13(13\overline{4})[111]$ tilt GB with a misorientation of 27.8° around the [111] axis. The
numerical details for determining the ground-state structure of the grain boundary is included in Appendix A.1, and the side-view and top-view of the ground state structure of the GB are shown in Fig. 4.1. The GB area, A_{tot} , for the considered GB is determined as 45.4 Å². DFT calculations are used to determine the bind-



Figure 4.1: Ground state structure of the $\Sigma 13(13\overline{4})[111]$ GB viewed along [111] direction (side view) and $[13\overline{4}]$ direction (top view). Both the top and the side views have identical indexing and GB sites are labeled in decreasing order of their Voronoi volume. B1 and B2 represent the bulk sites used in diffusion calculations. (Courtesy of Dr. Daniel Scheiber)

ing energies of Fe and Bi at different GB sites using the approach highlighted in Appendix A.2. Further, the temperature dependence of self and solute diffusion in metals is typically described using an Arrhenius relationship with two parameters, the pre-exponential factor D_0 , and the activation energy, E_a . For a vacancy-mediated diffusion of substitutional solute, the activation energy at T = 0 K can be written as [126]:

$$E_a = E_m + E_f + E_b \tag{4.1}$$

where E_m is the migration barrier, E_f is the vacancy formation energy, and E_b is the solute-vacancy binding energy. The computational details to determine these barriers from DFT calculations are summarized in Appendix A.3.

4.3 Solute enrichment

4.3.1 Grain boundaries

Based on the binding energy profile obtained with the DFT calculations, the solute excess at the grain boundary as a function of temperature is calculated using the White-Coghlan segregation model [46], where the probability of occupancy for each site can be determined from:

$$\frac{c_{GB}^{i}}{1 - c_{GB}^{i}} = \frac{c_{0}}{1 - c_{0}} \exp\left(-\frac{E_{seg}^{i}}{k_{B}T}\right)$$
(4.2)

Here, c_{GB}^{i} is the concentration of solute at GB site *i*, c_{0} is the bulk concentration of solute, k_{B} is the Boltzmann constant and *T* is the temperature in K. The total solute excess (Γ_{DFT}) at the grain boundary in atoms/nm² is then the sum of individual occupancies projected onto the habit plane as,

$$\Gamma_{DFT} = \frac{1}{A} \sum_{i}^{N_{GB}} (c_{GB}^{i} - c_{0})$$
(4.3)

where N_{GB} is the total number of grain boundary sites in a GB unit cell with area A. Grain boundary sites are identified as sites with non-zero segregation energies and the maximum distance between these GB sites perpendicular to the GB plane is defined as the GB width. In this description, the GB surface density is determined as $\Gamma_0 = N_{GB}/A$.

4.3.2 Phase interfaces

Contrary to the grain boundaries, the reference energy of phases on either side of the interface is different in DFT calculations at T = 0 K [120]. As a result, relative energies with respect to one of the two phases are reported, e.g. relative energies of Nb in a coherent FCC/BCC interface in Fe with respect to the BCC phase are shown in Fig. 4.2a. In this example, Nb is a ferrite stabilizer and has lower



Figure 4.2: (a) Relative energies and (b) Binding energies for Nb segregation across an FCC/BCC interface [120]. The interface width is shown with dash-dotted lines.

internal energy in the BCC phase at T = 0 K. Solute segregation, however, is an interface phenomenon and, therefore, should remain unaffected by bulk energies. First, the bulk energy of each phase is determined from either end of the interface where the difference between the relative energies for two consecutive sites is smaller than 0.02 eV. The distance between these sites on either end is considered as the interface width. A linear variation between the bulk energies is taken as the reference energy [120], and the binding energy at each site is determined from the difference between the reference and relative energies determined from DFT calculations as shown in Fig. 4.2b. Then, the interface enrichment is determined from Eq. (4.2) and Eq. (4.3) similar to the grain boundaries.

4.4 Effective segregation energies

For a thick interface where the solute can segregate to the interface, the chemical potential of the substitutional solute, in the dilute limit, can be described as [50],

$$\mu = \mu_0 + k_B T \ln[c(x)] + U(x) \tag{4.4}$$

where, μ_0 is the chemical potential in the bulk, e.g. α phase in α/α grain boundaries and α/β phase boundaries, and U(x) is the segregation potential at the interface. In contrast to Eq. (4.2), *c* is a continuous function of *x* where *x* is the distance from the habit plane of the GB. For phase interfaces, U(x) is described using an asymmetric wedge with two parameters, *E* and $2\Delta E_P$, where *E* is the effective segregation energy and $2\Delta E_P$ is the difference in the bulk energies of individual phases. Naturally, $2\Delta E_P = 0$ corresponds to a special case of grain boundaries. Similar to the methodology described in Sec. 4.3.2, a symmetric binding energy profile is determined for both phase interfaces and grain boundaries.

Cahn-Lücke-Stüwe [50, 51] demonstrated that the composition, c(x), at the GB, agrees locally with the Langmuir-McLean isotherm under the dilute limit approximation $c(x) = c_0 \exp(-U(x)/k_BT)$. As a result, the excess solute at a stationary grain boundary or GB enrichment (Γ_{CLS}) in atoms per area is determined as [34]:

$$\Gamma_{CLS} = N_{\nu} \int_{-\delta_{SD}}^{\delta_{SD}} [c(x) - c_0] dx$$
(4.5)

where N_v is the number of atoms per unit volume at the grain boundary, and $2\delta_{SD}$ is the interface thickness. Using the triangular potential variation in U(x) as shown in Fig. 2.2, the GB excess can be simplified as:

$$\Gamma_{CLS} = \Gamma_0 c_0 \left\{ \frac{k_B T}{E} \left[1 - \exp\left(-\frac{E}{k_B T}\right) \right] - 1 \right\}$$
(4.6)

here, $\Gamma_0 = N_v [2\delta_{SD}]$ is the surface density in the continuum model that is equivalent to the surface density determined in the atomistic model. The effective segregation energy is determined by considering equal enrichment in the continuum and the atomistic model, i.e., $\Gamma_{CLS} = \Gamma_{DFT}$. Similar to the grain boundary, the effective segregation energy for phase interface is determined using Eq. (4.3), and Eq. (4.6) with the solute binding energy profile shown in Fig. 4.2b. The additional parameter in phase interfaces, $2\Delta E_P$ is related to the difference in standard state energies of the bulk phases which varies with the temperature and can be determined from the equilibrium partition coefficients, $c_{eq}^{\beta}/c_{eq}^{\alpha} = \exp(-2\Delta E_P/k_BT)$ in the dilute limit, where c_{eq}^{α} and c_{eq}^{β} are the equilibrium solute composition in α and β phase, respectively.

4.5 Solute drag modeling

For grain boundaries with triangular segregation potential, Cahn [50] indicated that the solute drag pressure (ΔG_{SD}) for a GB migrating in steady-state conditions takes a particular form in the dilute limit as,

$$\Delta G_{SD} = \frac{\alpha_{SD} c_0 v}{1 + \beta_{SD}^2 v^2} \tag{4.7}$$

where, *v* is the GB velocity, α_{SD} and β_{SD} are solute drag parameters dependent on the effective segregation energy (*E*), temperature (*T*), and trans-GB diffusivity of solute element (*D*) such that [50]:

$$\alpha_{SD} = \frac{N_{\nu} [2\delta_{SD}] [k_B T]^2}{DE} \left[sinh\left(\frac{E}{k_B T}\right) - \frac{E}{k_B T} \right]$$
(4.8)

and

$$\beta_{SD}^2 = \frac{\delta_{SD} \alpha_{SD} k_B T}{2N_v D E^2}.$$
(4.9)

In this framework, the GB velocity is described as:

$$v = M_{int} (\Delta G - \Delta G_{SD}) \tag{4.10}$$

where, M_{int} is the intrinsic GB mobility and ΔG is the driving pressure.

For an α/β phase boundary, both the 'force-based' [55] and the 'energybased' [54] solute drag approaches consider a thick interface with different properties than the bulk, e.g. with an asymmetric potential well defined by *E* and ΔE_P as highlighted in Sec. 4.4 [55]. In either approach, the composition profile of solute elements across the interface is determined for a given composition in product phase, $c^{\alpha/\beta}$, and velocity, *v*, of the growing phase under the assumption of steady-state partitionless growth using Fick's diffusion [54], as

$$-\nu[c(x) - c^{\alpha/\beta}] = J \tag{4.11}$$

The diffusional flux (J) is given by reaction rate theory,

$$J = \frac{D(x)}{RT}c(x)[1-c(x)]\frac{\partial\widetilde{\mu}}{\partial x}$$
(4.12)

where $\tilde{\mu} = \mu_B - \mu_A$ is the diffusion potential with A and B as solute and solvent species, respectively, and D(x) is the diffusion coefficient. The composition profile for v = 0 with E = -12 kJ/mol and $\Delta E_P = -3$ kJ/mol is shown in Fig. 4.3a. For a given velocity, the solute drag pressure from the Purdy-Brechet (PB) model is determined similarly to the CLS model, as [55].

$$\Delta G_{SD,PB} = N_{\nu} \int_{-\delta_{SD}}^{\delta_{SD}} [c(x) - c^{\alpha/\beta}] \frac{\partial U}{\partial x} dx \qquad (4.13)$$



Figure 4.3: (a) Composition profile in a stationary interface with E = -12 kJ/mol and $\Delta E_P = -3$ kJ/mol (b) Solute drag pressure as a function of normalized velocity from different models.

Alternatively, the energy dissipation due to the solute diffusion inside the in-

terface or the solute drag pressure given by Hillert and Sundman (HS) [54] is determined as,

$$\Delta G_{SD,HS} = N_{\nu} \int_{-\delta_{SD}}^{\delta_{SD}} [c(x) - c^{\alpha/\beta}] \frac{\partial \widetilde{\mu}}{\partial x} dx \qquad (4.14)$$

Fig. 4.3b shows that the solute drag from the HS model is negligible at low and high velocities and increases for intermediate velocities, whereas the PB model results in non-zero solute drag pressure for low velocities that originates due to the spike at the interface [56]. The operating interface velocities for given $c^{\alpha/\beta}$ are then determined where the driving pressure across the interface,

$$\Delta G_{chem,int} = \sum_{i=1}^{n} c_i^{\alpha/\beta} [\mu_i^{\beta/\alpha} - \mu_i^{\alpha/\beta}]$$
(4.15)

exactly balances the interface friction, v/M_{int} , and the solute drag pressure. Here, μ_i , and c_i are the chemical potential and the composition of individual components at the interface in a model α - β system, and the driving pressure is counted per mole of the growth of the product phase.

4.6 Phase field modeling

4.6.1 Introduction

In the phase field approach, the microstructure is described by either conserved or non-conserved phase field parameters that are continuous functions of space and time. Conserved parameters may include local composition fields, whereas non-conserved parameters contain information about the phase and/or grain orientation [211]. In a microstructure, each grain/phase *i* is described by a separate non-conserved phase field parameter, e.g., ϕ_i , that takes a value of 1 in the bulk and gradually decreases at the interface to 0 outside the grain/phase. The total Gibbs free energy is described as an integral over the local free energy densities that include contributions from the bulk free energy, interface energy, chemical energy, strain energy, etc., as,

$$G = \int_{\Omega} [G_{int} + G_{chem} + G_{strain} + \dots] d\Omega$$
(4.16)

In all the formulations, an interface energy density (G_{int}) is defined, which includes (1) a potential that has a minimum for the bulk grains/phases, e.g., doublewell or multi-well potential, and (2) a gradient energy density that is responsible for the diffuse interface. The microstructure and the phase field parameters evolve in order to reduce the total free energy of the system with time according to the Allen-Cahn [212] and Cahn-Hilliard [213] equations for non-conserved and conserved fields, respectively, as

$$\frac{\partial \phi}{\partial t} = -L \frac{\delta G}{\delta \phi} \tag{4.17}$$

$$\frac{\partial c}{\partial t} = \nabla \cdot \left(M_c \nabla \frac{\delta G}{\delta c} \right) \tag{4.18}$$

here, *L* is a kinetic constant, M_c is the diffusion mobility of the solute element. The main difference among various phase field models lies in the treatment of different energy contributions to free energy. For grain growth simulations, Eq. (4.17) is used, whereas for phase transformation simulations, both Eq. (4.17) and Eq. (4.18) are implemented to solve for the composition and phase field parameters.

4.6.2 Grain growth

A multi-phase field model proposed by Fan and Chen [156] is used to simulate grain growth in ultrapure materials with and without solutes. The total free energy is constructed using the interface energy density (G_{int}) and an additional energy density (G_d) that imposes a retarding pressure on the grain boundaries simulating the solute drag of solutes during grain growth. Shahandeh et al. [192] provided a detailed derivation of the model, and the critical points of the models are summarized below. The interface energy density is defined as,

$$G_{int} = m_G \left[\sum_{i=1}^p \frac{\phi_i^4}{4} - \sum_{i=1}^p \frac{\phi_i^2}{2} + \sum_{i=1}^p \sum_{j \neq i}^p \lambda_{G,ij} \phi_i^2 \phi_j^2 + \frac{1}{4} \right] + \frac{\kappa_G}{2} \sum_{i=1}^p (\nabla \phi_i)^2 \qquad (4.19)$$

such that multiple degenerate minima exist at $(\phi_1, \phi_2, ..., \phi_p) = (1, 0, 0, ..., 0)$, (0, 1, 0, ..., 0), ..., (0, 0, 0, ..., 1), where each configuration corresponds to a different grain. *p* is the number of coexisting grains at any point in space, m_G is the maximum free energy barrier between two grains, $\lambda_{G,ij}$ is a model parameter, and κ_G is the gradient energy coefficient. Unless otherwise stated, $\lambda_{G,ij}$ is taken as 1.5 in all the simulations that lead to a symmetric equilibrium profile of phase field parameters [174].

To introduce the solute drag pressure [192], artificial free energies per unit volume, G_i and G_j are assigned to grains *i* and *j*, respectively such that a solute drag pressure $\Delta G_{ij} = G_j - G_i$ can be imposed as a friction pressure to drag a migrating grain boundary. G_d is the additional energy that interpolates these free energies using an auxiliary variable $\eta_{ij} = (\phi_j - \phi_i + 1)/2$, which assumes a value of 0 in grain *i* ($\phi_i = 1, \phi_j = 0$), 1 in grain *j* ($\phi_i = 0, \phi_j = 1$) and varies smoothly at the grain boundary. As a result, G_d for two grains is defined as,

$$G_d = 3\sum_{i=1}^2 \sum_{j\neq i}^2 \left(\frac{\eta_{ij}^3}{3} - \frac{\eta_{ij}^2}{2}\right) \Delta G_{ij} + \frac{1}{2}\sum_{i=1}^2 G_i$$
(4.20)

The grain structure evolution is then determined from,

$$\frac{\partial \phi_i}{\partial t} = L_G \left[\nabla \cdot \frac{\partial G_{int}}{\partial \nabla \phi_i} - \frac{\partial G_{int}}{\partial \phi_i} - \frac{\partial G_d}{\partial \phi_i} \right]$$
(4.21)

where L_G is the kinetic constant. Using $\phi_i = 1 - \phi_j$, $\partial G_d / \partial \phi_i$ is determined as $3\phi_i\phi_j\Delta G_{ij}$, and considering that each pair of order parameters ϕ_i and ϕ_j con-

tributes to $\partial G_d / \partial \phi_i$, the final evolution equation simplifies to,

$$\frac{\partial \phi_i}{\partial t} = L_G \left[\kappa_G \nabla^2 \phi_i - m_G \left(\phi_i^3 - \phi_i + 2\phi_i \sum_{j \neq i}^p \lambda_{G,ij} \phi_j^2 \right) - 3\phi_i \sum_{j \neq i}^p \phi_j \Delta G_{ij} \right] \quad (4.22)$$

Here, κ_G , m_G , and L_G are related to the physical GB properties such as GB thickness (2 δ), GB energy (γ), and GB mobility (*M*) for $\lambda_{G,ij} = 1.5$, as [174, 192],

$$\kappa_G = \frac{3}{4}\gamma[2\delta] \tag{4.23}$$

$$m_G = \frac{6\gamma}{[2\delta]} \tag{4.24}$$

$$L_G = \frac{4}{3} \frac{M}{[2\delta]} \tag{4.25}$$

Note that the grain boundary properties such as the mobility (M_{ij}) , energy (γ_{ij}) , and solute drag (E_{ij}) can be anisotropic and depend on the misorientation between grains *i* and *j*. The anisotropy can be included in the phase field method by formulating the model parameters as a function of local field variables. For instance, anisotropic grain boundary mobility (M_{ij}) between grains *i* and *j* is used to determine L_{ij} using Eq. (4.25), and L_G is determined as [174]:

$$L_{G} = \frac{\sum_{i}^{p} \sum_{j \neq i}^{p} L_{ij} \phi_{i}^{2} \phi_{j}^{2}}{\sum_{i}^{p} \sum_{j \neq i}^{p} \phi_{i}^{2} \phi_{j}^{2}}$$
(4.26)

For anisotropic GB energies, an approach proposed by Moelans [174] is used that is summarized in Appendix B. The solute drag pressure parameterized from the atomistic simulations is used as ΔG_{ij} such that individual grain boundaries between grain *i* and *j* may have different effective segregation energies (E_{ij}). In this approach, all the effects of the solute-GB interactions are considered to be included in the velocity-dependent solute drag pressure. Therefore, explicit concentration evolution is not considered in the phase field simulations for grain growth. The GB velocity between grain *i* and *j* is determined from $v = \frac{\partial \phi_i}{\partial t} / |\nabla \phi_i|$ as proposed by Shahandeh et al.[192]. An iterative scheme is used to solve Eq. (4.22) for an accurate determination of phase field parameters and grain boundary velocity. The algorithm determines the velocity from the $\partial \phi_i / \partial t$ at the previous timestep and evaluates the $\partial \phi_i / \partial t$ at the current time step from Eq. (4.22) and Eq. (4.7). Subsequently, a new velocity is computed, and the process is repeated until the convergence in velocity is achieved.

4.6.3 Phase transformation

Similar to grain growth, an approach is presented to simulate solute drag during phase transformation in mesoscale. A single phase field model proposed by Wheeler, Boettinger, and McFadden [194] (WBM) is used which explicitly considers solute segregation at a planar interface between α and β phase. This model considers the interface to be a mixture of both α and β phase with identical composition, i.e., $c = c^{\alpha} = c^{\beta}$ [201], which limits the model applicability to nano-scale simulations [214]. Further details of the model formulation and its limitations are summarized in Chapter 8 for the convenience of the reader.

The solute drag pressure from these simulations is determined from Eq. (4.10). Here, the interface velocities are obtained from the phase field simulations by monitoring the interface displacement, and the chemical driving pressure across the interface ($\Delta G_{chem,int}$) is evaluated from the simulations analogous to the sharpinterface approach, i.e.,

$$\Delta G_{chem,int} = G^{\beta}(c^{\beta/\alpha}) - G^{\alpha}(c^{\alpha/\beta}) - \widetilde{\mu}^{\beta/\alpha}[c^{\beta/\alpha} - c^{\alpha/\beta}]$$
(4.27)

where, G^{α} , G^{β} are the bulk free energies of α and β phase, and $c^{\alpha/\beta}$, $c^{\beta/\alpha}$ are the interfacial concentrations on the α and β side of the interface, respectively [215]. Fig. 4.4a shows a schematic of the solute concentration profile during interface migration. In a diffuse interface approach, the interfacial compositions are not clearly defined, and as a result, the composition from either end of the interface at $\phi = 0.01$ and $\phi = 0.99$ with additional 5 points from outside the interface is used

to linearly extrapolate the composition to $\phi = 0.5$, that is then used to determine the chemical driving pressure as shown in the schematic free energy in Fig. 4.4b. It is worth mentioning that the compositions at $\phi = 0.01$ and $\phi = 0.99$, and con-



Figure 4.4: (a) Composition profile of a moving interface without solute segregation. The interfacial composition, $c^{\beta/\alpha}$ and $c^{\alpha/\beta}$ are shown by extrapolating the composition from either end of the interfaces to $\phi = 0.5$ (b) Schematic for determination of chemical driving pressure across the interface from interfacial concentrations.

sequently, the determined interfacial compositions represent outer points of the interface and remain unaffected by solute segregation at the interface.

Kim, Kim, and Suzuki [216] (KKS) proposed a phase field model that relaxes the limitations of the WBM model such that the interface width can be artificially increased while preserving the phase transformation kinetics. As a result, the KKS model is used to simulate phase transformation in the microstructure scale. The solute drag pressure from nano-scale simulations, i.e., using the WBM model, is used to parameterize the friction pressure that is used in the KKS model to account for solute drag in mesoscale simulations without resolving the solute segregation at the interface. Similar to the WBM model, the details of the KKS model are included in Chapter 8.

4.6.4 Numerical implementation

Phase field equations for conserved and non-conserved parameters are non-linear Partial Differential Equations. This work uses an explicit finite difference method with a forward Euler scheme in space and time to discretize the partial differential equations on a uniform square grid. A five-point stencil as shown in Fig. 4.5 is used to determine the Laplacian and gradients as,

$$\nabla^2 \phi_{i,j} = \left(\frac{\phi_{i+1,j} + \phi_{i-1,j} - 2\phi_{i,j}}{\Delta x^2}\right) + \left(\frac{\phi_{i,j+1} + \phi_{i,j-1} - 2\phi_{i,j}}{\Delta x^2}\right)$$
(4.28)



Figure 4.5: Five-point stencil for discretization in a square grid.

A sparse data structure is used to store phase field parameters that have nonzero values locally at each grid point. The number of active parameters varies in space depending on the topological arrangement of grains in a microstructure, a maximum of 8 fields are stored at each point [192]. Consequently, all the phase fields with $\phi_i < 10^{-5}$ are not stored in the active parameter list. The explicit Euler integration in time is conditionally stable and, as a result, a time step is chosen as,

$$\Delta t = k_t \min\left(\frac{\Delta x^2}{M_{max}\gamma_{max}}, \frac{\Delta x^2}{D_{max}}\right)$$
(4.30)

where, M_{max} , and γ_{max} are the maximum mobility and maximum grain boundary energy of all the grain boundaries in the microstructure, and D_{max} is the maximum diffusivity in any phase in the microstructure. k_t is an adjustable parameter that varies between 0 and 1 depending on the dimensions of the simulation.

4.6.5 Modeling benchmarks

The phase field model for grain growth and phase transformation is implemented in C programming language, and the appropriate model parameters such as time step, interface width, and initial grain size for grain growth, are determined using accuracy analysis. A circle is initialized in a 2D domain discretized in 400 × 400 domain with a grid size of 0.06 µm as shown in Fig. 4.6a. A higher value of $k_t = 0.5$ results in interface destabilization. As a result, k_t is chosen as 0.1 in all the simulations. Isotropic interface mobility is taken as 5×10^{-11} m⁴/s and γ as 1 J/m². Under ideal conditions, the area of a shrinking circle (A_c) follows $d(A_c)/dt = -2\pi M\gamma$, and the radius of a shrinking circle follows, $R^2 - R_0^2 = -2M\gamma t$. Fig. 4.6b shows the effect of time stepping using k_t in Eq. (4.30) on the shrinkage rate of a circle.

For accurate simulations, the grid spacing should be much smaller than the smallest internal length scale, i.e., grain boundary width in the case of grain growth. While resolving grain boundaries with a large number of grid points imposes restrictions on the simulation domain size, fewer interface points may lead to artificial grain boundary pinning [217] or mesh-induced anisotropy [218]. Depending on the accuracy requirements, the grain boundary width is typically resolved in 4 or more grid points for grain growth simulations [219]. Fig. 4.7a compares the sensitivity of the number of interface points (L_{GBP}) with the shrinkage rate of a circle determined from the analytical solution. For $L_{GBP} = 3, 4, 8, 12$,



Figure 4.6: (a) Initial simulations domain with a circular grain (b) Normalized radius as a function of time for different time constant.



Figure 4.7: (a) Comparison of shrinkage rates for different GB resolution. The analytical solution is also shown in red. (b) Shrinkage rates as a function of driving pressure considering solute drag with an effective segregation energy of 40 kJ/mol and varying trans-GB diffusivities.

deviations of 4.4%, 2%, 0.03% and -0.03% are obtained from the simulations, respectively. Therefore, $L_{GBP} = 4$ is chosen as a compromise between accuracy and computational efficiency. Note that McKenna et al. [220] also performed a sensitivity analysis and suggested that the grain boundary width should be resolved in at least 6 points. However, the grain boundary width used in that study is 1.35 times thicker than that defined by Moelans et al. [157] for identical parameters. The current study follows the latter definition of GB width such that 6 points suggested by McKenna et al. [220] would correspond to 4 points in the present study in agreement with the benchmark simulations. Furthermore, Fig. 4.7a also indicates that the simulations deviate from the analytical solution when the grain diameter is smaller than five times the grain boundary width. As a result, the initial average grain size during grain growth simulations is considered to be at least five times larger than the grain boundary width.

Solute drag pressure given by Eq. (4.7) is introduced as a friction pressure in the phase field model with an effective segregation energy of 40 kJ/mol, and trans-GB diffusivity of 5×10^{-15} m²/s. During the simulation, the circular grain shrinks, resulting in an increase in the driving pressure with a decrease in the radius of curvature. Fig. 4.7b shows that the velocity of the interface agrees reasonably well with the analytical solution.

Grain boundary properties such as GB energy modify the force balance at triple junctions. A three-grain geometry is used with constant flux boundary conditions. The grain boundaries indicated with γ_{12} , γ_{13} , and γ_{23} have grain boundary energies of 1, 1, 0.5 J/m² respectively, and are considered to be isotropic in the other case. Fig. 4.8 shows the equilibrium structure for these anisotropic cases, where the analytical triple junction angles, i.e. 151° and 120° are in agreement with the phase-field simulations, i.e. 154° and 120°, respectively [221].

4.7 Mean field modeling of grain growth

Phase field simulations and, consequently, the average grain size evolution considering anisotropic segregation energy is rationalized using a mean-field grain growth model. For curvature-driven grain growth, the grain growth rate, i.e., the change in average grain radius (\overline{R}) with respect to time, is commonly described as the product of the representative GB mobility and the driving pressure which can be written as,

$$\frac{\partial \overline{R}}{\partial t} = k_1 M_{rep} \left(\frac{k_2 \gamma_{rep}}{\overline{R}} - k_3 \Delta G_{SD, rep} \right)$$
(4.31)



Figure 4.8: Equilibrium triple junction geometry for two cases (a) anisotropic energy where $\gamma_{12} = 1 \text{ J/m}^2$, $\gamma_{13} = 1 \text{ J/m}^2$, $\gamma_{23} = 0.5 \text{ J/m}^2$ and, (b) isotropic grain boundary energy.

where k_1 , k_2 and k_3 are scaling constants, γ_{rep} is the representative grain boundary energy, M_{rep} is the representative mobility, and $\Delta G_{SD,rep}$ is the solute drag pressure, given by Eq. (4.7), due to an impurity and/or alloying element with a representative segregation energy (E_{rep}) . For ideal grain growth with isotropic GB mobilities and no solutes, Eq. (4.31) leads to the well-known parabolic grain growth relationship with a geometrical constant $k (= 2k_1k_2)$, i.e., $\overline{R}^2 - \overline{R}_0^2 = kM_{rep}\gamma_{rep}t$, where \overline{R}_0 is the initial average grain radius. As shown by Shahandeh and Militzer [222], k_2 is determined using the product of the average grain radius and the average curvature in the microstructure, whereas k, and subsequently, k_1 is obtained from the slope of $\overline{R}^2 - \overline{R}_0^2$ vs. time from ideal grain growth simulations.

In the presence of solutes, grain boundaries may transition from the highvelocity to the low-velocity limit depending on the local curvature distribution in the microstructure such that only a few GBs are loaded with solutes and migrate slowly, whereas others move independently of the solute concentration. In this regime, an averaged distribution of the solute drag pressure that is a function of local GB velocity distributions in the microstructure is different than the solute drag pressure due to the average grain growth rate in the phenomenological grain growth model. As a result, a scaling constant k_3 is added to the phenomenological model that incorporates the differences due to the different averaging techniques.

Chapter 5

Solute drag assessment of grain boundary migration in Au

5.1 Introduction¹

The primary aim of this chapter is to rationalize the migration of a specific grain boundary (GB) using the Cahn-Lücke-Stuwe (CLS) solute drag model, highlighted in Section. 2.2.3, in combination with the Density Functional Theory (DFT) calculations. For this work, the available experimental data on GB migration in ultra-pure Au [60] is utilized where a 30°<111> tilt GB migrated during recrystallization heat treatments at different temperatures ranging from 500-610 K such that the apparent activation energy for GB migration varied with temperature as shown in Fig. 2.4. The deviation was attributed to the segregation of Fe that was present in 20 ppm, but there were also other solutes present at lower concentration levels, in particular 2 ppm Bi, that were considered to have negligible effects on GB migration. In contrast, Scheiber [223] found in a recent DFT study on binding energies to the $\Sigma 5(021)[100]$ tilt GB in Au that Bi is the strongest segregant fol-

¹The results presented in this chapter have been published. See A. Suhane, D. Scheiber, M. Popov, V. I. Razumovskiy, L. Romaner, M. Militzer, Solute drag assessment of grain boundary migration in Au, *Acta Materialia* **224** (2022) 117473.

lowed by Al, while all other impurities present in the experimentally investigated ultra-pure Au including Fe showed either weak or anti-segregation tendencies. Al exhibited attractive segregation with weaker binding energies compared to Bi. Given that the concentration of Al (0.5 ppm) in the Au sample is lower than that of Bi, the role of Al is assumed to be negligible. Thus, the effect of Fe and Bi on the observed GB migration rates is investigated in the present analysis. First, DFT calculations are performed to quantify the binding energies of Fe and Bi to the $\Sigma 13(134)$ [111] GB in Au which is close to the experimental GB and also accessible to DFT calculations. Further, activation energies for solute diffusion across the GB are determined with DFT calculations. Note that the above-mentioned DFT calculations are performed by Dr. Daniel Scheiber and Dr. Maxim Popov, respectively, at Materials Center Leoben in consultation with all the authors in [224]. An approach to translate the solute binding energies determined from DFT calculations to the effective segregation energy, E, in the CLS model is proposed based on the GB enrichment. The concluded parameters from DFT calculations are compared to those obtained from the conventional CLS solute drag model and the uncertainties of the proposed analysis are critically discussed.

5.2 Binding energy of solutes

Different GB sites in the $\Sigma 13(13\overline{4})[111]$ GB are shown in Fig. 4.1, and Fig. 5.1 shows the binding energy of solutes, Fe and Bi, as a function of the Voronoi volume of the corresponding GB sites normalized by the site volume of bulk Au. Bi has significantly larger binding energies than Fe, similar to what was obtained in the previous study for a $\Sigma 5$ tilt GB [223]. Interestingly, most of the sites are repulsive for Fe, whereas all the GB sites are attractive for Bi. This difference can be attributed to the atomic size of solutes and can be rationalized using the Eshelby model for segregation [223, 225]. Bi has a larger atomic size than Au whereas Fe is a smaller atom than Au [226]. Ignoring electronic contributions, oversized solutes release strain energy at sites with excess volume whereas smaller solutes prefer GB sites which have a smaller volume compared to the bulk. It can



Figure 5.1: DFT calculated binding energies to different sites in the $\Sigma 13$ GB for Fe and Bi as a function of the normalized Voronoi volume. Bi interactions refer to a case where sites 1 and 2 are substituted with Bi atoms, and the segregation energy corresponding to Bi segregation at other GB sites is calculated. (Courtesy of Dr. Daniel Scheiber)

be observed from Fig. 5.1 that all the GB sites have excess volume compared to the bulk, and site 1 with the largest excess volume is found to be the strongest segregating site for Bi which is also the most repulsive site for Fe.

For Bi, multiple GB sites, i.e., sites 1, 2, 3, 4 have appreciable binding energies. Simultaneous Bi occupancy of each GB site will, however, deviate from the dilute limit approximation. Thus, the influence of Bi-Bi interactions on the binding energies is determined at these sites. To investigate the Bi-Bi interactions at the GB, the most favorable site (site 1) is substituted with Bi, and then the binding energy at an additional GB site is computed using the approach described in Appendix A.2. In this analysis, the next favorable site after site 1 is site 2 which is found to have the same binding energy as without Bi interaction. For further interaction of Bi with occupied GB sites, site 1 and 2 are substituted with Bi, and the binding energy for the third Bi atom to other GB sites is calculated using Eq. (A.4). The addition of a third Bi atom to the GB results in strong repulsive

interactions such that the magnitude of binding energies for most additional sites is significantly reduced. As shown by the open symbols in Fig. 5.1, the strongest binding energy for GB sites other than sites 1 and 2 is now -0.3 eV whereas it would be -0.8 eV if Bi-Bi interactions were not considered.

5.3 Effective segregation energy from DFT calculations

5.3.1 GB enrichment

While the DFT calculations provide binding energies at T = 0 K, the concentration of solute atoms at a GB site *i* at elevated temperatures is determined from Eq. (4.2). The total number of solute atoms per area is obtained by summing over the concentrations for all the GB sites and taking its projection at the GB plane. The contribution of each GB site towards the GB enrichment and of Bi considering Bi-Bi interactions is shown in Fig. 5.2. Note that the enrichment due to GB



Figure 5.2: Total GB excess and contribution from individual GB site as a function of temperature using binding energies calculated from DFT at T = 0 K for Bi with interaction.

sites 3, 4, 6, and 7 as shown in Fig. 4.1 is added twice to obtain the total GB enrichment. The probability of occupancy of a GB site increases with decreasing temperature. Depending on the magnitude of the binding energy, each site is completely occupied below a critical temperature. Only sites 1 and 2 are completely occupied in the temperature range of interest, i.e. 500 - 610 K, and lead to a significant GB enrichment of ~ 5 atoms/nm². Note that the interactions are negligible for these two sites. On the other hand, Fe has weak segregation and anti-segregation tendencies at the GB. The strongest binding energy of Fe (to site 6) is comparable to that for Bi with interactions to site 3 (see Fig. 5.1). Fig. 5.2 indicates significant GB enrichment at site 3 for Bi only below 200 K. As a result, GB enrichment of Fe is negligible in the temperature range of interest and would suggest a negligible solute drag due to Fe segregation on GB migration in Au.

Uncertainties in the predicted GB enrichment may result from the uncertainties in DFT calculations. Comparing several DFT studies on identical GBs and solute species shows a variation in binding energies depending on the simulation setup, i.e. different k-points, energy cutoff etc. [227–230]. For example, Scheiber et al. [227] and Wu et al. [228] reported binding energies of Re in W at different sites in $\Sigma 3(111)[1\overline{10}]$ GB with a 15% difference in their magnitude. Assuming a $\pm 10\%$ variation in individual site binding energies, the uncertainty range for the GB enrichment of Bi is determined as shown by the shaded area in Fig. 5.2. The predicted GB enrichment does not vary in the experimental temperature range, 500-610 K, and therefore the numerical uncertainties related to the binding energy calculations from DFT can be excluded in the further analysis.

5.3.2 Effective segregation energy

For a triangular potential used in the CLS formalism, the total solute excess across the grain boundary that is responsible for solute drag pressure can be obtained from Eq. (4.5). It depends on *E*, GB width $(2\delta_{SD})$ and bulk composition of solute (c_0). The GB width is identified as 6 Å from the ground state GB structure shown in Fig. 4.1. Using the GB enrichment concluded from DFT calculations (see Fig. 5.2) and considering 2 ppm as the bulk concentration for Bi, E is shown to vary as a function of temperature in Fig. 5.3. For the experimental temperature



Figure 5.3: Effective segregation energy for Bi in CLS model for equal enrichment as obtained from White-Coghlan model [46] using the binding energies determined from DFT calculations.

range, *E* is estimated to vary between -0.59 to -0.72 eV. GB width, however, can also be defined based on the state of GB segregation, i.e. only GB sites 1 and 2 are occupied in the experimental temperature range, and both sites are located in the habit plane. Considering the lattice parameter as the GB width, the effective segregation energy varies between -0.60 to -0.74 eV.

5.4 Activation energy for solute diffusion

Apart from the effective segregation energy, solute diffusion also plays an important role in the solute drag theory. DFT calculations have been performed to quantify the activation energies for Bi diffusion in Au both in the bulk and at the GB. Bi is a substitutional solute and is considered to diffuse by a vacancy-mediated mechanism. For bulk diffusion, the activation energy is the sum of vacancy formation energy, vacancy-solute binding energy, and migration energy. Using the bulk supercell for Au, the calculated values for these three energies are 0.68 eV, -0.30 eV, and 0.46 eV, respectively, such that an activation energy of 0.84 eV is predicted for Bi diffusion in the Au FCC lattice.

The situation at the GB and its vicinity is much more complex as a multiplicity of different diffusion paths would have to be considered. Thus, the determination of the activation energy for solute diffusion across the GB using DFT is an expensive and challenging task. Considering that the solute atmosphere lags behind the migrating interface, the solute-vacancy jumps contributing to the fastest migration path are investigated for a Bi atom to travel from a bulk site to site 1 in the GB, i.e. the strongest segregating site. Significant reconstructions are observed due to the introduction of vacancies at a few GB sites which is consistent with the observations of vacancy instability in several high-energy GBs in Cu [133, 231]. Only the migration paths which are stable with respect to solute-vacancy exchanges are considered. The activation energies for each Bi jump along the considered migration paths from a bulk site to site 1 are given in Table 5.1. Here, as expected, each activation energy has a different value. In general, these values are lower than the activation energy for bulk diffusion even though in one case a higher value is predicted. From Table 5.1, it can be inferred that B2-7-1 is the fastest migration path among all the solute-vacancy exchanges investigated in the present study. The activation energies for individual jumps along this migration path are 0.54 and 0.59 eV, respectively.

Noting that different atomic jumps are possible in the vicinity of the grain boundary, and realizing the uncertainty about the starting site for the migration path constitutes a fundamental challenge to quantify the effective activation energy for trans-grain boundary diffusion in the solute drag model. For the abovementioned fastest diffusion path, one could conclude that the 0.59 eV is rate limiting, but if in addition, a jump from another bulk site into site B2 were needed, the activation energy for bulk diffusion would be rate limiting. Thus, the present DFT simulations would suggest an effective activation energy for the trans-grain boundary diffusion of Bi to fall into the range of 0.59 to 0.84 eV.

Table 5.1: Diffusion activation energies for individual jumps for different migration paths. Here sites 1, 4, 6, 7 are GB sites, and B1, B2 are bulk sites in Au GB indicated in Fig. 4.1.

	E_a	E_a	
Diffusion path	for first jump	for second jump	
_	(eV)	(eV)	
B1-6-1	0.58	1.04	
B1-4-1	0.68	0.67	
B2-7-1	0.54	0.59	

5.5 CLS solute drag analysis

5.5.1 Phenomenological parameters

DFT calculations indicate that Fe leads to negligible GB enrichment, whereas Bi has significant GB enrichment in the experimental temperature range. Grünwald and Haessner [60] did not realize that Bi is the decisive element for solute drag. As a result, the experimental GB migration rates are re-examined based on the CLS solute drag model considering Bi segregation to obtain the corresponding fit parameters, effective segregation energy, and trans-GB solute diffusivity.

According to Eq. (4.7) and Eq. (4.10), reasonable estimates of intrinsic mobility and driving pressure, along with the effective segregation energy and trans-GB solute diffusion, are essential to describe the GB velocity at a given temperature. Grünwald and Haessner [60] indicated that the driving pressure was constant at all investigated temperatures. They estimated an order of magnitude of the driving pressure as 10 cal/mol (43 J/mol) which is consistent with the typical range of driving pressure in cold-worked metals (10 - 100 J/mol) [52]. Having the driving pressure quantified and assuming negligible solute drag in the high-temperature regime permits one to estimate the intrinsic mobility. From Fig. 5.4, the activation energy for the intrinsic GB mobility, M_{int} , is obtained as 85 kJ/mol (0.88 eV). Then, the pre-exponential factor is determined to be 5 × 10⁻⁷ m⁴/Js. The



Figure 5.4: Comparison between the experimental GB migration rates with the CLS solute drag model considering Bi segregation.

estimated intrinsic mobility is consistent with the literature data. Würschum and Balluffi [232] investigated the migration of a high angle near- Σ 5 grain boundary in an Au bicrystal using in-situ transmission electron microscopy and concluded a grain boundary mobility with a pre-exponential factor of 9.5 × 10⁻⁷ m⁴/Js, and an activation energy of 0.82 eV. Further, an activation energy of 0.88 eV is also obtained as the activation energy for grain boundary self-diffusion in Au [233].

Using the above intrinsic mobility and driving pressure as well as the GB width concluded from DFT (0.6 nm), Eq. (4.7), Eq. (4.8), Eq. (4.9) and Eq. (4.10) can be combined to determine the GB velocity as a function of temperature with appropriate values of E, D_0 and Q_d where D_0 , Q_d are the pre-exponential factor and the activation energy for solute diffusion, respectively. Using least-square error analysis, the best fit of the experimental velocity data is obtained for effective segregation energy E = -0.69 eV, and a trans-GB solute diffusivity $D = 1.2 \times 10^{-11} \exp(-0.61 \text{ eV}/k_BT) \text{ m}^2/\text{s}$, as shown in Fig. 5.4. The resulting so-

lute drag pressure for 2 ppm Bi addition is displayed as a function of GB velocity in Fig. 5.5 for three different temperatures representing three velocity regimes in Fig. 5.4, i.e., high (> 590 K), low (< 568 K) temperature, and the intermediate transition region. It is evident from Fig. 5.5 that both the actual and the peak solute drag pressure increase with a decrease in temperature. The effect of solute diffusion on the temperature dependence of the velocity corresponding to peak solute drag pressure can also be inferred from Fig. 5.5. A decrease in solute diffu-



Figure 5.5: Solute drag pressure as a function of velocity for three experimental temperatures assuming $E_0 = -0.69$ eV, and $D = 1.2 \times 10^{-11} \exp(-0.61 \text{ eV}/k_B T) \text{ m}^2/\text{s}$. The solute drag pressure at each temperature for the velocity predicted from the CLS model is shown by solid circles.

sivity due to a decrease in temperature lowers the velocity at which the solute drag pressure peak occurs. Alternatively to Fig. 5.4, the GB velocity is displayed as a function of driving pressure in Fig. 5.6. At each temperature, the high-velocity regime, transition regime, and low-velocity regime can be identified as a function of driving pressure. In the high-velocity limit, the GB velocity is independent or has a negligible effect due to solute drag. In the low-velocity limit, the GB velocity limit, the GB velocity is controlled by the solute diffusivity across the GB. It can also be observed



Figure 5.6: Velocity as a function of driving pressure for three experimental temperatures. The applied driving pressure of 43 J/mol is shown by the dash-dotted line.

that the transition from high to low velocity exists for a narrow range of driving pressure. This representation provides further evidence for the narrow transition temperature range, i.e. 568 - 590 K in the present case.

5.5.2 Uncertainty analysis

Grünwald and Haessner [60] arrived at an order of magnitude for the driving pressure as 43 J/mol. Thus, it is critical to investigate the dependence of the CLS model parameters on the magnitude of driving pressure. For this purpose, the above driving pressure is increased and decreased, respectively, by 50% such that a driving pressure range of 22 - 64 J/mol is considered to identify the uncertainties in the CLS model parameters. The pre-exponential factor of the intrinsic mobility scales inversely with the driving pressure in order to replicate the GB velocities in the high-temperature region. The CLS parameters for different driving pressure assumptions are obtained by least-square fitting and summarized in Table 5.2. It can be observed that E, which determines the solute drag pressure, scales with the

driving pressure. Trans-GB diffusivity, on the other hand, remains comparatively insensitive to the driving pressure. The activation energy does not vary significantly (<5%) with the assumed driving pressure whereas the pre-exponential factor scales with the driving pressure but remains of the same order of magnitude.

$\Delta G (J/mol)$	$M_0 ({ m m}^4/{ m Js})$	<i>E</i> (eV)	$D_0 ({\rm m^2/s})$	Q_d (eV)
22	9.8×10^{-7}	-0.63	1.0×10^{-11}	0.63
43	5×10^{-7}	-0.69	1.2×10^{-11}	0.61
64	3.4×10^{-7}	-0.72	1.8×10^{-11}	0.61

Table 5.2: Variation in fit parameters $(M_0, E, D_0, \text{ and } Q_d)$ for different estimates of driving pressure.

Further, the migration rates were experimentally determined by identifying the location of the grain boundary for different temperatures using a light microscope. Considering the experimental scatter of GB velocity as 10%, a reasonable agreement with experimental GB migration rates is achieved for several values of solute diffusion coefficients, where D_0 ranges from $10^{-10} - 10^{-11}$ m²/s and Q_d varies between 0.61 eV to 0.74 eV. *E*, on the other hand, has a negligible variation (<5%) when considering the scatter in GB velocity and is found to scale primarily with the driving pressure.

5.6 Comparison of CLS parameters with DFT predictions

5.6.1 Effective segregation energy

Based on the above analysis, it can be seen that *E* derived from DFT calculations (-0.59 to -0.72 eV, see Fig. 5.3) falls essentially into the same range as the values obtained in the CLS solute drag model (-0.63 to -0.72 eV, see Table 5.2). The CLS solute drag analysis suggests that a constant *E* reproduces the experimental GB migration rates. In contrast, *E* determined from DFT calculations, i.e., Fig. 5.3,

indicates a temperature dependence of E such that it decreases with increasing temperature. In the former, the approximate solute drag pressure, i.e., Eq. (4.7) deviates from the exact solution of Eq. (2.3) for non-dilute conditions at the grain boundary, and using the exact solution may introduce temperature dependence in E. Further, in the DFT based analysis, the temperature dependence of E originates due to constant GB enrichment in the experimental temperature range as shown in Fig. 5.2. While GB excess determined from DFT calculations consider site-saturation, the CLS model, i.e., Eq. (4.6) is determined assuming the dilute limit at the grain boundary, i.e. without accounting for site-saturation. The CLS model, as a result, will provide an upper limit on the effective segregation energy.

In addition, DFT calculations in this study provide binding energies at T = 0 K whereas the binding energies or the Gibbs free energy of segregation (ΔG_{seg}^i) for site *i* at higher temperatures can be written as,

$$\Delta G_{seg}^{i} = E_{seg}^{i} - T\Delta S_{ex}^{i} + P\Delta V_{seg}^{i}$$
(5.1)

where, E_{seg}^{i} is the change in internal energy determined from the atomistic calculations at T = 0 K, ΔS_{ex}^{i} is the segregation entropy excluding the configurational entropy, P is pressure, and ΔV_{seg}^{i} is the change in volume when a substitutional solute is moved from the bulk to the grain boundary site. This formulation is appropriate because the configurational entropy is accounted for in the Langmuir-Mclean [41] or White-Coghlan [46] type of mixing models of segregation. The last term, $P\Delta V_{seg}^{i}$, is negligible for solids [234]. ΔS_{ex}^{i} , on the other hand, can be composed of vibrational, electronic, and magnetic entropy changes where the vibrational entropic contributions are expected to have a measurable impact on the segregation phenomenon [14], and, as a result, will also influence the effective segregation energies which is ignored in the present analysis. To the best of our knowledge, the vibrational entropy of Bi in Au GB is not available. Seah and Lea [235] analyzed the order of magnitude for vibrational entropy of Sn segregation in BCC Fe and arrived at a value of $4k_B$, where k_B is the Boltzmann constant. Other phenomenological studies based on experimental observations indicate the typical range of vibrational entropy for substitutional solutes to be within $\pm 10k_B$ [236, 237]. As a result, we performed a sensitivity analysis of *E* for a reasonable range of vibrational entropy (ΔS) where, for simplicity, we consider all the sites to have identical ΔS , and the term E_{seg}^i in Eq. (4.2) is replaced with $E_{seg}^i - T\Delta S$. Fig. 5.7 shows that a negative vibrational entropy is essential to reduce the effective temperature dependence of *E*. Based on the segregation entropy of -3.5k_B for Bi segregation in Cu determined by Divinski et al. [238], Bi in Au can indeed be expected to have a negative vibrational segregation entropy.



Figure 5.7: *E* variation with temperature for different vibrational entropy.

5.6.2 Trans-GB diffusion

The activation energy for solute diffusion obtained from an independent CLS solute drag analysis, i.e., 0.61 eV agrees with the activation energy of 0.59 eV determined for the fastest migration path from DFT calculations. This suggests that B2-7-1 is indeed a representative diffusion path for solute diffusion during GB migration. However, a good agreement between the activation energy determined from the DFT calculations and the CLS analysis should be interpreted with caution. The trans-GB diffusion coefficients obtained from the CLS solute drag analysis are strictly effective GB parameters. The DFT calculations, on the other

hand, provide only information on the activation energies for individual jumps at the stationary GB. Dynamic simulations such as Molecular Dynamics or Kinetic Monte Carlo would be required to evaluate an effective diffusion coefficient quantitatively. In this context, it is useful to refer to the simulation study of Cu self-diffusion in several high-coincidence GBs by Suzuki and Mishin [133], who demonstrated using hybrid Molecular Dynamics simulations that the effective activation energy is always higher but remains close to the fastest solute-vacancy exchange at the GB. While there are uncertainties in the merit of the quantitative DFT values for activation energies, the present analysis suggests that the activation energy of trans-GB diffusion of Bi is closer to the GB diffusion of Bi instead of the bulk diffusion.

The above is also further corroborated when assessing the magnitude of the pre-exponential factor for solute diffusion obtained from the CLS analysis. For bulk diffusion in a typical FCC metal, D_0 is about ~ 10^{-4} m²/s [239] but in the CLS analysis, a much smaller value of order 10^{-11} m²/s is obtained. Indeed for GB diffusion one may expect a smaller pre-exponential factor due to softer phonon modes. For example, Suzuki and Mishin [133] obtained a wide range of pre-exponential factors from their simulations of self-diffusion of Cu in different grain boundaries. In particular, they reported a pre-exponential factor of 4×10^{-9} m²/s for diffusion in a Σ 13 tilt GB, i.e. a GB which is similar to that investigated in the present study. As a result, one may consider the obtained pre-exponential factors for trans-GB diffusion of Bi in Au to be of reasonable magnitude. However, a quantitative comparison between the trans-GB diffusivity of Bi in Au with the bulk and GB diffusion is, at present, not possible due to the absence of any experimental data.

5.7 Summary

In the present study, the solute-affected grain boundary migration in Au is examined with the classical solute drag model of Cahn, Lücke, and Stüwe (CLS) and further rationalized with the solute-grain boundary interactions using DFT calculations. In particular, binding energies of solutes to the grain boundary sites determined from DFT calculations indicate Bi as the strongly segregating solute in Au compared to the other impurities present in the investigated Au sample. Based on the grain boundary enrichment, an approach is presented to determine the effective segregation energy of Bi. Further, DFT calculations are performed to determine the activation energy for Bi diffusion in the vicinity of the grain boundary and in the bulk. The effective segregation energy and the representative activation energy for Bi diffusion obtained from DFT calculations are found to be consistent with the CLS solute drag model. Several sources of uncertainties from both experimental and simulations are investigated, where, two quantities, i.e., the vibrational entropy and the quantitative determination of trans-GB diffusivity in the CLS solute drag model are currently, either inaccessible, or extremely expensive to determine from DFT calculations.

Even with these uncertainties, the proposed approach of predicting ranges of effective segregation energies from DFT using GB enrichment is a powerful methodology to link atomistic scale simulations with the phenomenological solute drag models that may be useful in identifying the solute trends on migration rates of grain boundaries in different systems. The latter is essential for describing grain growth and recrystallization where, however, in general the migration of a multiplicity of different grain boundaries is involved. In detail, the binding energies vary from boundary to boundary as documented with a number of DFT calculations for grain boundaries in W, Fe, and Au but the trends of ranking solutes in terms of their segregation strength are expected to be independent of the type of boundary for a given host metal [112, 210, 225, 228]. As a result, the binding energy analysis is of significant merit for trend predictions with important implications for alloy development where high-throughput DFT calculations can be used for the appropriate selection of solutes to optimize microstructural control during thermomechanical processing.

Chapter 6

Representative grain boundaries during anisotropic grain growth

6.1 Introduction¹

Most metals and alloys are polycrystalline and contain multiple grain boundaries (GBs) with anisotropic GB properties, such as mobility and energy, that evolve during grain growth. Furthermore, the presence of impurities can modify the migration rates of grain boundaries due to solute drag as discussed in the previous chapter. Several experimental and theoretical studies have shown that the solute segregation and drag vary with the GB structure. Despite the anisotropy, experimental grain growth kinetics can be reasonably described using representative GB properties for normal grain growth conditions where the grain size distribution follows a unimodal grain size distribution. The representative grain boundary properties in these studies, however, are empirical and determined by fitting to grain growth experiments.

As highlighted in Sec. 2.5.1, a variety of computational methods such as Phase

¹The results presented in this chapter have been published. See A. Suhane, M. Militzer, Representative grain boundaries during anisotropic grain growth, *Computational Materials Science* **220** (2023) 112048.

field, Monte Carlo, Cellular Automata have been used to simulate grain growth in both two and three dimensions. Curvature-driven grain growth in three dimensions is quantitatively different than in two dimensions due to the additional curvature component in the former that modifies the driving pressure for grain boundary migration. However, grain growth kinetics in terms of average grain size in three dimensions can be rationalized using two dimensional simulations by introducing a correction in the grain boundary mobility [222]. Grain boundary migration in the presence of segregated solutes can also be interpreted using effective mobilities, and therefore, two-dimensional simulations are sufficient to evaluate the qualitative role of solutes on grain growth kinetics. In contrast, three dimensional simulations are necessary to account for particle pinning during grain growth.

This chapter aims to quantify the representative GB properties from the anisotropic GB property distributions, particularly GB mobility and solute drag, in an initial non-textured microstructure. As a result, two-dimensional phase field simulations with friction pressure, as highlighted in Sec. 4.6.2, are utilized to investigate the role of (1) anisotropic mobility, (2) anisotropic solute drag, and (3) combined anisotropic mobility and solute drag on the average grain size evolution. A corresponding "representative GB" is introduced for each case considering a phenomenological grain growth model that fits the simulated average grain size evolution. A relationship is proposed to determine the representative GB properties for an arbitrary distribution of anisotropic GB properties in the initial microstructure. A detailed discussion is presented for the choice of the representative grain boundary properties for different initial GB property distributions.

6.2 Anisotropy in grain boundary properties

Grain boundary properties vary with GB structure that has five degrees of freedom. However, a complete description of GB properties is, at present, lacking. In this study, the GB properties are assumed to vary with the disorientation angle. Similar dependence has been used in the past to separate high-angle and low-angle grain boundaries, e.g., by Read-Shockley [240] and Huang-Humphreys [241] for GB energy and GB mobility, respectively. Analogous to the previous studies on anisotropic grain growth [161, 180, 184], the disorientation dependence is used in this study as a pragmatic approach to distribute anisotropic GB properties in the microstructure. The disorientation angle, $\Delta\theta$, between grain *i* and *j* is the minimum misorientation angle among the 24 geometrically equivalent representations for a cubic material in Bunge's convention [242], and is determined as

$$\Delta \theta = \min \left| \cos^{-1} \left\{ \frac{tr(O_{432} \Delta g_{ij}) - 1}{2} \right\} \right|$$
(6.1)

where, O_{432} is the symmetry operator for cubic crystal structure given in [243]. Δg_{ij} is the rotation matrix given as,

$$\Delta g_{ij} = g_i g_j^{-1} \tag{6.2}$$

where, g_i and g_j are the orientation matrix for grain *i* and *j* respectively. For a grain represented using three Euler angles, ψ_1 , θ_1 , and ψ_2 , the orientation matrix is given as:

$$g = \begin{bmatrix} \cos\psi_1 \cos\psi_2 - \sin\psi_1 \sin\psi_2 \cos\theta_1 & \sin\psi_1 \cos\psi_2 - \cos\psi_1 \sin\psi_2 \cos\theta_1 & \sin\psi_2 \sin\theta_1 \\ -\cos\psi_1 \sin\psi_2 - \sin\psi_1 \cos\psi_2 \cos\theta_1 & -\sin\psi_1 \sin\psi_2 + \cos\psi_1 \cos\psi_2 \cos\theta_1 & \cos\psi_2 \sin\theta_1 \\ \sin\psi_1 \sin\theta_1 & -\cos\psi_1 \sin\theta_1 & \cos\theta_1 \\ & & (6.3) \end{bmatrix}$$

In this study, three random Euler angles are generated for each grain in the microstructure, and the disorientation angle is calculated for each grain boundary. For a cubic polycrystalline material, this leads to a distribution that resembles the Mackenzie distribution [244] in disorientation space, as shown in Fig. 6.1a. In this study, two different disorientation-dependent functions are used to introduce anisotropy in GB properties. Unless stated otherwise, the same anisotropic functions are investigated for both GB mobility, M, and GB segregation energy, E, in the present simulations by using their maximum and minimum values, M_{max} ,


Figure 6.1: (a) Probability density of disorientation angle in the initial microstructure that resembles the Mackenzie distribution. [244]. (b) The fraction of grain boundaries (f_s) with low mobility/segregation energy as a function of critical disorientation angle considering step distribution. An example of $f_s = 0.5$ for $\Delta \theta_c = 42^\circ$ is shown with dashed lines.

 M_{min} and E_{max} , E_{min} , respectively, that are interchangeable in the relations below.

1) <u>Step distribution</u> - a critical threshold disorientation angle $(\Delta \theta_c)$ is defined such that the grain boundaries with smaller disorientation than $\Delta \theta_c$ are low mobility (M_{min}) GBs as opposed to high mobility (M_{max}) GBs that have a larger disorientation angle than $\Delta \theta_c$.

$$M = \begin{cases} M_{min} & \text{if } \Delta \theta < \Delta \theta_c \\ M_{max} & \text{if } \Delta \theta \ge \Delta \theta_c \end{cases}$$
(6.4)

In this approach, the choice of a critical disorientation angle determines the fraction of high and low mobility boundaries in the microstructure according to the associated Mackenzie-like texture distribution. Fig. 6.1b shows the fraction of low mobility grain boundaries (f_s) as a function of $\Delta \theta_c$ where for example $\Delta \theta_c = 29^\circ$, 42°, 49° corresponds to $f_s = 0.2$, 0.5, 0.8, respectively. The strength of anisotropy for GB mobility is characterized by the mobility ratio, $r = M_{max}/M_{min}$. An analogous distribution is defined for segregation energy distribution such that E_{max} corresponds to GBs with a high effective segregation energy, whereas E_{min} refers to GBs with a low effective segregation energy, and f_e corresponds to the fraction of grain boundaries with low effective segregation energy. In this case, the segregation anisotropy is quantified in terms of relative changes, i.e., $\Delta E = (E_{max} - E_{min})/E_{max}$.

2) <u>Gaussian Distribution</u> - a continuous function of disorientation angle where GB properties such as GB mobility (*M*) and effective segregation energy (*E*) are controlled by two variables, i.e., σ and $\Delta \theta_g$,

$$M = M_{max} \exp\left(-\frac{(\Delta\theta - \Delta\theta_g)^2}{2\sigma^2}\right)$$
(6.5)

where M_{max} is the maximum mobility at $\Delta \theta_g$, and σ determines the extent of variability in GB mobility in the microstructure in accordance with the texture distribution. For $\Delta \theta_g = 45^\circ$, $\sigma = 20^\circ$ leads to a minimum mobility of 0.08 M_{max} at a disorientation angle of 0° whereas for $\sigma = 100^\circ$ the minimum mobility is 0.9 M_{max} . Thus, taking $\sigma > 100^\circ$ will result in virtually no anisotropy in GB mobility. An analogous relationship can be defined for effective segregation energy where E_{max} corresponds to the largest segregation energy at $\Delta \theta_g$. Fig. 6.2 shows the frequency of the grain boundary properties in the initial microstructure weighted by the corresponding GB length for different values of σ and $\Delta \theta_g$. Each GB in the microstructure is classified into one of twenty bins to distinguish the fast and slow-moving grain boundaries. Three different cases with $\sigma = 20^\circ$, $\Delta \theta_g = 45^\circ$, and $\sigma = 20^\circ$, $\Delta \theta_g = 60^\circ$, and $\sigma = 10^\circ$, $\Delta \theta_g = 60^\circ$ are shown as Gauss-I, Gauss-II, and Gauss-III, respectively. The length averaged GB property, i.e., mobility (M_{avg}) or segregation energy (E_{avg}), for different cases is determined as,

$$M_{avg} = \frac{\int_{l_{gb}} M(\Delta\theta) \delta l}{\int_{l_{gb}} \delta l} \qquad E_{avg} = \frac{\int_{l_{gb}} E(\Delta\theta) \delta l}{\int_{l_{gb}} \delta l} \qquad (6.6)$$

and indicated with dashed lines in Fig. 6.2. Here, l_{gb} is the total grain boundary length, δl refers to a grain boundary segment, and $M(\Delta \theta)$ and $E(\Delta \theta)$ are GB mobility and GB segregation energy of the grain boundary segment, respectively.



Figure 6.2: Normalized GB mobility/segregation energy distribution for different values of σ and $\Delta \theta_g$. Gauss-I refers to $\sigma = 20^\circ$, $\Delta \theta_g = 45^\circ$, Gauss-II to $\sigma = 20^\circ$, $\Delta \theta_g = 60^\circ$, and Gauss-III distribution corresponds to $\sigma = 10^\circ$, $\Delta \theta_g = 60^\circ$ in Eq. (6.5). Length averaged property for each case is shown with dashed lines with their respective labels of Gaussian distribution.

6.3 Computational details

An initial two-dimensional microstructure is constructed using Voronoi tesselation, where the simulation domain is divided into a 2000 × 2000 grid, and a total of ~18000 grains are created with periodic boundary conditions in all directions. The initial microstructure is allowed to evolve considering ideal grain growth with isotropic grain boundary properties until it reached steady-state conditions. Fig. 6.3 shows the scaled 2D microstructure with ~14000 grains, which is considered as the starting microstructure to study the effect of anisotropic grain boundary properties on grain growth. Each grain in the starting microstructure is assigned a random orientation, i.e., three Euler angles $0^{\circ} < \psi_1$, θ_1 , $\psi_2 < 90^{\circ}$, and disorientation for each pair of grains is computed and stored in a database. Based on Eq. (6.4) and/or Eq. (6.5), anisotropic properties are assigned to the grain boundaries accordingly.

Grain boundaries are discretized in four grid points such that the initial av-



Figure 6.3: Polycrystalline microstructure with an average grain radius of 0.6 μ m in a domain size of 120 μ m \times 120 μ m. Only a quarter of the simulation domain is shown for clarity.

erage grain diameter is five times the grain boundary width for all simulations. Based on the grid size (Δx) of 0.06 µm, the initial average grain size (radius) is 0.6 µm. Grain boundary energy (γ) is considered constant and equal to 1 J/m². The time step (Δt) is fixed to 7.2 µs based on the stability condition. Unless stated explicitly, the maximum GB mobility (M_{max}) and segregation energy (E_{max}) are taken as 5 × 10⁻¹¹ m⁴/Js and 50 kJ/mol at 800°C, respectively, which lies within the range of segregation energies reported for different solutes, e.g., for Nb in BCC Fe [30, 112]. For all the simulations considering impurity segregation, the trans-GB diffusivity is chosen as 3 × 10⁻¹⁶ m²/s [30], and bulk composition (c_0) is considered as 10 ppm (atomic fraction) to stay within the dilute limit at the GB for different segregation energies. According to Cahn [50], a transition from high to low GB velocity depends on the driving pressure, which is related to the average grain size for curvature-driven grain growth [187]. As a result, the grain size is chosen such that a transition from high to low-velocity limit occurs during grain growth for the case of strongly segregated grain boundaries (E_{max}). Appropriate solute drag pressure is determined using the physical GB width of 1 nm in Eq. (4.7) that is different than the artificially wide GB width, i.e., 0.24 μ m, in the phase field simulations.

6.4 Anisotropic grain boundary mobility

First, using isotropic GB mobility in the absence of solutes, ideal grain growth simulations are conducted as a benchmark to determine the scaling constants k_1 and k_2 in Eq. (4.31). Fig. 6.4 shows the square of the average grain radius normalized with the initial average grain radius as a function of time normalized with $\overline{R}_0^2/M_{max}\gamma$ such that the slope corresponds to the geometrical constant k. For 2D grain growth, k is evaluated as 0.35 ± 0.03 , which is in agreement with



Figure 6.4: Normalized average grain size as a function of time normalized with $\overline{R}_0^2/M_{max}\gamma$ considering isotropic and anisotropic grain boundary mobility with no solutes, where f_s is the fraction of low mobility grain boundaries, and r is the mobility ratio between high and low mobility GBs.

the most recent large-scale vertex model (0.36) [165] and phase field simulations (0.35) [181]. Using the approach proposed by Shahandeh and Militzer [222], the constants k_1 and k_2 are obtained as 0.89 ± 0.06 , and 0.20 ± 0.03 respectively. To

reduce the complexity of the phenomenological mean-field model in Eq. (4.31), these scaling constants are assumed to be fixed in the later analysis, whereas a more detailed analysis of the variability of scaling constant, k_2 , with anisotropic mobility is given in Appendix C.1.

Fig. 6.4 also shows the grain size evolution for different choices of mobility ratio (r) and the fraction of low mobility grain boundaries (f_s) in the initial microstructure considering the step distribution. A decrease in grain growth rates with an increase in f_s and r can be observed from Fig. 6.4. Further, a linear relationship indicates that the anisotropic grain growth behavior can be described with the parabolic grain growth relationship using a representative GB mobility. However, further increasing the mobility ratio leads to an appreciable deviation from the ideal grain size distribution, where, in some cases, the average grain size cannot be clearly defined. Liu et al. [182] performed a systematic analysis and indicated that the effect of anisotropic mobility is most pronounced when high and low mobility grain boundaries are present in equal proportions. Fig. 6.5 shows the grain structure for ideal grain growth, r = 10 and r = 100 with $f_s = 0.5$ in the initial microstructure after the initial average grain size has been increased by a factor of 2.5 due to grain growth. In the case of r = 100, few grains grow more rapidly



Figure 6.5: Microstructure for (a) isotropic GB mobility, and two different mobility ratios for equal distribution of low (shown in grey) and high (shown in black) mobility grain boundaries ($f_s = 0.5$) is shown for (b) r = 10 and (c) r = 100 where $\overline{R}/\overline{R}_0 \sim 2.5$.

due to the mobility advantage that results in a longer tail of the grain size distribution in comparison to ideal grain growth. Indeed, the microstructures qualitatively indicate the occurrence of mild abnormal grain growth conditions for r = 100, and therefore, the phenomenological model for normal grain growth may not be applicable for mobility ratios that are equal to or larger than 100. In fact, Liu et al. [182] also suggested that the normal grain growth conditions prevail below a mobility ratio of 50 which is observed in the present simulations as well.

For moderate mobility anisotropy, i.e., r < 50 and considering the step distribution, Eq. (4.31) with no solute drag term is used to determine the representative mobilities (M_{rep}) that describe the average grain size evolution obtained from the phase field simulations. The normalized representative mobility for different combinations of r and f_s is shown in Fig. 6.6a. Kazaryan et al. [245] noted that a



Figure 6.6: (a) Representative mobility for different anisotropy parameters considering step distribution. Average mobility normalized with the maximum mobility (M_{max}) and the predicted mobility from Eq. (6.7) is shown for comparison. (b) Initial fraction vs steady-state fraction of low mobility grain boundaries for mobility ratio (r) = 2, 10, 50.

representative GB mobility can be obtained by averaging the grain boundary mobilities in the microstructure weighted by their GB length. The average mobilities (M_{avg}) simplified from Eq. (6.6), i.e. $f_s M_{min} + (1 - f_s) M_{max}$, normalized with the maximum GB mobility (M_{max}) are also shown in Fig. 6.6a. It can be noted that the representative mobilities obtained from the phase field simulations deviate from the averaged mobilities, and the deviation is strongest for the cases where slow and fast mobile boundaries are in equal proportions. Furthermore, the deviation also increases with mobility anisotropy.

The change in f_s during anisotropic grain growth simulation is quantified in Fig. 6.6b, where the fraction of low mobility grain boundaries in steady-state conditions is determined to be higher than in the initial microstructure. However, the associated decrease in the averaged mobility due to an increase in f_s is insufficient to rationalize the obtained representative mobilities from the phase field simulations. The present results indicate that the low mobility grain boundaries play a dominant role during microstructural evolution. With an increase in the mobility anisotropy, larger grains that may have grown due to their mobility advantage will be surrounded by smaller grains with low mobility grain boundaries that will then dominate the average grain size evolution. As a result, a relationship between the anisotropic GB mobility distribution in the initial microstructure and the representative mobility is determined from the phase field simulations as,

$$\frac{M_{rep}}{M_{max}} = \left(\frac{1}{r}\right)^{1.13f_s - 0.13}$$
(6.7)

Fig. 6.6a shows the predicted mobilities using Eq. (6.7) which replicates the representative GB mobilities obtained from the simulations.

Considering continuous mobility distributions in the disorientation space using Gaussian function, the relationship is extended to determine the representative mobility from anisotropic mobility distributions. Table 6.1 shows the representative mobilities determined from fitting the phase field simulations for three different cases of GB mobility distributions that are shown in Fig. 6.2. To account for the variability in the GB mobility distribution, the grain boundaries with mobility, M_i , in the initial microstructure are classified according to their normalized mobility ($M_{n,i} = M_i/M_{max}$) among 20 bins with a bin size of 0.05 as the normalized mobilities ($M_{n,i}$) can vary between 0 and 1. Accordingly, the GB mobility

Table 6.1: Normalized representative mobilities obtained from the phase field simulations, prediction from Eq. (6.8), and the averaged mobilities for different anisotropy parameters in Eq. (6.5).

Case	Anisotropy		Normalized GB Mobility			
	Parameters		(M/M_{max})			
	σ	$\Delta \theta_{\rm g}$	Simulation	Prediction	Average	
Gauss-I	20°	45°	0.85	0.86	0.84	
Gauss-II	20°	60°	0.58	0.52	0.60	
Gauss-III	10°	60°	0.03	0.11	0.30	

of each bin can be represented by a mobility ratio ($r_i = 1/M_{b,i}$), where $M_{b,i}$ is the average normalized mobility of the bin. The fraction of grain boundaries that occupy a particular bin is denoted by f_i , which is determined for different parameters in Eq. (6.5) and shown in Fig. 6.2. The representative GB mobility is then determined as follows:

$$\frac{M_{rep}}{M_{max}} = \prod_{i=1}^{N_g} \left(\frac{1}{r_i}\right)^{1.13f_i - 0.13/(N_g - 1)}$$
(6.8)

Here, N_g refers to the total number of occupied bins for different parameters that may be smaller than 20 depending on the simulation parameters. For instance, for the step distribution, there are only two types of grain boundaries, and therefore, $N_g = 2$ such that Eq. (6.8) is then consistent with Eq. (6.7). A reasonable agreement can be observed between the predicted representative mobility and those obtained from fitting the phase field simulations for all investigated cases. Length averaged normalized mobilities, M_{avg}/M_{max} that are shown in Fig. 6.2 are also listed in Table 6.1 for comparison.

6.5 Anisotropic grain boundary segregation

The role of solutes on the overall grain growth rates is first benchmarked for a case considering isotropic segregation energy (E) and isotropic mobility (M) for all the grain boundaries considering a bulk solute concentration of 10 ppm. Several

phase field simulations with different initial microstructures, and E = 20, 50, and 100 kJ/mol are used to parameterize the constant k_3 in the phenomenological grain growth model. The square of the normalized average grain radius as a function of normalized time for E = 50 kJ/mol is shown in Fig. 6.7a. In comparison to



Figure 6.7: (a) Normalized average grain size evolution for isotropic and anisotropic GB segregation. E_{rep} determined by fitting the simulation results to the grain growth model, and the corresponding mean grain size evolution is shown with dashed lines. (b) E_{rep} and the average segregation energy from Eq. (6.6) normalized with $E_{max} = 50$ kJ/mol is shown for different simulation parameters.

the case with no solutes, strong retardation in terms of overall grain growth and a deviation from the parabolic relationship can be observed from Fig. 6.7a, which is in agreement with previous studies [52, 192]. In fact, the deviation from the parabolic grain growth relationship is often attributed to the presence of impurities in the sample. In this case, the segregation parameters are chosen such that a transition from high to low-velocity exists for E = 50, 100 kJ/mol but not for E = 20 kJ/mol for the considered grain size. The phase field simulations, i.e., the average grain size evolution, are fitted with Eq. (4.31) considering E_{rep} as E and k_3 as the fit parameter. k_3 is obtained as 0.45 \pm 0.05 for the cases where the transition from high to low velocity occurred due to the increase in the average grain size and 1 otherwise. In the present study, at least a few grain boundaries

are in the transition regime for the anisotropic segregation parameters, and, as a result, k_3 is considered as 0.45 ± 0.05 for all scenarios. More quantitative details about the limits of k_3 and its dependence on the average grain size can be found in Appendix C.2.

The effect of anisotropic segregation energy on grain growth rates is investigated for an otherwise isotropic GB mobility, M_{max} . For step distribution, the segregation anisotropy is quantified using $\Delta E = (E_{max} - E_{min})/E_{max}$ such that for $E_{max} = 50 \text{ kJ/mol}$ and $\Delta E = 0.4$, there are two types of grain boundaries in the microstructure with high/low segregation energy of 50 kJ/mol and 30 kJ/mol, respectively. From Fig. 6.7a, it can be observed that an increase in the segregation anisotropy (ΔE) and the fraction of low segregation energy GBs (f_e) leads to faster grain growth rates. This is because the low segregation energy grain boundaries are less prone to be affected by solutes due to the associated relatively small solute drag pressure. Similar to the anisotropic mobility analysis, it is worthwhile to assess whether a representative segregation energy (E_{rep}) can be defined that describes the grain growth kinetics obtained from the anisotropic phase field simulations. The mean field model with $k_3 = 0.45$ replicates the phase field simulations considering E_{rep} as the fit parameter. As shown with the black dashed lines in Fig. 6.7a, introducing a representative segregation energy does satisfactorily account for the anisotropic segregation energy distribution on the evolution of the mean grain size. Fig. 6.7b shows E_{rep} for different combinations of f_e and ΔE . The average segregation energy (E_{avg}) weighted by the GB length, i.e., $f_e E_{min} + (1 - f_e) E_{max}$ normalized with the maximum segregation energy (E_{max}) is also shown for comparison. Indeed, there is a deviation between the average segregation energy and those obtained by fitting the phase field simulations. The simulations indicate a larger representative segregation energy than the average. This can be attributed to the GBs experiencing higher solute drag pressure that accentuates the dominant role of slow-moving grain boundaries analogous to those observed in anisotropic mobility simulations. However, in detail, the maximum deviation between the average and the representative segregation energies

is ~3 kJ/mol (or 30 meV), comparable to the resolution of segregation energies obtained from experiments or atomistic simulations. For instance, for the case of $f_e = 0.5$ and $\Delta E = 0.6$, the averaged energy is 35 kJ/mol, whereas 38 kJ/mol is determined from fitting the phase field simulations. Further, the final grain size can be another metric to compare the performance of average segregation energy in the mean-field grain growth model with the phase field simulations. For the three anisotropic cases shown in Fig. 6.7a, the deviation between the final grain size obtained from the phase field simulations and the grain growth model with the averaged segregation energies is <3%, which is smaller than the accuracy of typical experimental grain size measurements [11]. As a result, the average segregation energy may be considered appropriate to identify the representative segregation energy from the initial GB segregation energy distribution to describe the grain growth behavior.

Similar to the GB mobility anisotropy considerations in the previous section, the influence of a spectrum of segregation energies on the average grain size evolution is investigated using the disorientation-dependent Gaussian function. Selected simulation results are shown in Fig. 6.8 for different combinations of σ and $\Delta \theta_g$. For each case, the averaged segregation energy, i.e., E_{avg} from Eq. (6.6), is used with the phenomenological grain growth model to determine the mean grain size evolution that is shown in Fig. 6.8 with dashed lines. Regarding the final grain size, a deviation of 3%, 6%, and 5% is determined for Gauss-I, Gauss-II, and Gauss-III, respectively, considering the phase field simulations and the grain growth model with averaged segregation energy. As a result, the average segregation energy can be considered as a representative GB property that can be determined from the GB segregation energy distribution in the initial microstructure.

6.6 Combined anisotropic mobility and segregation

In practice, the GB mobility and segregation energy are anisotropic functions of the GB structure. As a result, it is useful to identify the combined effect of



Figure 6.8: Normalized average grain size evolution for different values of σ and $\Delta \theta_g$. The predictions from the phenomenological grain growth model considering average segregation energy weighted with GB length are shown with dashed lines.

both anisotropies on grain growth. It has been suggested that high mobility grain boundaries have higher excess volume and may, thus, have larger segregation energies [52]. However, a different dependence is observed for various temperatures in Al grain boundaries [14, 246]. It is likely that there is no general correlation between GB mobility and GB segregation energy for a particular solute. As a result, to limit the largely unknown configuration space of structure-dependent mobility and segregation anisotropy, the two functions, i.e., step distribution and Gaussian distribution function, are combined to distribute arbitrary mobility and segregation anisotropy in the microstructure. In total, five cases with varying complexity of GB anisotropy in terms of GB mobility and segregation energy are demonstrated in this study:

- Same functional dependence
 - Case I: Minimal anisotropy. Step distribution with critical disorientation angle of 42° is chosen such that the fraction of low mobility and low segregation energy boundaries, i.e., f_s and f_e is 0.5, mobility ratio (*r*) is chosen as 2 and $\Delta E = 0.2$ for segregation anisotropy.

- Case II: Moderate anisotropy. Step distribution with critical disorientation angle of 42° is chosen such that the fraction of low mobility and low segregation energy boundaries, i.e., f_s and f_e is 0.5, mobility ratio (r) is chosen as 10 and $\Delta E = 0.2$ for segregation anisotropy.
- Case III: Spectrum of segregation energy and mobility. Gaussian distribution for both mobility and segregation energy with $\sigma = 20^{\circ}$ and $\Delta \theta_g = 45^{\circ}$.
- Different functional dependence
 - Case IV: Mobility anisotropy is defined using the step distribution function with $\Delta \theta_c = 42^\circ$ leading to a fraction of low-mobile grain boundaries (f_s) as 0.5 and a mobility ratio of 10. Segregation anisotropy is defined using the Gaussian function with $\sigma = 20^\circ$ and $\Delta \theta_g = 60^\circ$.
 - Case V: Mobility anisotropy is defined using Gaussian function with $\sigma = 20^{\circ}$ and $\Delta \theta_g = 45^{\circ}$ whereas segregation anisotropy is defined using step distribution with a critical disorientation angle of 42° leading to a fraction of low-segregation energy grain boundaries (f_e) as 0.5 and $\Delta E = 0.4$.

Fig. 6.9 shows the average grain size evolution for the above-mentioned cases where a non-parabolic grain growth relationship is, in general, obtained due to the presence of solute drag. The dashed lines show the average grain size evolution using the grain growth model with the predicted representative GB properties, i.e., $E_{rep} = E_{avg}$ from Eq. (6.6) and M_{rep} from Eq. (6.8), for the associated GB property distributions. The predicted representative GB properties correspond to simulations considering individual anisotropies in GB mobility and segregation energies, respectively. Considering Case II as an example, the normalized representative mobility (M_{rep}/M_{max}) without any solute effects is determined as 0.38, whereas the representative (averaged) segregation energy considering isotropic GB mobility is obtained as 45 kJ/mol. As a performance metric, the relative deviation in the



Figure 6.9: Normalized average grain size evolution considering the combined effect of anisotropic mobility and segregation energy anisotropy. The prediction from the grain growth model with representative GB mobility, M_{rep} determined from Eq. (6.8), and representative segregation energy, $E_{rep} = E_{avg}$ determined from Eq. (6.6), are shown with dashed lines.

final grain size, as obtained from the phase field simulations and the phenomenological grain growth model, is determined as 1.8%, 4.6%, 3.8%, 13.2%, and 3% for the cases I through V. The largest discrepancy in the above-mentioned cases is comparable with typical errors reported in experimental grain size measurements, i.e., $\sim 10\%$ [11]. As a result, this reasonable agreement between the phase field simulations and the phenomenological model suggests that the representative GB properties can be identified independently from the anisotropic distribution of grain boundaries in terms of mobility and segregation energy.

6.7 Representative grain boundary properties

The results indicate that the representative GB mobility and representative segregation energy can be superimposed to describe the grain size evolution where both anisotropies in mobility and segregation are considered. Here, the sensitivity of the representative GB parameters is investigated by fitting it to the phase field simulations. Two specific cases, Case I and Case V are chosen to demonstrate the relationship between representative segregation energy and GB mobility, whereas a similar qualitative relationship is found for all the other investigated cases. Different values of E_{rep} and M_{rep} are considered in the phenomenological grain growth model, and the relative average deviation (ε) between the average grain size is determined from the phase field simulations and those predicted from the mean-field model such that:

$$\varepsilon(\%) = \sqrt{\frac{1}{N_t} \sum_{i=0}^{N_t} \left(\frac{R_i^{PF} - R_i^{GG}}{R_i^{PF}}\right)^2 \times 100}$$
(6.9)

where R_i^{PF} corresponds to the average grain size from phase field simulation at time t_i , R_i^{GG} corresponds to the average grain size from the grain growth model at time t_i , and N_t refers to the number of measurements that are used to determine the average deviation. $N_t = 30$ is considered for all the cases in the present study. A relative average deviation, $\varepsilon < 10\%$, corresponds to less than 10% average difference between the phase field simulations and the phenomenological grain growth model.

Fig. 6.10 shows the relative deviation between phase field simulations and phenomenological grain growth model for different values of representative grain boundary mobilities and representative segregation energies for both cases. It can be observed that the average grain size evolution can be described reasonably well ($\varepsilon < 10\%$) by considering multiple combinations of representative segregation energy and GB mobility. Qualitatively, a relationship between M_{rep} and E_{rep} is visible, where high segregation energy and high mobility in the grain growth model balance each other's effect leading to comparable grain growth rates. The relationship between M_{rep} and E_{rep} is, however, different in detail when comparing both cases.

More quantitatively, the relative average deviation for the optimum GB parameters (marked with 'x') is determined as 0.7% and 0.6% for Case I and Case V, respectively. The GB parameters, M_{rep} determined from Eq. (6.8) and E_{rep} from Eq. (6.6), that considered individual anisotropy of either GB mobility or segre-



Figure 6.10: Relative average deviation of the average grain size evolution for (a) Case I (b) Case V. Horizontal dashed lines correspond to the representative mobility predicted from Eq. (6.8) and vertical dashed lines correspond to the representative segregation energy determined from Eq. (6.6). The optimum fit values (x) and superposition of representative GB parameters (●) are also included for comparison

gation energy, respectively, are also indicated with dashed lines, and the superimposed GB parameters (marked with '•') are shown for both cases in Fig. 6.10. The relative average deviation for the superimposed GB parameters is determined as 1.7% and 3.3% for Case I and Case V, respectively. In these cases, the superimposed GB parameters are sufficient to describe the average grain size evolution for the simulations considering combined anisotropies in GB mobilities and segregation energies. Note that the relative average deviation is higher in Case V than in Case I. Case I considers identical step distribution for both GB mobilities and segregation energies, resulting in two groups of high mobility-high segregation energy GBs and low mobility-low segregation energy grain boundaries in the microstructure. The migration rate of grain boundaries increases with an increase in GB mobility and decreases with segregation energy. As a result, the effective anisotropy in migration rates is reduced in Case I due to the compensation of high mobility with high segregation energy and vice-versa. However, in Case V, Gaussian distribution for GB mobility and step distribution for segregation energy may lead to the presence of grain boundaries that have low mobilities and high segregation energy, for instance, for $\Delta \theta > 45^{\circ}$. Such a combination enhances the

anisotropy in migration rates as both GB mobility and segregation energy will reduce the migration rates further compared to GB groups considered in Case I. In these cases, the superimposed representative GB parameters determined from independent anisotropic simulations will lead to a relatively higher deviation from the optimum fit. Thus, the current approach, where the superimposed representative GB properties reasonably describe the grain size evolution, may not be applicable for cases where the combination of GB properties significantly increases the anisotropy in GB migration rates.

6.8 Grain size distribution

As indicated in Sec. 6.4, grain size distribution may change depending on the anisotropy in GB mobility and segregation energy. Fig. 6.11 compares the probability density of grain size normalized with the average grain size for different anisotropy parameters considering a step distribution in mobility and segregation energy. In all the cases, the grain size distribution is determined when the average grain size is increased by approximately a factor of two compared to the initial grain size. The grain size distribution for isotropic mobility with no solute drag follows the a Weibull distribution, given by $\left[\frac{\beta_w}{\alpha_w}\right]\left[\frac{x}{\alpha_w}\right]^{\beta_w-1}e^{-(x/\alpha_w)^{\beta_w}}$ where α_w and β_w are fit parameters, and x is the grain size normalized with the average grain size. Furthermore, adding anisotropy in GB mobility, i.e., r = 50, leads to a preferential growth of a few grains that modifies the tail of the distribution, and as a result, the grain size distribution also deviates from that for ideal grain growth. The anisotropy in segregation energy, i.e., $\Delta E = 40\%$, results in a relatively narrow distribution in comparison to the case of ideal grain growth, in agreement with previous studies that simulated grain growth considering isotropic segregation [187, 247]. The combined anisotropy, however, leads to even fewer grains that are larger than the average grain size compared to the anisotropic mobility simulations, and in this case, the corresponding grain size distribution falls in between the distribution determined from simulations with individual anisotropies.



Figure 6.11: Probability density of grain size normalized with the average grain size for different anisotropy parameters.

6.9 Grain boundary energy anisotropy

Conventional experiments that measure the migration rates of grain boundaries either report the reduced mobilities or absolute mobilities with an implicit assumption of isotropic grain boundary energy [14]. However, it is clear from both experiments and simulations that GB energy is also dependent on the GB structure and therefore affects the grain growth kinetics [248, 249]. Considering identical maximum GB energy, several large scale simulations which included a variability in GB energy have shown an overall decrease in grain growth rates in comparison to simulations with uniform grain boundary energy [180, 183, 184, 250]. As a result, the effect of a fixed reduced mobility anisotropy is examined on the grain growth kinetics and representative GB properties in the absence of solutes by considering anisotropy in GB energy and GB mobility, respectively. Two sets of simulations are performed using the step distribution, such that two types of grain boundaries are present in equal proportion ($f_s = 0.5$) in the initial microstructure. In one case, mobility anisotropy is considered such that the GB mobilities are defined as M_{max} and $M_{min} = 0.5M_{max}$, respectively, with isotropic GB energy $(\gamma_{max} = 1 \text{ J/m}^2)$. In the other case, GB energy anisotropy is considered such that the GB energy for grain boundaries is defined as γ_{max} and $\gamma_{min} = 0.5 \gamma_{max}$, respectively, with isotropic GB mobility (M_{max}). Both simulations, therefore, have an identical reduced mobility anisotropy. To include the GB energy anisotropy, the phase field model proposed by Moelans et al. [169], described in Appendix B, is used that reproduces the force balance between grain boundaries and triple junction angles for moderate GB energy anisotropy. The average grain size evolution as a function of normalized time for both cases is shown in Fig. 6.12. In both



Figure 6.12: Normalized average grain size evolution considering constant anisotropy of 2 in reduced mobility $(M\gamma)$. In both cases, two types of grain boundaries are present in equal proportions in the initial microstructure. A simulation with isotropic reduced mobility is shown for comparison, and representative reduced mobilities are shown with dashed lines.

sets of simulations, a parabolic grain growth relationship is observed indicating that a representative reduced mobility may be defined for each case of anisotropy. However, the representative reduced mobility is found to be dependent on the mobility or GB energy anisotropy, even for otherwise the same reduced mobility anisotropy. The normalized representative reduced mobility, i.e., the slope of \overline{R}^2 with $kM_{max}\gamma_{max}t$, is determined as 0.74 and 0.57 from simulations that considered GB mobility and GB energy anisotropy, respectively. The representative reduced mobility is lower for the case with GB energy anisotropy which affects the driving pressure, whereas GB mobility only affects the kinetics of grain boundary migration. Accordingly, for moderate GB energy anisotropies, either a representative GB energy may be defined from the latter simulations considering uniform GB mobility, or the representative GB mobility may be corrected for the anisotropy in GB energy, i.e., reduced by 20% in the above case when the anisotropy originates from GB energy as opposed to GB mobility. Note that GB energy anisotropy $(\gamma_{max}/\gamma_{min})$ is typically smaller than 2, and a 20% correction in GB mobility is relatively minor in comparison to GB mobility anisotropy that can vary by up to a factor of approximately 50 for normal grain growth conditions.

6.10 Summary

Experimental measurements of grain growth kinetics are traditionally rationalized using empirical grain growth models, which ignore the variability in GB properties. However, both experimental and theoretical approaches have revealed a strong structure dependence of GB properties that may also influence grain growth rates. In this study, the role of anisotropic GB properties, in particular GB mobility and segregation energy, on grain size evolution is investigated using 2D phase field simulations and the grain growth kinetics is rationalized using representative GB properties in a phenomenological grain growth model. In particular, two different disorientation-dependent functions are considered to distribute the anisotropic GB properties, mobility, and segregation energy, during grain growth. The simulations indicate that the well-known parabolic grain growth relationship is recovered for moderate anisotropy in GB mobility, i.e., when the minimum GB mobility is at most a factor of 50 smaller than the maximum GB mobility in the microstructure. In this regime, a relationship is proposed that determines the representative GB mobility from a distribution of GB mobilities in the microstructure. The effect of variability in solute segregation is considered using anisotropic solute drag pressure and segregation energy. Here, a friction pressure approach is used to simulate solute drag effects during grain growth simulations. The average segregation energy can be used in a mean-field grain growth model to describe the average grain size evolution in sufficient agreement with the phase field simulations.

In reality, solute segregation and GB mobility anisotropies coexist, and their

structure dependence is not necessarily correlated. The present simulation study indicates that the representative GB mobility and the representative segregation energy that are determined from independent phase field simulations considering only variability in GB mobility and solute segregation at the grain boundaries, respectively, may be superimposed to describe the average grain size evolution considering combined anisotropy in GB mobility and segregation energy. It should be emphasized that a realistic anisotropy in GB properties is not limited to the parametric distributions considered in the present work, i.e., step distribution and Gaussian distribution. Instead, any arbitrary distribution that corresponds to moderate anisotropy in GB properties may be used. Different distributions, as determined from experimental [251] and/or computational databases [136], can be used, for example, by generating a look-up table for segregation energies and intrinsic mobility as a function of GB disorientation angle. The representative segregation energy and representative GB mobility may be determined for these cases, and the corresponding mean grain size evolution can be verified with the anisotropic phase field simulations.

Chapter 7

Atomistically informed phase field study of austenite grain growth

7.1 Introduction¹

This chapter aims to combine the atomistic details, i.e., the binding energies of solutes to grain boundaries, with the grain growth modeling in the microstructure scale to verify whether a representative grain boundary (GB) can be defined to determine the solute trends that promote grain refinement in austenite. In this regard, DFT-based binding energies for five common alloying elements in steels, Nb, Ti, Mo, V, Mn, in nine different [001] symmetric tilt grain boundaries in FCC-Fe with increasing Σ value from 5 to 41, which is the largest known database for FCC-Fe reported by Ito and Sawada [117], is utilized to determine the variability in effective segregation energy of solutes. Using two-dimensional anisotropic phase field simulations of grain growth, a representative GB is defined, and the solute trends in terms of the solute drag effect for a range of bulk solute additions are discussed in light of the current experimental knowledge.

¹The results presented in this chapter have been published. See A. Suhane, D. Scheiber, V. I. Razumovskiy, M. Militzer, Atomistically informed phase field study of austenite grain growth, *Computational Materials Science* **228** (2023) 112300.

It should be highlighted that the DFT-based binding energies provided by Ito and Sawada [117] covers only a small subset of grain boundaries that exist in the microstructure. As a result, DFT simulations are useful to derive solute trends instead of a quantitative description of grain growth in the presence of solutes.

7.2 Numerical parameters

7.2.1 Solute drag parameters

Two key parameters, effective segregation energy and trans-GB diffusivity are essential to quantify the solute drag pressure due to solutes. The binding energy profiles of solutes in each of the nine GBs are taken from the results reported by Ito and Sawada [117]. As highlighted in Sec. 4.3.1, the maximum surface density from atomistic calculations is determined from N_{GB}/A that varies between 40 - 45 atoms/nm² for all the investigated grain boundaries. Considering the GB width $(2\delta_{SD})$ as 0.5 nm in accordance with the DFT calculations [117], N_{ν} , in Eq. (4.5) is determined to vary between 81 - 90 atoms/nm³ whereas $N_{\nu} = 90$ atoms/nm³ is determined from the lattice constant of FCC-Fe at 0 K. A 10% variation in N_{ν} corresponds to less than 30 meV difference in effective segregation energies for all investigated grain boundaries that is smaller than the accuracy of atomistic calculations. Therefore, $N_{\nu} = 90$ atoms/nm³ is used in all the subsequent simulations to determine the effective segregation energy of solutes.

Element	$D_0 ({\rm cm}^2/{\rm s})$	$Q(\mathrm{eV})$	D_{1273K} (×10 ⁻¹² cm ² /s)	Ref.
Nb	0.75	2.74	10.80	[252]
Ti	0.15	2.61	6.83	[253]
Мо	0.036	2.48	5.36	[253]
V	0.28	2.73	4.26	[253]
Mn	0.18	2.74	2.56	[253]

Table 7.1: Diffusion coefficients for the solute elements considered in the present study.

7.2.2 Computational details

Similar to the previous chapter, an initial two-dimensional structure with ~ 18000 grains is constructed using Voronoi tesselation considering periodic boundary conditions in all directions where the simulation domain of 2 mm \times 2 mm is divided into a 2000 \times 2000 grid. As a result, the grid size (Δx) is fixed as 1 μ m. The initial microstructure is allowed to evolve using Eq. (4.22) considering ideal grain growth with isotropic grain boundary properties and in the absence of solute drag until it reaches the scaling grain size distribution. The scaled microstructure is considered as the starting microstructure that contains ~ 14000 grains with an average grain size (radius) of 10 μ m. The grain size considered here corresponds to the typical order of magnitude of grain size observed during austenite conditioning during different thermomechanical heat treatments in steels. The grain boundary width is 4 μ m resolved in four grid points such that the initial average grain diameter is five times the grain boundary width. As shown in the previous chapter, a moderate variability in GB mobility and energy, on the one hand, and those for solute drag, on the other hand, can be separated to identify the properties of a representative GB. Thus, only the effective segregation energy (E) is considered anisotropic in the present study, and other GB properties, such as GB mobility and GB energy, are assumed to be isotropic for all the cases. The representative GB energy (γ_{rep}) is taken as 1 J/m² for austenite, and the representative GB mobility is assumed as $M_{rep} = 1.5 \times 10^{-11} \text{ m}^4/\text{Js}$ as suggested by Furumai et al. [74] for T = 1273 K. An isothermal heat treatment with a holding time (t_{sim}) of 400 s at 1273 K is considered to assess the grain growth kinetics. For all the simulations, the time step is fixed to 0.0065 s which satisfies the stability condition. For these parameters and in the absence of any solutes, a final grain size of 51 μ m is obtained from 2D phase field simulations.

Each grain in the scaled microstructure is assigned three random Euler angles, and the disorientation angle between each pair of grains, i.e., grain i and grain j, is determined and stored in a look-up table. Disorientation-dependent segregation energies are distributed in the microstructure by considering four types of grain

boundaries, i.e., GB-I, GB-II, GB-III, and GB-IV, as shown in Fig. 7.1. Three cutoff disorientation angles, $\Delta\theta_{12}$, $\Delta\theta_{23}$, and $\Delta\theta_{34}$ are defined to control the fraction of a particular GB type in the initial microstructure with randomly distributed Euler angles resulting in a Mackenzie-like distribution [182] (See Fig. 6.1a). Fig. 7.1 shows the initial microstructure that contains an equal fraction of four GB types by defining $\Delta\theta_{12} = 32^{\circ}$, $\Delta\theta_{23} = 42^{\circ}$, and $\Delta\theta_{34} = 49^{\circ}$. The effective segregation



Figure 7.1: Polycrystalline microstructure with an average grain size of 10 μ m in a domain size of 2 mm \times 2 mm. Only a quarter of the simulation domain is shown for clarity. (b) Four distinct GB types, shown with different colors, are considered, where each GB type has different effective segregation energy. *E* for ten ppm addition of Nb in four GBs is shown as an example.

energies, shown in Fig. 7.1, are determined for 10 ppm (atom fraction) addition of Nb in Σ 41(540)[001], Σ 5(310)[001], Σ 37(610)[001], Σ 29(520)[001] GBs, respectively.

The average grain size evolution from phase field simulations is rationalized using the grain growth model given in Eq. (4.31), and the geometrical constants, k_1 , k_2 , and k_3 are used based on the benchmarks shown in Sec. 6.4 and Sec. 6.5. As a result, k_1 and k_2 are taken as 0.89 and 0.20, respectively, for all the cases. For the average grain size of 10 µm, the driving pressure is sufficiently low such that the grain boundaries either remain unaffected by solutes for relatively low solute concentrations in the bulk or are in the low-velocity limit for higher bulk concentrations. As a result, k_3 is taken here as 1 for all cases.

7.3 Anisotropy in effective segregation energy

The effective segregation energies for different [001] symmetric tilt GBs, characterized by their Σ value, are determined from Eq. (4.3) and Eq. (4.5) using the binding energy data from DFT [117] for the bulk solute concentration of 10 ppm at 1273 K. These energies are compiled in Fig. 7.2 for Nb, Mo, Ti, V, and Mn ordered according to their atomic sizes. Here, a negative effective segregation energy corresponds to solute segregation, whereas a positive value corresponds to solute depletion at the grain boundary. The data indicates favorable segregation of all solutes, except Mn, in all the investigated GBs, with the largest solute, Nb, having the largest magnitude of the segregation energy. There is an appreciable variability in effective segregation energies among different GBs, e.g., the absolute difference between the maximum and minimum values is 0.34 eV, 0.38 eV, 0.21 eV, 0.37 eV, and 0.15 eV for Nb, Ti, Mo, V, and Mn, respectively. However, identical solute trends are determined for individual grain boundaries. As a reference, the effective segregation energies for the above order of solutes are determined as -1.11 eV, -0.78 eV, -0.53 eV, -0.12 eV, and 0.07 eV for the $\Sigma 5(310)[001]$ GB, and the average segregation energy $(E_{ave,gb})$ for all the nine GBs are -1.0 eV, -0.70 eV, -0.48 eV, -0.09 eV and 0.07 eV, respectively.

7.4 Phase field simulations

Two configurations of phase field simulations are considered, i.e. (1) isotropic segregation of solutes considering $\Sigma 5(310)[001]$ GB as the representative GB, (2) anisotropic segregation by considering an equal proportion of four GBs, i.e., $\Sigma 5(310)[001]$, $\Sigma 29(520)[001]$, $\Sigma 37(610)[001]$ and $\Sigma 41(540)[001]$ in the initial microstructure as shown in Fig. 7.1. For the latter, the weighted mean segregation energy (E_{avg}) of the microstructure is determined identical to Eq. (6.6), which



Figure 7.2: Effective solute segregation energy in [001] symmetric tilt GBs in FCC-Fe determined from DFT calculations [117]. $E_{avg,gb}$ corresponds to the average for all nine grain boundaries.

lies within 10 meV of the average segregation energy of all nine grain boundaries $(E_{avg,gb})$ and is therefore considered representative for anisotropic simulations.

Fig. 7.3 shows the normalized average grain size evolution from anisotropic grain growth simulations where \overline{R}_0 is the initial average grain size. While Nb, Ti, and Mo result in strong grain growth retardation compared to pure Fe, Mn and V have a negligible effect on grain growth rates due to their low effective segregation energies and solute drag pressures. Nevertheless, a parabolic grain growth rate is observed for all cases indicating that all grain boundaries are either in the low-velocity limit or remain almost unaffected by solutes during grain growth.

Fig. 7.4 shows snapshots of microstructures with Mo and V additions after 150 and 400 s, suggesting unimodal grain size distribution and normal grain growth in both cases, i.e., for a strongly and a weakly segregating solute. In comparison to the initial microstructure, the proportion of grain boundaries does not change significantly during grain growth, i.e., for the case of Mo, each type of grain boundary is present within $25 \pm 3\%$ even though the number of grains is reduced from ~ 14000 to ~ 1200 after 400 s. The average grain size evolution in Fig. 7.3 is used



Figure 7.3: Square of the normalized average grain size as a function of time from anisotropic phase field simulations for 10 ppm solute addition. Dashed lines are determined from the mean-field model considering $E_{rep} = E_{avg}$ for each solute.

to fit the mean-field model given by Eq. (4.31) with E_{rep} as the fitting parameter. E_{rep} , for each solute, is found to agree with the E_{avg} and the grain size evolution from the mean-field model, i.e., Eq. (4.31) with $E_{rep} = E_{avg}$ is shown with dashed lines in Fig. 7.3.

Further, the role of bulk solute content on grain growth is investigated by determining the effective segregation energy of individual GBs for a given solute concentration that is then used as an input for phase field simulations. For relatively low solute additions and strong segregating solutes such as Nb, the effective segregation energies are insensitive to the solute content, e.g., $c_0 < 100$ ppm, but vary with further increase in solute concentration due to site saturation. As opposed to the atomistic approach of determining the GB excess (Eq. (4.3)), the CLS solute drag model does not account for site saturation (Eq. (4.6)), and as a result, *E* effectively changes with the solute concentration. For instance, an increase in Nb content from 100 ppm to 1000 ppm corresponds to a variation in *E* from -1.11 eV to -0.74 eV for the $\Sigma 5(310)[001]$ GB.

Fig. 7.5a shows the final average grain size obtained from anisotropic simula-



Figure 7.4: Microstructure evolution for anisotropic grain growth simulations for 10 ppm addition of (a) V (b) Mo after 150 s and 400 s at 1273 K.

tions that decreases with an increase in bulk solute concentration for all solutes. The solute rankings, however, remain unaffected for a given bulk concentration. The final average grain size determined from the mean-field model considering $E_{rep} = E_{avg}$ shows almost perfect agreement with the phase field simulations, further validating the choice of E_{avg} for the representative segregation energy. Fig. 7.5b shows a reasonable agreement between the final average grain sizes obtained from isotropic simulations that considered $\Sigma 5(310)[001]$ GB as the representative GB and anisotropic simulations, suggesting that the $\Sigma 5(310)[001]$ GB may be a reasonable choice to determine the solute trends for grain refinement in austenite. It should be highlighted that the trends may be difficult to determine for



Figure 7.5: (a) Normalized final average grain size determined from anisotropic simulations as a function of solute concentration. Solid lines are determined by $E_{rep}=E_{avg}$ in the mean-field model. (b) Comparison of normalized final grain size determined from the anisotropic grain growth simulations and isotropic simulations with $\Sigma 5(310)[001]$ GB as the representative GB.

solutes that have overlapping segregation energies irrespective of their sign, e.g., Mn and V in the present case, which will lead to similar solute drag pressures during grain growth. For instance, isotropic simulations consistently over-predict final grain sizes for Mn and under-predict for V compared to anisotropic simulations. The overall final grain size and solute trends, in these cases, are dependent on the distribution of GB properties in the microstructure. In general, a higher amount of Mn (>0.3 - 2 wt. %) is added in steels in comparison to V (<0.1 wt.%), and as a result, Mn may become a more relevant element for grain refinement in comparison to V.

7.5 Solute trend parameter

The simulations show that the variability in effective segregation energies determined from atomistic calculations has a secondary effect on the solute rankings during grain growth, such that a single representative GB, e.g., the $\Sigma 5(310)[001]$ GB, is sufficient to estimate the relative potential of solutes in retarding grain growth in austenite. To further quantify the effects of the bulk solute concentration and effective segregation energy on grain growth, a solute trend parameter given by $|\Gamma_{GB}/D|$ is proposed, where both the GB excess (Γ_{GB}) and the bulk solute diffusivity (*D*) can be determined from atomistic simulations and/or experimental measurements.

Fig. 7.6a shows the solute trend parameter as a function of the normalized final grain size obtained from the isotropic simulations. Qualitatively, an increase in the trend parameter leads to grain refinement that is in agreement with the conventional solute drag studies where an increase in the GB excess and a decrease in bulk solute diffusivity is correlated with increased solute drag effects [50]. For



Figure 7.6: (a) Solute trend parameter $(|\Gamma_{GB}/D|)$ as a function of the normalized final grain size considering isotropic segregation energy. Here, $D = D_b$ is used. The normalized final grain size determined from Eq. (4.31) is shown with a solid line for comparison. (b) Sensitivity of trend parameter with representative GB mobility and trans-GB diffusivity. Solid markers correspond to simulations with increased GB mobility (100 M_{rep}), and open markers to simulations with increased trans-GB diffusivity ($D = 100D_b$), respectively.

different values of the trend parameter, E is determined from Eq. (4.5) for a given solute diffusivity and concentration, and the final grain size from the mean-field model is shown with a solid black line. The simulated and predicted final grain sizes for all the solutes fall on the master curve such that the solute additions that correspond to a trend parameter $< 10^{-6} \text{ s/nm}^4$ have virtually no effect on grain growth, whereas an increase in the trend parameter leads to a transition range, followed by negligible grain growth for trend parameters $> 10^{-3} \text{ s/nm}^4$.

The other model parameters, namely the representative mobility, and the trans-GB diffusivity are known with the least certainty. Thus, identical isotropic phase field simulations as above have been conducted, but with trans-GB diffusivities increased by a factor of 100 as well as with a 100 times larger representative mobility for selected cases, i.e., Mo and V. For the latter, the heat treatment time is adjusted according to $M_{rep} \propto 1/t_{sim}$ to obtain 51 µm as the final grain size in pure Fe. Fig. 7.6b shows that the transition range is insensitive to the scaling factor in trans-GB diffusion in the former case but shifts by approximately two orders of magnitude to 10^{-7} - 10^{-5} s/nm⁴ in the case of simulations with increased GB mobility. In the low-velocity limit, the solute drag pressure from Eq. (4.7) can be approximated by $\alpha_{SD}c_0v$, and effective mobility, according to $v = M_{eff}\Delta G$, is determined as $(1/M_{rep} + \alpha_{SD}c_0)^{-1}$ for a single grain boundary. An increase in the trans-GB diffusivity reduces both α_{SD} and the solute trend parameter, and therefore, the final grain size shifts along the same master curve. A similar increase in representative mobility, however, has a negligible effect on the effective mobility due to higher contributions from $\alpha_{sD}c_0$ compared to $1/M_{rep}$, especially for higher solute enrichment. As a result, a nearly identical effective mobility for a given $\alpha_{sp}c_0$ coupled with smaller heat treatment time results in smaller grain sizes for a higher representative mobility in comparison to simulations with a lower representative mobility.

7.6 Comparison with experiments

Relatively little information is available regarding the comparative effects of different solutes on austenite grain growth in ultrapure Fe as opposed to ferrite [30, 71]. Careful investigations of static and dynamic recrystallization in hot-rolled steels have quantified the role of dissolved solutes in reducing the recrystallization rates in austenite. In particular, Jonas and coworkers [254–257]

proposed in a series of studies a Solute Retardation Parameter (SRP) that captures the delay in recrystallization time by the addition of 0.1 at.% of alloying element in C-Mn steels, which is defined as,

$$SRP = log\left(\frac{t_x}{t_{ref}}\right) \times \frac{0.1}{at.\%} \times 100$$
(7.1)

where t_x is the time for the onset of recrystallization, and t_{ref} is the equivalent time in the reference steel (0.06 C-1.4 Mn -0.24 Si-0.024 Al in wt.%). In these experiments, the authors measured softening kinetics and assumed 10% softening at 1000 $^{\circ}$ C as the time for the onset of recrystallization. Since both recrystallization and grain growth involve migration of high-angle grain boundaries, albeit with different driving pressures, the solute trends are expected to follow a similar relationship even though grain growth rates will be quantitatively more influenced by solute additions due to the smaller associated driving pressures. Note that the SRP was evaluated for one level of solute addition for each alloying element, and as a result, no error bars were reported for the SRP. Further, solutes can have non-linear effects on grain growth rates. Thus, the SRP should be considered as an approximate indicator that characterizes solute effectiveness on grain growth retardation. Fig. 7.7 shows the SRP for the investigated alloying elements against the proposed solute trend parameter for 10 ppm solute additions as shown in Fig. 7.6a. The solute trend parameter is also determined for all the grain boundaries shown in Fig. 7.2, and the range for each solute with finite GB excess is shown as error bars in Fig. 7.7. A correlation between the solute trend parameter and the SRP is evident, indicating that the proposed trend parameter is a good measure to identify solutes that may promote grain refinement in austenite.

7.7 Validity of representative grain boundary

The simulations suggest that the $\Sigma 5(310)[001]$ GB, falling in the midrange of coincident GB energies [136], can be considered as a representative grain boundary to identify solutes that may promote grain refinement in austenite. Here, it is



Figure 7.7: Correlation between the solute retardation parameter (SRP) [255] and the solute trend parameter considering DFT based segregation energy determined for the $\Sigma 5(310)[001]$ GB and 10 ppm solute additions. The error bars indicate the range of the trend parameter determined for GBs with non-zero GB excess among the nine [001] tilt grain boundaries included in the DFT database.

discussed whether the sample space of investigated GBs is sufficient to support the conclusion of ignoring the structure dependence of the effective segregation energies for solute trend predictions in dilute alloys. Ito and Sawada [117] demonstrated a monotonic dependence between the Voronoi volume of GB sites and the site-specific binding energies for each solute, indicating elastic contributions as the dominant contributions towards the binding energy. One of the general conclusions is that the GB sites with larger Voronoi volumes show favorable segregation for all the solutes. Each GB has at least one site with a larger Voronoi volume as compared to that of regular lattice sites in the bulk and these larger GB sites control the GB enrichment in dilute systems. The sites investigated in the GB vicinity, i.e., 2.5 Å from the habit plane, spanned a Voronoi volume from 10 to 14 Å³ for all the nine grain boundaries such that the largest Voronoi volume in individual GBs is 16-27% higher than the bulk Voronoi volume in FCC-Fe. Here, the largest site in $\Sigma5(310)[001]$ GB is 21% higher than the bulk site. Mahmood et al. [258] investigated 22 symmetric tilt GBs and their metastable structures in Al, another FCC system, and observed a similar monotonous change in Voronoi volume and binding energy for Mg segregation. Similar to Ito and Sawada [117], they found that the strongest segregating site for Mg is the largest GB site with a Voronoi volume which is 30% larger than for the bulk sites in Al. Considering Voronoi volume as the primary indicator of segregation energy, it is reasonable to assume that the segregation trends in low coincident "general" grain boundaries will also be qualitatively similar to those observed for high-coincidence GBs.

7.8 Solute interactions

DFT calculations from Ito and Sawada [117] are applicable to dilute Fe-X alloys with X as the substitutional element, whereas, in reality, carbon in steels can further enhance or hinder solute segregation at austenite grain boundaries. All the investigated solutes in the present study are carbide formers and, therefore, are expected to have a tendency to co-segregate with carbon at the grain boundaries. Using a thermodynamic segregation model, for instance, the interaction coefficient between Mn-C (ω_{Mn-C}) is obtained as -0.5 eV [80], whereas DFT simulations suggest the interaction coefficient to vary between -0.1 eV to -0.55 eV depending on different GB sites for Mn and C in a $\Sigma 3(111)$ GB in BCC-Fe [118]. In low carbon steels, the carbon concentration profile in the austenite grain boundaries (c_C) reaches approximately 2 - 10 at.% [80, 259]. A first estimation would, therefore, suggest an increase in the effective segregation energy of Mn by $\omega_{Mn-C}c_C$, i.e., -0.01 to -0.05 eV in the presence of carbon. A similar increase in the effective segregation energy is expected for other carbide-forming solutes [80] that will increase the solute trend parameter marginally for these solutes for a given bulk composition. Additionally, the experiments that quantified SRP implicitly included the effect of carbon interactions [254–257], and their agreement with the solute trend parameter further suggests that the solute trends established in the
present study will not change significantly by including X-C interactions. On the other hand, solutes such as Si, Ni, and Co show repulsive interactions with carbon such that different solute trends may be obtained in the presence of carbon [80]. As a result, these interactions should be explicitly considered when determining the solute trends for these dissimilar solutes in terms of their interaction with C.

7.9 Summary

In this study, two-dimensional phase field simulations have been performed that considered binding energy profiles of several solutes (Nb, Ti, Mo, V, Mn) at different grain boundaries in FCC-Fe to determine the relative solute trends that affect austenite grain growth. The simulations suggest the solute ranking as $Nb > Ti > Mo > V \approx Mn$ in order of their effectiveness to retard grain growth rates. Anisotropic phase field simulations indicate a secondary role of segregation anisotropy on the solute trends such that different combinations of grain boundaries in the initial microstructure lead to identical solute trends. As a result, the $\Sigma 5(310)[001]$ GB, which is easily accessible to DFT simulations, is identified as a representative grain boundary. To further quantify the solute effects, a solute trend parameter is proposed that is defined as the ratio of GB enrichment and trans-GB diffusivity that quantitatively captures the grain size variation in austenite for a wide range of solute additions. The agreement of the solute trend parameter with experimental observations indicates that a representative GB, such as the $\Sigma 5(310)[001]$ GB, may be useful in identifying solute elements that promote grain refinement in austenite using high-throughput atomistic simulations. In this case, the solutes with overlapping effective segregation energies

Chapter 8

Solute drag during phase transformation in binary alloys

8.1 Introduction

This chapter aims to extend the atomistically informed phase field approach to simulate phase transformation in mesoscale. Similar to the grain boundary migration during grain growth, an appropriate solute drag pressure can be used as a friction pressure to simulate phase transformation in technical alloys [199]. A critical aspect is determining the solute drag pressure for which different formulations exist in the literature [54, 55, 107]. As a result, we consider a simplified binary system and perform phase field simulations in nanoscale that explicitly consider solute segregation at a moving interface. Two limiting cases for a binary system, i.e., partitioning and partitionless transformations, are simulated. The solute drag pressure, extracted from the phase field simulations, is then compared to the analytical predictions from the solute drag model. Upon identifying the solute drag, a friction pressure-based phase field model is proposed to extend the simulations to the microstructure scale which is first benchmarked with simulations that resolve the solute segregation at the interface. Finally, recommendations are made to extend the model to industrially relevant ternary Fe-C-X alloys with interstitial

C and one substitutional element (X).

8.2 Phase field model

8.2.1 Solute segregation at the interface

A single phase field model is used to simulate phase transformation in nanoscale in a binary system which considers a planar interface between α and β phase such that $\phi = 1$ corresponds to the α phase, and $\phi = 0$ to the β phase. As highlighted in Sec. 4.6.3, the model proposed by Wheeler, Boettinger, and McFadden [194] (WBM model) is used which explicitly resolves the solute segregation at the interface and considers the total free energy to be composed of interface energy density (G_{int}), chemical energy density that interpolates the bulk free energies of individual phases (G_{chem}), and a segregation energy density (G_{seg}) [201]. The interface energy density is defined as,

$$G_{int} = \frac{\varepsilon_P^2}{2} g(\phi) + \omega_P [\nabla \phi]^2$$
(8.1)

where ε_P and ω_P are model parameters similar to κ_G and m_G defined in Sec. 4.6. $g(\phi) = 16\phi^2[1-\phi]^2$ is a double well function. G_{chem} is given as,

$$G_{chem} = G^{\alpha}(c^{\alpha})h(\phi) + G^{\beta}(c^{\beta})[1 - h(\phi)]$$
(8.2)

where, G^{α} and G^{β} are free energy densities of α and β phase, respectively, where c^{α} and c^{β} are concentration fields at each point in the computational domain. $h(\phi) = 3\phi^2 - 2\phi^3$ is an interpolation function that takes a value of 0 at $\phi = 0$ and one at $\phi = 1$. Further, the segregation energy density is added as

$$G_{seg} = -cEp(\phi) \tag{8.3}$$

where E is the effective segregation energy, c is the concentration, and $p(\phi) = g(\phi)$ is considered in the present study such that the segregation, i.e., an increase in the interface concentration, occurs at the interface due to non-zero $p(\phi)$ that reduces the total free energy of the system.

In the WBM model, the interface is considered as a mixture of α and β phase with identical composition, i.e., $c = c^{\alpha} = c^{\beta}$ [201]. The phase field equation using Eq. (4.17), Eq. (8.1), Eq. (8.2) and Eq. (8.3) is determined as,

$$\frac{\partial \phi}{\partial t} = L_P \left[\varepsilon_P^2 \nabla^2 \phi - \omega_P g'(\phi) + c E p'(\phi) + h'(\phi) [G^\beta(c) - G^\alpha(c)] \right]$$
(8.4)

where, L_p is the kinetic constant, and $g'(\phi)$, $h'(\phi)$, $p'(\phi)$ are the partial derivatives with respect to ϕ . Here, the interface energy (γ) or width (2 δ) must be determined numerically in the absence of any analytical relationship [214]. Grönhagen and Ågren [186], and later Li et al. [188] used a similar model but for GB segregation and indicated ~ 10% increase and decrease in thickness and energy, respectively, for a factor of 10 increase in GB concentration in comparison to the bulk. Alternatively, similar to Zhang et al. [201], the model parameters are determined assuming a pure system and approximated as $\varepsilon_P = \sqrt{(2\delta)\gamma}$, $\omega_P = \frac{1}{16}[18\gamma/(2\delta)]$, and $L_P = [M_{int}/(2\delta)]$ in the present study [193, 201] where M_{int} is the intrinsic interface mobility. The concentration evolution is then defined using Eq. (4.18) with $M_c = \frac{D(\phi)}{\partial^2 G/\partial c^2}$ where $D(\phi)$ is the diffusion coefficient defined as [214, 260],

$$D(\phi) = [D^{\alpha}h(\phi) + D^{\beta}[1 - h(\phi)]] \left[\frac{D^{int}}{D^{\alpha}}\right]^{4h(\phi)[1 - h(\phi)]}$$
(8.5)

here, $D^{\alpha}, D^{\beta}, D^{int}$ are the diffusion coefficients in α, β phase and in the interface, respectively.

A challenge with the WBM model, however, is the excess contribution from the chemical-free energy to the interface energy due to the equal concentration condition [214]. Within the interface at equilibrium, the solute concentration varies continuously from c_{eq}^{α} to c_{eq}^{β} from $\phi = 1$ to $\phi = 0$ such that the chemical energy at each point in the interface is higher than the minimum energy corresponding to the common tangent. The excess energy, however, is negligible in comparison to the interface potential, i.e., $\omega_P g(\phi)$ for sharp interfaces or for small differences in equilibrium composition, i.e., $c_{eq}^{\beta} - c_{eq}^{\alpha}$, and therefore, solute segregation in thin interfaces can be simulated using this model.

8.2.2 Friction pressure method

Kim, Kim, and Suzuki [216] (KKS model) considered the total energy to be composed of interfacial energy density and chemical energy density given by Eq. (8.1) and Eq. (8.2), respectively. In contrast to the WBM model, Kim et al. [216] considered the solute concentration in the interface as a fraction-weighted average of phase compositions, i.e., c^{α} and c^{β} , such that

$$c = c^{\alpha} h(\phi) + c^{\beta} [1 - h(\phi)]$$
(8.6)

A unique solution to individual concentration fields, c^{α} and c^{β} , at each point is obtained by considering the equal diffusion potential, $\mu_B^{\beta} - \mu_A^{\beta} = \mu_B^{\alpha} - \mu_A^{\alpha} = \tilde{\mu}$ in each phase. For dilute systems, this further simplifies to $c^{\alpha}/c^{\beta} = c_{eq}^{\alpha}/c_{eq}^{\beta} = k_p$ where k_p is the equilibrium partition coefficient for a given T [196]. In this approach, the excess contribution to the interface energy due to the chemical free energy disappears, and the interface width can be artificially increased while preserving the interface kinetics. The model parameters, in this formulation, have the exact relationship with interface energy and width as have been approximated for the WBM model [170]. As a result, the KKS model can be used to simulate solute drag in the microstructure scale, however, adding a free energy density for segregation, i.e., Eq. (8.3), violates the constraint of equal diffusion potential at the interface and leads to incorrect equilibrium conditions [202]. Therefore, the KKS model is parameterized with a friction pressure that emulates the solute drag without resolving the solute segregation at the interface.

In the KKS model, the phase field equation is determined with an added con-

straint of equal diffusion potential using Eq. (4.17) as,

$$\frac{\partial \phi}{\partial t} = L_p \left[\varepsilon_P^2 \nabla^2 \phi - \omega_P g'(\phi) + h'(\phi) \Delta G_{eff} \right]$$
(8.7)

here, ΔG_{eff} is the effective driving pressure at each grid point. In the absence of solute drag, $\Delta G_{eff} = \Delta G_{chem,pf}$ where,

$$\Delta G_{chem,pf} = G^{\beta}(c^{\beta}) - G^{\alpha}(c^{\alpha}) - \widetilde{\mu}^{\beta}[c^{\beta} - c^{\alpha}]$$
(8.8)

is determined at each point in the interface [177]. In the presence of solutes, $\Delta G_{eff} = max(0, \Delta G_{chem,pf} - \Delta G_{SD})$ is used, where ΔG_{SD} is an appropriate solute drag pressure determined from either phase field simulations in nanoscale or analytical function that applies a retarding friction pressure at the interface. Note that c^{α} and c^{β} in this model are defined at each grid point and are different than $c^{\alpha/\beta}$ and $c^{\beta/\alpha}$ in the sharp interface models. In addition, it is suggested to average the driving pressure across the interface for increased stability [193]. For the undercooling considered in the present study, simulations with and without averaging the driving pressure led to identical phase transformation kinetics. Therefore, for simplicity, averaging is not performed in the presented simulations.

The concentration evolves according to Eq. (4.18), with $M_c = \frac{D(\phi)}{\partial^2 G/\partial c^2}$ where $D(\phi)$ is given by Eq. (8.5) and the denominator is determined as [198, 216],

$$\frac{1}{\partial^2 G/\partial c^2} = \frac{h(\phi)}{\partial^2 G^{\alpha}/\partial c^{\alpha^2}} + \frac{1 - h(\phi)}{\partial^2 G^{\beta}/\partial c^{\beta^2}}$$
(8.9)

In the present work, a simplified single phase field model is used to be consistent with the phase field model that explicitly considers segregation. In contrast, a more sophisticated model that utilizes double obstacle potential and multi-phase field formulation developed by Steinbach and coworkers [193, 195] can be coupled with an appropriate solute drag (friction) pressure for simulating phase transformation in mesoscale.

8.3 Computational details

Two phases, α and β , are considered in a binary A-B system with an ideal solution model such that their free energies are defined as:

$$G^{p} = [1-c]G^{p}_{A,0} + [c]G^{p}_{B,0} + RT\{[c]ln[c] + [1-c]ln[1-c]\}$$
(8.10)

where *p* represents a phase, and $G_{i,0}^p$ is the standard state free energy of component *i*. Here, $G_{i,0}^{\alpha}$ is taken as 0, and $G_{i,0}^{\beta} = B_i[T - T_i]/T_i$ with B_i and T_i as fit parameters that produce a linear phase diagram as shown in Fig. 8.1. A one-dimensional



Figure 8.1: Linear phase diagram for a model A-B system.

domain is initialized with 500 grid points with a grid spacing of 0.1 nm. The interface (2δ) is discretized in 12 points which is sufficient to resolve the gradients in concentration due to solute segregation at the interface. The time step (Δt) is chosen according to the numerical stability using Eq. (4.30). Unless otherwise stated, the solute diffusivities in the α , β phase, and at the interface are assumed, for simplicity, to be identical in the present simulations. Other relevant simulation parameters are listed in Table 8.1.

M _{int}	$0.0145 \exp(-140000/RT) \text{ m}^4/\text{Js}$
D^{lpha}	$2 \times 10^{-4} \exp(-170500/RT) \text{ m}^2/\text{s}$
D^{eta}	$2 \times 10^{-4} \exp(-170500/RT) \text{ m}^2/\text{s}$
Δt	$2 \times 10^{-12} \text{ s}$
2δ	1.2 nm
γ	0.45 J/m^2

 Table 8.1: Simulation parameters for phase field simulations

In these simulations, the grid size is comparable to the lattice constant, and an important question is whether the phase field model can capture the physical phenomena of phase transformation and grain growth on the atomistic scale. Danilov et al. [261] demonstrated that Molecular Dynamics and phase field approaches yield equivalent results for solidification in a two-phase Ni_xZr_{1-x} crystal-liquid sample where the free energy in the atomistic model is used to formulate the phase field model. Fu et al. [262] utilized an average bond order parameter from MD simulations and rescaled them to determine the phase field profile across the atomistic interface. Further, planar and multi-grain solidification simulations in Ni starting from the identical initial configurations resulted in a comparable transformation fraction with approximately 10% deviation between the phase field and MD simulations. As a result, we utilize phase field simulations to study the role of solute segregation on phase transformation kinetics using nanoscale simulations.

8.4 Binding energy from atomistic simulations

The relative energy profiles for different solutes, such as Nb, Mo, and Ni etc. in an FCC/BCC interface in Fe are reported by Jin et al. [120] using DFT calculations. Assuming a linear interpolation of the relative bulk energies from FCC to BCC at the interface as a reference, the binding energy profiles are determined that become independent of the bulk energies of either phase. Similar to the grain boundaries, the occupancy of each interfacial site is then determined using the White-Coghlan segregation model [46], and the total interfacial enrichment in atoms/nm² is determined using Eq. (4.3). Interfacial enrichment should ideally be independent of the bulk energy of individual phases, and as a result, Eq. (4.6) is used to determine the effective segregation energy, *E*, from the calculated interfacial enrichment. For 0.1 at.% in the BCC phase at T = 1073 K, *E* for Nb, Mo, and Ni is determined as -23 kJ/mol, -13 kJ/mol, and -6 kJ/mol, respectively. A temperature variation from 973 K to 1073 K, and a composition of the BCC phase from 0.1 at.% to 0.2 at.% results in a negligible change (<20 meV) in the effective segregation energy. Thus, we use E = -6, -12, -24 kJ/mol in the phase field simulations to investigate the solute drag effect.

8.5 Partitioning transformation

8.5.1 Simulation setup

The phase field model described by Eq. (8.4) for the phase field parameter, and Eq. (4.18) and Eq. (8.5) for composition, are used to simulate partitioning transformations. As highlighted previously, this model is referred to as the WBM model that is applicable to nanocrystalline materials. Fig. 8.2 shows the initial domain, which consists of 0.2 volume fraction of α phase in equilibrium with the β phase at T = 1073 K, corresponding to an average composition of 0.18 at.% B highlighted in Fig. 8.1. This corresponds to a domain size of 50 nm where the initial α film thickness is 10 nm, and the grain size of β phase is 40 nm with no flux boundary conditions for both phase field parameter and composition field. For different values of the effective segregation energies, the equilibrium composition profiles at T = 1073 K are shown in Fig. 8.2 which is considered as the initial condition for subsequent phase field simulations.

The mass conservation constrains the equilibrium α fraction to be 0.197, 0.22 and 0.33 for E = 0, -12, -24 kJ/mol, respectively. An undercooling of 50 K is applied such that the equilibrium composition of α and β phase at T = 1023 K is 0.149 at.% and 0.298 at.%, respectively and the equilibrium α volume fraction from the phase diagram increases to 0.79. Here, a change in the α fraction



Figure 8.2: The initial domain and the composition profile after equilibrium segregation in the case of partitioning transformation for different values of effective segregation energy.

from the initial fraction, Δf , is insensitive to the segregation energies due to a relatively small change in the solute concentration at the interface with a decrease in temperature. Therefore, the equilibrium Δf corresponds to approximately 0.59 at T = 1023 K for all the cases. The interface velocity during migration is determined by monitoring the interface displacement, and the driving pressure at a time instant is determined from Eq. (4.27) where the interfacial concentrations, i.e., $c^{\beta/\alpha}$ and $c^{\alpha/\beta}$ from outside the interface are determined by linearly extrapolating the composition from $\phi = 0.01$ and $\phi = 0.99$ with five additional points outside the interface, to $\phi = 0.5$. Note that five points from outside the interface fit reasonably well to a linear line, and using higher-order quadratic functions does not change the composition at the interface. The driving pressure determined in this way is independent of the interfacial segregation.

8.5.2 Comparison of solute drag pressure

Fig. 8.3 shows the composition profile for different times, t = 0, 40, and 81 µs for two cases, i.e., E = 0 and -12 kJ/mol, respectively. The interface position corresponding to $\phi = 0.5$, and the interfacial compositions, $c^{\beta/\alpha}$ and $c^{\alpha/\beta}$, are highlighted along with the equilibrium composition of α and β phase at T = 1023 K. The simulations indicate a slower transformation rate for higher segregation energy, where the interfacial concentrations differ from the equilibrium concentrations indicating deviation from local equilibrium conditions. An increase in the peak solute concentration in Fig. 8.3b is due to the increase in equilibrium α concentration and inherent segregation capacity that increases with a decrease in temperature.



Figure 8.3: Composition evolution in the absence and presence of segregation, i.e., (a) for E = 0 and (b) E = -12 kJ/mol, respectively, for an undercooling of 50 K.

Fig. 8.4a shows the chemical driving pressure such that a zero driving pressure corresponds to the local equilibrium at the interface. For non-zero driving pressures, α growth proceeds by long-range diffusion in the parent phase, where the diffusion within the interface consumes a part of the driving pressure that leads to slower migration rates in the case of solute segregation. The lower transformation rates can be interpreted as effective mobilities determined from the slope



Figure 8.4: (a) Variation in driving force with time, (b) velocity as a function of driving force where the slope corresponds to the effective mobility.

in Fig. 8.4b. The effective mobility, in this regard, decreases with an increase in the effective segregation energy. More rigorously, the solute drag pressure can be determined in the diffusional regime using $\Delta G_{SD} = \Delta G_{chem,int} - v/M_{int}$. Fig. 8.5 shows the solute drag pressure for different segregation parameters where the solute drag pressure decreases with a decrease in both interface velocity and effective segregation energy. The composition of the product phase, i.e. $c^{\alpha/\beta}$, and v determined from phase field simulations are used as an input to Eq. (4.14) to determine the solute drag pressure from the Hillert-Sundman model [54]. There is consistency between the solute drag model and phase field simulations such that the steady-state assumption in the former is reasonable for the present case of solute drag in a nanocrystalline binary alloy.

8.6 Friction pressure

Resolving solute segregation at the interface and simultaneously studying phase transformation on a microstructural scale is challenging due to the different length scales which would require huge computational resources. Additionally, the current framework, i.e., the WBM phase field method [201], can resolve segregation in the nanoscale, but its application is largely limited to smaller interfacial widths,



Figure 8.5: Comparison of solute drag pressure extracted from the phase field simulations and from Hillert and Sundman (HS) solute drag model [54].

i.e., few nms, due to the bulk energy contributions to the interface energy that increases with an increase in the interface width. The phase field model given by Eq. (4.18) and Eq. (8.7), also referred to as the KKS model, is used with a friction pressure that simulates the solute drag without resolving the solute segregation at the interface. Here, the solute drag description by Hillert and Sundman [54] is included as a friction pressure to account for solute drag. A CLS-like solute drag pressure, i.e., $av/1 + bv^2$, is used with *a* and *b* to fit the solute drag pressure, $\Delta G_{SD,HS}$, and is shown in Fig. 8.6a.

Fig. 8.6b compares the transformation kinetics from the phase field simulations that consider the solute segregation at the interface with the friction pressure simulations. In both cases, the equilibrium fraction change in α phase, Δf , is consistent with the phase diagram. A decrease in transformation kinetics is evident from both the simulations for E = -12 kJ/mol and -24 kJ/mol, where the friction pressure approach (KKS model) results in faster transformation kinetics in comparison to the simulations that resolved solute segregation at the interface (WBM model). The deviation between the WBM and the KKS model is due to



Figure 8.6: (a) Fit between the solute drag pressure determined from the Hillert and Sundman (HS) model and $av/1 + bv^2$ with *a* and *b* as fit parameters. (b) Comparison of the phase field simulations considering either solute segregation with the WBM model or friction pressure with the KKS model, respectively.

the imperfect fit between the CLS-like fit function and analytical solute drag that can be seen in Fig. 8.6a in the low-velocity regime such that the fit function results in lower solute drag pressure in comparison to the solute drag model for the same interface velocity.

As mentioned previously, the simulations with solute segregation are only valid for nanocrystalline materials. In these cases, the diffusion distances in the parent phase are comparable to the interface width resulting in non-negligible solute drag pressure for binary alloys. As a result, the role of diffusion length scale is investigated with the WBM model by considering different diffusivities in the bulk and at the interface. Fig. 8.7a shows the transformation kinetics from the phase field simulations considering $D^{int} = 100D^{\alpha}$ for E = -12 kJ/mol indicating no solute retardation even with segregation at the interface for higher interface diffusivities. Fig. 8.6a shows that the solute drag peak at around $v[2\delta]/D = 3$ where D is the trans-interface diffusivity. For higher trans-interface diffusivity, the peak shifts to higher velocities leading to lower solute drag pressures for the transformation velocities observed in the present simulations.



Figure 8.7: (a) Effect of interface diffusivity in nanoscale simulations considering solute segregation (b) Solute drag in microstructural length scale for binary alloys using friction pressure.

The phase field simulations with friction pressure can be extended to simulate interface migration in microcrystalline materials. The grid size is increased from 1 Å to 0.1 μ m in microcrystalline simulations for identical effective interface mobility [193]. The domain size, in these simulations, is 50 μ m corresponding to 10 μ m of α film thickness where the grain size of β phase is 40 μ m. Fig. 8.7b shows a negligible solute retardation due to segregation energy in microcrystalline materials confirming that the long-range diffusion is a rate-limiting step resulting in no solute drag for binary alloys. These partitioning simulations, however, correspond to the low-velocity limit, and therefore, in the following section, the role of solute drag on interface-controlled phase transformation, which corresponds to the high-velocity limit, is investigated using phase field simulations.

8.7 Massive transformation

8.7.1 Simulation setup

The nanocrystalline domain with a grid spacing of 0.1 nm is used to simulate partitionless transformations, where α phase with a volume fraction of 0.08, i.e.

4 nm thickness, is initialized with the alloy concentration $c_0 = 0.11$ at.% B also shown with a dotted line in Fig. 8.1. Sufficiently high undercooling may result in the formation of the product phase without any redistribution of solute across the interface. Thermodynamically, these massive transformations are possible below the T_0 temperature where the free energies of both phases are equal for the bulk composition of the alloy. A deviation from T_0 temperature in experiments can be rationalized by considering solute drag of substitutional elements, whereas appreciable solute diffusion at the interface further suppresses the start of the partitionless transformation at smaller undercooling below T_0 . As a result, in the present case of a model A-B system, the diffusivity is reduced by two orders of magnitude to mimic the Fe-X system and to suppress the partitioning transformation closer to T_0 in the absence of segregation. Simulations with the WBM model are performed at different temperatures to determine the thickening rate of α growth, where the temperature at which the product and parent phase have the same composition during interface migration is considered as the start of the partitionless transformation, e.g. in the absence of solute segregation the partitionless growth occurs at $T_0 - T = 11$ K which is considered as a reference.

8.7.2 Phase field simulations

The interface velocity for E = 0, -6, -12, and -24 kJ/mol is determined from the phase field simulations for different temperatures and a transition from partitioning to partitionless transformation is obtained from the simulations. For lower undercooling below the T_0 temperature, the solute starts to partition at the interface due to slower interface migration rates. In these cases, the interface velocity further decreases with an increase in the α film thickness. A representative velocity is determined from the simulations after the composition in the product phase has reached the equilibrium composition. For larger undercooling, the interface velocity reaches steady state within 1 µs indicating partitionless transformation. A kinetic transition from partitioning to partitionless transformation, indicated by an increase in the velocity by approximately an order of magnitude, can be observed from Fig. 8.8 at a critical undercooling that increases with an increase in the effective segregation energy. The velocity, in each case, has a maximum due to the competing effect of increasing chemical driving pressure and decreasing interface mobility and diffusion with a decrease in temperature.



Figure 8.8: Comparison of the Gibbs Energy Balance (GEB) model with phase field simulations.

Hillert et al. [263] determined the velocity for the partitionless growth using the Gibbs Energy Balance approach where the chemical driving pressure over the interface, i.e. Eq. (4.27), exactly balances the dissipation due to interface friction, i.e. v/M_{int} , and diffusion inside the interface, i.e. Eq. (4.14). Here, an equivalent description according to the Purdy-Brechet solute drag model is used, e.g. in Fe-Ni, Fe-Mn, and Fe-Co alloys [102], where the partitionless driving pressure, i.e. $\Delta G_t = G^{\beta}(c^{\alpha/\beta}) - G^{\alpha}(c^{\alpha/\beta})$ is balanced with the solute drag pressure, i.e. Eq. (4.13) and interface friction. Fig. 8.9 shows the application of the Gibbs Energy Balance model using the latter approach where the total driving pressure is shown with dashed lines and total dissipation due to the above-mentioned sources are shown with solid lines for different temperatures and E = -12 kJ/mol. For a lower undercooling, e.g., $T_0 - T = 10$ K, no solution exists, indicating that the partitionless transformation is not feasible at this temperature. For larger under-



Figure 8.9: Gibbs Energy Balance model for E = 12 kJ/mol.

cooling, multiple solutions exist for interface velocities, and several authors have considered the low-velocity or the high-velocity solution as the suitable velocity for interface migration [57, 263]. The interface velocities obtained from the phase field simulations are also shown in Fig. 8.9, which are found to agree with the high velocity solution from the Gibbs Energy Balance model. With this information, the model is further used to determine the critical temperature for partitionless growth that agrees with the phase field simulations as shown in Fig. 8.8. The minor deviations may be due to the slightly different descriptions of the interface properties in the phase field method and the solute drag model.

Among the equivalent formulations of the Gibbs Energy Balance model described above, the latter is also verified for partitioning transformations using $\Delta G_{SD,PB} = \Delta G_t - \Delta G_m$ and is shown in Fig. 8.10 for the phase field simulations performed in Sec. 8.5.2.

8.8 Implication for ternary Fe-C-X alloys

The simulations suggest that the steady-state solute drag models are equally applicable to determine the kinetics in both high and low-velocity limits of transforma-



Figure 8.10: Comparison of the solute drag pressure determined from the phase field simulations considering total driving force for partition-less transformation and Purdy-Brechet solute drag model.

tions in a binary alloy. Further, similar to Zhu et al. [199], the solute drag pressure can be incorporated into the phase field simulation using a friction pressure approach. For industrially relevant ternary alloys, such as Fe-C-X, the interface velocity is determined by the long-range diffusion of carbon, and substitutional segregation may lead to solute drag in microcrystalline materials even though the diffusion of solutes at the interface is higher than the bulk. As shown above for binary alloys, both the Purdy-Brechet [55] and Hillert-Sundman [54] model lead to identical results but care must be taken in using the appropriate driving pressure to determine the interface migration rates. As a result, it is recommended to use the parameterized Hillert-Sundman solute drag model [54] as a friction pressure in the phase field simulations where the chemical free energy for different phases can be directly used from thermodynamic databases without any explicit assumption of the interfacial conditions such as Para Equilibrium or No Partition Local Equilibrium condition in ternary alloys.

8.9 Summary

Phase field simulations have been performed to explicitly simulate solute segregation and solute drag at the interface. Using a model binary system, the solute drag from the phase field simulations is found to be in agreement with the steady-state solute drag model for both partitioning and partitionless transformations. The former corresponds to a low-velocity limit, whereas the latter corresponds to the high-velocity branch of solute drag, suggesting that both limits are well captured in the conventional solute drag models. These results provide promising evidence in support of the solute drag models suggesting that the steady-state assumption may be reasonable for binary alloys in nanocrystalline materials. The simulations can be further treated as a benchmark for solute drag models.

The simulations suggest a non-negligible solute drag pressure for nanocrystalline alloys where the diffusion distance in the parent phase is comparable to the interface width. Of particular importance is the role of solute diffusion which shows that a higher interface diffusion in comparison to bulk diffusion, results in decreased solute drag pressure for partitioning transformations. In this regard, a systematic analysis of the role of unequal diffusivities in the parent and product phase would be useful that is not accessible from analytical solute drag models.

An approach is proposed to incorporate the atomistic solute-interface interactions via effective segregation energies into the phase field models that can be used to simulate morphological evolution during phase transformations. A friction pressure approach, that is different than the method proposed by Zhu et al. [199], is verified to reproduce the phase transformation kinetics in agreement with the phase field simulations which explicitly considers solute segregation at the interface. Further, suggestions to extend the approach to ternary alloys are made where care must be taken in utilizing the appropriate solute drag model depending on the driving pressure considered in the phase field simulations.

Chapter 9

Conclusions and Future Work

9.1 Conclusions

In this work, an atomistically-informed phase field model is developed for grain growth and phase transformation in binary alloys. In Chapter 5, Chapter 6, and Chapter 7, a systematic approach is presented to investigate the role of solutes on grain growth kinetics considering the atomistic details of solute segregation.

Chapter 5 rationalized the experimental migration rates of a well-characterized grain boundary in Au during recrystallization heat treatments using Density Functional Theory calculations of binding energy and solute diffusivity across the grain boundary in combination with a solute drag model. Here, the atomistic calculations suggest that Bi is the strongest segregating impurity among all the other impurities in the Au sample. More importantly, Chapter 5 provides the key to linking atomistic details of solute segregation to the phenomenological solute drag model, where in detail, the total grain boundary enrichment is used to determine the effective segregation energy for solutes, which can be used to identify the grain boundary migration rates in the presence of solutes and/or impurities.

During grain growth, a network of grain boundaries evolve where the grain boundaries may have structure or misorientation-dependent properties such as grain boundary mobility or solute drag. Chapter 6 integrates the phenomenological solute drag model to the phase field method and delineates the role of GB anisotropy in terms of mobility and solute drag on grain growth kinetics. The 2D phase field simulations reveal that a representative grain boundary mobility and a representative segregation energy can be quantitatively defined for uniformly textured microstructures despite the anisotropy in GB properties. Furthermore, the combined effect of anisotropic mobility and anisotropic solute drag on grain growth can be described by superimposing the representative mobility and representative segregation energy determined from simulations that considered individual anisotropies. As a result, the representative mobility for a given host metal can be determined from either atomistic databases [136, 251] or grain growth experiments in ultra pure alloys, whereas the representative solute segregation energies can be determined from atomistic calculations that can be used to evaluate the average grain size evolution in the presence of solutes.

Chapter 7 uses this model approach to determine the effect of Nb, Mo, Ti, Mn, and V on austenite grain growth. Using the atomistic segregation data for nine different symmetric tilt grain boundaries in FCC-Fe and a representative mobility from experiments, the anisotropic phase field simulations indicate a secondary role of the variability in solute binding energies on the grain growth rates. As a result, a high coincidence $\Sigma 5(310)[001]$ GB, which is relatively easily accessible to DFT calculations, is proposed as a representative grain boundary that is used to determine the solute trends in agreement with experimental observations.

The proposed atomistically-informed approach is then extended in Chapter 8 to phase transformation in binary alloys where the binding energy profiles of solute elements such as Nb, Mn, and Mo in semi-coherent FCC/BCC interface are available. The solute drag pressure from a phase field model that explicitly accounts for solute segregation agrees with the conventional solute drag model in nanocrystalline materials for partitioning and partitionless phase transformations. An appropriate friction pressure is parameterized from the solute drag model, which is then used in a phase field model to simulate phase transformation kinetics in microcrystalline materials. The simulations suggest a non-negligible

solute drag pressure in nanocrystalline materials but result in practically no solute drag effect in microcrystalline materials during partitioning transformations. These differences are attributed to the comparable diffusion distances in the interface and in the parent phase in nanocrystalline materials. The kinetic transition from partitioning to partitionless transformation, however, depends on the interface diffusion, and therefore, would lead to an appreciable solute drag in both nano and microcrystalline materials. In Fe-C-X alloys, the interface migration rates are controlled by long range diffusion of carbon where the substitutional solute may remain partitionless due to diffusivity differences between C and X. The associated solute drag due to X may modify the microstructural evolution in ternary steels. As a result, recommendations are made to extend the approach to industrially relevant ternary Fe-C-X systems.

In this respect, the key novelty of the thesis is the approach to link atomistic simulations with microstructure evolution models such that the proposed atomistically informed approach can be used to identify the role of different solutes on microstructure evolution in metals and alloys. In particular for austenite grain growth, the solute trends determined from the proposed approach are found to be in agreement with the experimental observations. These physically motivated models, e.g. similar to the grain growth and phase transformation models in the present study, can be utilized to develop alloy design strategies to produce e.g. the next generation of high-strength steels. Alternatively, the operational process parameters for downstream processes, such as austenite conditioning and/or cooling, during steel production may be corrected according to the residual/impurity content that will be increased by the adoption of scrap-based steel production to reduce the emissions due to steel manufacturing.

9.2 Recommendations for future work

Despite encouraging results, the present work benefited from several simplifying assumptions that may not be applicable to other material systems. As a result, the following future research directions can be considered, partly to relax the sim-

plifying assumptions, and partly to improve the models developed in the present work:

- In Chapter 5, reasonable estimates of grain boundary mobility in Au are available from high-temperature data where the GB migration rates are unaffected by the solutes. The same is, however, not apriori available for other grain boundaries in different material systems. Here, opportunities exist from experimental and theoretical approaches to determine the GB mobility in the absence of solutes. In-situ measurement techniques such as Laser Ultrasonics for Metallurgy [264] or Laser Scanning Confocal Microscopy [265] can be used to measure grain growth rates in ultra-pure materials to calibrate the effective mobilities in ultra-pure materials. On the other hand, MD simulations can be used to determine the GB mobilities but remain limited due to the accuracy of the interatomic potentials. Here, a new class of Machine Learning interatomic potentials that can reach DFT accuracy, and also allow transferability to unknown atomic environments are promising [266] and can be used to determine the GB migration rates.
- Trans-GB diffusivity of solutes remains an unknown parameter, and more focussed atomistic studies are required to determine their reasonable estimates. Here, DFT simulations for a large number of configurations near the grain boundary can be coupled with Kinetic Monte Carlo simulations that can access longer time scales relevant to substitutional diffusion. In this regard, a trans-GB diffusivity database of solutes in different host elements will greatly benefit the solute drag community.
- $\Sigma 5(310)[001]$ tilt GB can be used as a representative GB to determine the role of solutes and/or impurities on grain growth and recrystallization. The proposed solute trend parameter can be used with high-throughput atomistic calculations to rapidly screen solute elements based on their potential to retard grain growth rates in austenite. For steels, the interaction of carbon with solutes needs to be quantified, as well as other potential energetic inter-

actions between different solutes. In a first approximation, DFT simulations can provide insights into these interactions [267].

- The solute drag model presented in this work is applicable to dilute systems which needs to be modified to include the interactions between the segregating elements at different grain boundary sites. The recent theoretical development from Alkayyali et al. [268], and Mishin et al. [269] provides a framework to extend the conventional solute drag formalism.
- The anisotropic phase field simulations in the present work considers the interaction of anisotropic GB mobility and segregation energy on grain growth in two dimensions. Additional large-scale 3D simulations that account for different textures are required to extend the proposed relationship for representative GB properties. Further, the grain boundary energy also changes with solute segregation and the structure dependence of GB energy with the segregation energy in the context of grain growth requires more attention.
- Industrial steels contain at least one substitutional solute along with carbon, where carbon partitions across the interface and interface migration is controlled primarily by the long-range diffusion of carbon. The substitutional solute, however, does not partition under industrial cooling conditions. The atomistic approach suggested in the present study can be used to systematically assess the influence of solutes on the phase transformation kinetics in ternary Fe-C-X alloys for different processing conditions.

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Appendix A

Atomistic calculation details

A.1 Computational setup

Density Functional Theory calculations are performed with the software Vienna Ab-initio Simulation Package using the projector augmented wave-functions [209, 270–272]. The revised Perdew-Burke-Ernzerhof Exchange Correlation functional [273] is employed as this permits to reproduce the bulk properties of Au, as shown in detail by Haas et al. [274]. For example, a lattice parameter of 4.0812 Å is obtained in agreement with the experimental results [274]. The potentials for Au, Bi, and Fe are chosen according to the recommendations from the simulation software [275]. All calculations with Fe are spin-polarized. For all the calculations, an energy cut-off of 300 eV is employed. The k-point mesh is chosen as $7 \times 8 \times 1$ for the GB cell with the dimensions $7.069 \times 6.453 \times 41.620$ Å³ containing 54 atoms, and $4 \times 4 \times 4$ for the cubic bulk cell with 108 atoms. Ionic relaxations are performed with a convergence criterion of a force per atom of 0.009 eV/Å which results in a converged value of the binding energy with a variation of less than 0.01 eV.

The ground state structure of the $\Sigma 13(13\overline{4})[111]$ tilt GB considered in Chapter 5 with DFT calculations is obtained using the γ -surface approach [227], where two grains at the GB are shifted with respect to each other to identify the lowest

energy structure. The GB energy is computed using

$$\gamma_{GB} = \left(E_{GB} - E_{FS}\right) / A_{tot} \tag{A.1}$$

where E_{GB} and E_{FS} denote the total energies of slabs containing the same amount of atoms and the same cell dimensions but one with a GB and one without a GB, respectively. The energy is normalized by the GB area, A_{tot} . In both cases, the free surfaces of the periodic images are separated by 10 Å of vacuum and in the GB slab, the distance between the free surface and GB is taken larger than 10 Å. It is checked explicitly with convergence calculations that at these distances, the interactions between the interfaces are below 0.01 eV. See [227] for further details on the computation of GB energies. This approach yields a GB energy of 0.59 J/m².

A.2 Binding energy

For an alloying element X, the binding energy to site i in the GB is computed as [225, 276]

$$E_{seg}^{i} = E_{GB}(N-1, X@i) - E_{GB}(N) - E_{ref}^{X}$$
(A.2)

where $E_{GB}(N)$ is the total energy of the GB slab with 54 atoms and $E_{GB}(N - 1, X@i)$ is the total energy of the same GB slab but the atom X is placed at the substitutional site *i*. The binding energy is computed using the reference energies of the alloying element in the bulk, $E_{ref}^X = E(M - 1, X) - E(M)$, with E(M) being the total energy of a cubic bulk FCC Au cell with 108 atoms and E(M - 1, X) as the total energy of the same cell but with one Au atom replaced by an atom X. Note that the sign convention is such that a negative E_{seg}^i corresponds to a favorable segregation at the GB site *i*.

In Sec. 5.2, the Bi-Bi interactions are determined by substituting the strongest segregating site (see site 1 in Fig. 4.1) and then the binding energy for the next strongest segregating site (see site 2 in Fig. 4.1) is determined analogous to

Eq. (A.2) using,

$$E_{seg}^{i,Bi@1} = E_{GB}(N-2,Bi@1,Bi@i) - E_{GB}(N-1,Bi@1) - E_{ref}^{Bi}$$
(A.3)

where, $E_{GB}(N-1,Bi@1)$ corresponds to the total energy of the structure with a Bi atom at site 1, $E_{GB}(N-2,Bi@1,Bi@i)$ corresponds to the total energy of the structure with Bi at site 1 and at another GB site *i*, and E_{ref}^{Bi} is the reference energy of Bi in the bulk. For further interaction of Bi with occupied GB sites, the binding energy is calculated by substituting site 1 and 2 with Bi and adding the third Bi atom to other GB site using,

$$E_{seg}^{i,Bi@1\&2} = E_{GB}(N-3,Bi@1\&2,Bi@i) - E_{GB}(N-2,Bi@1\&2) - E_{ref}^{Bi} \quad (A.4)$$

where, $E_{GB}(N-2, Bi@1\&2)$ corresponds to the total energy of the structure with Bi atoms at sites 1 and 2. $E_{GB}(N-3, Bi@1\&2, Bi@i)$ is the total energy of the structure with Bi at sites 1 and 2 and at another GB site *i*.

A.3 Activation energy for solute diffusion

For a vacancy-mediated diffusion of substitutional solute, the activation energy at T = 0 K can be written as [126]:

$$E_a = E_m + E_f + E_b \tag{A.5}$$

where E_m is the migration barrier, E_f is the vacancy formation energy, and E_b is the solute-vacancy binding energy. The migration barrier is defined as the energy difference between the saddle point and the initial configuration [277]. Here, the climbing-image Nudged Elastic Band [278] as implemented in the Transition State Tools [279] is used with five intermediate images. The energies of the intermediate configurations along the transition path are minimized in all directions except for the reaction path, and the maximum energy is taken as the saddle point.

The defect formation energy, E_f , is computed as:

$$E_f = E(N - 1, V) - \frac{N - 1}{N} E(N),$$
(A.6)

where E(N-1,V) is the total energy of the supercell containing N-1 host atoms and one vacancy. E_b is defined here as:

$$E_b = E(N - 2, X, V) - E_{ref}^X - E(N - 1, V)$$
(A.7)

where E(N-2,X,V) and E(N-1,V) are the total energies of supercells representing a cell with a bound solute atom and a vacancy and an isolated vacancy in the cell, respectively. E_{ref}^X is the same as for the calculation of the binding energy in Eq. (A.2).

Appendix B

Phase field model for anisotropic grain boundary energy

The phase field model proposed by Moelans et al. [169, 221] is used to simulate the variability in GB energy. As highlighted in Sec. 6.9, the phase field model parameters L_G , $\lambda_{G,ij}$, κ_G , and m_G in Eq. (4.22) are determined for a given maximum (γ_{max}), and minimum GB energy (γ_{min}), GB mobility (M), and GB width (2 δ) as follows:

- First, $\gamma_{init} = 0.5(\gamma_{max} + \gamma_{min})$, is determined.
- m_G is then calculated as,

$$m_G = \frac{6\gamma_{init}}{[2\delta]} \tag{B.1}$$

- $Q_{ij} = \gamma_i / 6\gamma_{init}$ is calculated for maximum and minimum energy grain boundaries.
- Subsequently, $\lambda_{G,ij}$ is determined as,

$$\frac{1}{\lambda_{G,ij}} = 103.3970 Q_{ij}^6 - 165.3930 Q_{ij}^5 + 105.3469 Q_{ij}^4 - 44.5566 Q_{ij}^3 + 24.7348 Q_{ij}^2 - 11.2572 Q_{ij} + 1.9996$$
(B.2)

• $f_{0,ij}$ is determined from $\lambda_{G,ij}$ as,

$$\sqrt{f_{0,ij}} = -0.07296 \left(\frac{1}{\lambda_{G,ij}}\right)^5 + 0.35784 \left(\frac{1}{\lambda_{G,ij}}\right)^4 - 0.68325 \left(\frac{1}{\lambda_{G,ij}}\right)^3 + 0.63578 \left(\frac{1}{\lambda_{G,ij}}\right)^2 - 0.48566 \left(\frac{1}{\lambda_{G,ij}}\right) - 0.53703$$
(B.3)

- $\kappa_{G,ij}$ is then determined as $6f_{0,ij}\gamma_{init}[2\delta]$.
- The model parameter, κ_G , from Eq. (4.23) for a grain boundary between grain *i* and *j*, is then determined using

$$\kappa = \frac{\sum_{i}^{p} \sum_{j \neq i}^{p} \kappa_{G,ij} \phi_{i}^{2} \phi_{j}^{2}}{\sum_{i}^{p} \sum_{j \neq i}^{p} \phi_{i}^{2} \phi_{j}^{2}}$$
(B.4)

 L_G is determined from Eq. (4.25) for all the cases with only anisotropic GB energy. Note that the functions for $f_{0,i}$ and $\lambda_{G,ij}$ are polynomial fits to the exact relationship between GB energy and phase field model parameters and remain applicable for $\gamma_{max}/\gamma_{min} < 55$ [221].

Appendix C

Scaling Constants

C.1 Driving pressure

The anisotropic phase field simulations in Chapter 6 considered two types of grain boundaries, each with different mobilities, i.e., maximum mobility (M_{max}) and minimum mobility (M_{min}) , characterized by the mobility ratio (r) and the fraction of low mobile grain boundaries (f_s) . The scaling constant k_2 that is defined as the product of average radius (\overline{R}) and average curvature ($\overline{\kappa}_R$) in Eq. (4.31) is determined for different values of r and f_s and is shown in Fig. C.1. In comparison to isotropic grain growth, the width of grain size distribution increases with an increase in mobility ratio and reaches a maximum for an equal proportion of low and high mobile grain boundaries for fixed mobility ratio (See Fig. 6.5). Consequently, k_2 also varies with anisotropic parameters. Using $\overline{R}^2 - \overline{R}_0^2 = 2k_1k_2M_{rep}\gamma t$, $k_1 k_2 M_{rep}$ is determined from phase field simulations for different anisotropy parameters. Alternative to the approach where k_1 and k_2 were fixed from ideal grain growth simulations to determine M_{rep} for other anisotropic simulations, $k_1 M_{rep}$ can be determined considering k_2 from anisotropic simulations. However, it is apriori not clear whether k_1 can be assumed to be constant for anisotropic simulations, and as a result, determining M_{rep} is not possible. As a result, the isotropic approach, i.e. with fixed k_1 and k_2 values, is considered in the main text.



Figure C.1: k_2 as a function of mobility ratio (*r*) and fraction of low mobile grain boundaries (f_s). k_2 determined from isotropic phase field simulation is shown with the dashed line.

C.2 Solute drag

Phase field simulations are performed considering isotropic solute segregation energy, E, and isotropic mobility in the presence of solutes. The average grain size evolution from simulations, shown in Fig. C.2, is used to fit with the phenomenological grain growth model, Eq. (4.31), considering representative GB mobility as E, and k_3 as fit parameter. The fit parameters for each simulation are listed in Table. C.1.

Considering the equation of motion for individual grain boundaries as $v = M(\Delta G - \Delta G_{SD})$ and $\Delta G_{SD} = \alpha_{SD}c_0v/(1 + \beta_{SD}^2v^2)$, it is possible to determine the critical driving pressure (ΔG_{tr}) for the transition from the high to the low-velocity limit. An abrupt transition exists if $M\alpha_{SD}c_0 \ge 8$, whereas a smooth transition exist for $1 < M\alpha_{SD}c_0 < 8$ and no transition for $M\alpha_{SD}c_0 < 1$, such that:

$$\Delta G_{tr} = \begin{cases} \frac{\sqrt{P}}{M\beta} \left(1 + \frac{M\alpha_{SD}c_0}{1+P}\right) & \text{if } M\alpha_{SD}c_0 \ge 8\\ \frac{1+0.5M\alpha_{SD}c_0}{M\beta} & \text{if } 1 < M\alpha c_0 < 8 \end{cases}$$
(C.1)



Figure C.2: Normalized average grain size as a function of time normalized with $\overline{R}_0^2/M_{max}\gamma$ for phase field simulations considering isotropic grain boundary mobility and isotropic segregation. Fit with the phenomenological grain growth model is shown with dashed lines.

Table C.1: Fit parameter k_3 considering fit of the grain growth model with the average grain size evolution determined from phase field simulations. For the considered initial microstructure, the product $(M\alpha_{sD}c_0)$ and the ratio of grain size where the transition from high to low velocity occurs (\overline{R}_{tr}) with the initial average grain size (\overline{R}_0) is shown for reference.

E	$M\alpha_{SD}c_0$	$\overline{R}_{tr}/\overline{R}_0$	<i>k</i> ₃
(kJ/mol)	(-)	(-)	(-)
20	1.5	8	1
50	33	2.2	$0.45 {\pm} 0.05$
100	4794	1.1	0.45 ± 0.05

Here, $P = 0.5(M\alpha_{sD}c_0 - 2 + \sqrt{M\alpha_{sD}c_0(M\alpha_{sD}c_0 - 8)})$. A schematic for three cases of $M\alpha_{sD}c_0$ is shown in Fig. C.3, and the critical driving pressure from Eqn. (C.1) is shown with dashed lines. The average grain size for the transition can also be estimated using $\Delta G_{tr} = k_2 \gamma / \overline{R}$. Considering that the maximum grain size is approximately twice the average grain size due to the grain size distribution in the



Figure C.3: Schematic for GB velocities as a function of driving pressure for different $M\alpha c_0$. The critical driving pressure for the two cases, determined from Eq. (C.1), is shown in dashed lines.

microstructure and that the average grain size increases with an increase in time during grain growth, the transition range can be defined as $1/c < \overline{R_{tr}}/\overline{R_0} < c$ where c=4 for an increase in average grain size by a factor of 2 during the simulations. In this regime, the averaged solute drag pressure depends on the local GB velocities of the individual grain boundaries that will differ from the averaged GB velocity considered in the phenomenological grain growth model. Table C.1 shows the corresponding $\overline{R_{tr}}/\overline{R_0}$ and $M\alpha_{SD}c_0$ for the three cases of isotropic segregation such that E = 50 kJ/mol and 100 kJ/mol corresponds to simulations where the driving forces are in the transition range, and therefore, the scaling constant k_3 that is different than 1, is used in the phenomenological grain growth model.