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Abstract

Thermodynamics and Kinetics of Aluminum Alloys

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There is growing interest in and demand for lightweight, age-hardenable alloys such as aluminum (Al) alloys in the transportation sector. This interest is due to the potential for reducing vehicle mass and thereby improving fuel economy. Precipitation microstructures improve the mechanical properties of materials, such as yield stress, by impeding the motion of dislocations. That is, the distribution and shape morphology of precipitates have a significant impact on the materials’ properties. Therefore, understanding the mechanisms of microstructure evolution is very important to material design. The microstructure of the precipitate is strongly influenced by the interfacial stability, which is closely connected to the atomic-scale crystal structure of the precipitate phase, the matrix phase, and the interface between the two phases. For this reason, it is vital to understand the thermodynamic and kinetic behavior of strengthening precipitate phases at a variety of length scales for designing structurally strong Al alloys. This work aims to understand phase stability and the growth/coarsening mechanism of Al-based precipitates. We utilize computational methods (i.e., first-principles calculation based on density
functional theory (DFT) and phase-field model (PFM)) and develop analytical theories to investigate the thermodynamics and kinetics of a variety of Al precipitates at various length-scales.

In this study, we: 1) investigate the energetically-favored interfacial structure at coherent and semi-coherent Al₂Cu (θ'//α-Al interfaces for the growth and coarsening studies; 2) search for the lowest energy crystal structure of the ternary (Al-Li-Cu) T₁ phase in order to resolve controversial topic found in many experimental studies; 3) perform atomic-scale DFT calculations of defect properties, solute partitioning, and interfacial stability of the Al₃Cu₂Mg₉Si₇ (Q) precipitate to explain Q-phase off-stoichiometry in experiments, find a potential solute to make the Q-phase energetically stable for coarsening resistance, and to derive a low-energy structure for future growth and coarsening studies; 4) examine the growth of equilibrium Al₂Cu (θ') morphology using the phase-field method with parameters supplied by first-principles calculations in order to elucidate fundamental physics for the high aspect ratio of θ’ precipitates in experiments of binary Al-Cu alloys; and 5) develop a general theory of phase coarsening (Ostwald ripening) for a prolate spheroidal particle in a multicomponent alloy by accounting for the anisotropic effects of interfacial energy and geometry in order to analyze anisotropic shape effects on the growth and coarsening law. These thermodynamic and kinetic studies at atomistic- and micro-scales will move the field of structure metal alloys forward, shedding light on fundamental issues in design of strengthening precipitates in Al alloys.
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Table of Contents

Abstract 3
Acknowledgements 5
List of Tables 11
List of Figures 13
Chapter 1. Introduction 17
  1.1. Motivation 19
  1.2. Material Objectives 19
Chapter 2. Methodology 26
  2.1. Density Functional Theory (DFT) 26
  2.2. Phase Field Model (PFM) 27
Chapter 3. Interfacial stability of $\theta'$ // Al in Al-Cu alloys 30
  3.1. Introduction 31
  3.2. Methodology 34
    3.2.1. First-principles Methodology 34
    3.2.2. Formation and Defect formation energy 35
    3.2.3. Segregation energy 36
    3.2.4. Interfacial energy 37
  3.3. Results and Discussions 37
3.3.1. Stability analyses of the occupancy of interstitial Cu at the coherent 
(001)$_\theta$//(001)$_{Al}$ interface

3.3.2. Stability analyses of the semi-coherent (001)$_\theta$//(001)$_{Al}$ interfacial 
energies with different interface configurations

3.4. Conclusions

Chapter 4. First-principles study of crystal structure and stability of $T_1$ (Al-Cu-Li) 
precipitates in Al-Li-Cu alloys

4.1. Introduction

4.2. Methodology

4.2.1. First-principles Methodology

4.2.2. Formation energy

4.3. Five previously-proposed $T_1$ crystal structures from experiments

4.4. Results and Discussions

4.4.1. A modification of the Li (2) position in the structure by Van Smaalen et al.

4.4.2. Comparison of relative stability of $T_1$ crystal structures based on DFT energetic calculations

4.4.3. Search for $T_1$ stable phase from CE calculation in ternary Al-Li-Cu system

4.5. Conclusions

Chapter 5. Energetics of native defect, solute partitioning and interfacial energy of $Q$ 
precipitates in Al-Cu-Mg-Si alloys

5.1. Introduction
5.2. Methodology

5.2.1. First-principles Methodology

5.2.2. Formation energy

5.2.3. Native defect (i.e., vacancy and anti-site) formation energy

5.2.4. Partitioning energy of solutes

5.2.5. Interfacial energy

5.3. Results and Discussions

5.3.1. Native defects (i.e., vacancy and anti-site) analysis

5.3.2. A prediction for partitioned elements to \( Q \)-phase

5.3.3. A search for lowest energy and structure of the interface

5.4. Conclusions

Chapter 6. Phase-field modeling of \( \theta' \) precipitation in Al-Cu alloy

6.1. Introduction

6.2. Methodology

6.2.1. Free energy

6.2.2. Fourth-rank term for interfacial anisotropy

6.2.3. Elastic contribution to the total free energy

6.2.4. Constructing the phase field model

6.2.5. Interfacial energy

6.3. Results & Discussions

6.3.1. Comparisons with past DFT and PFM studies
## List of Tables

1.1  Alloy design requirement matrix  
4.1  The space group, lattice parameters, and atomic coordinates of the proposed crystal structures of the $T_1$ phase  
4.2  Fractional occupancy of the lattice sites corresponding Fig. 4.1 and Table 4.1 based on the previous literatures  
4.3  Lists of formation energies (eV/atom) were calculated in this work for stable compounds in a binary Al-Cu, Al-Li, and ternary Al-Li-Cu system.  
4.4  Formation energies calculated of $T_1$ atomic models  
4.5  First-principles calculated (VASP) atomic coordinates of relaxed $T_1$ structure $(Al_6Cu_4Li_3)$ corresponding Fig. 4. (b).  
5.1  Comparison of $Q$-phase compositions reported in the literature.  
5.2  Calculated formation energies (eV/atom) to draw convex hull (Fig. 5.1) in quaternary Al-Cu-Mg-Si system.  
5.3  Chemical potential of Al, Cu, Mg, and Si based on the predicted equilibrium reaction phases (reference phases).  
5.4  First-principles defect formation energy for vacancies in $Q$-phase $(Al_3Cu_2Mg_9Si_7)$  
5.5  First-principles defect formation energy for anti-site defects in $Q$-phase
5.6 Summary for site preference of solutes partitioned to $Q$-phase based on DFT energies

5.7 Diffusivity (at 200 °C) of elements in Al

5.8 Calculated interfacial energies of $(11\overline{2}0)_{Q}//(510)_{Al}$ with different terminations (different species)

6.1 Parameters used in the simulation

6.2 Simulation (non-dimensional) parameters

6.3 Experimentally determined average values for two-dimensional length, thickness, and aspect ratio for equilibrium $\theta'$ precipitate in Al-Cu.

6.4 Elastic parameters used in the simulation. Each column corresponds to the equilibrium morphology in Fig. 6.7 (a)-(e).

6.5 Quantitative measurement of $\theta'$ precipitates corresponding Figs. 6.8 (a)-(e).
List of Figures

1.1 Yield strength and ultimate tensile strength (MPa) data for A356 compared to GM project objectives. 22
1.2 Flow chart of multiscale modeling 24
3.1 Atomic models for the coherent $(001)_{\theta'}/(001)_{Al}$ interface with or without interstitial Cu atoms 38
3.2 The calculated convex hull in binary Al-Cu 39
First-principles formation energies of the interface $\alpha$-Al/$\theta'$-Al$_2$Cu ($N$-atom supercells) as a function of $1/N$ for the coherent interface with or without interstitial Cu atoms
3.3 Si solute segregation energies as a function of distance from the coherent interfaces with or without interstitial Cu atoms 40
3.4 Relaxed atomic models for the semi-coherent $(010)_{\theta'}/(010)_{Al}$ interface with different interfacial configurations 45
Interfacial energy calculation for the semi-coherent $(010)_{\theta'}/(010)_{Al}$ interface with different interfacial configurations
4.1 The proposed atomic models for the $T_1$ phase 57
4.2 Atomic structure of the modified model of Van Smaalen et al. proposed in this work 63
4.3 The calculated convex hull based on formation energies of stable compounds in Al-Li-Cu ternary system

4.4 Formation energy (eV/mixing atom) as a function of different fractions of Al in Al-Cu (1) mixed layers (Al$_{8+x}$Cu$_{12-x}$Li$_6$) in the modified model of Van Smaalen et al.

Relaxed supercells of the two ground-state structures (Al$_6$Cu$_4$Li$_3$, Al$_{13}$Cu$_7$Li$_6$)

4.5 The calculated convex hull based on formation energies of stable compounds (Table 4.3) in Al-Li-Cu ternary system

4.6 Calculated formation energies (eV/solute atoms) as a function of fraction of Cu and Li.

5.1 Calculated convex hull based on computed formation energies in a quaternary Al-Cu-Mg-Si system.

5.2 Schematic diagram of crystal structure of Q-phase (Al$_3$Cu$_2$Mg$_9$Si$_7$)

5.3 First-principles calculated partitioning energies of various solutes to Q-phase

5.4 Proximity histogram in APT experiments for various solute elements

5.5 Relaxed super cell of the (1120)$_Q$//(510)$_{\alpha}$ interface

6.1 Chemical free energies of $\theta'$ phase and the matrix $\alpha$-Al as a function of Cu composition in Al-Cu

6.2 Relaxed supercells used for the first-principles interfacial energy calculations of coherent (001) $\theta'$ // (001) $\alpha$-Al and semi-coherent (010) $\theta'$ // (010) $\alpha$-Al interfaces.
First-principles formation energies of the interface $\alpha$-Al/$\theta'$-Al$_2$Cu ($N$-atom supercells) as a function of $1/N$ for the coherent and semi-coherent interfaces

6.3 The equilibrium $\theta'$ morphology (with interfacial energy anisotropy only) changes depends on grid conditions.

6.4 The equilibrium $\theta'$ morphology with interfacial energy anisotropy changes depends on different methods.

6.5 The equilibrium $\theta'$ morphology with interfacial and elastic energy (with elastic inhomogeneity) anisotropy

6.6 Computed aspect ratio as a function of characteristic length (nm) in the 2-D simulation.

6.7 The equilibrium $\theta'$ morphology with interfacial and elastic energy anisotropy. The elastic parameters for (a)-(e) corresponds to (a)-(e), listed in Table 6.3.

6.8 Quantitative measurement of $\theta'$ plate-shaped precipitate with different elastic conditions corresponding Figs. 6.7 (a)-(e).

7.1 The dependence of the diffusional shape factor $f$ on the aspect ratio

7.2 The polar plot of dimensionless interfacial ($\sigma$) energy

The dimensionless chemical potential ($\mu$) vs. the normal angle ($\theta$) to the interface with respect to $x$-axis by solving Eq. (7.34) including our proposed energy model (Eq. (36))

7.3 A dimensionless two-dimensional (2D) physical shape from our proposed energy model based on the wulff construction and Eq. (33) and (34) with a constant
chemical potential

7.4 The dependence of the interfacial energy anisotropy shape factor on the aspect ratio

The dependence of the Gibbs-Thomson shape factor on the aspect ratio.

7.5 The various shape factors in a coarsening law

7.6 The Gibbs tetrahedron of a two-phase equilibrium in a quaternary system

A graphical representation of a composition profile of component $j$ as a function of equivalent radius $r$
CHAPTER 1

Introduction

Recently, a major shift has occurred in the United States public’s perception of the importance of automobile fuel efficiency. There are several reasons why people’s interest has shifted to fuel efficiency in the automobile industry. The first reason is that we are susceptible to rising oil prices, due to its limited availability. Another reason for the increased awareness of fuel consumption is related to the pollution emitted by automobiles as a result of fuel combustion. Previous research has shown that carbon dioxide (CO₂) generated by burning gasoline and diesel fuel in automotive engines has influenced global climate change significantly[1]. One of the ways to aid in an automobile’s fuel economy is to remove the cast iron cylinder block liners and replace them with a lighter material, such as aluminum (Al), which serves to reduce vehicle weight for improved fuel efficiency.

The development of integrated computational materials engineering (ICME) design enables the optimization of materials, manufacturing processes, and component designs by integrating and utilizing computational resources long before components are manufactured. The field of high-temperature cast aluminum alloys for automotive applications is one example of an area in need of an integrated approach through experimentation and theory. Currently, commercial cast Al alloys show drastically reduced room temperature mechanical properties (e.g., yield strength, ultimate tensile strength, or fatigue properties) above a high temperature (250°C) due to coarsening of the strengthening precipitate phases. Thus, it is necessary to develop a thermally
stable microstructure based on thermodynamic and kinetic studies of high-temperature Al alloys to facilitate the design of high-temperature alloys for future applications.

This work focuses on understanding the underlying thermodynamics and kinetics of phase stability and the growth/coarsening mechanism of Al alloys. This investigation is structured as follows: Chapter 1 contains a brief overview of our project motivation and material objectives for our study are introduced. Chapter 2 represents a brief overview of methodologies for quantum-mechanical first-principles calculations based on density functional theory (DFT) and phase-field method (PFM), which are used throughout this work. Chapter 4, 5, and 6 provide DFT calculations that investigate the thermodynamic stability of bulk and interface structures at an atomic-scale. Chapter 4 focuses on the thermodynamic stability of the interfacial structure at the coherent and semi-coherent Al2Cu (θ')/α-Al interfaces for future nucleation, growth, and coarsening studies. Chapter 5 determines the energetically stable crystal structure of the T1 phase (Al-Cu-Li) to resolve the experimental controversy that currently exist in the literature. The determination of crystal structure is the most fundamental step in designing strengthening alloys. Chapter 6 calculates defect properties, solute partitioning energies, and interfacial energy of the Al3Cu2Mg0Si7 (Q) precipitate. Our work aims to understand the off-stoichiometry of the Q-phase in experiments, find a potential solute to make the Q-phase energetically stable for coarsening resistance, and derive a low-energy structure for the future growth and coarsening studies. Chapter 7 covers phase-field simulations with parameters supplied by first-principles methods in order to examine the growth of equilibrium Al2Cu (θ') morphology. The work in this chapter elucidates on fundamental physics for the high aspect ratio of θ' precipitates in experiments involving binary Al-Cu alloys. Chapter 8 describes the general theory of Ostwald ripening for a
spheroidal (non-spherical) particle in multicomponent alloys. This analytic description enables a fundamental understanding of anisotropic shape effects in relation to growth and coarsening laws. Finally, Chapter 9 summarizes findings and discusses avenues for future work.

1.1. Motivation

In the U.S., 30% of total energy consumption is attributed to transportation, of which 90% comes from petroleum consumption[2]. Therefore, the Department of Energy Vehicle Technologies Office (VTO) set a goal to reduce the weight of powertrains by 25% in the year 2025. Achieving this goal would mitigate the U.S. dependence on foreign petroleum and reduce greenhouse gas emissions. In order to achieve this, the design of advanced high-temperature cast aluminum alloys is essential.

Traditional alloy development has an approach that requires trial and error, large expenditures of time, money, and materials to perform experiments to optimize material properties. Thus, our project team (General Motors (Detroit, MI), QuesTek Innovations (Evanston, IL), and Northwestern (Evanston, IL)) aims to design a new lightweight cast-alloy with the desired high-temperature properties by the ICME approach, which is based on thermodynamic and kinetic fundamental studies.

1.2. Material Objectives

Currently, the most commonly used cast Al alloys for cylinder head applications are A356, 319, and AS7GU (A356+0.5%Cu)[3] in automotive applications. The A356 shows good room
temperature ductility and fatigue properties, but has a dramatic drop of tensile strength at 200°C due to coarsening of the Mg$_2$Si ($\beta$) precipitate phases. The Cu containing 319 is significantly strengthened by the Al$_2$Cu ($\theta'$) phase[4]. The 319 alloy also has a weakness at high temperature due to rapid coarsening of the $\theta'$ precipitates. The AS7GU alloy is a variant of the A356 with 0.5 wt.% Cu and is strengthened by $Q$ precipitates, which has an enhanced creep resistance and tensile strength at room and high temperature compared to A356 and 319[5]. All three alloys have drastically reduced room temperature mechanical properties (e.g., yield strength, ultimate tensile strength, and fatigue properties) if exposed to temperatures higher than 250 C due to continued coarsening of their strengthening phases. Therefore, it is important to reduce the coarsening rate in order to maintain the mechanical properties at room temperature. Bridge valve in cylinder heads are especially susceptible to fatigue fracture due to exposure at increased temperatures.
<table>
<thead>
<tr>
<th>Property</th>
<th>Temperature</th>
<th>Baseline DOE Cast Al</th>
<th>Baseline DOE Proposal</th>
<th>GM Proposal</th>
</tr>
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<tbody>
<tr>
<td>Ultimate Tensile Strength (MPa)</td>
<td>Room Temp.</td>
<td>227.5</td>
<td>275.8</td>
<td>300</td>
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<tr>
<td></td>
<td>150</td>
<td>N/A</td>
<td>N/A</td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>51.7</td>
<td>N/A</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>N/A</td>
<td>65.5</td>
<td>65.5</td>
</tr>
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<td>Room Temp.</td>
<td>165.5</td>
<td>206.8</td>
<td>210</td>
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<tr>
<td></td>
<td>150</td>
<td>N/A</td>
<td>N/A</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>34.5</td>
<td>N/A</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>N/A</td>
<td>44.8</td>
<td>45</td>
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<td>3.5</td>
<td>&gt; 3.5</td>
</tr>
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<td>75.8</td>
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</tr>
<tr>
<td></td>
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<td>N/A</td>
<td>N/A</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>N/A</td>
<td>N/A</td>
<td>50</td>
</tr>
<tr>
<td>Density</td>
<td>Room Temp.</td>
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<td>&lt; 6.4</td>
<td>&lt; 6.4</td>
</tr>
<tr>
<td>Fluidity</td>
<td>-</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Same as 319</td>
</tr>
<tr>
<td>Hot Tearing Resistance</td>
<td>-</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Same as 319</td>
</tr>
<tr>
<td>Manufacturing Cost</td>
<td>-</td>
<td>-</td>
<td>&lt; 110% Baseline</td>
<td>&lt; 110% Baseline</td>
</tr>
</tbody>
</table>

Table 1.1. Alloy design requirement matrix, set by DOE and General Motors (GM)
Table 1.1 shows the design requirements needed in future cylinder head applications as specified by the DOE and GM. The baseline properties are from Table 7[5]. The target properties outlined by the DOE and GM show higher than baseline properties across all temperature ranges. For example, room temperature ultimate tensile strength (UTS) and yield strength (YS) need to be improved to 300 MPa and 210 MPa, respectively. Fig. 1 shows a comparison of UTS and YS properties between the A356 alloy and GM targets based on testing temperature. As shown in Fig. 1., room temperature properties are already achieved by current A356 alloys, but the UTS and YS of the A356 alloy drops approximately 85% from room temperature to 250°C. Thus, this
needs to be improved by utilizing thermally stable coarsening resistant strengthening precipitates.

Thus, our aim is to optimize a thermally stable microstructure in order to facilitate the design of novel alloys that meet the increasingly higher demands of future applications. Importantly, computationally driven materials development (i.e., Integrated Computational Material Engineering (ICME)) can reduce time and costs by uniting materials science with engineering in terms of product development.
Figure 1.2. Flow chart of multiscale modeling[7]: Fundamental properties, microstructural implementation, outputs, and materials response (predicted properties). Arrows indicate the transmission of information between different length scale approaches. Red colors (boxes and arrows) represent the related properties in this study.

In an ICME approach, multiscale materials modeling across different time and length scales to develop robust, accurate, and predictive simulations of material behaviors has garnered much attention in the materials community. Fig. 2 illustrates how the microstructure evolution affects the material properties across various length scales. As seen here, the complexity in the relationship between structure and property, have a large number of computational methods to aid in describing the microstructure evolution. The red arrows and boxes are investigated in
this study. Detailed information and background about ICME and multiscale modeling is well described in the minerals, metals, & materials Society (TMS) reports[6, 7].
CHAPTER 2

Methodology

In computational alloy design, multiscale materials modeling has been an interesting topic due to the predictive simulations of materials behavior in significantly reducing the time and cost of developing new materials and manufacturing processes. The representative methods for understanding and predicting the atomistic and microstructural interaction in a material are first-principles calculations based on density functional theory (DFT) and phase field modeling (PFM). In this work, we employ DFT and PFM to understand the thermodynamic and kinetic behavior of strengthening aluminum (Al) precipitates, in order to optimize microstructures in Al alloys for enhancing their mechanical properties at high temperature.

2.1. Density Functional Theory (DFT)

For the practical implementation of Hohenberg–Kohn theorems[8] and density functional theory, Kohn-Sham Ansatz[9] assumes that the ground state density can be calculated by solving a system where Kohn-Sham (KS) non-interacting particles replace the interacting electrons in the true system. The results, following Martin[10] are the KS equations, given by

\[
(H_{KS}^\sigma - \epsilon^\sigma_i)\psi^\sigma_i(r) = 0
\]  
(2.1)

\[
H_{KS}^\sigma = -\frac{1}{2} \nabla^2 + V_{KS}^\sigma(r)
\]  
(2.2)
\[ V_{KS}^\sigma(r) = V_{ext}(r) + V_{Hartree}(r) + V_{xc}^\sigma(r) \]  \( (2.3) \)

\( H_{KS}^\sigma \) is the KS Hamiltonian, and \( \epsilon_i^\sigma \) is the energy of the non-interacting electron in the auxiliary KS system. \( V_{KS}^\sigma(r) \) is the effective KS potential. \( V_{ext}(r) \) is the potential due to the nuclei and other external fields. \( V_{Hartree}(r) \) is the potential due to the exchange and correlation. The last term, \( V_{xc}^\sigma(r) \), is the most difficult to treat as there is no functional form for it other than the case for a homogenous electron gas. Thus, the homogeneous electron gas model is the basis functional for the approximation to the exchange-correlation energy. In this work, we considered the Generalized Gradient Approximation (GGA) where the exchange-correlation energy now depends on the value of the electron density and its gradient at the point in consideration[11, 12], using the Perdew-Burke-Ernzerhof (PBE) functional[13]. The Vienna Ab-initio Simulation Package (VASP)[14-16] is used in this work. Detailed information on DFT calculations is explained in Chapters 3, 4, and 5.

2.2. Phase Field Model (PFM)

The phase-field model (PFM) has become an important and extremely versatile technique for simulating structure evolution at a microscale. Thanks to the diffuse-interface approach, it allows us to study the evolution of arbitrarily complex grain morphologies without any presumptions about their shape or mutual distribution. Specifically, we don’t need to track the location of the interface explicitly. PFM also allows for a straightforward account of different thermodynamic driving forces for microstructure evolution, such as bulk, interfacial, and elastic energies[17], as shown below.
\[
F = \int f(c_1, ..., c_n, \eta_1, ..., \eta_p) + \sum_{i=1}^{n} \alpha_i (\nabla c_i)^2 \\
+ \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \beta_{ij} \eta_i \nabla_j \eta_k d^3 r + \int \int G(r - r') d^3 r d^3 r'
\]

(2.4)

The first integral term describes the bulk free energy function \( f \) and the gradient energy terms \( \alpha_i, \beta_{ij} \) from short-range chemical interactions locally. There are two types of field variables \( c \) and \( \eta \), the conserved and non-conserved field variables, respectively. The non-zero gradient term at and around interfaces contributes interfacial energy. The second integral represents the contribution to the total free energy from the long-range interactions, such as elastic interaction, which is dependent upon the field variables.

The time-dependent behavior of the phase field variables is solved in order to describe microstructure evolution using the Cahn-Hilliard and Allen-Cahn equations[18-21], respectively, for the example of binary A-B alloys,

\[
\frac{\partial c_i(r, t)}{\partial t} = \nabla M_{ij} \nabla \frac{\delta F}{\delta c_j(r, t)}
\]

(2.5)

\[
\frac{\partial \eta_p(r, t)}{\partial t} = -L_{pq} \frac{\delta F}{\partial \eta_q(r, t)}
\]

(2.6)

where \( M_\eta, L_{pq} \) are atom and interface mobility. The objective in phase-field modeling then becomes finding the solution to the two kinetic equations (Eq. (2.5) and (2.6)). There are many numerical methods for solving the kinetic equations in phase-field method. In most cases, the simple second-order finite-difference method on a uniform spatial grid with explicit-time
stepping is used. In this work, we use semi-implicit Fourier-spectral method to solve the phase-field equations for the sake of computational efficiency. According to the previous work by Chen and Shen[22], the computational efficiency is at least two orders of magnitude greater in two-dimensions when compared to the explicit finite-difference method.
CHAPTER 3

Interfacial stability of $\theta'$/Al in Al-Cu alloys

The metastable phase, $\text{Al}_2\text{Cu}$ ($\theta'$), is a well-known strengthening precipitate in aluminum alloys. We investigate the thermodynamically stable interfacial structure at the coherent and semi-coherent $\theta'$/\(\alpha\)-Al interfaces using atomic-scale density functional theory (DFT) calculations. Our results show that the recently proposed occupancy of interstitial Cu atoms at the coherent $(001)_{\theta'}/(001)_{\text{Al}}$ interface by Bourgeois et al. increases the total energy, and does not yield Si segregation behavior in agreement with the previous results obtained using atom probe tomography (APT) showing strong segregation at the interface. Thus, we suggest that the coherent interface without interstitial Cu atoms corresponds to the equilibrium state, and the observed occupancy of interstitial Cu atoms at the coherent $(001)_{\theta'}/(001)_{\text{Al}}$ interface is due to kinetic effects. For the semi-coherent interface, we investigate the energetics of various interfacial configurations with different matches between the number of unit-cells of $\alpha$-Al and $\theta'$. The results show that the semi-coherent interfacial energy does not significantly depend on these interfacial configurations or misfit strains. This DFT result, though somewhat surprising, is consistent with previous results obtained by molecular dynamics (MD) simulation based on the modified embedded-atom method (MEAM).
3.1. Introduction

Precipitation hardening represents a significant source of strength in aluminum alloys and Al₂Cu (θ′) is one of the most common and effective strengthening precipitate phases[23-25]. In Al-Cu alloys, a series of metastable precipitate phases are formed from the decomposition of a supersaturated solid solution during precipitation[26, 27]. At relatively low aging temperatures, the universally accepted sequence of steps for the Al-Cu precipitation process is: Alₜₜₜ → Guinier Preston (GP I zones) → θ'' (GP II zones) → θ’ → θ[28, 29]. (At higher aging temperatures, the GP zones may be bypassed, and θ’ formed directly from the solid solution.) The atomic-crystal structure of the θ’ phase is a CaF₂ structure, but, when embedded in an Al matrix, it adopts a tetragonally distorted version of a cubic fluorite (C1) structure with lattice constants of a = 4.04 Å and c = 5.80 Å. The morphology of the θ’ precipitate is a plate-like morphology with an extremely high aspect ratio (θ’ plates are typically 1-10 nm in thickness and 0.1-1 μm in length[9]), and this high aspect ratio serves an important role as an effective strengthening component. There are two different crystallographic interfacial orientations of the plate-shaped precipitate phase. One is a coherent interface (001)₀///(001)ₐ on the broad faces of the plate, and the other is a semi-coherent interface with (010)₀///(010)ₐ around the rim of the plates[30]. To optimize and control precipitation strengthening, it is essential to understand the morphology and distribution of precipitate phases. The interfacial energy plays a significant role in determining the precipitate morphology, since it in part determines the height of the energy barrier for nucleation and the number density of nuclei, thereby influencing the size
distribution of the precipitate. Also, knowledge of interfacial energies coupled with misfit strains can be used to determine the growth and equilibrium morphology of precipitates, both of which are influenced by the anisotropy of interfacial and strain energy. Thus, a detailed understanding of the thermodynamically stable interfacial structure and its energy is a key step for understanding various precipitate-related phenomena.

The crystal structure and the interfacial energy of the \( \theta'//\alpha\)-Al interfaces have been studied previously[30-32]. Recently, Bourgeois et al.[33] proposed a new structure for the coherent interface that was different from the previously accepted structures[34-36] based on \((001)_{\theta'}\) of the precipitate. They referred to their finding as an intermediate phase in the growth of the \( \theta' \) precipitate, and referred to the structure as a “GP (I) zone-like interface”. The newly proposed interface has a different composition and crystal structure, with extra interstitial Cu atoms at the coherent interface \( \theta' // \alpha\)-Al. Bourgeois et al. argue that during the evolution of the precipitates, the Cu atoms move from these interstitial positions to create new lattice sites of \( \theta' \), thereby causing growth of the \( \theta' \) precipitate. Thus, these interstitial Cu atoms are responsible for precipitate ledge growth. In order to clearly understand the energetic effect of this interstitial Cu occupancy on the interfacial stability, we perform interfacial energy calculations for both the previously proposed structure as well as this newly-proposed one.

The semi-coherent interfacial energy (around the rim of \( \theta' \) precipitates) is an important component to the nucleation energy barrier, and information regarding interfacial energy coupled with misfit strains is also important to understanding precipitate growth. For example, the calculated interfacial energies and lattice misfit strains can be incorporated into a meso-scale phase field model to understand the equilibrium \( \theta' \) morphology[35, 36]. At a semi-coherent
interface, there are periodic variations of residual misfit in magnitude and sign because of different interfacial configurations during particle thickening[30]. According to recent literature, a $\theta'$ thickness distribution shows a discontinuous variation with $0.5c_{\theta'}$ steps and the $3.5c_{\theta'}$ was also commonly observed for 200 °C/24 hours ageing, and not only for $2c_{\theta'}$[37]. In the previous work by Hu et al.[34], molecular dynamics (MD) simulations based on the modified embedded-atom method (MEAM) were used to calculate semi-coherent interfacial energies with different interfacial configurations, and the results showed that an interfacial configuration $2c_{\theta'}: 3a_{Al}$ with misfit strain (-4.29%[34] or -5.1%[36]) is energetically favored. However, their study did not investigate the $7c_{\theta'}: 10a_{Al}$ ($= 3.5c_{\theta'}: 5a_{Al}$) configuration, which is the lowest misfit strain (-0.3%[36] or +0.45%[38]) among all the possible combinations of number of unit-cells of $\alpha$-Al and $\theta'$ up to 10 unit cells. This configuration is important because when a semi-coherent interface has $7c_{\theta'}: 10a_{Al}$ ($= 3.5c_{\theta'}: 5a_{Al}$) configuration, the effect of elastic energy anisotropy becomes smaller. This strongly influences equilibrium $\theta'$ morphology. The lengthening kinetics are also strongly influenced by a thickness-dependent misfit strain[39]. Thus, we investigate the thermodynamic stability of interfaces with different configurations (combinations of different number of unit-cells of $\alpha$-Al and $\theta'$) including the $7c_{\theta'}: 10a_{Al}$ ($= 3.5c_{\theta'}: 5a_{Al}$) configuration by using first-principles DFT calculations.

Here, we perform atomic-scale density functional theory (DFT) calculations to explore the energetically-favored interfacial structure and and energies at the coherent and semi-coherent $\theta'$//$\alpha$-Al interfaces. We find the recently proposed occupancy of interstitial Cu atoms at the coherent (001)$_{\theta'}$//(001)$_{Al}$ interface raises the energy of this interface and hence is not thermodynamically favored. Also, the interstitial Cu atoms change the calculated segregation
behavior of Si atoms to this interface, which leads to inconsistencies with experimental atom probe tomography (APT) results. For the semi-coherent interface, we investigate several energetically favored interfacial configurations with different matches between the number of unit-cells of $\alpha$-Al and $\theta'$. The results show that semi-coherent interfacial energy is not sensitive to the semi-coherent interfacial configurations or misfit strains. Our analysis of the energies and structures of $\theta'$ interfaces will be helpful for future studies of the nucleation and evolution of these precipitates.

3.2. Methodology

3.2.1. First-principles methodology

We performed first-principles DFT calculations using the Vienna Ab initio Simulation Package (VASP)[14, 15] and projector-augmented wave potentials[16]. We utilized the PBE parameterization of the generalized gradient approximation (GGA-PBE)[13] for all calculations. All structures were relaxed with respect to all cell-internal and cell-external degrees of freedom at an energy cutoff of 450 eV (for formation energy calculations, 520 eV is used). In the calculation of formation energy, gamma-centered k-point meshes were constructed to achieve at least 9,000 k-points per reciprocal atom, and the convergence of the energy differences was within 1 meV/atom. For interfacial energy calculations, k-point meshes were used to achieve approximately 10,000 k-points per reciprocal atom. And different super cell sizes (from 31 to 75 atoms for a coherent interface, from 84 to 451 atoms for a semi-coherent interface) were tested for convergence of the energy differences within interfacial energy on the order of 5-10%. In the calculation of solute segregations, 2x2x1 super cells (180 and 188 atoms) were used to achieve
the partitioning energy of each bulk phase, and a 7x7x1 k-point mesh was used to achieve 9,000 k-points per reciprocal atom for convergence of energy differences within 0.03 eV/a solute atom. A k-point mesh “1” for the direction of out of the interface was enough for convergence within 0.02 eV/a solute atom. Especially, near the interface with interstitial Cu atoms, an 8x8x1 k-point mesh was used for convergence within 0.01 eV/a solute atom.

3.2.2. Formation and defect formation energy

The equation for calculating formation energy is shown below:

$$\Delta H^{eq}(Al\alpha Cu\beta) = E(Al\alpha Cu\beta) - [x_A E^{eq}(Al) + x_B E^{eq}(Cu)]$$  \hspace{1cm} (3.1)

where the equilibrium formation enthalpy (eV/atom), $\Delta H^{eq}(Al\alpha Cu\beta)$ for a binary compound $Al\alpha Cu\beta$ is given by the energy of $Al\alpha Cu\beta$ relative to the composition-weighted average of the energies of the pure constituents each in their equilibrium crystal structures. $E(Al\alpha Cu\beta)$, $E^{eq}(Al)$, and $E^{eq}(Cu)$ are the energies (per atom) of the compound $Al\alpha Cu\beta$ and constituents, Al and Cu, respectively, each relaxed to their equilibrium geometries. $x_A = a/(a + b)$ and $x_B = b/(a + b)$ are the concentrations of Al and Cu, respectively. The equation for calculating defect formation energy is shown below:

$$\Delta E_{\text{Defect}} = E_{(\text{Defect})} - E_{(\text{Pristine})} - \sum_m \mu_m$$

$$= E_{(Al_2Cu, r' + \text{interstitial Cu atom})} - E_{(Al_2Cu, r')} - \mu_{Cu}$$ \hspace{1cm} (3.2)

$$E_{Al} = \mu_{Al}, E_{(Al_2Cu, r')} = 2\mu_{Al} + \mu_{Cu}$$
where $E_{(Al_2Cu, \theta' + \text{interstitial Cu atom})}$ is the energy per formula unit of bulk $\theta'$ with interstitial Cu atoms, as shown in Fig. 3.1 (d). Since the chemical potential for Al is the same in both the Al matrix $\mu_{Al}(\text{matrix})$ and in $\theta'$ phase $\mu_{Al}(\theta')$, $\mu_{Cu}$ can be extracted by the energies of two different stable phases, $E_{Al}$ and $E_{(Al_2Cu, \theta')}$.  

### 3.2.3. Segregation energy

Segregation energies can be calculated using the following equation:

$$
\Delta E_{\text{seg}} = \Delta E_{\text{sol}}(\text{interface}) - \Delta E_{\text{sol}}(\text{bulk})
= E(Si \rightarrow Al_i) - E(Si \rightarrow Al_b)
$$

(3.3)

This equation is used for the Al lattice sites in an Al matrix or at an Al sub-lattice site in $\theta'$. The sites that have a sign convention of $\Delta E_{\text{seg}} < 0$ are energetically favorable compared to Al bulk-like sites in the matrix. In addition to the segregation at Al sites, we also considered solute segregation at Cu sites within $\theta'$. For example, when segregation occurs at the coherent $\theta'_i^{Cu}$ layer in Fig. 3.3, then:

$$
\Delta E_{\text{seg}} = \Delta E_{\text{sol}}(\text{int}) - \Delta E_{\text{sol}}(\text{bulk}) = E(Si \rightarrow \theta'_i^{Cu}) - E(Si \rightarrow Al_b) + \mu_{Cu} - \mu_{Al}
$$

$$
\mu_{Al}(\text{matrix}) = \mu_{Al}(\theta')
$$

(3.4)

$$
2\mu_{Al}(\theta') + \mu_{Cu}(\theta') = E(\theta')
$$

where $E(\theta')$ is the energy per formula unit of bulk $\theta'$, i.e., the chemical potential for Al is the same in both the Al matrix $\mu_{Al}(\text{matrix})$ and in the $\theta'$ phase $\mu_{Al}(\theta')$.  

3.2.4. Interfacial energy

We construct supercells of $\theta'$ and $\alpha$-Al to calculate the interfacial energies of the $\theta'/\alpha$-Al interfaces. The energy of formation relative to the energies of $\alpha$-Al and $\theta'$ phases can be written as the follows:

$$\Delta E^f = \delta E_{cs}(\alpha, \theta') + 2\sigma A/N$$  \hfill (3.5)

where $\Delta E^f$ is the formation energy of the super cell relative to $\alpha$-Al and $\theta'$, $\Delta E_{cs}(\alpha, \theta')$ is the coherency strain caused by the lattice mismatch between $\alpha$-Al and $\theta'$, and $N$ is the total number of atoms in the super cell, and $\sigma$ and $A$ are the interfacial energy and area, respectively. Based on the above equation, we can obtain the interfacial energy from the slope of $\Delta E^f/N$ vs. $1/N$ as shown in Fig. 3.2 (b) and 3.4 (b). Detailed information of this approach is well described in the literature[36].

3.3. Results and Discussions

3.3.1. Stability analyses of the occupancy of interstitial Cu at the coherent $(001)_{\theta'}/(001)_{\alpha}$ interface
Figure 3.1. Relaxed atomic models for the coherent (001)$_{\theta'}$/(001)$_{Al}$ interface used in our first-principles calculations: (a) without occupancy of interstitial Cu atoms; (b) with occupancy of interstitial Cu atoms at the interface. The blue spheres represent Al atoms, the orange spheres represent Cu atoms, and the red spheres represent interstitial Cu atoms at the interface, respectively. Dashed lines indicate the bulk structures of $\alpha$-Al, $\theta'$ and $\theta'$ with interstitial Cu atoms, respectively; (c) The unit cell of the bulk $\theta'$ crystal structure (1x1x2 super cell) is shown in green, and the black dotted-line is the unit cell of the bulk $\theta'$ corresponding to the dashed line in (a); (d) The unit cell of the bulk ($\theta'$, 2C$_{θ'}$) with interstitial Cu atoms (red spheres) is shown by the black-dotted line.
Figure 3.2. (a) First-principles calculated energetics from Eq. (3.1) of equilibrium Al-Cu compounds: The equilibrium phase of tetragonal (C16) structure of Al$_2$Cu ($\theta$) is not on the convex hull based on the calculation at $T = 0$ K. This was explained by the role of the vibration entropy of $\theta$ and $\theta'$, which were found to be crucial for the stability of $\theta$ phase[40]. We observed that bulk $\theta'$ was on the convex hull, but the formation energy of the bulk ($\theta'$, 2$\theta'$) with interstitial Cu atoms, as shown in Fig. 3.1 (d), is not. (b) First-principles formation energies of (001)$_{\theta'}/$(001)$_{Al}$ N-atom super cells as a function of $1/N$ for the interface with or without interstitial Cu atoms, as shown in Fig. 3.1 (a) and (b). The energies of the large-cell calculations were fitted to straight lines, and the interfacial energies ($\sigma$) were extracted from the slopes, $2\sigma A$, of these lines by Eq. (3.5).
Figure 3.3. (a) and (b) Relaxed atomic models for the coherent (001)\(\beta_1\)/\(\beta_1\) interface: The blue spheres represent Al atoms, the orange spheres represent Cu atoms, and the red spheres represent interstitial Cu atoms (on \(\theta_1\)-plane), respectively. The black atom in the supercell illustrates the position of a Si atom at a bulk-like site in the Al matrix. (Sub) lattice planes are labeled according to their position relative to the interface planes. For example, \(Al_1\) refers the Al plane adjacent to the interface; \(Al_b\) refers to a bulk-like plane in the Al matrix; and \(\theta_1^{Cu}\) refers to the interfacial Cu layer within the \(\theta_1\) precipitate. (c) Calculated Si solute segregation energies by Eq. (3.3) and (3.4) as a function of distance from the coherent interfaces. Two segregation energies are reported for each layer. The blue points represent Si solute at the coherent interface with the interstitial Cu atoms at interface, and the red points represent Si solute at the coherent interface without interstitial Cu atoms at interface.
Fig. 3.1 (a) and (b) show the two proposed coherent \( (001)_{\theta^'/\theta} // (001)_{Al} \) interfaces. Fig. 3.1 (a) corresponds to the prevalently believed concept of a coherent interface, which has a cutting-edge in a bulk \( \theta^' \) structure. Fig. 3.1 (b) is the new and recently proposed structure by Bourgeois et al.[33]. The difference between the two structures involves occupancy by interstitial Cu atoms at the interface, as indicated as red atoms in Fig. 3.1 (b) and (d). Before investigating the thermodynamic stability of the occupancy of interstitial Cu atoms at the coherent \( (001)_{\theta^'/\theta} // (001)_{Al} \) interface, we focused on the effect of the interstitial occupancy on the thermodynamic stability of the bulk \( \theta^' \) precipitate in order to choose the common reference phases in binary Al-Cu. The binary convex hull shows that the occupancy of interstitial Cu atoms made bulk \( \theta^' \) unstable, which was not on the calculated convex hull, as shown in Fig. 3.2 (a). Accordingly, the defect formation energy of interstitial Cu atoms in bulk \( \theta^' \) shows a positive value (0.33 eV/defect) by Eq. (3.2), which means the interstitial occupancy is not energetically favorable in the bulk \( \theta^' \) precipitate.

In terms of interface stability, according to the work by Bourgeois et al.[33], the occupancy of interstitial Cu atoms (shown in Fig. 3.1 (b)) can lower the energy of the system by 0.11 eV per Cu atom. For energetic comparison between Fig. 3.1 (a) and (b), they choose two reference phases, pure Al and a dilute solid solution (an isolated Cu substitutional point defect in Al) to evaluate the energetic effect of an additional (interstitial) Cu atom. After the occupancy of interstitial Cu atoms at the interface, the Cu atoms move to the new lattice site of \( \theta^' \) lowering the energy of the system by 0.38 eV per Cu atom, which means the interface (Fig. 3.1 (a)) becomes thicker by \( 0.5c_{\theta^'} \). Thus, they argued that “interfacial segregation of solute Cu is energetically favorable, but ultimately less so than incorporation of solute into a new unit of \( \theta^' \) through
thickening.” To clarify the energetic effect of interstitial occupancy on interfacial thermodynamic stability, we perform interfacial energy calculations at zero temperature in this work. Since the Cu chemical potential is lowest for $\alpha$-Al and $\theta'$ at 0K as shown in Fig. 3.2 (a), we choose $\alpha$-Al and $\theta'$ for reference phases for comparison between two interfacial energies in common. In other words, since the two-phase equilibrium in binary Al-Cu is between $\alpha$-Al and $\theta'$, $\text{Al}_2\text{Cu} (\theta')$ is the lowest energy state (“per Cu”) in equilibrium with $\alpha$-Al at 0K. The dilute solute Cu atoms in Al matrix are not considered in our 0K approach because the solubility of Cu in Al shows a pretty small solubility ($0.00044 X_{Cu}$) even at finite temperature (200 °C) based on recent thermodynamic (CALPHAD) modeling of Al-Cu system[41-43]. Fig. 3.2 (b) shows that the coherent interface has an interfacial energy of 0.20 J/m². However, a much larger interfacial energy of 0.39 J/m² was obtained for the interface with occupancy of interstitial Cu atoms, indicating that the interstitial occupancy is not energetically preferred based on our computation. That it, interstitial Cu atoms decrease interfacial stability compared to an interface without interstitial Cu atoms based on two stable phases in binary Al-Cu, $\alpha$-Al and $\theta'$.

Commercial cast aluminum alloys are complex multi-component systems, and Si is a common element in these alloys. The study of the interfacial segregation of the solute atom is important because the interfacial energy of the matrix-precipitate interface is strongly influenced by the chemistry of the interface, thereby influencing the micro-morphology of precipitates, For example, According to the literature[44], Si has a role in catalyzing the heterogeneous nucleation of GPII zones and $\theta'$ precipitates by interfacial segregation in the Al-Cu system. Here, to investigate the effect of interstitial occupancy by Cu atoms on the segregation of Si solute in a ternary alloying system, we compared the segregation energies of the Si solute both interfaces to
previous APT results by Biswas et al.[44, 45]. The previous APT and thermodynamic DFT results[44, 45] showed that Si atoms strongly segregate at the coherent interface. Specifically, previous first-principles calculations (validated by red points in our work, as shown in Fig. 3.3 (c)) aptly explained the experimental segregation behavior based on non-interacting solute atoms at the coherent interface without interstitial Cu atoms. However, in Fig. 3.3 (c), our calculation shows that the Si atoms are not preferentially segregated at the interface with the interstitial Cu atoms ($\Delta E_{seg} > 0.1$ eV/atom solute on $Al_i$-$\theta'^{Cu}_{1-1}$ planes), which is in disagreement with the previous APT results. Since Si segregation occurs with a thermodynamic driving force, as explained by a previous work[44], we can predict that the interface without occupancy of interstitial Cu atoms is thermodynamically stable in a multi-component Al alloy system when considering the Si segregation of the APT results. Also, strained $\theta'$ precipitates from the occupancy of interstitial Cu atoms present less solute partitioning for the Si solute. The blue point is higher than the red point on the $\theta'^{Cu}_b$ plane in Fig. 3.3 (c).

To sum up this section, APT shows preferential Si segregation to this interface. Without the interstitial Cu (which is also the lowest energy interface), DFT calculations agree with APT about Si segregation. However, including the interstitial Cu (which is a higher energy interface), DFT calculations show anti-segregation of Si, in disagreement with APT. Thus, the energy of the interface with Cu interstitials is higher, and does not yield segregation behavior in agreement with experiment. Therefore, we concluded that a coherent interface without interstitial Cu atoms corresponds to a low energy interfacial state between the $\alpha$-Al and $\theta'$ phases in binary Al-Cu. The observed occupancy of interstitial Cu atoms at the coherent $(001)_{\theta'/}(001)_{Al}$ interface is energy-lowering, but could be observed as a kinetic pathway during growth. It is also possible
that the Cu atoms directly move to $\theta'$ lattice sites during the growth, not through the interstitial sites at the interface, similar to the direct $\theta'$ formation regardless of GP zone. In order to clarify this mechanism precisely, future studies (e.g., dilute Cu segregation at an interface super cell) will be needed.

3.3.2. Stability analyses of the semi-coherent $(001)_{\theta'}/(001)_{Al}$ interfacial energies with different interface configurations
Figure 3.4. (a) Relaxed atomic models for the semi-coherent \((010)_{\theta'}/(010)_{Al}\) interface with different interfacial configurations (2c\(_{\theta'}\): 3\(a_{Al}\), 3c\(_{\theta'}\): 4\(a_{Al}\), and 7c\(_{\theta'}\): 10\(a_{Al}\) (= 3.5c\(_{\theta'}\): 5\(a_{Al}\)), which corresponds to lattice misfit strains, -5.1\%[36], +6.8\%[36], and -0.3\%[36]) were used in our first-principles calculations (b) First-principles formation energies of \((010)_{\theta'}/(010)_{Al}\) \(N\)-atom super cells as a function of \(1/N\) for the interface, as shown in (a). The energies of the large-cell calculations were fitted to straight lines, and the interfacial energies (\(\sigma\)) were extracted from the slopes, 2\(\sigma\)A, of these lines by Eq. (3.5). The interface with the 7c\(_{\theta'}\): 10\(a_{Al}\) (= 3.5c\(_{\theta'}\): 5\(a_{Al}\)) configuration has a higher
slope, but also a relatively higher interfacial area of larger supercells, and as such, extracted interfacial energies can be similar.

Semi-coherent interfacial energy around the rim of $\theta'$ precipitate is higher than the coherent interfacial energy at the broader side of $\theta'$ precipitate, and as such, it is responsible for the energetic barrier for nucleation due to higher energy compared to coherent one. One interesting aspect is that the residual misfit strains at a semi-coherent interface vary with different interfacial configurations during the thickening process[30]. Moreover, lengthening kinetics are affected by a thickness-dependent misfit strain based on the previous literature[39]. Thus, the information about semi-coherent interfacial energy coupled with misfit strains is crucial for the study of $\theta'$ morphology.

We investigated the relationship between interface configuration and its interfacial energy, i.e., how many $\theta'$ and $\alpha$-Al unit cells match each other. Previously, Hu et al.[14] calculated the interfacial energies of $\theta'$ precipitates and studied the energetically favored configuration of critical nuclei using MD simulation with an empirical potential, and found that the interfacial configuration $2c_{\theta'}:3a_{Al}$ with a misfit strain (-4.29%[34], -5.1%[36], or -4.3%[38]) was energetically favored. They argued that the semi-coherent interfacial energy is not significantly influenced by the interface configurations, although it increases slightly with an increase of stress-free strain. However, in the previous work, the smallest misfit strain (-0.3%[36] or +0.45%[38]) case of $7c_{\theta'}:10a_{Al}$ (the $3.5c_{\theta'}:5a_{Al}$), which is among all the possible combinations of unit cells of $\theta'$ and $\alpha$-Al, was not studied. According to recent literature, a $\theta'$ thickness distribution shows a step variation with 0.5 $c_{\theta'}$. Not only for $2c_{\theta'}$, the thickness of $3.5c_{\theta'}$ was
also commonly observed for 200 °C/24 hours ageing [37]. Thus, we additionally investigated the thermodynamic stability of a semi-coherent interface with different configurations including a $7c_{\theta'}:10a_{Al}$ ($= 3.5c_{\theta'}:5a_{Al}$) match using first-principles calculations.

Fig. 3.4 shows the calculated interfacial energies at semi-coherent interfaces with different interfacial configurations, $2c_{\theta'}:3a_{Al}$, $3c_{\theta'}:4a_{Al}$, and $7c_{\theta'}:10a_{Al}$ ($= 3.5c_{\theta'}:5a_{Al}$). Each interfacial configuration corresponds to different lattice misfit strains reported in the literature, which are -4.29%[34] or -5.1%[36], +6.8%[36] or +7.67%[34], and -0.3%[36] or +0.45%[38], respectively. For the configuration of $7c_{\theta'}:10a_{Al}$ ($= 3.5c_{\theta'}:5a_{Al}$), we choose very large super cells with a $7c_{\theta'}:10a_{Al}$ configuration instead of choosing $3.5c_{\theta'}:5a_{Al}$ because the $7c_{\theta'}:10a_{Al}$ configuration satisfies the periodic boundary condition of Cu atoms along the [001] axis in Fig. 4.4 (a). As shown in Fig. 4.4 (b), the three calculated interfacial energies were similar (0.52, 0.51, and 0.51 J/m$^2$), which is comparatively consistent with the previous literature[34] using MD simulation. Thus, we conclude that misfit strain energy does not significantly influence the semi-coherent interfacial energy. In other words, the semi-coherent interfacial energy is not significantly dependent upon the interface configurations. As such, the difference of local geometry due to different interface configurations can be considered not significant at a constant crystallographic orientation. For the large misfit strain configuration (i.e., $3c_{\theta'}:4a_{Al}$), the increased bulk energies due to large misfit strain are offset by the increased super cell energy due to large interface stress.
3.4. Conclusions

This study focused on the thermodynamic stability of the coherent \((001)_{\theta'/(001)_{\text{Al}}}\) and semi-coherent \((010)_{\theta'//(010)_{\text{Al}}}\) interfaces. Utilizing reference (stable) phases, \(\theta'\) and \(\alpha\)-Al in binary Al-Cu, we investigated the recently proposed interfacial structure with the occupancy of interstitial Cu atoms. We found that the interstitial Cu occupancy increases the total energy, which means that the interfacial stability of a coherent interface decreases. In ternary Al-Cu-Si, the interstitial Cu atoms change the segregation behavior of the Si atoms; a tendency that is inconsistent with the previous results obtained using atom probe tomography (APT), which showed that strong segregation existed at the interface. Therefore, we conclude that a coherent interface without interstitial Cu atoms corresponds to an equilibrium state based on stable phases, \(\alpha\)-Al and \(\theta'\). And, the future kinetic study will be needed to explain the experimentally observed occupancy of interstitial Cu atoms at the coherent interface in the future. Additionally, we investigated the energetically favored interfacial configuration at a semi-coherent interface, a match between different numbers of unit-cells of Al and \(\theta'\), for the future study of nucleation or growth of \(\theta'\) precipitate. The results demonstrate that a semi-coherent interfacial energy does not significantly depend on the semi-coherent interfacial configurations or misfit strains.
CHAPTER 4

First-principles study of crystal structure and stability of $T_1$ precipitates in Al-Li-Cu alloys

Aluminum-lithium-copper alloys have a low density, high elastic modulus and high specific strength. Due to this combination of properties, alloys strengthened with the ternary (Al-Li-Cu) $T_1$ phase have attracted a great deal of interest especially in aerospace applications. Determining the atomic structural information of the precipitate is a fundamental step in developing a basis for advanced alloy design; however, even though many experimental studies have addressed the $T_1$ crystal structure, it still remains the subject of some controversy. Here, we use density functional theory (DFT) calculations to investigate the structure and composition of the $T_1$ phase by comparing the energetic stability of five previously-proposed models of the crystal structure of $T_1$. The DFT formation energy of these proposed $T_1$ crystal structures was calculated using a special quasi-random structure (SQS) approach to describe a disordered Al-Cu sub-lattice. In conflict with the experimental phase diagram (which shows $T_1$ as a stable phase), DFT of all five proposed models result in an energetically unstable $T_1$ phase. We search for a new, lower-energy structure of $T_1$ using a cluster expansion approach method, and find a new structural model with DFT energy that is stable (at $T = 0K$), i.e., on the calculated convex hull of the Al-Li-Cu ternary system. However, this new predicted phase does not have a tie-line with Al (i.e., does not form a stable two-phase equilibrium with Al), but the formation energy of the phase is very close to the
energy required to make a tie-line with Al ($\Delta E = 0.013$ eV/atom), which could be affected by finite temperature entropic effects (i.e., vibrational entropic stabilization).

### 4.1. Introduction

Al-Li-Cu alloys are known to offer an attractive combination of properties for various structural applications, especially in aerospace[46-48]. These alloys generally have a low density, a high elastic modulus, and high specific strength, largely attributed to highly efficient precipitation strengthening[46, 48]. The addition of Li by ~1 at.% can reduce the total density of an alloy by ~3% (the solid solubility of Li varies from ~4.2 wt.% at ~600°C to < 1wt.% at 100°C in binary aluminum-lithium alloy[49, 50]). In the ternary Al-Li-Cu system, the stable Al-rich phases which appear in the phase diagram under equilibrium conditions are Al$_2$Cu ($\theta$), AlLi ($\delta$), Al$_2$CuLi ($T_1$), Al$_6$CuLi$_3$ ($T_2$) and Al$_{7.5}$Cu$_4$Li ($T_B$)[51-53]. In addition, there are a variety of metastable phases found in the Al-Cu and Al-Li systems, namely GP zones, $\theta''$, $\theta'$, and Al$_3$Li ($\delta'$)[51]. One of the important, well-studied stable phases is the $T_1$ phase (Al$_2$CuLi) because it is the major strengthening precipitate phase in many Al-Li-Cu alloys[54]. The $T_1$ phase is generally reports to have a stoichiometry of Al$_2$CuLi. We show below, however, a new structure and stoichiometry of this phase. However, for simplicity of notation, we will refer to the stoichiometry of the phase generally as Al$_2$CuLi nominally, and will specifically point out deviations to this stoichiometry as appropriate.

When $T_1$ is embedded in an Al matrix, it is usually observed as a very thin plate with ~1.3 nm thickness, which is approximately equal to the five times the distance between close-packed
$\{111\}$ Al planes$^{[46]}$. This phase is hexagonal with a space group $P6/mmm$ ($a_\theta = 0.496$ nm, $c = 0.935$ nm) established by Hardy and Silcock using X-ray powder diffraction$^{[55]}$. To control alloy microstructures and ultimately mechanical properties, it is vital to understand the nucleation and growth of the $T_1$ phase during precipitation, and as such, establishing an accurate atomic-crystal structure is a key fundamental insight. For example, according to previous reports, plastic deformation prior to the ageing process and secondary alloying elements, such as Ag and Mg, can play important roles in promoting the nucleation of $T_1$ precipitate$^{[56-59]}$. In order to fully understand those effects, knowledge about the $T_1$ crystal structure is a premise. Even though there have been considerable experimental efforts devoted to determining the $T_1$ crystal structure, the topic still remains somewhat controversial. Therefore, there is a pressing need to clarify the atomic structure of the thermodynamically stable $T_1$ phase for establishing the structure of the precipitate.

Five atomic models of the $T_1$ crystal structure have been proposed in the literature$^{[54, 60-65]}$. A detailed description of these models is given in Section 4.4 below. Here we present a brief summary of the previously proposed structures. The proposed $T_1$ structure models can be categorized into two main types. A first family of models is based on that the stacking of four hexagonal layers ($c = 0.935$ nm $\approx 4 \times 0.233$ nm) analogous to the $\{111\}$ planes of the Al matrix. The representative structure is the model by Huang et al.$^{[60]}$ in 1987. Later, Cassada et al.$^{[61]}$ and Howe et al.$^{[62]}$ proposed a modification of atomic coordination and different decoration of each layers in the structure of Huang et al.$^{[60]}$. In 1990, Van Smaalen et al.$^{[63]}$ proposed the representative structure of a second family of $T_1$ models utilizing single crystal X-ray diffraction based on a $T_1$ bulk phase. Their atomic structure showed several differences in comparison to the
previous structure by Huang et al.[60] in spite of the same space group and similar lattice parameter. The main difference is that the $T_1$ structure does not consist of a stacking of four hexagonal layers spaced by 0.233 nm but shows several corrugated Al-Li layers. However, Wang et al.[66] argued that the structure based on the work by Huang et al.[60] appears more likely to be true instead of the other proposed structures, and there is a lack of further supporting research for the model by Van Smaalen et al.[63]. They also suggested that the other $T_1$ structures could originate from when the $T_1$ phase is formed by the dissociation of dislocations by a stacking-fault mechanism[66, 67].

Thus, the structure model by Huang et al.[60] was, until recently, the generally accepted structure for the $T_1$ precipitates in aluminum. However, in 2011, the two independent studies, by Donnadieu et al.[64] and Dwyer et al.[65] determined that the $T_1$ precipitate embedded in Al matrix was actually very close to that of the bulk $T_1$ phase proposed by Van Smaalen et al.[63] based on aberration-corrected electron microscopy[64, 65]. They also argued that at very small sizes the particles may exhibit off-stoichiometric composition compared to bulk $T_1$ phase by Van Smaalen et al.[63]. However, the reported structures were not identical to each other in terms of the presence of the Li atoms at the edge of a unit-cell. For example, Dwyer et al.[65] argued that the reason of the difference is because Donnadieu et al.[64] only considered images at the certain direction, where Li atoms are masked[65]. From the above descriptions of the large number of experimentally reported structural models, it is clear that although much is known about the $T_1$ precipitate, its crystal structure remains controversial.

In this paper, we perform an energetic evaluation via accurate DFT calculation to compare the relative stability of the different suggested atomic models. First-principles DFT calculations
have been widely used to successfully deduce various properties of precipitate phases, specifically in Al alloys[40, 68-74], as well as in other systems[75-81]. For example, Wolverton[72] performed DFT calculations to validate crystal structures of Al-Cu-Mg, Al-Cu-Mg-Si, and Al-Zn-Mg precipitates using DFT energies, and we will apply an analogous approach here to the $T_1$ phase. The validation or determination of precipitate crystal structures based on DFT calculations provides only an initial step, but this knowledge of the crystal structure is a necessary step to allow connections of DFT with other computational approaches. For example, the information of thermodynamic stability of precipitates can be utilized for bulk energetics to be incorporated into CALPHAD type databases[82-86]. Also, the information of crystal structure can be used to calculate interfacial energies, which can be incorporated into phase-field model (PFM) to determine mechanical properties by understanding microstructure evolution[35, 36, 87-90]. But, calculation of these thermodynamic and interfacial properties from DFT requires knowledge of the precipitate crystal structure.

To help solve the long-standing controversial problem of the $T_1$ precipitate crystal structure in Al-Li-Cu alloys, we perform an atomic-scale analysis of the structure and energetics of the various proposed candidate crystal structures of the $T_1$ phase. We perform DFT calculations of all previously suggested models, and evaluate the relative stability of these models. We use two theoretical methods special quasi-random structure (SQS)[91] and cluster expansion (CE)[92-94], to describe the configuration of disordered and ordered Al-Cu sub-lattice in the $T_1$ structure. Based on our DFT energies combined with the SQS method for describing the disordered sub-lattice, it is shown that all experimentally proposed $T_1$ models are energetically unstable, which is in conflict with experimental observations. Thus, we search for a new, lower-energy structure.
of $T_1$ phase based on previous experimental reports by using the CE method. Based on the CE method, we propose a new structure of $T_1$ phase, and find that the DFT energy of our new finding structural model is stable (at $T = 0K$) on the calculated convex hull of the Al-Li-Cu ternary system. The new structural information of the $T_1$ phase proposed here can provide key information to use in future computational modeling efforts of Al-Li-Cu alloys, and ultimately can impact novel Al-Li-Cu alloy designs.

4.2. Methodology

4.2.1. First-principles Methodology

DFT calculations were performed with the Vienna Ab initio Simulation Package (VASP) and projector-augmented wave potentials\cite{14-16}. We utilized the PBE parameterization of the generalized gradient approximation (GGA-PBE)\cite{13} for all calculations. All structures were fully relaxed with respect to volume as well as all cell-internal and cell-external degrees of freedom at an energy cutoff of 520 eV. Static calculations were subsequently performed after fully relaxation of the structures. Gamma-centered k-point meshes in both relaxation and static calculations were constructed to achieve at least 10,000 k-points per reciprocal atom. Based on these settings, convergence of formation energy was achieved within 1 meV/atom.

The two dimensional Al-Cu (1) mixed sub-lattice configuration (Fig. 4.1) was made by using a special quasi-random structure (SQS) approach\cite{91}. In the current work, we fixed the number of Al-Cu mixed layers to 12 atoms because of the limitation of large supercell size due to computational cost, and thus established two SQSs (Table 2.). Subsequently, the number of atoms in a super cell was approximately ~50 or ~70 atoms (2x12 atoms for mixed Al-Cu layers)
depending on different models. To evaluate the stability of the $T_1$ structure, as shown in Fig. 4.2 (b), with respect to Al and Cu fractions on Al-Cu (1) sites (Fig. 4.2 (b)), a cluster expansion (CE) approach[92-94] was used. In the CE calculation, 24 effective cluster interaction (ECI) coefficients, including 11 pairs, 9 three-body, and 2 four-body interactions, were used to achieve the final cluster expansion for Al$_{8+x}$Cu$_{12-x}$Li$_6$ by fitting 84 ordered input structures (26 atoms per a cell). The cluster expansion has the predictive power with a cross-validation score of 0.013 eV/mixing atom. The CE and SQS methods were implemented in the Alloy Theoretic Automated Toolkit (ATAT) software suite[95-98].

We utilized the Open Quantum Material Database (OQMD)[99, 100] to search for stable compounds in a ternary Al-Li-Cu system. All the phases involved were recalculated in this work (due to the fact that we use a higher energy cutoff than is used in OQMD). Subsequently, the recalculated DFT energies for all phases (both those previously in OQMD and newly calculated DFT energies for $T_1$ phases) were utilized to plot a convex hull in the ternary Al-Li-Cu system to examine their relative phase stability.

### 4.2.2. Formation energy

For the purpose of evaluating relative stabilities of various experimentally proposed $T_1$ structures, we calculated formation enthalpies based on the following equations.

$$
\Delta H^{eq}(Al_{a}Cu_{b}Li_{c}) = E(Al_{a}Cu_{b}Li_{c}) - [x_{A}E^{eq}(Al) + x_{B}E^{eq}(Cu) + x_{C}E^{eq}(Li)]
$$

(4.1)

Here, the equilibrium formation enthalpy (eV/atom), $\Delta H^{eq}(Al_{a}Cu_{b}Li_{c})$ for a ternary $T_1$ compound Al$_a$Cu$_b$Li$_c$ is given by the energy of Al$_a$Cu$_b$Li$_c$ relative to the composition-weighted
average of the energies of the pure constituents each in their equilibrium crystal structures. \( E(Al_aCu_bLi_c), E^{eq}(Al), E^{eq}(Cu) \) and \( E^{eq}(Li) \) and are the energies (per atom) of the compound \( Al_aCu_bLi_c \) and constituents, Al, Cu, and Li, respectively, each relaxed to their equilibrium geometries. \( x_A = a/(a+b+c), x_B = b/(a+b+c) \) and \( x_C = c/(a+b+c) \) are the concentrations of Al, Cu, and Li, respectively. In section 4.4.3, we will discuss thermodynamic stability of \( T_1 \) phase in equilibrium with Al matrix. Thus, we calculated the formation enthalpies per solute atoms (eV/solute atoms) based on the following equation.

\[
\Delta H^{eq}(Al_aCu_bLi_c) = \frac{E(Al_aCu_bLi_c) - [x_A E^{eq}(Al) + x_B E^{eq}(Cu) + x_C E^{eq}(Li)]}{x_B + x_C} \tag{4.2}
\]

This energy represents the thermodynamic stability of any compounds \( (Al_aCu_bLi_c) \) when equilibrium with Al matrix.

4.3. Five previously-proposed \( T_1 \) crystal structures from experiments
Figure 4.1. Atomic models for $T_1$ phase: (a) Huang et al.[60], (b) Howe et al.[62], (c) Van Smaalen et al.[63], (d) Donnadieu et al.[64], and (e) Dwyer et al.[65] The structures are shown along [1100] direction (y-axis). The z-axis represents (0001), which corresponds to the normal direction of {111} Al plane. Light blue spheres represent Al atoms, orange spheres represent Li atoms, and dark blue spheres represent the disordered sub-lattice of Al and Cu. The notations on the right of the atomic stacking layers in each crystal structure (i.e. Li (1), Al (3)) correspond to the atomic coordinates as listed in Table 4.1 and 4.2.
<table>
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<tbody>
<tr>
<td>Lattice Å</td>
<td>4.965 Å</td>
<td>4.965 Å</td>
<td>4.954 Å</td>
<td>4.94 Å</td>
<td>4.96 Å</td>
</tr>
<tr>
<td>(a=b, c)</td>
<td>9.345 Å</td>
<td>9.345 Å</td>
<td>9.327 Å</td>
<td>9.33 Å</td>
<td>14.18 Å</td>
</tr>
<tr>
<td>Li (1)</td>
<td>(0 0 0.5)</td>
<td>(⅔ ⅔ 0.5)</td>
<td>(⅓ ⅔ 0.5)</td>
<td>(⅓ ⅔ 0.5)</td>
<td>(⅓ ⅔ 0.5)</td>
</tr>
<tr>
<td>Al (3)</td>
<td>(⅓ ⅔ 0.5)</td>
<td>-</td>
<td>(0 0 0.3568)</td>
<td>(0 0 0.3568)</td>
<td>(0 0 0.4062)</td>
</tr>
<tr>
<td>Al-Cu (1)</td>
<td>(⅓ 0.25)</td>
<td>Al (⅔ ⅔ 0.75)</td>
<td>(⅔ 0.2363)</td>
<td>(⅔ 0.2363)</td>
<td>(⅔ 0.3237)</td>
</tr>
<tr>
<td></td>
<td>(⅓ 0.25)</td>
<td>Cu (⅓ ⅔ 0.25)</td>
<td>(⅔ 0.2363)</td>
<td>(⅔ 0.2363)</td>
<td>(⅔ 0.3237)</td>
</tr>
<tr>
<td></td>
<td>(0 ⅔ 0.25)</td>
<td>Cu (0 ⅔ 0.75)</td>
<td>(0 ⅔ 0.2363)</td>
<td>(0 ⅔ 0.2363)</td>
<td>(0 ⅔ 0.3237)</td>
</tr>
<tr>
<td>Li (2)</td>
<td>(⅓ ⅔ 0)</td>
<td>-</td>
<td>(0 0 0.051)</td>
<td>-</td>
<td>(0 0 0.1993)</td>
</tr>
<tr>
<td>Al (2)</td>
<td>(0 0 0)</td>
<td>(⅔ ⅔ 0)</td>
<td>(⅔ 0 0)</td>
<td>(⅔ 0 0)</td>
<td>-</td>
</tr>
<tr>
<td>Al-Cu (2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(⅔ 0.1612)</td>
</tr>
<tr>
<td>Al-c</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(0 0 0)</td>
</tr>
</tbody>
</table>

Table 4.1. The space group, lattice parameters, and atomic coordinates of the proposed crystal structures[60, 62-65] of the $T_1$ phase were used for DFT calculations in this work. The listed coordinates, which correspond to Fig. 4.1, are fractional with respect to a hexagonal cell. A dash (-) indicates no pertinent data (N/A).
Table 4.2. Fractional occupancy of the lattice sites corresponding Fig. 4.1 and Table 1 based on the previous literatures[60, 62-65]. A dash (-) indicates no pertinent data (N/A).

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<tbody>
<tr>
<td>Al-Cu (1)</td>
<td>0.5 Cu/0.5 Al or 0.35(0.65) Cu/0.65(0.35) Al</td>
<td>0.56 Cu/0.44 Al</td>
<td>0.9 Cu/0.1 Al</td>
<td>0.2-0.4 Cu/0.6-0.8 Al</td>
<td></td>
</tr>
<tr>
<td>Al-Cu (2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1-0.2 Cu/0.8-0.9 Al</td>
<td></td>
</tr>
<tr>
<td>Li (1)</td>
<td>Li</td>
<td>Li</td>
<td>Li</td>
<td>0.2 Li/0.8 Al</td>
<td></td>
</tr>
<tr>
<td>Li (2)</td>
<td>Li</td>
<td>-</td>
<td>0.66 Li</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Many previous reports over several decades have pursued the crystal structure of the $T_1$ phase. Based on previous experimental data[60, 62-65], five representative atomic models of the $T_1$ phase were proposed and are shown in Fig. 4.1 (a)-(e). In the early work, Huang et al.[60] proposed a crystal structure for $T_1$, as portrayed in Fig. 4.1 (a), based on stacking planes analogous to the $\{111\}$ Al planes[60]. The structure is composed of a series of stacking layers, such as ABAB ..., where A planes are Al-Li ordered layers (close-packed) of Li and Al in 2:1 and 1:2 ratios respectively, which are located on the basal plane and the medium plane ($z=0$ and 1/2), and the inner B planes are randomly disordered sub-lattice of Al and Cu atoms, which are non-close packed ($z = 1/4$ and 3/4).

Later, Howe et al.[62] proposed a very similar $T_1$ structure compared to that proposed by Huang et al.[60], but with several differences shown in Fig. 4.1 (b). In Howe et al.[62] model, only Al atoms were on the basal plane ($z=0$), while the middle plane ($z=1/2$) had only Li atoms.
And, the Al-Cu mixed layers (Fig. 4.1 (b)) were closed-packed planes where disordered 0.5Al/0.5Cu or ordered layers (each Cu atom is surrounded by six Al atoms, and vice versa). The two Al-Cu (1) configurations in a cell (Fig. 4.1 (b) and Table 4.1) are not identical each other. So the structure is composed of four close-packed stacking layers, A₁B₂A₃C, instead of ABAB[62]. Cassada et al.[61] also proposed a similar $T₁$ structure with a modification of Huang et al.[60], which is also composed of four close-packed stacking layers[61]. All the layers (Al-Li and Al-Cu) are randomly disordered in the structure by Cassada et al.[61], and as such, this structure was not chosen for performing DFT calculation in this work. Instead, the ordered structure by Howe et al.[62] was chosen for our first-principles study, which is supposed to have lower energy than the disordered structure by Cassada et al.[61].

In 1990, Van Smaalen et al.[63], based on a crystallographic study by X-ray diffraction, proposed a significantly different $T₁$ structure compared to the previous structures by Huang et al.[60], Cassada et al.[61], and Howe et al.[62]. Unlike the previous suggestions, the structure by Van Smaalen et al.[63] displays corrugated Al-Li layers (Al (3) and Li (1) sites and Al (2) and Li (2) sites, shown in Fig. 4.1 (c)) instead of flat planes corresponding to the (111) Al type planes, as shown in Fig. 4.1 (c). For example, Al (3) and Li (2) are on $z=0.3568$ and $z=0.051$, respectively, and not $z=0.5$ and $z=0$, as shown in Table 4.1. Due to the difference in inner structure between Huang et al.[60] model and Van Smaalen et al.[63] model, the distance between the two Al-Cu mixed layers in a cell increased to 0.492 nm as compared to 0.467 nm in the previous models based on the stacking of four (111)-type layers.

Until recently, due to lack of further supporting research for the model by Van Smaalen et al.[63], the structure model by Huang et al.[60] was, until recently, the generally accepted
structure for the $T_1$ precipitates in Al-Li-Cu alloys. However, in 2011, the recent high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) studies by Donnadieu et al.[64] found that the corrugated layer structure derived from X-ray studies by Van Smaalen et al.[63]. Around the same time, Dwyer et al.[65] proposed the $T_1$ precipitate structure, which is also very close to the structure from Van Smaalen et al.[63], as shown in Fig. 4.1 (c) and (e). According to the argument by Donnadieu et al.[64], the structure by Van Smaalen et al.[63] has a very close distance of 0.095 nm between two Li (2) atoms (z-position (0.051) in Table 4.1) with consideration of the mirror symmetry. Since it is smaller than the atomic radius 0.152 nm of a Li atom, they argued that only one of the two sites could be occupied, leading to an occupation factor equal to 0.5 instead of the 0.66 given by Van Smaalen et al.[63] In section 4.5.1, we discuss atomic coordination and partial occupancy of Li (2) sites since the two Li (2) atoms are overlapped due to periodic images when more than half the Li (2) sites (non zero at z-axis) are occupied. Donnadieu et al.[64] also argued the composition of the layers could be different in the precipitates compared with that of the bulk stable phase. For example, they proposed a new model for the $T_1$ precipitate with the correction of the Li (2) replaced by Al when compared to the structure by Van Smaalen et al.[63]. They found that their modified model shows closer intensity to small-angle X-ray scattering (SAXS) than the structure by Van Smaalen et al.[63] in terms of crystal structure of $T_1$ precipitate. However, around the same time, Dwyer et al.[65] proposed the structure which is different from the structure by Donnadieu et al.[64]. Dwyer et al.[65] model has Li (2) sites, and they argued that the results by Donnadieu et al.[64] only considered the image from the $<110>_{\alpha}$ direction, where Li (2) sites are masked[65].
In terms of crystallographic space group of the $T_1$ phase, all the structures show hexagonal with a space group symmetry of $P6/mmm$ except for the structure (hexagonal, $P6mm$) proposed by J. M. Howe et al., as shown in Table 4.1. Since the structure by J. M. Howe et al.\cite{62} does not have a mirror plane perpendicular to the six-fold axis due to a difference of coordination between two Al-Cu (1) layers in a cell, listed in Table 4.1, it shows $P6mm$, not $P6/mmm$. The detail information, such as the fractional occupancy of atomic coordinates, is listed in Table 4.2.

4.4. Results and Discussions

4.4.1. A modification of the Li (2) position in the structure of the work by Van Smaalen et al.
Figure 4.2. (a) A periodic cell (1x1x2 super cell) of atomic structure of Van Smaalen et al.[63] (Fig. 4.1. (c)). When the partial occupancy of Li is chosen as 0.5 based on the argument from Donnadieu et al.[64], Li (2) atoms move to the same plane (c-axis) of Al (2) sites during relaxation of a cell. (b) Atomic structure of the modified model of Van Smaalen et al.[63], proposed in this work. (c) Calculated energy differences of displacement (z-axis) of 0.5 Li (2) atoms in the modified model with respect to the c-axis of position of Al (2) sites as shown in (b). The y-axis represents energy difference
divided by number of atoms (2x1x1, 26 atoms) in a super cell. The red and blue indicate that Al-Cu (1) sites are occupied by only Cu atoms or Al atoms, respectively. (d) Computed XRD pattern for the structure of Van Smaalen et al.[63] and the modified model with the radiation source of Cu Kα with a wavelength of 1.5418Å.

As mentioned in Section 4.3, we need to clarify the atomic coordination of Li (2) in the structure by Van Smaalen et al.[63], shown in Fig. 4.2 (a), for performing DFT calculations before investigating relative stabilities of proposed T1 structures. In the paper by Donnadieu et al.[64], they argued that only one of the two sites could be occupied, leading to an occupation factor equal to 0.5 instead of the 0.66 given by Van Smaalen et al.[63]. Accordingly, we chose the fraction 0.5 of Li (2) in the structure by Van Smaalen et al.[63] for performing DFT calculations. The 0.5 Li (2) atoms move toward the plane (z-axis) of Al (2) layers during DFT relaxation, when the atoms are chosen as layers or alternately configuration, as shown in Fig. 4.2 (a). Thus, based on our calculations, we chose a slightly modified structure, as shown in Fig. 2 (b), from the work of Van Smaalen et al.[63] to calculate DFT formation energy, as shown in section 4.5.2. Our modified T1 structure has a fully occupied Li (2) site, where z=0, not 0.66 at z=0.051, which is listed in Table 4.1. Fig. 4.2 (c) shows variation in energy difference for displacement of Li (2) along the z-axis with respect to the z-position of the Al (2) layer. This also represents that the T1 structure has lowest energy when the z-position of Li (2) equals to zero, as same with one of Al (2) layer. In terms of crystallographic space group, our modified structure (the correction of Li (2) position and occupancy in the structure by Van Smaalen et al.[63] also shows same space group of P6/mmm (Hexagonal) with assumption of disordered sub-lattice of Al-Cu (1).
Since the structure by Van Smaalen et al.[63] was proposed based on single crystal X-ray diffraction, we computed XRD pattern for the structures of Van Smaalen et al.[63], and that of a modified structure. Based on our computed XRD pattern for both structures, there are no distinct differences, as shown in Fig. 4.2 (d). Thus we can argue that it is difficult to elucidate the exact position of Li (2) atoms in experiment because Li atoms are weakly scattered for both X-rays and electrons in experiment. The structure by Dwyer et al.[65] also has the same issue of position and partial occupancy of Li (2) atoms when considering mirror-symmetry. However, since Dwyer et al.[65] proposed only a one unit-cell structure of $T_1$ precipitate embedded in an Al matrix, they did not consider overlapping Li (2) atoms due to periodic images when more than half the Li (2) sites (non zero at z-axis) are occupied. In order to perform DFT calculation with periodicity for the structure by Dwyer et al.[65], thus we choose the structure sandwiched between {111} planes of $\alpha$-Al, followed by the information of atomic coordination in Table I in the previous paper[65].

4.4.2. Comparison of relative stability of $T_1$ crystal structures based on DFT energetic calculations
Table 4.3. Lists of formation energies (eV/atom) were calculated in this work from Eq. (4.1) for various compounds in a binary Al-Cu, Al-Li, and ternary Al-Li-Cu system. We utilized the Open Quantum Material Database (OQMD)[99, 100] to search for stable compounds in a ternary Al-Li-Cu system, and to recalculate DFT energies for them. These calculations were used to draw a convex hull (Fig. 4.3) in an Al-Li-Cu ternary system to evaluate the relative stability (hull distance) of five different $T_1$ phase models. The formation energies of compounds with an * indication are newly proposed $T_1$ phases, as discussed in section 4.4.3.

<table>
<thead>
<tr>
<th></th>
<th>Al-Cu</th>
<th>Al-Li</th>
<th>Al-Cu-Li</th>
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<tbody>
<tr>
<td>$\Delta H_f$</td>
<td>$\text{(eV/atom)}$</td>
<td>$\text{(eV/atom)}$</td>
<td>$\text{(eV/atom)}$</td>
<td>$\text{(eV/atom)}$</td>
<td>$\text{(eV/atom)}$</td>
</tr>
<tr>
<td>$\text{Al}_2\text{Cu (GP)}$</td>
<td>-0.092</td>
<td>$\text{Al}_2\text{Li (}\delta')$</td>
<td>-0.097</td>
<td>$\text{AlCuLi}_2$</td>
<td>-0.191</td>
</tr>
<tr>
<td>$\text{Al}_2\text{Cu (}\theta, \theta')$</td>
<td>0.156, -0.175</td>
<td>$\text{AlLi (}\delta)$</td>
<td>-0.182</td>
<td>$\text{AlCu}_3\text{Li}$</td>
<td>-0.225</td>
</tr>
<tr>
<td>$\text{AlCu}$</td>
<td>-0.213</td>
<td>$\text{Al}_2\text{Li}_3$</td>
<td>-0.189</td>
<td>$\text{Al}_6\text{Cu}_4\text{Li}_3^*$</td>
<td>-0.239</td>
</tr>
<tr>
<td>$\text{AlCu}_3$</td>
<td>-0.189</td>
<td>$\text{Al}_4\text{Li}_9$</td>
<td>-0.157</td>
<td>$\text{Al}_{13}\text{Cu}_7\text{Li}_6^*$</td>
<td>-0.218</td>
</tr>
</tbody>
</table>

Table 4.4. Formation energies calculated from Eq. (4.1) of $T_1$ atomic models[60, 62-65]. We chose the modified structure (Fig. 4.2 (b)) from the model by Van Smaalen et al.[63] as discussed in section 4.3. Two different SQSs are used to describe the approximately...
disordered configurations of Al-Cu (1) sub-lattice. In the Howe et al.[62] model, the specific ordered configuration of Al-Cu (1) has been described in the previous literature. A dash (-) indicates no pertinent data (N/A). We draw the convex hull, as shown in Fig. 4.3, through lowest energy path (stable phases) in ternary Al-Li-Cu system, and then compute the hull distances for comparing relative stabilities. The hull distance represents the distance (eV/atom) to the calculated convex hull of Al-Li-Cu under the same composition.

Figure 4.3. The calculated convex hull based on formation energies of stable compounds (Table 4.3.) in Al-Li-Cu ternary system. The indicated phases are stable phases in ternary Al-Li-Cu system. Blue circles represent five different $T_1$ models (a: Huang et al.[60], b: Howe et al.[62], c: Modified Van Smaalen et al.[63], d: Donnadieu et al.[64], and e: Dwyer et al.[65]. As shown in Table 4.4, the hull distances for all the $T_1$ models are the positive values, which means unstable in ternary Al-Li-Cu system.

To evaluate relative stability of five different models for $T_1$ phase, we calculated formation energies from Eq. (4.1) of various compounds to draw convex hull (Fig. 4.3) in ternary Al-Li-Cu system, as shown in Table 4.3. Table 4.4 represents calculated formation energy from Eq. (4.1)
to compare the relative stability of the five different models based on information from the $T_1$ crystal structures. Except for the model of Howe et al.[62] with ordered configuration of Al-Cu (1), the other four models have the same two-dimensional configuration comprised of Al-Cu mixed (disordered) layers (Al-Cu (1)), as shown in Fig. 4.1 and Table 4.1. As such, we commonly put the two configurations from SQS method (Table 4.4.). The configurations of the two Al-Cu (1) mixed layers in a cell are chosen identically. We fixed the fraction of Al and Cu atoms to be 0.5 in common, and in the Dwyer et al.[65] structure, the Al-Cu (2) layer was assigned to be pure Al.

Since the compositions of the structures are not identical each other, we couldn’t compare the energies directly. Thus, we calculated hull distance from the formation energies of five different models to the convex hull under the same composition as listed in Table 4.4. Among the five different structures, the modified model of Van Smaalen et al.[63] was the closest to the convex hull (lowest hull distance), which means it is the most stable among five different models. The family of models (structures by Huang et al.[60] and Howe et al.[62]) based on the stacking of four hexagonal layers similar to \{111\} planes of the Al matrix shows less stable than the family of a structure with corrugated Al-Li layers, as shown in Table 4.4. However, the major finding is that all of the five previously-proposed models for $T_1$ crystal structure have energies above the convex hull, and hence none of these models produce a $T_1$ phase that is thermodynamically stable.

Since the $T_1$ phase is observed as a stable phase in the experimental phase diagram of Al-Li-Cu, our finding of positive hull distance for all of these models is inconsistent with the experimental phase diagram. Hence, we conclude that all five models of the structure are likely
incorrect, and some lower energy structure must therefore exist. Based on our structure, configurational entropy given by ideal mixing on the Al-Cu layer (24 atoms) can stabilize $T_1$ phase by $\sim 0.017$ eV/atom at 350°C, but this energy is not sufficient to be stable. We focus specifically on the disordered Al-Cu (1) configurations as a potential avenue to lower the energy of the phase. To search for a new, lower-energy structure of $T_1$, we used a cluster expansion (CE) method for the modified structure by Van Smaalen et al.\cite{63} to determine the configuration dependent energy with consideration of all the possible configurations of Al-Cu (1) sites, which is described in section 4.4.3.

4.4.3. Search for $T_1$ stable phase from CE calculation in ternary Al-Li-Cu system

![Figure 4.4](image.png)

Figure 4.4. (a) Formation energy (eV/mixing atom) as a function of different fractions of Al in Al-Cu (1) mixed layers ($\text{Al}_{8+x}\text{Cu}_{12-x}\text{Li}_6$) in the modified model of Van Smaalen et al.\cite{63}, as shown in Fig. 4.2 (b). Blue points indicate the energies predicted by cluster expansion for possible structures, and the black points indicate the energies of DFT
calculated ground states. Two ground state energies (Al$_6$Cu$_4$Li$_3$, Al$_{13}$Cu$_7$Li$_6$) are observed.

(b) Relaxed supercells of the two ground-state structures (Al$_6$Cu$_4$Li$_3$, Al$_{13}$Cu$_7$Li$_6$).

Figure 4.5. The calculated convex hull based on formation energies of stable compounds (Table 4.3.) in Al-Li-Cu ternary system. The indicated phases are stable phases in ternary Al-Li-Cu system. The red (Al$_6$Cu$_4$Li$_3$) and green (Al$_{13}$Cu$_7$Li$_6$) points indicate the two ground state structures computed from the CE calculation, as shown in Fig. 4.4. Al$_6$Cu$_4$Li$_3$ is a stable phase on the calculated convex hull of Al-Li-Cu ternary system. Indeed, the calculated hull distance from Al$_{13}$Cu$_7$Li$_6$ to the convex hull, including the new Al$_6$Cu$_4$Li$_3$ ($T_1$) phase, is very small (0.003 eV/atom). The red dotted line indicates a lack of tie-line between the calculated $T_1$ phase and Al matrix at 0K.
Figure 4.6. (a) Calculated formation energies (eV/solute atoms) from Eq. (4.2) as a function of fraction of Cu and Li. These energies represent the thermodynamic stability
when equilibrium with Al matrix. The red (Al₆Cu₄Li₃) and green (Al₁₃Cu₇Li₆) points indicate the two ground state $T_1$ structures computed from the CE calculation, as shown in Fig. 4.4. (b) Calculated formation energies in the range of -0.55 and -0.35 eV/solute atoms in Fig. 4.6 (a). When we draw the tie-line with Al₂Cu ($\theta$) and AlLi ($\delta$) rather than Al₂Cu ($\theta'$) and Al₃Li ($\delta'$) based on experiment[51-53], the energies from newly-proposed $T_1$ models are below the tie-line between experimental stable phases, Al₂Cu ($\theta$) and AlLi ($\delta$).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Atomic coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li (1)</td>
<td>(0.485 0.841 0.5)</td>
</tr>
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<tr>
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<td></td>
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<td>(0.023 0 0.647)</td>
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<tr>
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<td>(0.477 0.2 0.353)</td>
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<tr>
<td>Al-Cu (1), Al</td>
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<tr>
<td>Al-Cu (1), Cu</td>
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</tr>
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<td>(0.508 0 0.765)</td>
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Table 4.5. First-principles calculated (VASP) atomic coordinates of relaxed $T_1$ structure (Al₆Cu₄Li₃) corresponding Fig. 4. (b). The listed coordinates are fractional with respect to a supercell (lattice constants of a=4.941 Å, b=8.641 Å and c=9.232 Å)
In section 4.4.2, we find that all five models of the $T_1$ structure are unstable with respect to the ternary Al-Li-Cu convex hull (Fig. 4.3). In order to find a new, lower-energy structure of $T_1$, we used CE method to examine the configuration-dependent energy with consideration of all the possible configurations of Al-Cu (1) sites. Since the modified structure by Van Smaalen et al.[63] has lowest hull distance (most stable) among five different $T_1$ models shown in Table 4.4, we chose this structure as the basis for performing the CE. The dependence of the formation energy of $T_1$ on the substitution arrangement of Al-Cu atoms was described with a cluster expansion and coefficients, which were fitted to selected first-principles total-energy calculations. Based on the CE calculation, two 0 K ground state structures on the convex hull were found to be (Al$_6$Cu$_4$Li$_3$ and Al$_{13}$Cu$_7$Li$_6$), and it was shown that these two structures have lower energies, in terms of their convex hull distance, than any of the previous-proposed models of $T_1$. In fact, including these phase in the construction of the convex hull of the Al-Li-Cu ternary system, as shown in Fig. 4.4 (b), we find that one of these two phases appears on the convex hull as a stable, T=0K compound. Based on this, we propose our new Al$_6$Cu$_4$Li$_3$ structural model as a stable $T_1$ structure on the calculated convex hull of the Al-Li-Cu ternary system at 0K. In addition, the calculated hull distance from Al$_{13}$Cu$_7$Li$_6$ to the convex hull, including the new Al$_6$Cu$_4$Li$_3$ ($T_1$) phase, is very small (0.003 eV/atom). Thus, the Al$_{13}$Cu$_7$Li$_6$ ($T_1$) phase also might an off-stoichiometric stable phase of $T_1$ at high temperature.

The $T_1$ phase is not only observed as a stable phase in the experimental phase diagram, but there is also a two-phase region between $T_1$ and the Al solid solution observed. Hence, this means that the $T_1$ phase should not only appear on the convex hull, but also should have a tie-line
with Al. The formation energy of our new Al₆Cu₄Li₃ (T₁) phase is on the convex hull, but does not show a tie-line with Al (Fig. 4.5). However, its energy of this phase by only 0.013 eV/atom would form a tie-line with Al. Thus, the tie-line with Al may be explained by other high temperature effects (i.e., vibrational entropic stabilization of Al₂Cu (θ)[40]). To understand thermodynamic stability of T₁ phase in equilibrium with the Al matrix, we calculated formation energies per solute atoms from Eq. (4.2), as shown in Fig. 4.6 (a) and (b). According to the experimental phase diagram[51-53], Al₂Cu (θ) and AlLi (δ) phases are stable phases rather than the metastable phases of Al₂Cu (θ’) and Al₃Li (δ’). When we chose Al₂Cu (θ) and AlLi (δ) instead of Al₂Cu (θ’) and Al₃Li (δ’) to draw tie-line, the calculated energy of Al₆Cu₄Li₃ (T₁) is low enough to make a tie-line with Al as shown in Fig. 4.6 (b). This strongly suggests that our model for T₁ should be stable, and possess a tie-line with Al at finite temperatures. However, a calculation of the entropic contributions will be the subject of a future study.

According to the experimental phase diagram of the Al-Li-Cu system, there are other Al-rich stable phases, such as Al₆CuLi₃ (T₂) and Al₇.₅Cu₄Li (T₉), under equilibrium conditions[51-53]. In this work, we did not consider the thermodynamic stability for Al₆CuLi₃ (T₂) and Al₇.₅Cu₄Li (T₉) due to lack of information of partial occupancies in a significantly large supercell. To understand the broader landscape of T₉ stability in a ternary Al-Li-Cu system, future studies can investigate the stability of the two phases (Al₆CuLi₃ (T₂) and Al₇.₅Cu₄Li (T₉)) and also account for the effects of high temperature excitations.
4.5. Conclusions

In this paper, first-principles DFT calculations were performed to address a long-standing controversial problem regarding the $T_1$ crystal structure in Al-Li-Cu alloys. To evaluate the relative stability among five different experimentally suggested models, the DFT formation energies of the various experimentally suggested $T_1$ crystal structures were calculated using a special quasi-random structure (SQS) approach to describe a disordered Al-Cu sub-lattice. DFT of all five models gives energies that are not on the lowest-energy convex hull, in conflict with the experimental phase diagram. To search for a new, lower-energy structure of $T_1$ corresponding to a stable phase in experimental phase diagram, we use cluster expansion (CE) method. Based on the CE method, we suggest a new structure (Al6Cu4Li3), and find that the DFT energy of this new structural model is stable (at $T = 0K$) on the calculated convex hull of the Al-Li-Cu ternary system. The newly predicted phase still does not have a tie-line with Al (again, in contrast with the experimental phase diagram), but the formation energy of the phase is very close to the energy required to make a tie-line with Al. The energy difference is only 0.013 eV/atom, which will require studies accounting for high temperature effects (i.e., vibrational entropic stabilization) in the future. We note that our proposed new structure of $T_1$ phase can help facilitate a wide variety of new modeling approaches for Al-Li-Cu alloys, such as multiscale modeling of microstructural phenomenon from phase-field methods and more accurate phase diagram calculations based on CALPHAD.
CHAPTER 5

Energetics of native defect, solute partitioning, and interfacial energy of $Q$ precipitate in Al-Cu-Mg-Si alloys

The compound $\text{Al}_3\text{Cu}_2\text{Mg}_9\text{Si}_7$, is known as the $Q$-phase and forms as a thermodynamically stable precipitate during solidification and aging in the quaternary Al-Cu-Mg-Si system. It is crucial to achieve basic information of thermodynamic parameters to design strengthening precipitates for advanced alloys. Here, we perform atomic-scale density functional theory (DFT) calculations of defect properties, solute partitioning, and interfacial stability of the $\text{Al}_3\text{Cu}_2\text{Mg}_9\text{Si}_7$ ($Q$) precipitate. We find: (i) simple native point defect (i.e., vacancies and anti-sites) thermodynamics can partially explain experimentally observed off-stoichiometry, such as the observed variation of $\text{Al}_{3+\delta}\text{Cu}_2\text{Mg}_{9-\delta}\text{Si}_7$ (Mg-deficient and Al-rich) in experiment. (ii) Calculated solute-partitioning energies of common solutes allow us to define general rules for site-preference in the $Q$-phase in terms of electronic structure and atomic radius. To validate our DFT predictions, we perform atom-probe tomography (APT) experiments for six-different elements (Zn, Ni, Mn, Ti, V, and Zr). The results show that the partitioning behavior of solutes Ni, Zn, and Mn are consistent with DFT predictions, but the transition elements (Ti, V, and Zr), which are anomalously slow diffusers in Al, partitioned to the $Q$-phase as opposed to DFT predictions. (iii) For the low energy interface $(11\bar{2}0)_Q//(510)_{\text{Al}}$ for the needle shaped $Q$-precipitate, we survey various terminations and orientations and derive a low-energy structure. We find Cu is the
nearest atom to the interface, which is in agreement with previous literature on Cu interfacial segregation at the $Q' \parallel \alpha$-Al interface. The computed lowest energy (0.52 J/m$^2$) and corresponding structure can be applicable to future multi-scaling modeling of microstructural evolution.

5.1. Introduction

Lightweight, age-hardenable alloys such as those based on aluminum are of growing interest in the transportation sector, where their use has the potential to reduce vehicle mass and thereby improve fuel economy. Many industrial aluminum alloys currently in use in the automotive industry have a variety of solute elements, often including silicon, magnesium, and copper. In the quaternary Al-Cu-Mg-Si system, the equilibrium phase, Q-phase, is found in a wide variety of aluminum alloys, including wrought 2xxx (Al-Cu-Mg-Si), 6xxx (Al-Mg-Si) with Cu additions, and cast alloys such as 319, which is one of the multicomponent commercial alloys that is frequently used for engine blocks and related power train applications[101, 102]. The equilibrium Q-phase has been widely used for strengthening in an Al matrix[103-105]. It is generally known to have a hexagonal crystal structure (P$\bar{6}$, $a = 10.35$-$10.40$ Å and $c = 4.02$-$4.05$ Å) with 21 atoms in a primitive cell[72, 106, 107]. The micro-morphology of the Q-phase precipitate exhibits a lath or needle-like morphology. Typical dimensions of Q-phase precipitates were reported to be in the range of 2.0-5.0 nm$^2$ in cross-section and 60-100 nm in length, depending upon aging conditions[108]. It is commonly known that the Q-phase has a $\{510\}_\alpha$ habit plane, and its orientation relationship with the $\alpha$-Al matrix can be $[0001]_Q \parallel [001]_\alpha$ and
Although the $Q$-phase has been regarded as an important strengthening phase in commercial Al alloys for a long time, there is still a lack of fundamental thermodynamic understanding of it. Knowledge of simple atomic-scale quantities, such as the stoichiometry and lattice parameters of the precipitate are fundamental steps in developing a basis for advanced alloy design. However, the information of chemical composition of $Q$-phase remains controversial. For example, there have been various stoichiometric compositions, such as $\text{Al}_4\text{Cu}_2\text{Mg}_8\text{Si}_7[106]$, $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6[110, 111]$, $\text{Al}_4\text{Cu}_1\text{Mg}_5\text{Si}_4[25]$, and $\text{Al}_{17}\text{Cu}_9\text{Mg}_{45}\text{Si}_{29}$ ($\sim\text{Al}_{3.5}\text{Cu}_2\text{Mg}_{9.5}\text{Si}_6$)[112, 113] reported from various experimental studies. First-principles calculations based on density functional theory (DFT) have previously been used to examine the formation enthalpies of various compositions of $Q$, and determined that $\text{Al}_3\text{Cu}_2\text{Mg}_9\text{Si}_7$ has the lowest energy at $T=0K[72]$, and is thus proposed to be the stoichiometric ground state composition for $Q$. Most experimental measurements of $Q$ phase are in the form of precipitates in equilibrium with an Al matrix, which would naturally make them off-stoichiometric with Al-rich compositions. The off-stoichiometries are due to native defects such as, vacancy or anti-site defects, which occur at finite temperatures, it is necessary to examine experimental stoichiometries in terms of an analysis of native defects. Also, the information of thermodynamic stability of precipitates with defects can be utilized for bulk energetics in computer coupling of phase diagrams and thermochemistry (CALPHAD, CALculation of PHAse Diagrams) databases[82].

The study of the effects of alloying elements is also important because solutes can play a role in influencing the nucleation or coarsening rates of precipitation or changing interfacial stability via interfacial segregation, thereby influencing the morphology of precipitates. For example,
with respect to $Q$-phase, significant partitioning of Zn to the interior of $Q$-phase precipitates was recently observed by atom-probe tomography (APT) experiments[114]. With respect to other Al-based precipitates, there are already plenty of reports about solute behavior (i.e., partitioning or segregation). However, except for the finding of Zn partitioning to $Q$ precipitate, other possible minor elements, which could be candidates to make $Q$-phase energetically more stable for coarsening resistance, have not yet been discovered.

In order to understand precipitation strengthening, it is essential to study interfacial energy since it is responsible for the energetic barrier in nucleation and growth, thereby influencing the morphology of the precipitate. Precipitate growth is influenced by interfacial and strain energy anisotropy, making it important to consider interfacial energies and their effects on misfit strains. Thus, fundamental knowledge about a thermodynamically stable interfacial structure and its energy is a key step for understanding various precipitate-related phenomena. Recently, Fiawoo et al.[115] found multiple interface orientations perpendicular to the long dimension of the lath or needle with accounting for atomic row matching based on rotations about the long axes ($[0001]_Q // [001]_\alpha$) by using atomic resolution High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM). They showed the $\{510\}_\alpha$ plane is the majority of examined Q- precipitates. However, the detailed atomic structure (the chemistry of the interface) was not well characterized. Thus, a low-energy interfacial structure in atomic-scale needs to be obtained using atomic DFT calculations for more-effective coarsening-related studies.

Therefore, even though the $Q$-phase has a long history and is a key-strengthening phase in a group of commercially important aluminum alloys, fundamental knowledge such as
stoichiometry, solute-interaction, and interfacial structure is poorly understood because of lack of knowledge about the aforementioned atomic-scale studies. First-principles calculations based on DFT have been successfully employed to provide key information about energetics, kinetics, diffusion and phase stability in alloy systems[68-70, 73, 75-81]. Thus, we perform DFT calculations of defect properties, solute partitioning, and the stability of the interfacial structure of the equilibrium stable precipitate, Al$_3$Cu$_2$Mg$_9$Si$_7$ (Q). Specifically, we calculated vacancy and anti-site defect formation energies to explain previously suggested various off-stoichiometries of Q-phase precipitates in Al alloys. In addition, we address solute interactions with Q-phase in search of alloys designed to make Q-phase energetically more stable for coarsening resistance. We calculate solute-partitioning energies of various solutes and analyze the results of our calculations to search for the key physical effects. We also perform atom-probe tomography (APT) experiment to validate our DFT predictions. Finally, since the study of the atomic-interfacial structure between precipitates and matrix is essential for advanced computational alloy design, we therefore survey various terminations and orientations to derive a low-energy structure of the interface (11$ar{2}$0)$_Q$//(510)$_{Al}$, perpendicular to the long dimension of the lath or needle.

5.2. Methodology

5.2.1. First-principles methodology

We performed first-principles DFT calculations using the Vienna Ab initio Simulation Package (VASP)[14, 15] and projector-augmented wave potentials[16]. We utilized the PBE
parameterization of the generalized gradient approximation (GGA-PBE) [13] for all calculations. All structures were relaxed with respect to all cell-internal and cell-external degrees of freedom at an energy cutoff of 450 eV (for formation energy calculations, 520 eV is used) and k-point meshes were used to achieve at least 9,000 k-points per reciprocal atom. We chose a formation energy difference of 1 meV/atom to be sufficient for a convergence criterion. For the calculation of defect formation energies, 1x1x3 and 1x2x3 supercells containing 63 and 126 atoms, respectively, were used for the Q-phase to achieve an energy difference convergence value of approximately ~0.03 eV/defect. The solute partitioning calculations were performed using supercells: a 4x4x4 supercell containing 256 atoms was used for α-Al, and 1x1x3 and 1x2x3 supercells containing 63 and 126 atoms, respectively, were used for the Q-phase to achieve an energy difference of ~0.03 eV/solute. In the case of interfacial energy calculations, we used a super cell of 94 and 188 atoms, and the k-point density and supercell size were enough for convergence of the energy difference to within less than 0.015 J/m^2.

5.2.2. Formation energy

We calculated formation energies based on the following equations.

\[
\Delta H^{eq}(A_aB_bC_cD_d) = E(A_aB_bC_cD_d) - [x_A E^{eq}(A) + x_B E^{eq}(B) + x_C E^{eq}(C) + x_D E^{eq}(D)]
\]

(5.1)

where the equilibrium formation enthalpy, (eV/atom), \(\Delta H^{eq}(A_aB_bC_cD_d)\), for any quaternary compound \(A_aB_bC_cD_d\) is given by the energy of \(A_aB_bC_cD_d\) relative to the composition-weighted average of the energies of the pure constituents each in their equilibrium crystal structures.
\( E(A_aB_bC_cD_d), E^{eq}(A), E^{eq}(B), E^{eq}(C), \) and \( E^{eq}(D) \) and are the energies (per atom) of the compound \( A_aB_bC_cD_d \) and constituents, A, B, C and D, respectively, each relaxed to their equilibrium geometries. \( x_A = a/(a+b+c+d), x_B = b/(a+b+c+d), x_C = c/(a+b+c+d) \) and \( x_D = a/(a+b+c+d) \) are the concentrations of A, B, C and D, respectively.

### 5.2.3. Native defect (i.e., vacancy and anti-site) formation energy

Defect formation energies are computed from the following formula:

\[
\Delta E_{\text{defect}}' = E_T - \sum n_i \mu_i
\]  

\( E_T \) represents the total ground state energy of the super cell plus defect as calculated, \( n_i \) represents the number of atoms of element \( i \) in the super cell, and \( \mu_i \) represents the chemical potential of that element. In order to calculate native defect formation energies, we need to compute the chemical potentials. To do that, it is first necessary to determine the various phases that are in equilibrium with the Q-phase. We utilized the grand canonical linear programming (GCLP) method[116] to search for equilibrium phases in a quaternary Al-Cu-Mg-Si system in the open quantum material database (OQMD)[99, 100]. The convex hull based on re-calculated DFT energies (Table 5.2) is shown in Fig. 5.1. The chemical potentials are then obtained using a series of equations for the equilibrium of the various phases on the convex hull. For example, for equilibrium between \( \alpha \)-Al, Si, \( \text{Al}_2\text{Cu} (\theta^\prime) \), and \( Q \), we would solve the following equations for the chemical potentials:
\[
\mu_{Al} = E_{FCC\ Al} \\
\mu_{Si} = E_{diamond\ Si} \\
2\mu_{Al} + \mu_{Cu} = E_{\theta'(Al_2Cu)} \\
3\mu_{Al} + 2\mu_{Cu} + 9\mu_{Mg} + 7\mu_{Si} = E_Q
\] (5.3)

5.2.4. Partitioning energy of solutes

The difference in the formation energy for a solute in \( Q \) and the formation energy for a solute in the \( \alpha \)-Al matrix is defined as the solute partitioning energy (\( E_p \)). The solute partitioning calculations are evaluated based on the following equation:

\[
E_p = E\ (solute \rightarrow Q) - E\ (Q) - E\ (solute \rightarrow Al) + E\ (Al) + \mu\ (x) - \mu\ (Al)
\] (5.4)

A negative value indicates that solute atoms prefer the \( Q \)-phase over the \( \alpha \)-Al matrix. Conversely, a positive value suggests that it is energetically favorable for solute atoms to partition to \( \alpha \)-Al rather than into \( Q \)-phase. \( E\ (solute \rightarrow Q) \) and \( E\ (solute \rightarrow Al) \) are the energies of \( Q \) and \( \alpha \)-Al supercells, with each containing one solute atom. In the same manner, \( E\ (Q) \) and \( E\ (Al) \) are the energies of pristine \( Q \) and \( \alpha \)-Al supercells without solute. \( \mu\ (x) \) refers to the chemical potential of the atom, \( x \) (Al, Cu, Mg or Zn) in \( Q \), which is displaced by a substitutional atom, and \( \mu\ (Al) \) is the chemical potential of an Al atom, same as the pure energy of Al. Previously, Ravi and Wolverton[117] showed that the majority of commercial alloys (e.g. 319, 356, 6111 and 6022) fall into one of two different equilibriums depending on the relative amounts of Cu and Mg (\( Al+Si+Al_2Cu+Q \) or \( Al+Si+Mg_2Si+Q \)) based on CALPHAD methods.
The calculated chemical potentials of Al, Cu, Mg, and Si stayed at most 2 meV/atom from the two situations above, listed in Table 5.3. In this work, we chose the reference phases \( \text{Al} + \text{Si} + \text{Al}_2\text{Cu} + Q \) for the Cu-rich alloy (e.g. 319), which were shown in the previous experiments[111, 114]. As such, the chemical potentials of Al, Cu, Mg, and Si are determined by Eq. (5.3).

5.2.5. Interfacial energy

To calculate the energies of the \( Q//\alpha\)-Al coherent interface, we construct interfacial supercells. The interfacial energy of the supercell is the supercell formation energy divided by its cross-section area. The supercell formation energy can be calculated as the difference between the total energy of the supercell and the energy of the pure bulk phases, \( Q \) and \( \alpha\)-Al, based on the following equation:

\[
\sigma = E[SC] - \left( E_{\text{Al bulk}}^{\text{epi}}(a_{\perp}, a_{\parallel}^{\text{Al}}, \hat{G}) + E_{Q \text{ bulk}}^{\text{epi}}(a_{\perp}, a_{\parallel}^{Q}, \hat{G}) \right) / 2\text{Area} \tag{5.5}
\]

where \( E[SC] \) is the energy of the interfacial super cell. If the two phases (\( Q \) and \( \alpha\)-Al) are perfectly lattice matched, the supercell formation energy contributes directly to the interfacial energy. On the other hand, if the two phases are not perfectly lattice matched, there is a resulting energy penalty to be matched coherently across the interface. To reflect this coherency strain effect, the \( Q \) and \( \alpha\)-Al phases are deformed in an epitaxial geometry. Both phases are fixed to a common lattice constant \( a_{\perp} \) perpendicular to \( \hat{G} \) (an orientation perpendicular to the interfacial plane), and the energy of each phase is individually minimized with respect to the lattice constant \( a_{\parallel} \) parallel to \( \hat{G} \) for the energy of each strained phase. However, the \( Q//\alpha\)-Al interface supercell
has one additional atom at the termination of $Q$-phase in a supercell compared to the bulk $Q$-phase structure because of different periodic boundary conditions. As such, we utilize the chemical potential approach to calculate the interfacial energy based on the following equation:

$$\sigma_1 + \sigma_2 = E[SC, Al_{a}Cu_{b}Mg_{c}Si_{d}] - \left(a\mu_{Al} + b\mu_{Cu} + c\mu_{Mg} + d\mu_{Si}\right)/\text{Area}$$

$$\mu_{Al} = E_{Al \text{ bulk}}^{\text{epi}}(a_\perp, a_{Al}^{\perp}, \mathbf{G})$$

$$3\mu_{Al} + 2\mu_{Cu} + 9\mu_{Mg} + 7\mu_{Si} = E_{Q \text{ bulk}}^{\text{epi}}(a_\perp, a_{Q}^{\perp}, \mathbf{G})$$  \hspace{1cm} (5.6)

$$\mu_{Si} = E_{\text{diamond Si}}$$

$$2\mu_{Al} + \mu_{Cu} = E_{\theta'(Al_{2}Cu)}$$

Moreover, the two interfaces in the supercell are not symmetrically equivalent. That is, we only can determine the summation of interfacial energies for the two different interfaces in a cell. In order to extract an interfacial energy for the symmetry-distinct interface, we established three different supercells with three symmetry-distinct interfaces and solve the simultaneous equations for calculating an interfacial energy for the symmetry-distinct interface.

### 5.3. Results and Discussions

#### 5.3.1. Native defects (i.e., vacancy and anti-site) analysis
<table>
<thead>
<tr>
<th>Composition</th>
<th>Author</th>
<th>Physical situation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₄Cu₃Mg₆Si₇</td>
<td>Arnberg et al.</td>
<td>Single crystal</td>
<td>[106]</td>
</tr>
<tr>
<td>Al₇Cu₃Mg₈Si₆</td>
<td>Phragmen et al.,</td>
<td>Single crystal</td>
<td>[110, 111]</td>
</tr>
<tr>
<td></td>
<td>Clayron et al.</td>
<td>Q-precipitates in Al matrix</td>
<td></td>
</tr>
<tr>
<td>Al₆Cu₄Mg₆Si₄</td>
<td>Mondolfo et al.</td>
<td>Q-precipitates in Al matrix</td>
<td>[25]</td>
</tr>
<tr>
<td>Al₃.₅Cu₂Mg₉.₅Si₆</td>
<td>Loffler et al.</td>
<td>95% Q-phase</td>
<td>[112, 113]</td>
</tr>
<tr>
<td>Al₃Cu₂Mg₆Si₇</td>
<td>Wolverton</td>
<td>DFT calculations of stoichiometric ground state</td>
<td>[72]</td>
</tr>
<tr>
<td>Al₃Cu₂.₃Mg₈.₂Si₆.₅</td>
<td>Bobel A.</td>
<td>Q-precipitates in Al matrix</td>
<td>[118]</td>
</tr>
</tbody>
</table>

Table 5.1. Comparison of Q-phase compositions reported in the literatures[25, 72, 106, 110-113, 118].
Figure 5.1. Calculated convex hull based on computed formation energies by Eq. (5.1) in a quaternary Al-Cu-Mg-Si system. Indicated compounds are stable phases, as listed in Table 5.2. We utilized OQMD[99, 100] to search for stable compounds in a quaternary Al-Cu-Mg-Si system, and to recalculate DFT energies (Table 5.2) for them. The equilibrium phase of the tetragonal (C16) structure of Al$_2$Cu ($\theta'$) is not the stable phase in the calculation at T = 0 K. This was explained by the role of the vibration entropies of $\theta$ and $\theta'$, which were found to be unexpectedly important for this phase[40]. As such, the cubic fluorite (C1) structure, Al$_2$Cu ($\theta'$), is chosen in this work. The red-circles and -lines indicate stables phases and the tie-lines connected to the $Q$-phase, are used in section 5.4.2 and 5.4.3.
<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\Delta E_f$ (eV/atom)</th>
<th>Space group</th>
<th>Prototype</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$Cu$_2$Mg$_5$Si$_7$</td>
<td>-0.154</td>
<td>P6</td>
<td>Th$_2$S$_2$</td>
</tr>
<tr>
<td>Al$_2$Cu ($\theta$, $\theta'$)</td>
<td>-0.156, -0.175</td>
<td>Fmmm, Fm$\bar{3}$m</td>
<td>Al$_2$Cu, CaF$_2$</td>
</tr>
<tr>
<td>Mg$_2$Si</td>
<td>-0.162</td>
<td>Fm$\bar{3}$m</td>
<td>CaF$_2$</td>
</tr>
<tr>
<td>Al$_2$Cu$_4$Mg$_2$</td>
<td>-0.237</td>
<td>Pm$\bar{3}$m</td>
<td>Mg$<em>2$Zn$</em>{11}$</td>
</tr>
<tr>
<td>Cu$_2$Mg$_6$Si$_7$</td>
<td>-0.184</td>
<td>Fm$\bar{3}$m</td>
<td>Mn$_{23}$Th$_6$</td>
</tr>
<tr>
<td>Cu$_2$Mg$_5$Si</td>
<td>-0.239</td>
<td>P63/mmc</td>
<td>Laves-MgZn$_2$</td>
</tr>
<tr>
<td>Al$<em>{10}$Mg$</em>{23}$</td>
<td>-0.019</td>
<td>R$^3$</td>
<td>Co$_3$Cr$_2$Mo$_3$</td>
</tr>
<tr>
<td>Al$<em>2$Mg$</em>{17}$</td>
<td>-0.024</td>
<td>I$\bar{3}$m</td>
<td>Mn(cl58)</td>
</tr>
<tr>
<td>AlCu</td>
<td>-0.213</td>
<td>C2/m</td>
<td>AlCu</td>
</tr>
<tr>
<td>Cu$_{13}$Si$_4$</td>
<td>-0.072</td>
<td>I$\bar{3}$d</td>
<td>Cu$_{13}$Si$_4$</td>
</tr>
<tr>
<td>AlCu$_3$</td>
<td>-0.189</td>
<td>Pmmm</td>
<td>AlCuZn$_2$</td>
</tr>
<tr>
<td>Al$_2$CuMg</td>
<td>-0.183</td>
<td>Cmcm</td>
<td>Al$_2$CuMg</td>
</tr>
<tr>
<td>Cu$_2$Mg</td>
<td>-0.147</td>
<td>Fd$\bar{3}$m</td>
<td>Cu$_2$Mg</td>
</tr>
<tr>
<td>CuMg$_2$</td>
<td>-0.119</td>
<td>Fddd</td>
<td>CuMg$_2$</td>
</tr>
</tbody>
</table>

Table 5.2. DFT calculated formation energies (eV/atom) of compounds in the quaternary Al-Cu-Mg-Si system used to construct the convex hull (Fig. 5.1)
Table 5.3. Chemical potential of Al, Cu, Mg, and Si based on the predicted equilibrium reaction phases (reference phases). We utilized GCLP method[116] to search for reference phases in OQMD[99, 100]. The formation energies of reference phases are listed in Table 5.2.

Figure 5.2. Schematic diagram of crystal structure of $Q$-phase ($Al_3Cu_2Mg_9Si_7$)[72]. There are 21 atoms, and 9-symmetry distinct sites ($Al$, $Cu_1$, $Cu_2$, $Mg_1$, $Mg_2$, $Mg_3$, $Si_1$, $Si_2$, $Si_3$) in a cell. The space group is $P\overline{6}$ and the prototype is Th$_7$S$_{12}$.

<table>
<thead>
<tr>
<th>Defect site</th>
<th>Native defect formation energy, $\Delta E_f^d$ (eV/defect)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SC 63 (1x1x3)</td>
</tr>
<tr>
<td>$V_{Al}$</td>
<td>1.67</td>
</tr>
<tr>
<td>$V_{Cu1}$</td>
<td>0.59</td>
</tr>
<tr>
<td>$V_{Cu2}$</td>
<td>0.43</td>
</tr>
<tr>
<td>$V_{Mg1}$</td>
<td>1.33</td>
</tr>
<tr>
<td>$V_{Mg2}$</td>
<td>1.10</td>
</tr>
<tr>
<td>$V_{Mg3}$</td>
<td>1.40</td>
</tr>
<tr>
<td>$V_{Si1}$</td>
<td>1.47</td>
</tr>
<tr>
<td>$V_{Si2}$</td>
<td>1.29</td>
</tr>
<tr>
<td>$V_{Si3}$</td>
<td>1.54</td>
</tr>
</tbody>
</table>
Table 5.4. First-principles defect formation energy for vacancies in $Q$-phase ($Al_3Cu_2Mg_9Si_7$) by Eq. (5.2). The chemical potentials for the calculation of each defect are listed in Appendix A. The vacancies are labeled such that $V_{Al}$ refers to a vacancy on the Al site. The defect with lower energies are highlighted in bold, and the Cu vacancies are clearly lower in energy than other vacancies in $Q$-phase.

<table>
<thead>
<tr>
<th>Defect site</th>
<th>$\Delta E_f^d$ (eV/defect)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SC 63 (1x1x3)</td>
</tr>
<tr>
<td>Al$_{Cu1}$</td>
<td>0.41</td>
</tr>
<tr>
<td>Al$_{Cu2}$</td>
<td>0.50</td>
</tr>
<tr>
<td>Al$_{Mg1}$</td>
<td>0.38</td>
</tr>
<tr>
<td>Al$_{Mg2}$</td>
<td>0.27</td>
</tr>
<tr>
<td>Al$_{Mg3}$</td>
<td>0.11</td>
</tr>
<tr>
<td>Al$_{Si1}$</td>
<td>0.54</td>
</tr>
<tr>
<td>Al$_{Si2}$</td>
<td>0.65</td>
</tr>
<tr>
<td>Al$_{Si3}$</td>
<td>0.74</td>
</tr>
<tr>
<td>Cu$_{Al}$</td>
<td>0.80</td>
</tr>
<tr>
<td>Cu$_{Mg1}$</td>
<td>1.21</td>
</tr>
<tr>
<td>Cu$_{Mg2}$</td>
<td>1.05</td>
</tr>
<tr>
<td>Cu$_{Mg3}$</td>
<td>1.20</td>
</tr>
<tr>
<td>Cu$_{Si1}$</td>
<td>0.86</td>
</tr>
<tr>
<td>Cu$_{Si2}$</td>
<td>1.24</td>
</tr>
<tr>
<td>Cu$_{Si3}$</td>
<td>1.07</td>
</tr>
<tr>
<td>Mg$_{Al}$</td>
<td>0.49</td>
</tr>
<tr>
<td>Mg$_{Cu1}$</td>
<td>1.36</td>
</tr>
<tr>
<td>Mg$_{Cu2}$</td>
<td>1.06</td>
</tr>
<tr>
<td>Mg$_{Si1}$</td>
<td>1.61</td>
</tr>
<tr>
<td>Mg$_{Si2}$</td>
<td>1.71</td>
</tr>
<tr>
<td>Mg$_{Si3}$</td>
<td>1.94</td>
</tr>
<tr>
<td>Si$_{Al}$</td>
<td>0.52</td>
</tr>
<tr>
<td>Si$_{Cu1}$</td>
<td>0.54</td>
</tr>
<tr>
<td>Si$_{Cu2}$</td>
<td>0.90</td>
</tr>
<tr>
<td>Si$_{Mg1}$</td>
<td>1.50</td>
</tr>
<tr>
<td>Si$_{Mg2}$</td>
<td>1.02</td>
</tr>
<tr>
<td>Si$_{Mg3}$</td>
<td>1.12</td>
</tr>
</tbody>
</table>
Table 5.5. First-principles defect formation energy for anti-site defects in \(Q\)-phase (Al\(_3\)Cu\(_2\)Mg\(_9\)Si\(_7\)) by Eq. (5.2). The used chemical potentials used for the calculation of each defect are listed in Table 4. The anti-site defects are labeled such that \(Al_{Cu1}\) refers to an Al atom on a Cu1 site. The lower energies are highlighted in bold. The lowest energy anti-site found is for Al on Mg sites. These defect calculations are consistent with experimental measurements of compositions for \(Q\)-phase that are Al-rich and Mg-deficient (see Table 5.1.), and suggest that these \(Q\)-phase precipitates are off-stoichiometric, Al-rich versions for the ground state compound.

The most fundamental step in developing a basis for advanced alloy design is to establish the stoichiometry and corresponding parameters in atomic-scale, such as lattice parameter of the precipitate. However, the stoichiometry of \(Q\)-phase has been a long-standing controversy in \(Q\)-phase studies, as shown in Table 5.1. Previously, Wolverton investigated the formation energies using first-principles calculation, and Al\(_3\)Cu\(_2\)Mg\(_9\)Si\(_7\) was regarded as the lowest energy stoichiometry[72]. Native defects such as, vacancies or anti-site defects can occur at finite temperatures, and can alter the composition of the \(Q\)-phase, particularly when embedded in an Al-rich matrix. Hence, we will explore the defect energies of a large number of vacancies and anti-sites in \(Q\)-phase, and will interpret our calculations in light of the experimentally reported compositions of the \(Q\)-phase. We define the off-stoichiometry of \(Q\)-phase with respect to Al\(_3\)Cu\(_2\)Mg\(_9\)Si\(_7\), which has the lowest energy in DFT calculations.

The DFT calculated convex hull in the quaternary Al-Cu-Mg-Si system was shown in Fig. 5.1 based on the compounds and computed formation energies as listed in Table 5.2. To calculate native defect formation energies, we need to choose reference (stable) phases. The reference phases in Table 5.3 were chosen based on stable decomposition reaction pathways obtained by using a GCLP method[116] in the open quantum material database (OQMD)[99, 100]. Among
the 9 symmetry-distinct sites in Q-phase, as shown in Fig. 5.2, vacancy defect formation energy on a Cu site shows the lowest value among 9 vacancies, as listed in Table 5.4, meaning that a vacancy can be formed most easily at the Cu site. This can be understood by examining the crystal structure of Q-phase, which is based on the prototype Th$_7$S$_{12}$ structure, where the two Cu atoms occupy the interstitial sites in the structure, not the sub-lattice of Th$_7$S$_{12}$ structure like Al, Mg, and Si atoms do. Also, we can understand the lowest energy of vacancy of a Cu atom based on the fact that there is a metastable phase, called $B'$ (Al$_3$Mg$_6$Si$_7$)[119-121], in the Al-Mg-Si system, which has the same crystal structure as the Q-phase without Cu atoms.

Of all the formation energies of all the native defects, Al$_{Mg^3}$ has the lowest formation energy listed in Table 5.5, 0.11 eV/defect. Interestingly, none of the other defects are close in heat of formation, the closest being the Al$_{Mg^2}$ anti-site substitution at 0.27 eV/defect, which is almost three times as large. Generally, for the compositions proposed in the experimental literature (Table 5.1), the Mg content is underestimated and the Al content is overestimated as compared to Al$_3$Cu$_2$Mg$_9$Si$_7$. Thus, we suggest that the Q-phase can be observed to substitute Al atoms at the Mg sites relatively easily. For example, the observed Al$_4$Cu$_2$Mg$_6$Si$_7$[106] in experiment is the result of anti-site defects of Al$_{Mg^3}$ in the Al$_3$Cu$_2$Mg$_9$Si$_7$ Q-phase.

Based on the dilute mean-field expression at 300°C, $3\exp\left(-\Delta E_f^d/kT\right)$ (the factor of 3 coming from 3-Mg3 sites in the Q-phase crystal structure, shown in Fig. 5.2), Al should occupy approximately 30% of Mg3 sites. There are a couple of reasons that this value of 30% might underestimate the total off-stoichiometry (i.e., the true off-stoichiometry would likely be even larger): (i) these concentrations are not dilute, and hence the dilute expression likely breaks down and underestimate the true off-stoichiometry, (ii) vibrational entropies (not considered here) have
been shown to significantly enhance off-stoichiometries in ordered compounds, and (iii) the Mg chemical potential was found by assuming equilibrium with ordered compounds, but in an actual Al alloy, the Mg displaced from the $Q$-phase could go back into solid solution. Taking the Al-Mg solid solution as the chemical potential for Mg would lower the $\text{Al}_\text{Mg}$ defect energy even further, thereby raising the extent of the off-stoichiometry.

As for the observed $\text{Al}_4\text{Cu}_2\text{Mg}_8\text{Si}_6[110, 111]$ compound, it is noted that this structure is $\text{Al}_4\text{Cu}_2\text{Mg}_8\text{Si}_7[106]$ with an $\text{Al}_\text{Si}$ defect. Looking at the heats of formation for various defects in the case of deficient Si atoms, the lowest energy ones are the $\text{Al}_\text{Si1}$, $\text{Al}_\text{Si2}$, and $\text{Al}_\text{Si3}$ defects. This suggests that it is possible that this structure is the result of off-stoichiometry in alloy compositions where there is a lack of both Mg and Si. However, as with other structures resulting from multiple defects, a full treatment would require calculation of the interactions of similar defect energies such as, $V_{\text{Cu}}$ or $\text{Al}_{\text{Cu}}$ with $\text{Al}_\text{Si}$. For the case of the observed structure $\text{Al}_4\text{Cu}_1\text{Mg}_5\text{Si}_4$, off-stoichiometries cannot be easily explained by simple native point defect thermodynamics. Additionally, the $\text{Al}_{17}\text{Cu}_0\text{Mg}_{45}\text{Si}_{29}$ ($\text{Al}_{3.5}\text{Cu}_2\text{Mg}_{9.5}\text{Si}_6$)$[113]$ compound is not simply understood by our computed point defects because it has a $\text{Mg}_\text{Si}$ defect, which is of a higher in energy compared to other anti-site defects of $\text{Mg}_x$. Therefore, in order to gain a more complete picture of the defect landscape and explain all the observed off-stoichiometric compositions, further work probing the effects of finite temperature, entropic considerations, and interaction energies of multiple vacancies is necessary.

5.3.2. A prediction for partitioned elements to $Q$-phase
Figure 5.3. First-principles calculated partitioning energies of various solutes to $Q$-phase by Eq. (5.3). A negative (or positive) value indicates solute prefers locating into sub-lattice in $Q$ (or $\alpha$-Al) over locating $\alpha$-Al (or $Q$).
Figure 5.4. Proximity histogram in APT experiments for various solute elements, (a) Zn, (b) Ni, (c) Mn, (d) Ti, (e) V, and (f) Zr aged at 200°C for 24 hours[118].
Table 5.6. Summary for site preference of solutes partitioned to $Q$-phase based on DFT energies ($\Delta E_p < -0.1$ eV/solute)

<table>
<thead>
<tr>
<th>Preference sites in $Q$-phase</th>
<th>Solutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Zn, Ag, Au, Ni, Co</td>
</tr>
<tr>
<td>Mg</td>
<td>Sr, Ba</td>
</tr>
<tr>
<td>Si</td>
<td>Au, Ga, Ge, Sn</td>
</tr>
</tbody>
</table>

Table 5.7. Diffusivity (at 200 °C) of elements in Al[120-128]. As seen here, the transition elements show anomalous low diffusivities in Al.

<table>
<thead>
<tr>
<th>Elements</th>
<th>$D$ at 200 °C ($m^2s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (Self-diffusion)</td>
<td>$2.80 \times 10^{-19}$</td>
</tr>
<tr>
<td>Cu</td>
<td>$6.32 \times 10^{-20}$</td>
</tr>
<tr>
<td>Mg</td>
<td>$1.25 \times 10^{-18}$</td>
</tr>
<tr>
<td>Si</td>
<td>$1.86 \times 10^{-19}$</td>
</tr>
<tr>
<td>Zn</td>
<td>$1.13 \times 10^{-18}$</td>
</tr>
<tr>
<td>Ni</td>
<td>$3.35 \times 10^{-20}$</td>
</tr>
<tr>
<td>Mn</td>
<td>$9.46 \times 10^{-26}$</td>
</tr>
<tr>
<td>Zr</td>
<td>$1.40 \times 10^{-28}$</td>
</tr>
<tr>
<td>Ti</td>
<td>$2.21 \times 10^{-30}$</td>
</tr>
<tr>
<td>V</td>
<td>$5.65 \times 10^{-34}$</td>
</tr>
</tbody>
</table>

The study of solute-precipitate interaction is very important because solutes can play a role in increasing the nucleation rate of the precipitate or changing interfacial stability via interfacial segregation, thereby influencing the micro-morphology of precipitates. With respect to other Al-based precipitates, there are already plenty of reports about solute behavior (i.e., partitioning or
segregation). For example, experimental APT results have shown that Si atoms prefer partitioning into the Cu sub-lattice in Al$_2$Cu ($\theta'$) precipitates over partitioning into $\alpha$-Al, and this was explained by a strong thermodynamic driving force, as predicted by DFT calculations[44, 45].

According to recent experimental APT results, significant partitioning of Zn into the cores of $Q$-phase precipitates was observed, and the paper argued that Zn may play a role in increasing the nucleation rate of $Q$-phase[114]. They argued that this phenomenon was caused by a kinetic effect arising from slow Zn diffusion and/or nucleation effects, since Zn incorporation in all sub-lattices of the $Q$-phase is energetically unfavorable based on the previous DFT calculation. In Fig. 5.3, our calculation also indicates that the solute partitioning of Zn is favorable on the $\alpha$-Al matrix over most of the sub-lattices in the $Q$-phase. However, Zn is energetically favorable on the Cu sub-lattice in $Q$-phase over $\alpha$-Al matrix ($\Delta E_p \approx -0.1$ eV/solute). This discrepancy may be caused by different relaxation schemes. All the structures were relaxed with respect to all cell-internal and -external degrees of freedom in this work. But, only position of atoms were optimized under fixed experimental lattices in the previous work[114]. Therefore, we suggest that thermodynamic effects can explain Zn solute partitioning to $Q$-precipitates as being similar to Si partitioning to $\theta'$ precipitates.

Except for the finding of Zn partitioning to $Q$ precipitates, other possible minor elements, which could be candidates to make $Q$-phase energetically more stable for coarsening resistance, have not yet been explored. In order to consider minor elements, we calculated solute partitioning energies of various solutes in this work. Fig. 5.3 summarizes the calculated
partitioning energy $E_p$ of various solutes to the $Q$-phase for each of the nine symmetry distinct substitutional sites. We adopt a sign convention where a negative partitioning energy indicates that solute partitioning to the $Q$-phase is energetically favorable. We recognize types of site preference: Zn, Ag, and Au prefer the Cu site, Sr and Ba have a preference for the Mg site, and Ga, Ge, and Sn prefer the Si sites in $Q$-phase, as listed in Table 5.6. Therefore, each element shows a preference for sites that have similar electronic structures. Also, larger solutes, such as Sr and Ba, prefer substitution onto Mg sites in $Q$-phase, because Mg has the largest atomic radius among the other elements (Al, Cu, and Si) in $Q$-phase. We can understand this result in terms of chemical and physical effects, and determined the general rules for site-preference of solute in $Q$-phase in terms of electronic structure and atomic radius.

Recently, Bobel[118] performed APT experiments for various solute elements (Zn, Ni, Mn, Ti, V, and Zn) in order to validate DFT predictions. The proximity histogram is shown in Fig. 5.4. Similar to Zn behavior, solute Ni shows partitioning to the $Q$-phase, which is consistent with our prediction based on DFT calculations. The Mn solutes did not demonstrate any markable partitioning of Mn to the Q-phase in Fig. 5.4. This is also in agreement with our first-principle calculations, in that Mn was not found to partition to the $Q$-phase. Contrary to the first-principle calculated partitioning energies of this study, it was experimentally observed that Ti, V, and Zr all partitioned to the $Q$-phase precipitates as shown in Fig. 5.4. Table 5.7. shows the transition elements (e.g. Ti, V, and Zr) show anomalous low diffusivities in Al. It is possible that due to the slow diffusivity of Ti, Zr, and V that the elements become trapped in the $Q$-phase leading to a non-equilibrium partitioning like effect. It is also important to consider the approximations of the DFT calculations performed, such as non-interacting solutes and 0K non-finite temperature.
These additional effects could change the calculated partitioning energies, motivating the need for a finite-temperature DFT study. As well as in first-principles, uncertainties exist in the APT study. The low alloying content of the elemental additions lead to large compositional error within the \(Q\)-phase precipitates. Larger alloy additions and longer aging times could reduce the noise associated with small atomic counts in the proxigram analysis for these elements.

### 5.3.3. A search for lowest energy and structure of the interface \((1\overline{1}20)_Q/(510)_{Al}\)

Figure 5.5. (a) Schematic diagram of unit-cells of \(Q\)-phase \((1\overline{1}20)_Q\) and \(\alpha\)-Al \((510)_{\alpha}\), respectively. These unit-cells are constructed by using the below rotation matrix. (b) For constructing a lowest-energy interface super cell, we search energy variations by moving the cell (terrace) of \((510)_{\alpha}\) along the x-axis. The interfacial energy variation shows 0.52, 0.66, and 0.86 J/m\(^2\) as a function of mismatching along the x-axis. In terms of mismatching along the y-axis, both \(Q\)-phase and \(\alpha\)-Al unit-cells have two-independent
planes. As such, the two possible structures were studied after matching along the x-axis. (c) Relaxed super cell of the \((11\bar{2}0)_Q//(510)_A\) interface.

\[
\begin{pmatrix}
5 & 1 & 0 \\
-1 & 5 & 0 \\
0 & 0 & 1
\end{pmatrix}
\text{for } (510)_\alpha, 
\begin{pmatrix}
1 & 1 & 0 \\
0 & 2 & 0 \\
0 & 0 & 1
\end{pmatrix}
\text{for } (11\bar{2}0)_Q
\]

Rotation matrix for \((510)_\alpha\) and \((11\bar{2}0)_Q\) supercells with respect to \((100)_\alpha\) and \((1000)_Q\)

<table>
<thead>
<tr>
<th>1(^{st}) nearest atom to interface</th>
<th>2(^{nd}) nearest atom to interface</th>
<th>3(^{rd}) nearest atom to interface</th>
<th>Interfacial energy ((J/m^2)) ((11\bar{2}0)_Q//(510)_A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Mg or Al</td>
<td>Mg</td>
<td>0.72</td>
</tr>
<tr>
<td>Cu</td>
<td>Mg</td>
<td>Si</td>
<td>0.66</td>
</tr>
<tr>
<td>Cu</td>
<td>Si</td>
<td>Al</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Table 5.8. Calculated interfacial energies of \((11\bar{2}0)_Q//(510)_A\) with different terminations (different species) by Equation 4 and 5. When Cu and Si are the nearest atoms to the interface, the interface structure is lowest in energy.

Thermodynamic properties, such as interfacial energy between dissimilar phases, are critical to understanding the micro-morphology of precipitates in Al alloys. For example, the interfacial energy can control the nucleation energy barrier, thereby influencing precipitate size distribution. Even though \(Q\)-phase is a key-strengthening phase in a group of commercially important alloys, its related thermodynamic properties, interfacial structure and energy, have not been investigated extensively. It is commonly known that the \(Q\)-phase has a \(\{510\}_\alpha\) habit plane, and its orientation relationship with the \(\alpha\)-Al matrix can be denoted as \([0001]_Q//[001]_\alpha\) and \((11\bar{2}0)_Q//(510)_\alpha\).
Here, for the $(1\bar{1}0)_Q/(510)_\alpha$ interface, we survey various terminations and orientations and derive a low-energy structure for the first time.

Fig. 5.5 (a) shows the process of making an interfacial supercell. The repeat distance along the $(150)$ directions of the aluminum matrix is $0.404 \times \sqrt{36} = 1.03$ nm. This is about the same as the lattice parameter of the $Q$-phase (1.04 nm), thus the misfit strain is approximately 1.1%. Along the direction $[0001]_Q// [001]_\alpha$, the misfit strain between two primitive cells is approximately to -0.8%. So, the $(1\bar{1}0)_Q/(510)_\alpha$ interface is very coherent. When we constructed the interfacial supercell, there were three degree of freedom: 1) matching between two cells along the x-axis, as shown in Fig. 5.5 (b); 2) matching between two cells along the y-axis; and 3) termination of $Q$-phase corresponding to different species at the interface. In terms of the x-axis and y-axis degrees of freedom, we search energy variations by moving the cell (terrace) of $(510)_\alpha$ along the x-axis with accounting for the y-axis degree of freedom. In terms of mismatching along the y-axis (the direction $[0001]_Q// [001]_\alpha$), both $Q$-phase and $\alpha$-Al unit-cells have two-independent planes. As such, the two possible structures were studied after matching along the x-axis. The interfacial energy variation shows approximately 0.52, 0.66, and 0.86 J/m$^2$ as a function of mismatching along the x-axis, as shown in Fig. 5.5 (b). Since the distinct atomic-scale interfacial structure has not yet been found experimentally, we then tested different terminations for each of the different elements in the $Q$-phase structure to derive a low-energy structure.

Our calculations indicate that the lowest interfacial energy is approximately 0.52 J/m$^2$ for termination with a combination of Cu and Si atoms as shown in Table 5.8. It reveals that $\alpha$-Al
favorably bonds with the Cu-termination interface among different elements in the $Q$-phase. According to the previous report by Matsuda et al.[129], Cu segregation was detected at the $Q’/\alpha$-Al interface in an Al-Cu-Mg-Si alloy using energy-filtered transmission electron microscopy. $Q’$ is the precursor phase of the $Q$-phase, and also has the same lath morphology of $Q$ with a cross-section elongated along $\langle 510 \rangle_\alpha$. Thus, our finding that Cu is the nearest atom to the interface is in agreement with previous literature on Cu interfacial segregation. Also, according to a recent experiment, replacement of Mg with Cu in Al-Mg-Si alloys minimizes the strain energy caused by the difference in atomic sizes[130], so this is also agreement with that Cu-terminated interfacial energy is lower than Mg-terminated interfacial energy based on our computation

### 5.4. Conclusions

In this paper, the primary findings of our study using first-principles calculations can be summarized as follows:

1. By using a defect super cell approach, the previous experimentally observed off-stoichiometry of $Q$-phase can be partially explained as being the result of native defects in the $Q$-phase. Among native defects (vacancy and anti-site) formation energy calculations of $Q$-phase ($Al_3Cu_2Mg_9Si_7$), the defect of $Al_{Mg}$ shows the lowest energy (0.11, 0.27, and 0.38 eV/defect), which means the observed variation of $Al_{3+\delta}Cu_{2Mg_{9-\delta}}Si_7$ (Mg-deficient and Al-rich) in experiment can be understood by the result of anti-site defect of Al on Mg sites in the $Q$-phase. Based on the dilute mean-field expression, the underestimation of off-stoichiometry
is 30%, but the true off-stoichiometry would likely to be larger. However, in order to gain a more complete picture of the defect landscape to explain the other observed compositions such as, $\text{Al}_4\text{Cu}_1\text{Mg}_5\text{Si}_4$ a more complicated defect formation mechanism will need to be considered, such as the effects of finite temperature, entropic considerations, and multi-defect clustering.

2. The Zn partitioning to $Q$-phase, which was observed in the experimental APT, can be explained by a thermodynamic driving force similar to that driving Si partitioning to $\theta'$ precipitates. Based on our computation, solute partitioning of Zn on Cu sub-lattice in the $Q$-phase over Al matrix is energetically favorable. In addition to solute Zn, we calculated solute-partitioning energies of various conventional solutes, and we have defined general rules for site-preference of a solute in the $Q$-phase in terms of electronic structure and atomic radius. To validate our DFT predictions, we performed atom-probe tomography (APT) experiments for six-different elements (Zn, Ni, Mn, Ti, V, and Zr). The results show that the partitioning behavior of Ni, Zn, and Mn solutes are consistent with DFT predictions, but the slow diffusing transition elements (Ti, V, and Zr) in Al partitioned to the $Q$-phase precipitates, which is inconsistent with DFT predictions. We surmise that the discrepancy is caused either by trapping in the $Q$-phase leading to a non-equilibrium partitioning like effect due to slow diffusivity, or due to not accounting for finite temperature effects in the DFT calculations.

3. For the coherent $(11\bar{2}0)_Q // (510)_{Al}$ interface, we surveyed various terminations and orientations and derived a low-energy structure. We find Cu is the nearest atom to the interface, which is in agreement with previous literature on Cu interfacial segregation at the
The calculated interfacial energy of the lowest energy structure is approximately 0.52 J/m². The lowest interfacial energy and corresponding structure can be applicable to a wide variety of purposes such as multi-scale modeling for the future study of microstructural problems.
CHAPTER 6

Phase-field modeling of $\theta'$ precipitation in Al-Cu alloys

We examine the equilibrium morphology of Al$_2$Cu ($\theta'$) precipitates in Al-Cu alloys using a phase field method with the parameters supplied by first-principles density functional theory (DFT) calculations. The phase field method employed allows for an interfacial energy that is highly anisotropic: there are missing high-energy orientations and corners on the Wulff shape. This high degree of anisotropic interfacial energy yields a plate-shaped equilibrium $\theta'$ precipitate in two-dimensions and a disk-like shape in three dimensions. Also, we consider the effects of a mismatch in elastic-moduli (elastic inhomogeneity) of Al and $\theta'$, elastic anisotropy, as well as tetragonal misfit strain anisotropy to gain a fuller picture of the elastic energy contributions to the morphology of $\theta'$ precipitates. Based on our phase-field modeling, the results show that the aspect ratio of the precipitate morphology with the anisotropy of interfacial and strain energies as given by DFT is significantly smaller than the aspect ratio observed in the experiment after long aging times (~50 hrs.). Specifically, the computed length (54 nm) is almost ten-times smaller than the length (~580 nm) observed in the Al-Cu experiment with similar precipitate thickness (~10 nm). Thus, we conclude that the experimental morphology after long aging times (~50 hrs.) is strongly influenced by the kinetics of precipitate growth.
6.1. Introduction

As described in Chapter 3.1, a major strengthening phase in Al-Cu alloys is the metastable Al$_2$Cu (θ') precipitate. θ' has the CaF$_2$ crystal structure, but, when embedded in an Al matrix, it shows a tetragonally distorted version of the cubic fluorite (C1) structure with lattice constants of $a = 4.04$ Å and $c = 5.80$ Å[32]. The precipitates adopt a plate-shaped morphology. Thus, there are specific orientation relationships between the precipitate and the Al matrix. One is a coherent interface (001) θ' // (001) α-Al on the broad faces of the plate, and the other is a semi-coherent interface with (010) θ' // (010) α-Al around the rim of the plates[30]. The morphology shows an extremely high aspect ratio of θ' plate (typically 1-10 nm in thickness and 0.1-1 μm in length)[131], which is key to effective strengthening components. The aspect ratio of θ' plates is varied (often ~40 and higher) depending on aging conditions and the processing history.

In order to understand the physics responsible for the high aspect ratio of θ' precipitates, Vaithyanathan et al.[35, 36] employed a multiscale approach based on first-principles calculations, mixed-space cluster expansion, Monte Carlo simulations and the phase-field method, to investigate the growth and coarsening of θ' precipitates during aging in Al-Cu alloys. The input parameters to the phase-field model were derived from first-principles DFT calculations: free-energy of precipitate and solid solution phases, interfacial energies for both coherent and semi-coherent interfaces, stress-free lattice parameters and elastic constants. Phase-field modeling (PFM) was then done to analyze the effects of various physical contributions to θ' precipitate morphology. By including various anisotropic contributions to the model,
Vaithyanathan et al.[35, 36], showed that quantitative predictions of the equilibrium aspect ratio (~20) of $\theta'$ precipitates are obtained, in good agreement with experiments, only when interfacial and strain anisotropies are both included. Therefore, they argued that the plate-shaped morphology of $\theta'$ with large aspect ratios was caused by a combination of interfacial and elastic energy anisotropies.

However, there are several issues that need to be addressed in the previous phase-field modeling by Vaithyanathan et al.[35, 36]. First, they controlled the shape of $\theta'$ precipitate by changing grid spacing used in the solution of the phase field equations to obtain the equilibrium shape[132]. However, intentionally utilizing a numerical artifact from an insufficiently small grid is not a solution of the partial differential equations of the phase-field model because the solution of differential equations should yield an equilibrium shape that does not vary with the grid-spacing. In particular, the Wulff shape (equilibrium particle shape based on orientation dependence the interfacial energy) should be constant regardless of grid spacing. At the time of Vaithyanathan et al.’s [35, 36] work, it was not clear how to stabilize nearly faceted interfaces in a phase field calculation. Moreover, including the work by Vaithyanathan et al.[35, 36], there are several other studies[87, 133] that use the PFM to compute the equilibrium morphology of $\theta'$ where the shape was described as elliptic or lens-shape, which is not in agreement with an experimental $\theta'$ plate-shaped morphology. Thus, a flat or faceted surface needs to be included in the PFM to accurately account for the actual plate-shape of a $\theta'$ precipitate. Lastly, in the previous studies[35, 36, 87, 133] using the PFM, the elastic energy was determined using the assumption that the elastic constants of the $\theta'$ phase were the same as the Al matrix, the so-called a homogenous modulus approximation. However, the mismatch in elastic moduli ($C_{11}$) of
an Al matrix and $\theta'$ precipitate is almost a factor of $\sim2$. Therefore, it is also necessary to investigate the effect of the elastic inhomogeneity.

In this work, we present a phase field method with the parameters supplied by first-principles methods to elucidate the physical factors controlling the equilibrium $\theta'$ morphology in Al-Cu alloys based on the above considerations. Specifically, we chose a circularly equivalent radius instead of grid-spacing for non-dimensionalisation to independently control grid-spacing to precipitate a shape. We utilized the higher order terms in the gradient energy to allow for a highly anisotropic interfacial energy with missing orientations and corners on the Wulff shape. Also we examine the effects of various elastic contributions, including: elastic inhomogeneity and anisotropy, and tetragonal misfit strain anisotropy to the equilibrium shape of precipitate. Our phase-field model is thus helpful for understanding whether the morphologies of $\theta'$ precipitates observed in experiments in Al-Cu alloys are of a kinetic or thermodynamic origin. The approach can also be used to examine many other plate-shaped precipitates in a variety of metal alloys.

### 6.2. Methodology

#### 6.2.1. Free energy

In a binary Al-Cu alloy, we can describe the $\theta'$ precipitate microstructure by a composition and long-range order parameter fields[17]. The chemical free energy of the microstructure, including the bulk, interfacial and elastic energies, is then expressed as the follows:

$$F_{\text{total}} = F_{\text{bulk}} + F_{\text{int}} + F_{\text{elastic}}$$  \hspace{1cm} (6.1)
\[ F_{bulk} + F_{int} = \int \left[ f(c, \eta) + \frac{\alpha}{2} (\nabla c)^2 + \frac{\beta_{ij}}{2} \frac{\partial^2 \eta}{\partial x_i \partial x_j} + \gamma_{ijkl} s_{ijkl} \right] dV, \]

where \(\alpha\) and \(\beta_{ij}\) are gradient energy coefficients for composition and order parameters, respectively. \(\beta_{ij}\) is a second-rank tensor with zero diagonal terms to incorporate the tetragonal coherent \((\beta_{11})\) and semi-coherent \((\beta_{22})\) interfacial energies\([35, 36, 132]\). \(\gamma_{ijkl}\) is an effective fourth-rank tensor to describe faceted surfaces in two-fold symmetry which will be described in section 6.3.2.2. The bulk free energy (Fig. 6.1) describing phase-separation and order-disorder transformation is expressed as the following polynomial in \(c\) and \(\eta\)[36],

\[
f(c, \eta_1, \eta_2, \eta_3) = A_1(c - C_1)^2 + A_2(C_2 - c)(\eta_1^2 + \eta_2^2 + \eta_3^2) + A_{41}(\eta_1^4 + \eta_2^4 + \eta_3^4)
+ A_{42}(\eta_1^2\eta_2^2 + \eta_2^2\eta_3^2 + \eta_3^2\eta_1^2) + A_{61}(\eta_1^6 + \eta_2^6 + \eta_3^6)
+ A_{62}(\eta_1^4\eta_2^2 + \eta_2^4\eta_3^2 + \eta_3^4\eta_1^2) + A_{63}(\eta_1^2\eta_2^2\eta_3^2)
\]

where \(C_1\) and \(C_2\) are constants close to the equilibrium compositions of solid solution matrix and \(\theta'\) precipitates, respectively. The coefficients were calculated based on first-principles calculation in the previous literature\([36]\), as shown in Table 1.

### 6.2.2. Fourth-rank term for interfacial anisotropy

In this work, we used a fourth-rank tensor for interfacial energy anisotropy to describe faceted interfaces. The presence of symmetry in the crystal reduces the number of independent terms in the tensor\([134]\). Thus, we take into account tetragonal symmetry, which is an assumed
property of the phase that is being simulated. There are six unique values necessary to completely define the tetragonal $\gamma_{ijkl}$ tensor.

$$
\begin{pmatrix}
\gamma_{11} & \gamma_{12} & \gamma_{13} & 0 & 0 & 0 \\
\gamma_{12} & \gamma_{11} & \gamma_{13} & 0 & 0 & 0 \\
\gamma_{13} & \gamma_{13} & \gamma_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & 1/4 \gamma_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & 1/4 \gamma_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & 1/4 \gamma_{66}
\end{pmatrix}
$$

(6.4)

We investigate a coefficient along the plane’s normal direction (defined by its direction cosines $hkl$). A new coordinate system (identified using primes ($'$)) is constructed as follows.

$$
\gamma'_{1111} = a_{1i}a_{1j}a_{1k}a_{1l}\gamma_{ijkl}
$$

$$
= a_{11}^4 \gamma_{11} + a_{12}^2 a_{12}^2 \gamma_{12} + a_{13}^2 a_{13}^2 \gamma_{13} + a_{12}^2 a_{11}^2 \gamma_{112} + a_{12}^4 \gamma_{11} + a_{12}^2 a_{13}^2 \gamma_{13}
$$

$$
+ a_{13}^2 a_{11}^2 \gamma_{113} + a_{13}^2 a_{12}^2 \gamma_{13} + a_{13}^4 \gamma_{33} + a_{12}^2 a_{13}^2 \gamma_{44} + a_{11}^2 a_{13}^2 \gamma_{44}
$$

$$
+ a_{11}^2 a_{12}^2 \gamma_{66}
$$

(6.5)

The direction of a unit vector is given along $(a_{11} \ a_{12} \ a_{13})$, then $a_{11}$, $a_{12}$, and $a_{13}$ can be replaced by Miller indices $h$, $k$, and $l$ respectively.

$$
a_{11} = h, \ a_{12} = k, \ a_{13} = l
$$

(6.6)

And using the following relation,

$$
h^4 + k^4 + (al)^4 = 1 - 2(h^2k^2 + k^2(al)^2 + (al)^2h^2)
$$

(6.7)

the equation can then be further reduced to
\[ \gamma'_{1111} = \gamma_{12} + \frac{1}{2\gamma_{66}} + \left( \gamma_{11} + \gamma_{12} - \frac{1}{2\gamma_{66}} \right) h^4 + \left( \gamma_{11} + \gamma_{12} - \frac{1}{2\gamma_{66}} \right) k^4 + (\gamma_{33} - \frac{(2\gamma_{13} + \gamma_{44})^2}{2(2\gamma_{12} + \gamma_{66})}) l^4 \]

(6.8)

\[ a = \gamma_{11} - \gamma_{12} - \frac{1}{2\gamma_{66}} \]

(6.9)

And finally rewritten in tensor form yielding the following.

\[ \gamma_{ijkl} = \gamma'_{1111} = (\gamma_{11} - a) + a(h^4 + k^4 + \zeta l^4) \]

\[ \gamma_{11} - a = \gamma_i, \quad a = \gamma_a \]

(6.10)

The tetragonal anisotropy in interfacial properties requires three parameters: the isotropic fourth-rank coefficient \( \gamma_i \), and the anisotropic fourth-rank coefficient \( \gamma_a \) and \( \zeta = b/a \). The coefficient \( \zeta \) is responsible for two-fold symmetry. Using the form of \( \gamma_{ijkl} \) for tetragonal materials from Eq. (6.5), we get the following equation of \( \gamma_{ijkl}s_{ijkl} \) in Eq. (6.2).

\[ \gamma_{ijkl}s_{ijkl} = \gamma_i \sum_{i=1}^{3} \sum_{j=1}^{3} s_{ijij} + \gamma_a(s_{1111} + s_{2222} + \zeta s_{3333}) \]

(6.11)

\[ s_{ijkl} = \frac{\partial^4 \eta}{\partial x_i \partial x_j \partial x_k \partial x_l} \]

6.2.3. Elastic contribution to the total free energy

The elastic contribution to the total free energy is needed to account for elastic energy contribution to \( \theta' \) morphology. The total free energy for elasticity is given by:
where $\sigma_{ij}^{el}$ is the elastic stress and $\varepsilon_{ij}^{el}$ is the elastic strain, given by the follows:

$$\varepsilon_{ij}^{el} = \varepsilon_{ij} - \varepsilon_{ij}^0$$  \hspace{1cm} (6.13)

$\varepsilon_{ij}^0$ is the position dependent eigenstrain field and $\varepsilon_{ij}$ is the total strain,

$$\varepsilon_{ij} = \frac{1}{2} \left\{ \frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i} \right\}$$  \hspace{1cm} (6.14)

$u$ is the displacement field. We assume that the $\alpha$-Al and $\theta'$ precipitate obey linear elasticity:

$$\sigma_{ij}^{el} = C_{ijkl} \varepsilon_{ij}^{el}$$  \hspace{1cm} (6.15)

where $C_{ijkl}$ is the position-dependent elastic modulus tensor. The eigenstrain is an explicit function of order-parameter:

$$\varepsilon_{ij}^0(\eta) = \beta(\eta) \varepsilon_{ij}^T \delta_{ij}$$  \hspace{1cm} (6.16)

$$\beta(\eta) = \eta^3(10 - 15\eta + 6\eta^2)$$  \hspace{1cm} (6.17)

$$\varepsilon_{ij}^T = \begin{pmatrix} \varepsilon_{11}^T & 0 \\ 0 & \varepsilon_{22}^T \end{pmatrix}$$  \hspace{1cm} (6.18)

where $\varepsilon_{ij}^T$ is a constant that determine the strength of the eigenstrain. $\varepsilon_{ij}^T$ is second rank tensor to reflect tetragonal anisotropy with zero diagonal terms in this work. $\delta_{ij}$ is the Kronecker delta and $\beta(\eta)$, Wang’s interpolation function[135], is a scalar function of order-parameter. The elastic modulus tensor is also an explicit function of order parameter. The composition dependent elastic constants can be described as the follows:
\[ C_{ijkl}(c) = C_{ijkl}^{eff} + \alpha(\eta)\Delta C_{ijkl} \tag{6.19} \]

where \( \alpha(\eta) \) is a scalar function of order parameter.

\[ \alpha(\eta) = \frac{1}{2} \left\{ \eta^3(10 - 15\eta + 6\eta^2) \right\} \tag{6.20} \]

\[ \Delta C_{ijkl} = C_{ijkl}^p - C_{ijkl}^m \tag{6.21} \]

\( C_{ijkl}^p \) and \( C_{ijkl}^m \) are the elastic moduli tensor of the precipitate and matrix phases, respectively, and \( C_{ijkl}^{eff} \) is an effective modulus to calculate the 0th order approximation of solution by Eq. (6.38).

According to the literature, when \( C_{ijkl}^{eff} \) equals \( \frac{1}{2}(C_{ijkl}^p + C_{ijkl}^m) \), the number of iterations for convergence can be minimized[136]. To obtain the elastic energy, and hence the variational derivative of elastic free energy, we need to solve the following equation of mechanical equilibrium on domain \( \Omega \).

\[ \frac{\partial \sigma_{ij}^{el}}{\partial r_j} = 0 \tag{6.22} \]

The solution for the equilibrium equation is periodic on domain \( \Omega \) because the elastic moduli and eigenstrains are periodic on \( \Omega \). The strain field \( \epsilon(r) \) is also periodic, so the displacement field \( u(r) \) can be regarded as follows[137]:

\[ u = E \cdot r + u^* \tag{6.23} \]

where \( u^* \) is a displacement field that is also periodic on \( \Omega \) and \( E \) is a constant, homogeneous strain tensor, which assumed to be symmetric. \( E \) represents the mean strain tensor of the cell as the follows:
\[ \langle \varepsilon_{ij} \rangle = E_{ij} \]  
(6.24)

with the following definition for the mean \( \langle \cdot \rangle \) of a quantity \( \cdot \):

\[ \langle \cdot \rangle = \frac{1}{V} \int_{\Omega} \cdot \, d\Omega \]  
(6.25)

where \( V \) is the volume of the representative domain \( \Omega \). If we indicate the periodic strain by \( \varepsilon_{ij}^* \) (such that \( \langle \varepsilon_{ij}^* \rangle = 0 \)), the strain that we derive from the displacement equation becomes

\[ \varepsilon_{ij} = E_{ij} + \varepsilon_{ij}^* \]  
(6.26)

where

\[ \varepsilon_{ij}^* = \frac{1}{2} \left\{ \frac{\partial u_i^*}{\partial r_j} + \frac{\partial u_j^*}{\partial r_i} \right\} \]  
(6.27)

We can also define the mean stress on the domain \( \Omega \) as follows:

\[ \langle \sigma_{ij}^{el} \rangle = \frac{1}{V} \int_{\Omega} \sigma_{ij}^{el} d\Omega \]  
(6.28)

The mean stress equals the applied stress \( \sigma_{ij}^A \) [137-139]. Substituting for \( \sigma_{ij}^{el} \) from Eq. (6.17), we obtain

\[ \sigma_{ij}^A = \frac{1}{V} \int_{\Omega} C_{ijkl}(E_{kl} + \varepsilon_{kl}^* - \varepsilon_{kl}^0) d\Omega \]  
(6.29)

By using the definition in Eq. (6.27), we can define the following mean quantities:

\[ S_{ijkl} = \left( \langle \{C_{ijkl}\} \rangle \right)^{-1}, \langle \{\varepsilon_{ij}^*\} \rangle = \langle \{C_{ijkl}\varepsilon_{kl}^*\} \rangle, \]  
(6.30)

\[ \langle \{\sigma_{ij}^0\} \rangle = \langle \{C_{ijkl}\varepsilon_{kl}^0\} \rangle \]
Using the above equations, we obtain the followings.

\[ E_{ij} = S_{ijkl} [\sigma_{kl}^A + \{\sigma_{kl}^0\} - \{\sigma_{kl}^*\}] \]  

(6.31)

We can rewrite the following equation of mechanical equilibrium given a periodic order parameter \( \eta \) on \( \Omega \):

\[ \frac{\partial}{\partial r_j} \{ C_{ijkl} (E_{kl} + \varepsilon_{kl}^* - \varepsilon_{kl}^0) \} = 0 \]  

(6.32)

with the constraint

\[ E_{ij} = S_{ijkl} (\sigma_{kl}^A + \{\sigma_{kl}^0\} - \{\sigma_{kl}^*\}) \]  

(6.33)

and the boundary condition, \( \varepsilon_{kl}^* \) is periodic on \( \Omega \). Substituting for \( C_{ijkl} \) and \( \varepsilon_{kl}^0 \) in terms of order parameter, and \( \varepsilon_{kl}^* \) in terms of the displacement field in equation, and using the symmetry properties of the elastic constants and strains, we obtain the following:

\[ \frac{\partial}{\partial r_j} \left\{ C_{ijkl}^{\text{eff}} + \alpha(\eta)\Delta C_{ijkl} \right\} \left( E_{kl} + \frac{\partial u_i^*(r)}{\partial r_k} - \varepsilon_{kl}^0 \delta_{kl}\beta(\eta) \right) = 0 \]  

(6.34)

\[ \left[ C_{ijkl}^{\text{eff}} \frac{\partial^2}{\partial r_j \partial r_k} + \Delta C_{ijkl} \frac{\partial}{\partial r_j} \left( \alpha(\eta) \frac{\partial}{\partial r_k} \right) \right] u_i^*(r) \]

\[ = C_{ijkl}^{\text{eff}} \delta_{kl} \frac{\partial \beta(\eta)}{\partial r_j} - \Delta C_{ijkl} E_{kl} \frac{\partial \alpha(\eta)}{\partial r_j} + \Delta C_{ijkl} \varepsilon_{kl}^0 \delta_{kl} \frac{\partial \{\alpha(\eta)\beta(\eta)\}}{\partial r_j} \]  

(6.35)

The above equation of mechanical equilibrium can be solved numerically using a fast Fourier transform (FFT)-based iterative method. We begin with the 0\(^{th}\) order approximation to the solution by assuming that \( \Delta C_{ijkl} = 0 \). Thus, equation reduces to:
\[
C_{ijkl}^{\text{eff}} \frac{\partial^2 u^*_i(r)}{\partial r_j \partial r_k} = C_{ijkl}^{\text{eff}} \varepsilon_{kl} \frac{\partial \beta(\eta)}{\partial r_j} \tag{6.36}
\]

Taking \( \sigma_{ij}^T = C_{ijkl}^{\text{eff}} \varepsilon_{kl} \delta_{kl} \)

\[
C_{ijkl}^{\text{eff}} \frac{\partial^2 u^*_i(r)}{\partial r_j \partial r_k} = \sigma_{ij}^T \frac{\partial \beta(\eta)}{\partial r_j} \tag{6.37}
\]

The above equation can be solved in Fourier space. If we indicate the Fourier transform of a quantity \((\cdot)\) by \(\{(\cdot)\}_g\),

\[
\{(\cdot)\}_g = \int_\Omega (\cdot) \exp(-2\pi g' \cdot r) \, dr \tag{6.38}
\]

where \(J = \sqrt{(-1)}\). Defining \(G^{-1}_{ij}\) as \(C_{ijkl}g_jg_k\) (where \(g = 2\pi g'\)), we can write the solution in the Fourier space as follows:

\[
\{(u^*_i)^0\}_g = -J G_{ij} \sigma_{ij}^T g_j \{\beta(\eta)\}_g \tag{6.39}
\]

where the superscript on \(u^*_i\) indicates the order of approximation. Starting with the zeroth order approximation, we refine the solution. We write the \(n^{th}\) order refined solution using the \((n-1)^{th}\) order solution as follows:

\[
\{(u^*_i)^n\}_g = -J G_{ij} \Lambda^{-1}_{ij} g_j \tag{6.40}
\]

where

\[
\Lambda^{-1}_{ij} = \sigma_{ij}^T \{\beta(\eta)\}_g - \Delta C_{ijkl} E^{n-1}_{mn} \{\alpha(\eta)\}_g + \Delta C_{ijkl} \varepsilon_{kl} \delta_{mn} \{\alpha[\eta(r)] \beta[\eta(r)]\}_g \\
- \Delta C_{ijkl} \left\{ \alpha[\eta(r)] \frac{\partial (u^*_m)^{n-1}(r)}{\partial r_n} \right\}_g \tag{6.41}
\]
and \( E_{mn}^{n-1} \) is the homogeneous strain calculated from the \((n-1)^{th}\) order approximation of solution. The solution procedure yields periodic displacement \( u^* \) and homogeneous strain \( E \), and hence strain field \( \varepsilon_{ij}, \varepsilon_{el}^* \) and \( \sigma_{el}^* \). Thus, we solve the equation of mechanical equilibrium at each time step. Every time step, we get \( 0^{th} \) order solution and then, refine the \( 0^{th} \) order solution to get higher order until convergence is achieved. If the error in displacement is less than a given value, \( 10^{-10} \) in this work, the iteration is stopped. The calculation of error is based on the follows:

\[
\text{Error} = \left( \sum_{i=1}^{M} \sum_{j=1}^{N} (u^{n+1}(i,j) - u^n(i,j)) \cdot (u^{n+1}(i,j) - u^n(i,j)) \right)^{1/2} (6.42)
\]

where \( u^n(i,j) \) and \( u^{n+1}(i,j) \) are the displacement solutions at the grid point \((i,j)\). \( M \) and \( N \) are the total number of grid points in the x and y-directions. Substituting for \( \varepsilon_{el}^* \) and \( \sigma_{el}^* \) in equation, and using the definition of \( \mu_{el}^* \), we obtain the variational derivative of elastic free energy as follows, which is the same in [136, 140]:

\[
\frac{\delta E_{el}}{\delta \eta_p} = \mu_{el}^* = \frac{1}{2} \alpha'(\eta) \Delta C_{ijkl} \left( E_{ij} + \varepsilon_{ij}^* - \varepsilon_{ij}^0 \right) \left( E_{ij} + \varepsilon_{ij}^* - \varepsilon_{ij}^0 \right) \beta'(\eta) \varepsilon_{ij}^T \delta_{ijkl} \left( E_{ij} + \varepsilon_{ij}^* - \varepsilon_{ij}^0 \right) (6.43)
\]

### 6.2.4 Constructing the phase field model

The temporal evolution of the microstructure in the phase-field model is obtained by numerically solving the Cahn-Hilliard equation for composition and the Allen-Cahn equation for the order parameter, as follows:
where \( M \) is the solute mobility and \( L \) is the interfacial kinetic coefficient. The temporal evolution equations in dimensionless form are:

\[
\frac{\partial c}{\partial t^*} = M^* \nabla^2 \left[ \frac{\partial f^*}{\partial c} - \xi \nabla^2 c \right] \tag{6.46}
\]

\[
\frac{\partial \eta}{\partial t^*} = - \left[ \frac{\partial f^*}{\partial \eta} - \psi_{ij} \frac{\partial^2 \eta}{\partial x_i \partial x_j} + 2\gamma_{ijkl}^* s_{ijkl} + \frac{\delta E_{el}^*}{\delta \eta} \right] \tag{6.47}
\]

\[
s_{ijkl} = \frac{\partial^4 \eta}{\partial x_i \partial x_j \partial x_k \partial x_l}
\]

\[
r^* = \frac{r}{l}, \quad M^* = \frac{M}{l^2}, \quad M = \frac{Dc(1-c)}{RT}, \quad f^* = \frac{f(c, \eta)}{|\Delta f|}
\]

\[
E_{el}^* = \frac{E_{el}}{|\Delta f|}, \quad \xi = \frac{\alpha}{|\Delta f| l^2}, \quad \psi_{ij} = \frac{\beta_{ij}}{|\Delta f| l^2}, \quad \gamma_{ijkl}^* = \frac{\gamma_{ijkl}}{|\Delta f| l^4}
\]

where the quantities with asterisk (*) represent the dimensionless values corresponding dimensional quantities. \( l \) represents the characteristic length scale, which is chosen as physical quantity of circularly equivalent radius in this work. And \( \Delta f \) represents the characteristic free energy, which is the maximum driving force for phase transformation from the constructed bulk free energy, as shown in Fig. 6.1. The temporal equations are solved numerically using the semi-implicit Fourier-Spectral method[141] until the convergence of \( \frac{dc}{dt^*} \) is achieved to \( \sim 10^{-4} \) to assume the computed shape as equilibrium.
6.2.5 Interfacial energy

In the phase-field description, the interfacial energy $\sigma$ for a system described by both the composition and an order parameter has been given previously [18, 36, 132, 142]:

$$\sigma = 2 \int_{c_{eq}}^{c} \left[ \frac{\alpha}{2} \Delta f(c) \right]^{1/2} \left[ 1 + \sum_p \frac{\beta_{ij}}{\alpha} \left( \frac{d\eta}{dc} \right)^2 \right] dx = \int \left[ \alpha \left( \frac{dc}{dx} \right)^2 + \beta_{ij} \left( \frac{d\eta}{dx} \right)^2 \right] dx \quad (6.48)$$

where $\Delta f(c) = f(c) - f_{eq}(c)$ represents the excess free energy associated with the material in the interface, as shown in Fig. 6.1. $\alpha$ and $\beta_{ij}$ are gradient energy coefficients for composition and order parameters in Eq. (6.2). The fourth-order coefficient $\gamma_{ijkl}$ is described in Eqs. (6.5)-(6.12). We perform one-dimensional simulations to obtain the coefficients from the DFT free energy (Fig. 6.1) and interfacial energies (Fig. 6.2) along with Eq. (6.57) and (6.58). The coefficients are listed in Table 6.1.

6.3. Results and Discussions

6.3.1. Comparisons with past DFT and PFM studies
<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value used</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1, A_2, A_{41}, A_{61}$</td>
<td>1622.6, 1075.1, -536.6, 536.6 (meV/atom)</td>
<td>[36]</td>
</tr>
<tr>
<td>$C_{r1}, C_{r2}$</td>
<td>0.002, 0.3333</td>
<td>[36]</td>
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<td>$C_{a1}, C_{a1}^*$</td>
<td>0.0013, 0.3322</td>
<td>[36]</td>
</tr>
<tr>
<td>$D$</td>
<td>$10^{-18}$ (m$^2$/s)</td>
<td>[143]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$3.065 \times 10^{-10}$ (J/m)</td>
<td></td>
</tr>
<tr>
<td>$l$</td>
<td>$10 \times 10^{-9}$ (m)</td>
<td></td>
</tr>
<tr>
<td>$\Delta f$</td>
<td>34 (meV/atom)</td>
<td>[36]</td>
</tr>
<tr>
<td>$L$</td>
<td>0.2451 (eV/atom * s)</td>
<td>[35, 36]</td>
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<tr>
<td>$\beta_{11}, \beta_{22}$</td>
<td>$9.375 \times 10^{-11}, 7.08 \times 10^{-10}$ or $6.903 \times 10^{-10}$ (J/m)</td>
<td></td>
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<tr>
<td>$\gamma_l, \gamma_a$</td>
<td>6.903 $\times 10^{-10}$ (J/m)</td>
<td>[35, 36]</td>
</tr>
<tr>
<td>$b/a$</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>$\alpha(\eta)$</td>
<td>${\eta^3(10 - 15\eta + 6\eta^2)} - \frac{1}{2}$</td>
<td>[136]</td>
</tr>
<tr>
<td>$\beta(\eta)$</td>
<td>${\eta^3(10 - 15\eta + 6\eta^2)}$</td>
<td>[136]</td>
</tr>
<tr>
<td>$C_{ijkl}^{\text{eff}}$</td>
<td>$\frac{1}{2}(C_{ijkl}^p + C_{ijkl}^m)$</td>
<td>[136]</td>
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<td>$C_{ijkl}^m, C_{ijkl}^p, C_{ijkl}^m$</td>
<td>1.102, 0.548, 0.304 (Mbar)</td>
<td>[144]</td>
</tr>
<tr>
<td>$C_{ijkl}^p, C_{ijkl}^p, C_{ijkl}^p$</td>
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<tr>
<td>$e_{ijkl}^1, e_{ijkl}^2$</td>
<td>0.007, -0.051</td>
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Table 6.1. Phase-field coefficients used in this simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value used</th>
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<tbody>
<tr>
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<tr>
<td>$N \times N \times N$, 3D</td>
<td>512x512x512</td>
</tr>
<tr>
<td>$\Delta x^* = \Delta y^*$</td>
<td>0.0067</td>
</tr>
<tr>
<td>$dt^*$</td>
<td>$3 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Allowed error in displacements | Less than $10^{-10}$

Table 6.2. Simulation (non-dimensional) parameters
Figure 6.1. Chemical free energies of $\theta'$ phase and the matrix $\alpha$-Al as a function of Cu composition in Al-Cu. The coefficients of the free energies literature values[36, 132].

Figure 6.2. (a) Relaxed supercells used for the first-principles interfacial energy calculations of coherent (001) $\theta'$ // (001) $\alpha$-Al and semi-coherent (010) $\theta'$ // (010) $\alpha$-Al interfaces. Blue and orange circles represent Al and Cu atoms, respectively. Dashed lines indicate the $1a_{\theta'} = 1a_{\alpha Al}$ and $2a_{\theta'} = 3a_{\alpha Al}$ relationships of the coherent and semi-coherent interfaces, respectively. (b) First-principles formation energies of the interface $\alpha$-Al/$\theta'$-$\text{Al}_2\text{Cu}$ ($N$-atom supercells) as a function of $1/N$ for both interfaces. The interfacial energies ($\sigma$) are extracted from the slopes, $2\sigma A$, by Eq. (3.5). The size of super cells is chosen large enough to avoid interface-interface interactions for relatively small super cells based on the previous literature[36]. The detail information is explained in Chapter 3.
Figure 6.3. The equilibrium $\theta'$ morphology (with interfacial energy anisotropy only) changes depend on grid conditions. This simulation is done to validate the previous method of grid-spacing-controlled shape based on the literature[36, 132]. The initial condition is commonly assumed to a rectangle (3:1) following the literature[35, 36, 132]. (a) $N = 1024 \times 1024$, $h = 0.02$, (b) $N = 1024 \times 1024$, $h = 0.0067$, and (c) $N = 342 \times 342$, $h = 0.02$. Here, $N$ is the number of grids in simulation and $h$ is grid-spacing. (a) vs. (b) represent the effect of grid-spacing ($h$) to $\theta'$ morphology as shown in the literature[36, 132]. When the grid is insufficiently small compared to the interfacial width at coherent interface (top and bottom interfaces), the coherent interface becomes flat, this results in excessive lengthening in (a). (b) vs. (c) represent the effect of grid-density in a constant simulation box (a constant particle size). The shape morphology (i.e., aspect ratio) also changes depend on grid-density when the grid-density is insufficiently high.

Our phase-field modeling is performed using first-principles input parameters from previous work[35, 36, 132]. The chemical free energies of $\theta'$ phase and the matrix $\alpha$-Al are shown in Fig.
6.1. The input parameters are listed in Table 6.1 and 6.2, and details about the DFT calculations are well-explained in the literature[36]. Since interfacial energies for both coherent and semi-coherent interfaces are an important factor for determining precipitate morphology, we re-examined the values in this work. In order to calculate the energies for isolated interfaces, the minimum size of super cells was chosen in line with previous literature[36] in order to avoid interface-interface interactions for relatively small super cells. In Chapter 3, our DFT calculations show that the interfacial energies of 0.20 J/m² and 0.52 J/m² for both interfaces are in close agreement with earlier first-principles DFT calculations[35, 36, 145] shown in Fig. 3.2.(b) and 3.4.(b). The small difference comes from different (pseudo) potentials and exchange-correlation functionals. According to Nie[146], there is a relatively large shear component of ~0.33 associated with the α-Al → θ' transformation when θ' precipitate has single unit cell in thickness constrained within α matrix. The shear strain we employ has not taken into this account, since the minimum thickness of the θ' is two unit cells of θ' as observed in experiment, which has a tetragonal misfit strain due to a thickness of three unit cells of α-Al that minimizes the misfit[38, 147].

Recently, Laure Bourgeois et al.[33] proposed a new structure, distinct from the previously accepted structure based on a simple (001)θ' termination of the precipitate. The newly-proposed interface shows a different composition and crystal structure compared to the bulk θ' structure[34-36], and has interstitial Cu atoms at the coherent interface θ' // α-Al. In Chapter 3., we have performed detailed DFT investigation of theses interfacial structures, and found that the interface with Cu interstitials is higher in energy, and does not yield Si segregation behavior in agreement with an experiment in Al-Cu-Si. Thus, we choose the previously-adopted structure
based on (001)\(\theta^\prime\) termination of the bulk precipitate structure without interstitial Cu atoms (top image in Fig. 6.2. (a)) in this work.

In the previous work by Vaithyanathan et. al.[35, 36, 132], the characteristic length scale \(l\) was chosen as the grid-spacing in a simulation, and the size and “shape (aspect ratio)” of the \(\theta^\prime\) precipitate was controlled by this grid-spacing[132]. When the grid is insufficiently small compared to interfacial width (generally larger than one-sixth of interfacial width), the grid may not be small enough to describe the correct profile of the order parameter in the interface, leading to a numerical artifact that renders the interfaces relatively flat. Since a finer grid-spacing requires more computational effort, the previous work compromised between the discretization artifact and the computational effort, and chose a grid-spacing such that the precipitate aspect ratio is close to that given by the interfacial energy anisotropy. The comparison between Fig. 6.3 (a) and (b) show that the size and the shape of \(\theta^\prime\) precipitate changes with these two values of grid spacing, and as such, the flat surface in Fig. 6.3 (a) is due to a numerical artifact at the coherent interface. The size of the simulation box in Fig. 6.3 (b) and (c) was fixed in order to analyze the difference of a particle shape depending on grid density with the same particle size. As shown in Fig. 6.3 (c), the precipitate also has a flat surface with a numerical artifact at coherent interfaces when the grid density is not sufficiently high.

The Cahn Hilliard and Allen Cahn equations should be solved consistently, and the equilibrium Wulff shape, which is based on interfacial energy as a function of the crystallographic orientation of the interface, should also be independent of the grid spacing. If the facet in the Wulff shape is stabilized artificially by a large grid spacing, it then becomes unclear how elastic energy will affect the equilibrium shape. Therefore, we employ a different
approach to capture the faceted coherent interface and yield the proper Wulff shape. A circularly equivalent radius ($l$, in Table 1.) is chosen as a characteristic length instead of grid spacing for non-dimensionalization. Since our ultimate goal is to compare precipitate shapes (such as the aspect ratio of precipitate) in the simulation versus that in the experiment, we choose a physical length of 10 nm as a characteristic length based on the experimental literature[4].

6.3.2. Equilibrium shape of precipitate with interfacial energy anisotropy

Figure 6.4. The equilibrium $\theta'$ morphology with interfacial energy anisotropy changes depends on different methods. (a) Elliptic shape is described by a second-rank tensor coefficient ($\beta_{ij}$) with zero diagonal terms in Eq. (6.2) and (6.47). (b) Plate-shape is described by additional fourth-order terms in Eq. (6.2) and (6.47). By comparing (a) and (b), the faceted coherent interfaces of $\theta'$ precipitates can be described by the high-order
terms (Eq. (6.10) and (6.11)). (c) 3-dimensional (3D) plate-shape with the fourth-order terms. In the 3D plot, the precipitate is visualized by the isoconcentration Cu = 0.15 surfaces.

The considerable literature on the phase-field modeling of \( \theta' \) precipitation has yielded elliptical or lens shaped precipitates in two-dimensions[35, 36, 87, 133]. We also employ two gradient coefficients (\( \beta_{11} \) and \( \beta_{22} \)) retained as a second rank tensor to incorporate the (tetragonal) anisotropy in interfacial energy. However this is insufficient for describing the flat surface of actual \( \theta' \) plate-shaped precipitates as shown in Fig. 6.4 (a). Previously, a fourth-rank term has been used to describe the shape of four-fold symmetry precipitates[142, 148-150]. In order to allow for missing orientations, we employ the additional four-rank term as described in Eq. (2) with the resulting 2-dimensional (2-D) Wulff shape of the precipitate shown in Fig. 6.4 (b). This is the shape that minimizes the total interfacial area for a fixed volume of precipitate. The \( \zeta \) coefficient controls the aspect ratio of the Wulff shape.

When interfacial anisotropy is sufficiently high, the equilibrium morphology has corners and edges where there are certain missing high-energy orientations on the Wulff shape[151]. As such, this high degree of anisotropy can yield a plate-shaped morphology of equilibrium \( \theta' \) precipitate shown in Fig. 6.4 (b). To closely describe the thermodynamic stable shape of a precipitate[33], we would like to have the curvature at the corners of the precipitate as sharp as possible. Therefore, we investigated how the three coefficients (\( \gamma_i, \gamma_d, \zeta \)) in Eq. (6.10) and (6.11) influence precipitate morphology under fixed coherent and semi-coherent interfacial energies from first-principles calculations in Fig. 6.2 (b).
First, we need to choose a negative value of the anisotropic coefficient $\gamma_a$ in Eq. (6.10) and (6.11) to obtain elongated plate-like precipitate shape because a minimum energy is needed along the <100> directions. This is the same as cubic anisotropy as used previously[142]. If the coefficient $\gamma_a > 0$, the equilibrium shape will be an elongated diamond. Under the assumption that the coordinate $l$ is along the coherent interface direction, $\zeta$ (in Eq. (6.10) and (6.11)) is chosen as a positive value. Second, the curvature at the corners can be controlled by the isotropic coefficient $\gamma_l$. As we increase the coefficient $\gamma_l$, the curvature at the corner becomes larger. But, the aspect ratio of precipitate becomes smaller (interfacial energy anisotropy changes), which is unlike the case for cubic anisotropy, because we have the additional term $\zeta$ for tetragonal anisotropy (two-fold symmetry). When we fix the other constants, except for $\gamma_l$, $\gamma_l$ should be larger than $-\zeta\gamma_a$ because the high-order term should be non-negative, otherwise the system will be unstable. As such, we choose $\gamma_l = -\zeta\gamma_a$ to make the corner as sharp as possible.

Fig. 6.4 (b) shows that the shape of the precipitate is close to the actual plate-shape of precipitate based on our model with a fourth-order term, as compared to an elliptic shape, as shown in Fig. 6.4 (a). We also performed the 3-dimensional (3-D) simulation. Fig. 6.4 (c) shows the 3-D plate-shape precipitate with flat surfaces on top and bottom of the precipitate.

In this work, the grid spacing was chosen as one-sixth of interfacial width, which is in the range of $\eta_{0.1} \sim \eta_{0.9}$. To validate our calculation under the convergence of grid density, we tested a finer grid, which was one-ninth of interfacial width, and find that the computed shape of precipitate does not change as the grid size is decreased.
6.3.3. Equilibrium shape of precipitate with interfacial and elastic energy anisotropy

Figure 6.5. (a) The equilibrium $\theta'$ morphology with an isotropic interfacial energy and elastic energy (with elastic inhomogeneity) anisotropy. (b) The equilibrium $\theta'$ morphology with interfacial and elastic energy (with elastic inhomogeneity) anisotropy without a high-order terms $\gamma_{ijkl}$ in Eq. (6.3) and (6.48). (c) The equilibrium $\theta'$ morphology with interfacial and elastic energy (with elastic inhomogeneity) anisotropy with the high-order terms. (d) 3-D plate-shape with the high-order terms. In the 3D plot, the precipitate is visualized by the isoconcentration Cu = 0.15 surfaces. For the 3-D simulation, the particle size is chosen to be relatively small and the homogenous modulus approximation (Al modulus) is used for computational efficiency. (a), (b) vs. (c) represents that the strong effect of interfacial energy anisotropy on the shape.
Figure 6.6. Computed aspect ratio as a function of characteristic length (nm) in the 2-D simulation. The largest particle in the simulation corresponds to the particle in Fig. 6.5 (c). The aspect ratio increased as characteristic length increased because the elastic energy is proportional to the size of the precipitate.

<table>
<thead>
<tr>
<th></th>
<th>Al-Cu[45] (225°C, ~50hrs.)</th>
<th>PFM (This work)</th>
</tr>
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<tbody>
<tr>
<td>Length</td>
<td>~580 nm</td>
<td>54 nm</td>
</tr>
<tr>
<td>Thickness</td>
<td>~14 nm</td>
<td>10 nm</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>~50</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Table 6.3. Experimentally determined average values[152] for two-dimensional length, thickness, and aspect ratio for equilibrium $\theta'$ precipitate in Al-Cu-Si and Al-Cu. The computed particle size by PFM corresponds to the largest particle in Fig. 6.6. As seen in here, the computed length (54 nm) is almost ten-times smaller than the length (~580 nm) observed in the Al-Cu experiment under similar thickness (~10 nm).

Since the equilibrium Wulff shape does not have the aspect ratio seen in experiment, it is necessary to consider the effects of elastic stress. We thus examined the equilibrium $\theta'$ morphology with a combination of interfacial and elastic anisotropies. The elastic constants
and eigenstrain are determined from first-principles calculations and given in the literature[36, 144]. Given the difference in moduli between Al and \( \theta' \), we must account for the effects of an elastic constant inhomogeneity on the equilibrium \( \theta' \) morphology using Eq. (17). Also, we assumed a misfit at semi-coherent interface does not change with particle size. Based on the literature[36], the lattice misfit strain at a semi-coherent interface is -5.1% in the configuration of \( 2c_{\theta'}:3a_{Al} \).

Fig. 6.5 (a) shows the equilibrium shape of a precipitate with isotropic interfacial energy. Due to the strain energy anisotropy the precipitate assumes an elliptical shape. In contrast, when only including \( \beta_{ij} \) terms in the interfacial energy (Eq. (3)) and thus not allowing for missing orientations, the precipitate attains a lens-shape, see Fig. 6.5 (b). Allowing for missing orientations on the Wulff shape, and a nearly faceted interface shows that elastic stress does not induce a qualitative change the Wulff shape, but does change the aspect ratio. By comparing Fig. 6.5 (a), (b) and (c), it is clear that interfacial energy anisotropy is important in determining the equilibrium shape of the precipitate. The effects of the elastic energy on the \( \theta' \) morphology is proportional to the size of the precipitate, as shown in Fig 6.6.

The computed length (54 nm) of the equilibrium \( \theta' \) precipitate morphology with interfacial and elastic energy (including elastic inhomogeneity) anisotropies is almost ten-times smaller than its length (~580 nm) in the Al-Cu experiment with similar thickness (~10 nm) used in this work (Table 6.3). Thus, it is clear that kinetics is playing an important role in setting the shapes observed in experiment.

Si catalyzes the heterogeneous nucleation of \( \theta' \) precipitate, thereby influencing the microstructure of the alloy[44, 152]. Specifically, \( \theta' \) precipitates in the ternary Al-Cu-Si alloy
are more densely distributed, have lower aspect ratios at the same temperature compared to when in binary Al-Cu alloy[152]. Even in the case of lower aspect ratio morphology in ternary Al-Cu-Si alloy, the computed aspect ratio of the equilibrium $\theta'$ precipitate morphology with interfacial and elastic energy (including elastic inhomogeneity) anisotropies is about a factor of 4 for an equivalent particle radius of 15 nm, which is five-times smaller than the experimentally observed aspect ratio of ~20 in Al-Cu-Si alloy at 190°C (~50 hrs.).

Based on an atom-probe tomography (APT) experiment[45], the change in interfacial energies by Si segregation ($\Delta\sigma = -11$ and 64 mJ/m$^2$ for coherent and semicoherent interfaces, respectively) is negligible compared to two interfacial energies (Fig. 6.2 (b)). Thus, we surmise that future kinetic studies about an interaction between the growth of $\theta'$ precipitates and segregated Si solutes will be needed to understand the role of Si solutes in lowering aspect ratio of $\theta'$ precipitates.

In terms of the growth mechanism of $\theta'$ precipitate, there is a high-energy barrier for ledge nucleation at the coherent interface due to a large misfit strain at the edges of a semi-coherent interface. As such, the thickening of the plate is an interface-controlled thickening behavior, which is much slower than diffusion-controlled lengthening[143]. For example, in the recent work by Li and Purdy[39], the aspect ratio of $\theta'$ precipitate with a thickness of 1.2 nm ($2c_{\theta'}:3a_{Al}$) configuration at semi-coherent interface shows an aspect ratio more than ~300 during the initial 20 minute aging time for an Al-Cu alloy single crystal at 230°C. Based on this mechanism, we conclude that a considerably-kinetically elongated $\theta'$ precipitate does not fully recover to the computed equilibrium aspect ratio of the shape even at very long aging times (~50
hrs.), especially at around 200°C. In other words, the experimental morphology after long aging times (~50 hrs.) is influenced strongly by kinetic considerations.

For the 3-D simulation in Fig. 6 (d), the particle size was chosen as a relatively small (a thickness of 30 nm and a length of 7.6 nm) and the homogenous modulus approximation (Al modulus) is used for computational efficiency. The effect of elastic inhomogeneity is not significant in this work (detailed information about elastic contribution to equilibrium morphology will be described in the section 3.4.). In 3-D simulation, the aspect ratio of the precipitate was approximately ~4 for the relatively small particle size. Since the aspect ratios of similar magnitudes were seen in both the 2-D and 3-D simulations, the 2-D computation yields a reasonable approximation to the equilibrium shape. However, it is likely that the kinetics computed using a 2-D calculation is quite different from that in 3-D[153].

6.3.4. Different elastic energy contributions to the equilibrium $\theta'$ morphology
Table 6.4. Elastic parameters used in this simulation. Each column corresponds to the equilibrium morphology in Fig. 6.7 (a)-(e). All the elastic parameters are determined from previous DFT calculations[35, 36, 144]. We investigate various strain energy contributions: (a) elastic inhomogeneity (as used in the section 3.3.), (b) elastic homogeneity (Al modulus), (c) elastic homogeneity ($\theta'$ modulus), (d) elastic anisotropy, (e) misfit strain anisotropy. In order to see the elastic anisotropic effect by comparing (a) and (d), the elastic constants (shear modulus) with an * indication are modified in order to satisfy $A_z = 2C_{44}/(C_{11} - C_{12}) = 1$ for both Al and $\theta'$. In (e), the misfit strain ($\varepsilon_{22} = -0.003$) is at the semicoherent interface with interfacial configuration of $3.5c_{\theta'}: 5a_{Al}$ based on literature[36].

<table>
<thead>
<tr>
<th>Case study</th>
<th>(a) Elastic inhomogeneity (Mbar)</th>
<th>(b) Elastic homogeneity (Al modulus)</th>
<th>(c) Elastic homogeneity ($\theta'$ modulus)</th>
<th>(d) Elastic anisotropy</th>
<th>(e) Misfit strain anisotropy</th>
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</thead>
<tbody>
<tr>
<td>$C_{11}^{m}$</td>
<td>1.102[144]</td>
<td>1.102</td>
<td>1.9</td>
<td>1.102</td>
<td>1.102</td>
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<tr>
<td>$C_{12}^{m}$</td>
<td>0.548[144]</td>
<td>0.548</td>
<td>0.8</td>
<td>0.548</td>
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<td>$C_{44}^{m}$</td>
<td>0.304[144]</td>
<td>0.304</td>
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<td>0.277*</td>
<td>0.304</td>
</tr>
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<td>$C_{11}^{p}$</td>
<td>1.9[36]</td>
<td>1.102</td>
<td>1.9</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>$C_{12}^{p}$</td>
<td>0.8[36]</td>
<td>0.548</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$C_{44}^{p}$</td>
<td>0.9[36]</td>
<td>0.304</td>
<td>0.9</td>
<td>0.55*</td>
<td>0.9</td>
</tr>
<tr>
<td>$\varepsilon_{11}^{T}$</td>
<td>0.007[36]</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
</tr>
<tr>
<td>$\varepsilon_{22}^{T}$</td>
<td>-0.051[36]</td>
<td>-0.051</td>
<td>-0.051</td>
<td>-0.051</td>
<td>-0.003[36]</td>
</tr>
</tbody>
</table>
Figure 6.7. The equilibrium $\theta'$ morphology with interfacial and elastic energy anisotropy. The elastic parameters for (a)-(e) corresponds to (a)-(e), listed in Table 6.3. (a) elastic inhomogeneity, (b) elastic homogeneity (Al modulus), (c) elastic homogeneity ($\theta'$ modulus), (d) elastic anisotropy, $A_z = 2C_{44}/(C_{11} - C_{12}) = 1$ for both Al and $\theta'$, (e) misfit strain anisotropy, $\varepsilon_{22} = -0.003$ with interfacial configuration of $3.5c_{\theta'}: 5a_{Al}$ based on literature[36]. By comparing (a) and (e), we can see that the effect of misfit strain anisotropy is the most significant. The detail quantitative analysis will be shown in Fig. 6.8 and Table 4.
Figure 6.8. Quantitative measurement of $\theta'$ plate-shaped precipitate with different elastic conditions corresponding Figs. 6.7 (a)-(e). (a) elastic inhomogeneity (b) elastic homogeneity (Al modulus), (c) elastic homogeneity ($\theta'$ modulus), (d) elastic anisotropy, (e) misfit strain anisotropy. The distance (nm) is from a center of the precipitate to surfaces where isoconcentration Cu = 0.15. The polar angles (with respect to x-axis) of 0 and ±90 represent semi-coherent and coherent axis, respectively. As seen here, the effects of elastic inhomogeneity between (a) and (b), and elastic anisotropy between (a) and (d) are not significantly effective. The precipitate shape is strongly controlled by the misfit strain anisotropy, as can be seen by comparing (a) and (e).

<table>
<thead>
<tr>
<th>Case study</th>
<th>Coefficients $2^{th}/0^{th}$</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic inhomogeneity</td>
<td>0.4116</td>
<td>0.3970 (-3.55 %)</td>
<td>0.4479 (8.80 %)</td>
<td>0.4095 (-0.52 %)</td>
<td>0.2518 (-38.82 %)</td>
<td></td>
</tr>
<tr>
<td>Elastic homogeneity (Al modulus)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elastic homogeneity ($\theta'$ modulus)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elastic anisotropy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Misfit strain anisotropy</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 6.5. Quantitative measurement of $\theta'$ precipitates corresponding Figs. 6.8 (a)-(e). From the distance in Fig. 6.8, we took the distance as a function of angle, then computed the Fourier transforms to obtain coefficient values. The values of $2^{nd}/0^{th}$ is associated
with aspect ratio of the shape. A parenthesis represents the relative change of values in percentage with respect to the value in (a). By comparing (a) and (e), the misfit strain anisotropy influences the precipitate shape significantly (-38.82 %).

In order to gain a fuller picture of the elastic energetic contribution to $\theta'$ morphology, we examine various strain energy contributions: elastic inhomogeneity, elastic anisotropy, and tetragonal misfit strain anisotropy. The elastic constants and eigenstrains are listed in Table 6.4. To see the effect of elastic anisotropy $A_z = 2C_{44}/(C_{11} - C_{12})$, the elastic constants of $C_{44}$ for $\alpha$-Al and $\theta'$ were changed from 0.304 and 0.9 to 0.277 and 0.55, respectively, to achieve $A_z = 1$. To see the effect of misfit strain anisotropy, we tested a misfit strain of -0.3\%[36] at the semi-coherent interface to make a lower misfit strain anisotropy. Figs. 6.7 (a)-(e) show the morphology of the precipitate with different elastic energies. In Fig. 6.8, the distances (nm) from the origin of the precipitates (in Figs. 6.7 (a)-(e)) were calculated by using a characteristic length. We also perform quantitative analysis to evaluate relative shape-differences. To do this, the distance from the origin was computed as a function of angle, then Fourier transforms were applied for the distance to obtain coefficient values, which are associated with the shape of a precipitate. In Table 6.4, the ratio of $2^{nd} / 0^{th}$ is associated with the aspect ratio of a shape and relative changes (parenthesis) were calculated with respect to the case of elastic inhomogeneity (a) as listed in Table 6.5. Based on our calculations, when compared with (a) and (b) in Table 6.3, the effect of elastic inhomogeneity is not significant even though the difference of elastic modulus ($C_{11}$) between $\alpha$-Al and $\theta'$ precipitate is almost a factor of ~2. The results also show that the aspect ratio of the precipitate shape is highest under elastic homogeneity with the $\theta'$ elastic modulus. Since the $\theta'$ elastic modulus was chosen as a homogenous modulus
approximation in previous literature[35, 36], the previously reported high aspect ratio of ~20 includes this effect. In Table 6.4, among various elastic contributions, the effects of elastic inhomogeneity and elastic anisotropy are negligible compared to that of tetragonal misfit strain anisotropy. Thus, we conclude that tetragonal misfit strain anisotropy is the most important elastic energy factor in deciding $\theta'$ precipitate morphology.

In this work, we have assumed a constant misfit strain at both coherent and semi coherent interfaces, respectively. Actually, during the growth of the precipitate, the misfit strain along a semi-coherent interface changes. In this case, during particle thickening there are periodic variations in magnitude and sign of the residual misfit at the semi-coherent interface because of different interfacial configurations[30]. Based on previous first-principles calculations, the configuration at a coherent interface is $1a_{\theta'}:1a_{Al}$, which has a misfit strain of 0.7%, and the lattice misfit strain at a semi coherent interface, -5.1%, is used based on the configuration of $2c_{\theta'}:3a_{Al}[36]$. Recently, another thickness of the $3.5c_{\theta'}$ was also commonly observed in binary Al-Cu for 200 °C/24 hours ageing, and not only for $2c_{\theta'}[37]$. For other configurations such as, $5c_{\theta'}:7a_{Al}$, $3.5c_{\theta'}:5a_{Al}$ ($= 7c_{\theta'}:10a_{Al}$), the misfit strains are +1.7%[36] (or 0.5% in experiment[147]) and -0.3% (or 0.45% in experiment[38]), respectively. In these cases, tetragonal misfit strain anisotropy becomes negligible because of similar magnitude of misfit strains for both coherent and semi-coherent, thereby decreasing strain energy anisotropy. For example, when a semi-coherent interface has a $3.5c_{\theta'}:5a_{Al}$ ($= 7c_{\theta'}:10a_{Al}$) configuration, the computed aspect ratio became lower (closer to a Wulff shape from interfacial energy anisotropy), as shown in Fig. 6.7 (e) and 8 (e). Here, we assumed the constant interfacial energy with different interfacial misfit configurations, since interfacial stress does not strongly affect the
semi-coherent interfacial energy as discussed in Chapter 3. The result of lower aspect ratio is still further from the high aspect ratio in the experiment, and supports our argument that the computed equilibrium morphology is difficult to observe experimentally due to the strong effects of interfacial kinetics.

Our phase-field modeling helps us understand the factors setting the equilibrium morphology of $\theta'$ precipitates by analyzing interfacial and strain energy anisotropy. In order to fully understand nature of $\theta'$ morphology with kinetic effects, such as ledge growth mechanism by the interstitial Cu atoms at the coherent interface proposed by Laure Bourgeois et al.[33], phase-field crystal (PFC) methodology, which performs on atomic and diffusive time scales, will be needed in the future work.

6.4. Conclusions

Here, we performed phase field modeling with the parameters supplied by first-principles DFT to investigate the underlying physics governing the high aspect ratio of equilibrium $\theta'$ precipitates in Al-Cu alloys. Our modeling method can be applicable for understanding shape origin in a wide variety of plate-shaped precipitates in metal alloys. Based on our computations, we conclude that:

1. A phase field method has been developed that allows for the high anisotropic interfacial energy needed to describe the shape of $\theta'$ precipitates. The model allows for missing orientations and corners on the Wulff shape, thus can be used to describe the faceted coherent interfaces of $\theta'$ precipitates.
2. The strongly anisotropic interfacial energy has a strong influence on the morphology of \( \theta' \) precipitates.

3. The tetragonal misfit strain anisotropy is the most important factor in deciding \( \theta' \) morphology when compared to effects of elastic inhomogeneity and elastic anisotropy.

4. The computed aspect ratio of the equilibrium precipitate morphology is significantly smaller than the equilibrium aspect ratio observed in the experiment and thus the experimentally measured \( \theta' \) morphology is strongly influenced by the anisotropic interfacial kinetics which are operative during precipitate growth.

5. Since the misfit strain anisotropy can become negligible during the growth of \( \theta' \), the aspect ratio of the equilibrium shape of the precipitate decreases with size.
CHAPTER 7

Ostwald ripening for a spheroidal particle in multicomponent alloys

We propose a general theory of Ostwald ripening for a spheroidal (non-spherical) particle in a multicomponent alloy. The analysis is valid for a non-ideal and non-dilute solution. Our model introduces two correction factors to the previous model of a sphere. The first factor concerns the diffusional growth rate equation. We solve the diffusion problem by using prolate spheroidal coordinates in order to derive the diffusional growth rate equation for a spheroid with a constant wulff shape. The result shows that the diffusional growth rate increases with an increasing particle aspect ratio due to increased specific surface area. The second factor involves the Gibbs-Thomson effect including the anisotropic effects of interfacial energy and the physical geometry of a spheroid. Based on the generalized Gibbs-Thomson equation for a spheroid, the pressure difference decreases with an increasing particle aspect ratio under a constant equivalent radius. Asymptotic analysis shows that the temporal exponents for the coarsening law of a spheroid are identical to sphere exponents. However, the amplitudes depend on the aspect ratio of a particle. Specifically, the rate constant of the average equivalent radius, the matrix supersaturations, and the particle composition decrease as the aspect ratio increases. The shape factor does not influence the directional vector information of the particle composition, which is similar to a mobility tensor.
7.1. Introduction

Ostwald ripening\cite{154, 155} or phase coarsening\cite{156, 157} is a well-known phenomenon that an increase in a multiphase micromorphology at the end of a first-order phase transformation process. The driving force for this process comes from lowering the total energy of the system by decreasing the interfacial area. The resulting reduction of interfacial area leads to increase in size of the coarsening phase. For example, the large precipitates grow due to the dissolution of small precipitates via a diffusive mass flow.

The general theory of Ostwald ripening was described first by Lifshitz and Slyozov\cite{157}, and Wagner\cite{156} (referred to here as LSW theory). In the LSW\cite{156, 157} theory, Gibbs-Thomson equation is associated with the interfacial curvature of a coarsening particle that decides the interfacial compositions. Further, the evolution of particle size distribution for non-interacting particles is described by a statistical approach in phase separations. The shape of the precipitates is assumed to be a sphere and the fixed precipitates are a small volume fraction in a system. They also assumed such a system for binary alloys where the coarsening occurs by the diffusion of a chemical component. In a binary system, interfacial compositions can be described by a local equilibrium approach (equality of the chemical potential at the interface). However, in a multicomponent system, the local equilibrium approach at the interface is insufficient to determine the interfacial compositions. Thus, an additional condition of interfacial mass balance needs to be utilized to develop the coarsening model in a complex system. For example, Kuehmann and Voorhees\cite{158} (referred to here as KV theory) used this condition to describe a coarsening model for the effects of a third element on the ripening behavior of a two-phase
system in a ternary system. The KV[158] theory is valid for a non-ideal and non-dilute solution, but neglects off-diagonal diffusion coefficients. Recently, their work was extended to higher-order alloy systems by Philippe and Voorhees[159] (referred to here as PV theory), and the off-diagonal diffusion coefficients are included in the overall ripening behavior.

There has been much effort put into addressing kinetic coarsening behavior, but most studies assumed a particle shape as a sphere. However, many microstructures in real materials are morphologically complex. As such, the ripening behavior is influenced by the geometrical factors of non-spherical interfaces, such as the local anisotropic field, and interface kinetics that depend on anisotropy. In order to generalize the coarsening model of non-spherical particles, it is necessary to solve the corresponding diffusion problem in non-spherical coordinates. Previously, Ham[160], Horvay and Cahn[161] proposed analytical time-dependent solutions for a spheroid with a boundary condition of fixed concentration at the interface under the assumption of a constant particle aspect ratio. E. Kozeschnik et al.[162] introduced geometrical shape factors, which provide an extension of the spherical model to needle- or disc-shaped particles. They argued that the growth rate of disk-shaped precipitates is lower than that of spherical particles with equal volume. Recently, Bardel et al.[163] used the needle-shaped Zener-Hillert approximation[164, 165] and applied it to a diffusion solution for the growth equation. They also predicted that growth rate decreases with an increasing aspect ratio. Recently, Holmedal et al.[166] developed the model with two correction factors accounting for the effects induced by the particle’s non-spherical shape on their growth kinetics. Interestingly, in contradiction to the investigations mentioned above, a positive dependence of the volumetric growth rate on aspect ratio was suggested by Holmedal et al.[166] based on Ham’s early works[167, 168]. The
variation in the literature may stem from various factors, i.e., different approximate solutions for the diffusion problem, assumption of isotropic interfacial energy for non-spherical particles, etc.

The purpose of this paper is to make a generalization about a coarsening model for a spheroidal (non-spherical) particle based on the previous theory for a sphere by the PV[159] theory. In order to develop the analytic description for coarsening rate for a spheroid, we solve the diffusion problem in non-spherical coordinates (i.e., prolate spheroidal coordinates) followed by the previous work in spherical coordinates for a sphere. Also, the effects of anisotropic interfacial energy and physical geometry are included in a Gibbs-Thomson equation. The long-term behavior of the average precipitate equivalent radius, the far-field supersaturations, and the number density of precipitates are determined with a shape factor based on the asymptotic analysis.

7.2. Development

In this section, we develop the analytic description of the Ostwald ripening process for a spheroidal particle: (i) the kinetic equation describing the growth rate of a single spheroidal particle of a given size and aspect ratio based on a mass conservation equation, (ii) the Gibbs-Thomson equation including anisotropic interfacial energy and physical geometry, and (iii) the temporal law for the long-time behavior of a coarsening based on a continuity equation governing the dynamics of the precipitate size distribution. This work is based on the PV[159] theory for a spherical particle in a multicomponent alloy, which is valid for a non-ideal and non-dilute solution.
7.2.1. The kinetic equation

The most fundamental work for describing the coarsening rate equation is to derive the
diffusional flux of a solute to the migrating matrix-precipitate interface. In order to reveal a
coarsening description of a spheroidal (non-spherical) particle, we utilize the following prolate
spheroidal coordinates \((\mu, v, \phi)\).

\[ x = a \sinh \mu \sin v \cos \phi, \quad y = a \sinh \mu \sin v \sin \phi, \quad z = a \cosh \mu \cos v \quad \text{(7.1)} \]

We assume that the diffusion coefficient is not dependent upon the composition and there is
no interaction between particles. The concentration at the particle surface is assumed to a
constant since it is an equilibriuim shape. Based on these assumptions, we solve Laplace’s
equation for each component in prolate spheroidal coordinates with constant concentration at the
interface \( \frac{\partial c}{\partial v} = \frac{\partial c}{\partial \phi} = 0 \). We solve,

\[ \nabla^2 c = 0 \quad \text{(7.2)} \]

with the boundary conditions:

\[ C_i(\mu) = C_i^a \quad \text{(7.3)} \]

\[ C_i(\mu) = C_i^\infty \quad \text{(7.4)} \]

The solution is,

\[ C_i(\mu) = \frac{(C_i^\infty - C_i^a)}{-\ln \left( \tanh \left( \frac{\mu}{2} \right) \right)} \ln \left( \tanh \left( \frac{\mu}{2} \right) \right) + C_i^\infty, \quad \text{for } i = 2 \ldots N \quad \text{(7.5)} \]

Here, we are taking \( i = 1 \) as not independent since sum of compositions is a constant. \( \mu \) is
the distance from the center of the spheroidal particle in prolate spheroidal coordinates, \( N \) is the
number of components in the alloy, $C_i$ is the mole fraction of component $i$ at $\mu$, $C_i^o$ is the composition at infinity, and $C_i^a$ is the composition of the a spheroidal particle at the interface ($\mu = U$). Under the assumption that the molar volumes of both phases are the same, the mass balance condition at the interface is

$$\left(C_j^B - C_j^a\right) \frac{dr}{dt} \cdot n = \sum_{k=2}^{N} D_{jk} \nabla C_k \cdot n \quad \text{for } j = 2 \ldots N$$

(7.6)

Here, $r$ is a position vector locating the interface (Eq. (1)) in prolate spheroidal coordinates. $D_{jk}$ is the diffusion matrix. Eq. $n (= \hat{n})$ is the outward point normal vector[169] as follows.

$$n = \frac{1}{\sqrt{\sinh^2 \mu + \sin^2 \nu}} \left( \cosh \mu \sin \nu \cos \phi \hat{i} \quad \cosh \mu \sin \nu \sin \phi \hat{j} \quad \sinh \mu \cos \nu \hat{k} \right)$$

(7.7)

In our coarsening model for a spheroidal particle, we assume a particle with a constant Wulff shape (a constant aspect ratio) during coarsening. Thus, we assume that the velocity vector in the left-hand side of Eq. (6) is only as a function of a variation of a scale factor, $a$, in prolate spheroidal coordinates given in Eq. (1). Using Eq. (1) and (7), the left-hand side of Eq. (6) is then,

$$\frac{dr}{dt} \cdot n = -\frac{\sinh \mu \cosh \mu}{\sqrt{\sinh^2 \mu + \sin^2 \nu}} \left( \frac{da}{dt} \right)$$

(7.8)

Using Eq. (5), the diffusional flux (right-hand side of Eq. (6)) is,
\[
\sum_{k=2}^{N} D_{jk} \nabla C_k \cdot n = \sum_{k=2}^{N} \frac{D_{jk}}{a \sqrt{\sinh^2 \mu + \sin^2 \nu}} \frac{dC_k}{d\mu} \bigg|_{\mu=U} = \frac{D_{jk}}{h_{\mu} (= h_v) \, d\mu} \bigg|_{\mu=U},
\]

Using Eq. (8) and (9), the mass balance equation Eq. (6) is,

\[
(C_j^\beta - C_j^\alpha) \frac{da}{dt} = \sum_{k=2}^{N} f(U) D_{jk} \frac{dC_k}{d\mu} \bigg|_{\mu=U} \quad \text{for } j = 2 \ldots N
\]

\[
f(\mu) = \frac{1}{a \sinh \mu \cosh \mu}
\]

The Eq. (7.10) is valid when there is no flux into the particle or the composition of a particle is uniform. Using Eq. (7.5) in Eq. (7.10) gives

\[
(C_j^\beta - C_j^\alpha) \frac{da}{dt} = \sum_{k=2}^{N} f(U) \frac{D_{jk}}{g(U)} (C_k^\infty - C_k^\alpha) \quad \text{for } j = 2 \ldots N
\]

\[
g(\mu) = -\sinh \mu \ln \left( \tanh \frac{\mu}{2} \right)
\]

Based on the Gibbs-Thomson effect, the interface properties (i.e., interfacial curvature and energy) induce a shift in local equilibrium concentrations. Assuming that this shift is small compared with the equilibrium compositions at a planar interface, we can replace the difference in the left-hand side of Eq. (11) with the differences in the equilibrium concentrations, \( C_j^\beta - C_j^\alpha = \overline{C}_j^\beta - \overline{C}_j^\alpha \). Here, \( \overline{C}_j \) is the equilibrium mole fraction of component \( j \) in the noted phase at a planar interface. By using \( \Delta \overline{C} = \overline{C}_j^\beta - \overline{C}_j^\alpha \) and \( C_{k}^\infty = C_k^\alpha \), we can describe the equation as

\[
\Delta \overline{C} = \overline{C}_j^\beta - \overline{C}_j^\alpha
\]
\[ \Delta \mathbf{C} \frac{da}{dt} = f(U) \frac{D}{g(U)} [\Delta \mathbf{C}^\alpha - \Delta \mathbf{C}^\beta] \]  

(7.12)

where \( D \) is the \((N - 1) \times (N - 1)\) diffusion matrix. To determine the growth rate, rewrite Eq. (12) as

\[ g(U)f(U)^{-1}D^{-1}\Delta \mathbf{C} \frac{da}{dt} = \Delta \mathbf{C}^\alpha - \Delta \mathbf{C}^\beta \]  

(7.13)

After multiplying both sides of Eq. (11) by \((\Delta \mathbf{C})^T \mathbf{G}^\alpha\)

\[ g(U)f(U)^{-1}(\Delta \mathbf{C})^T \mathbf{G}^\alpha D^{-1} \Delta \mathbf{C} \frac{da}{dt} = (\Delta \mathbf{C})^T \mathbf{G}^\alpha \Delta \mathbf{C}^\alpha - (\Delta \mathbf{C})^T \mathbf{G}^\alpha \Delta \mathbf{C}^\beta \]  

(7.14)

Where \( \mathbf{G}^\alpha \) is the Hessian matrix \( \mathbf{G}^\alpha = \mathbf{G}^\alpha_{m,i,j} \) for \( m, i, j = 2 \ldots N \). The diffusion matrix is the product of a mobility matrix \( \mathbf{M} \) and a thermodynamic factor \( \mathbf{G}^\alpha \), \( D = \mathbf{M} \mathbf{G}^\alpha \) or \( \mathbf{G}^\alpha D^{-1} = \mathbf{M}^{-1} \). Using the relation \((\Delta \mathbf{C})^T \mathbf{G}^\alpha \Delta \mathbf{C}^\alpha = V_m^\beta \Delta P \), \( \Delta P = \mathbf{P}^\beta - \mathbf{P}^\alpha \), which was derived in the PV[159] in multicomponent alloys, the variation of the scale factor, \( a \), in prolate spheroidal coordinates is

\[ \frac{da}{dt} = \frac{f(U)}{g(U)(\Delta \mathbf{C})^T \mathbf{M}^{-1} \Delta \mathbf{C}} [(\Delta \mathbf{C})^T \mathbf{G}^\alpha \Delta \mathbf{C}^\alpha - V_m^\beta \Delta P] \]  

(7.15)

As explained in the PV[159] theory, the first term in the brackets is responsible for the driving force for the precipitation process. Specifically, it is the energy when an infinitesimal amount of material from \( \alpha \) of the composition given by supersaturation is replaced by the \( \beta \) phase with an equilibrium composition. The analytic form of the pressure difference \( \Delta P \) for a spheroid will be shown in section 2.2. In order to derive the lengthening rate of a spheroidal particle, we use the following equations,

\[ k = \frac{l}{m} = \coth U , \quad l = a \cosh U , \quad m = a \sinh U , \quad l > m \]  

(7.16)
Here, $k$ is the aspect ratio of a particle. $l$ and $m$ are the distances from the center to a surface along the major (long) and minor (short) axes. Using Eq. (15) and (16), the lengthening rate along the long axis of a spheroidal particle is

$$\frac{dl}{dt} = \frac{da}{dt} \cosh U = \frac{f(U) \cosh U}{g(U) (\Delta C)^T M^{-1} \Delta C} \left[ (\Delta C)^T G^a \Delta C^\infty - V_m^\beta \Delta P \right] \quad (7.17)$$

The lengthening rate recovers the radius growth rate of a spherical particle (Eq. (28) in the PV[159] theory) in the limit $U$ goes to infinity. Eq. (7.17) can be expressed differently as a function of aspect ratio ($k$) and length ($l$) along the long axis.

$$\frac{dl}{dt} = \frac{f_l(k)}{l(\Delta C)^T M^{-1} \Delta C} \left[ (\Delta C)^T G^a \Delta C^\infty - V_m^\beta \Delta P \right] \quad (7.18)$$

$$f_l(k) = \frac{k}{-\sinh(\coth^{-1} k) \ln\left(\tanh\left(\frac{\coth^{-1} k}{2}\right)\right)} \quad (7.19)$$

Here, $f_l(k)$ represents a shape factor as a function of aspect ratio $k$, shown in Fig. 1 (a). For the limit of spheres, i.e., with $k = 1$, the shape factor $f_l(k)$ becomes to $f_l(k) = 1$ in Fig. 1 (a).

The lengthening rate along the short axis is shown as follows.

$$\frac{dm}{dt} = \frac{f_m(k)}{m(\Delta C)^T M^{-1} \Delta C} \left[ (\Delta C)^T G^a \Delta C^\infty - V_m^\beta \Delta P \right] \quad (7.20)$$

$$f_m(k) = \frac{f_l(k)}{k^2} \quad (7.21)$$
Here, $f_m(k)$ represents a shape factor when a growth rate is described along the short axis. We also derive the growth rate of a spheroid with the radius $R$ of an equivalent sphere, whose volume is identical to the spheroid,

$$R = \sqrt[3]{m^2l} \quad (7.22)$$

In order to investigate the dependence of the growth rate on the aspect ratio under a constant volume, we derive the growth rate equation as a function of a shape factor $f_R(k)$.

$$\frac{dR}{dt} = \frac{f_R(k)}{R(\Delta C)^T M^{-1} \Delta C} \left[ (\Delta C)^T G^\alpha \Delta C^\alpha - V_m^\beta \Delta P \right] \quad (7.23)$$

$$f_R(k) = \frac{f_i(k)}{k^4} \quad (7.24)$$

The volumetric growth rate of a spheroid with an equivalent radius $R$ is

$$\frac{dV}{dt} = \frac{4\pi R f_R(k)}{(\Delta C)^T M^{-1} \Delta C} \left[ (\Delta C)^T G^\alpha \Delta C^\alpha - V_m^\beta \Delta P \right] \quad (7.25)$$

We can also derive the diffusional flux by using a surface integral in prolate spheroidal coordinates to validate our description of the volumetric growth rate (Eq. (7.22)).

$$D \nabla C \cdot n = \frac{D}{a} \frac{dC}{\sqrt{\sinh^2 \mu + \sin^2 \phi}} d\mu \bigg|_{\mu = U} = \frac{D}{h_\mu} \frac{dC}{d\mu} \bigg|_{\mu = U} = \frac{D}{h_\mu \sinh U} C_1 \quad (7.26)$$

$$C_1 = \frac{(C_i^\infty - C_i^\alpha)}{-\ln \left( \tanh \left( \frac{U}{2} \right) \right)}$$

$$\int \int J \cdot dS = \int \int D \nabla C \cdot n \, dS = \int \int \frac{D}{h_\mu \sinh U} C_1 \, dS \quad (7.27)$$
As seen in Eq. (7.24), we could get the shape factor \( f_R(k) \) (Eq. (7.21)) when \( C_i^\infty - C_i^a \) and \( D \) are assumed to a constant.

\[
\begin{align*}
\left( \frac{D}{h_\mu \sinh U} \right) h_v h_\phi d\nu d\phi &= \int D C_1 a \sin \nu d\nu d\phi = 4\pi a D C_1 \\
&= 4\pi RD(C_i^\infty - C_i^a)f_R(k)
\end{align*}
\]

Figure 7.1. (a) The dependence of the diffusional shape factor \( f \) on the aspect ratio. \( f_l \) (Eq. (7.19)) represents a shape factor when the growth rate is described along the long axis, shown in Eq. (7.18). (b) The shape factor of \( f_m \) (Eq. (7.21)) corresponds the growth rate (Eq. (7.20)) along the short axis of a spheroid, and \( f_R \) (Eq. (7.24)) is a shape factor when the growth rate (Eq. (7.23)) is described for a spheroid with the radius \( R \) of an equivalent sphere.

Fig. 1 (a) and (b) show the computed shape factors in Eq. (19), (21), and (24) with increasing the aspect ratio. As seen in Fig. 1 (b), \( f_R \) increases with the aspect ratio of a spheroidal particle. In recent work by Holmedal et al.[166], the diffusional shape factor for a spheroid was expressed
in a more complicatedly form[166], but equals to $f_R$ (Eq. (24)) in Fig. 1 (b). The difference in the form comes from the alternative form of the prolate spheroidal coordinates $(\cos \mu, \cos \nu, \phi)$ instead of $(\mu, \nu, \phi)$ in Eq. (1).

In this work, we assume that there is no flux into the particle in the mass balance at the interface. Therefore, when a spheroidal particle has a higher aspect ratio, it has a larger specific surface area, thereby increasing the growth rate of a spheroid at constant concentration gradient due to increased specific surface area under the fully diffusion-controlled growth scenario.

We develop the equation of the interface compositions for a spheroidal particle. The composition of $\alpha$ at the interface can be directly determined using the flux balance in dyadic form of Eq. (7.11),

$$\Delta \mathbf{c} \frac{d \alpha}{dt} = f(U) \frac{D}{g(U)} (\mathbf{c}^\infty - \mathbf{c}^\alpha)$$  \hspace{1cm} (7.28)

where $\mathbf{c}^\infty$ is a vector of compositions at infinity, and $\mathbf{c}^\alpha$ is a vector of compositions in the $\alpha$ phase at the interface. By using Eq. (15), we obtain the composition at the matrix $\alpha$ at the interface,

$$\mathbf{c}^\alpha = \mathbf{c}^\infty - \frac{D^{-1} \Delta \mathbf{c}}{(\Delta \mathbf{c})^T M^{-1} \Delta \mathbf{c}} \left[ (\Delta \mathbf{c})^T G^\alpha \Delta \mathbf{c}^\infty - V_m \Delta P \right]$$  \hspace{1cm} (7.29)

Eq. (7.29) is same as Eq. (31) in the PV[159] theory for a spherical particle except for the pressure difference, which will be discussed in section 7.2.2. As explained in the PV[159] theory, the concentrations of the $\alpha$ phase are set by both the driving force for precipitation and
Gibbs-Thomson effect. To describe the composition of $\beta$ at the interface, we use the following equation\[159\]

$$G^\alpha \Delta C^\alpha = G^\beta \Delta C^\beta + \Delta P \Delta \vec{V} \quad (7.30)$$

Here, $\Delta C^\alpha = C^\alpha_i - \bar{C}^\alpha_i$, $\Delta C^\beta = C^\beta_i - \bar{C}^\beta_i$, and $\Delta \vec{V} = \vec{V}^\beta_i - \vec{V}^\beta_1$ for $i, j = 2 \ldots N$. By using Eq. (7.30) and (7.29),

$$C^\beta = \bar{C}^\beta + G^{\beta^{-1}} G^\alpha \left\{ \Delta C^\alpha - \frac{D^{-1} \Delta \bar{C}}{\left( \Delta \bar{C} \right)} \times \left[ (\Delta \bar{C})^T G^\alpha \Delta C^\alpha \right] \right\} - \Delta P G^{\beta^{-1}} \Delta \vec{V} \quad (7.31)$$

where $C^\beta$ is a vector of compositions in $\beta$, and $\bar{C}^\beta$ is a vector representing the equilibrium compositions. Eq. (28) is also same as Eq. (36) in the PV[159] theory for a spherical particle except for a pressure difference.

### 7.2.2. The Gibbs-Thomson effect

The Gibbs-Thomson effect gives the chemical potential (or the pressure difference under a constant molar volume) across interfaces. For a spherical particle precipitated in a dilute binary solid solution matrix, the total curvature (twice the mean curvature) is the same everywhere on the particle surface. However, the curvature varies along the surface for a spheroidal particle, thereby modifying the Gibbs-Thomson effect. For a non-spherical shaped particle to be in equilibrium, the interfacial energy must be anisotropy. The anisotropic interfacial energy thus needs to be included in the Gibbs-Thomson equation. The anisotropic shape that results from the interfacial energy anisotropy is also called the Wulff shape. In this work, we assume that
precipitates take a prescribed shape (a constant Wulff shape), and the aspect ratio, during their
growth, so that the shape of a particle is time independent and $\Delta P$ is not a function of position
along the surface. In order to determine the pressure difference, we use the following equation in
the literature[170].

$$
P = \frac{2(\sigma \sin \theta + \sigma_\theta \cos \theta) \cos \varphi - \sigma_\varphi \sin \varphi / \sin \theta}{x} = \frac{2(\sigma \sin \theta + \sigma_\theta \cos \theta) \sin \varphi - \sigma_\varphi \cos \varphi / \sin \theta}{y} = \frac{2(\sigma \cos \theta - \sigma_\theta \sin \theta)}{z} \tag{7.32}
$$

Where, $\sigma$ represents interfacial energy, $\theta$ is the angle made by a unit vector normal ($\mathbf{n}$) to the
interface with respect to the $z$-axis, and $\varphi$ is the azimuthal angle. The subscripts on $\sigma$ denote
differentiation with respect to $\theta$ and $\varphi$. If $\sigma_\varphi = 0$, then, Eq. (7.32) becomes

$$
\Delta P = \frac{2A \cos \varphi}{x} = \frac{2A \sin \varphi}{y} = \frac{2A}{R}, \quad A = \sigma \sin \theta + \sigma_\theta \cos \theta \tag{7.33}
$$

That is, the cross-sectional shape of a spheroid in $x$-$y$ plane is a circle of radius $R = 2A / \Delta P$.

Thus, the equilibrium shape is a prolate spheroid as long as $\sigma_\varphi = 0$. In the $x$-$z$ or $y$-$z$ planes,

$$
\Delta P = \frac{2(\sigma \cos \theta - \sigma_\theta \sin \theta)}{z} \tag{7.34}
$$

Let $z$ be a position of an ellipse surface along the long axis, $z = l \cos \vartheta$. Here, $\vartheta$ is a polar angle.

The relation between the normal angle ($\theta$) and the polar angle ($\vartheta$) shows

$$
\cos \theta = \left(\frac{1}{1 + k^2 \tan^2 \vartheta}\right)^{\frac{1}{2}}, \quad k = \frac{l}{m}, \quad l > m \tag{7.35}
$$
where $k$ is the aspect ratio of a particle. In order to include anisotropic interfacial energy in Eq. (32), we propose an analytic form of interfacial energy as a function of the interface normal angle ($\theta$) for a spheroid. The analytic formula with respect to normal angle ($\theta$) is,

$$
\sigma(\theta) = \sigma_0 \left( 1 + \sum_{n=1}^{\infty} \epsilon_{2n} \cos 2n\theta \right)
$$

(7.36)

In Eq. (7.36), $\sigma_0$ is a scale factor and $(1 + \sum_{n=1}^{\infty} \epsilon_{2n} \cos 2n\theta)$ has a role in revealing the anisotropy of interfacial energy (i.e., integral of $(1 + \sum_{n=1}^{\infty} \epsilon_{2n} \cos 2n\theta)$ equals to 1). The coefficients $\epsilon_{2n}$ have positive and negative values alternatively to induce a smooth curve on the surface of a spheroid. Since the cross-sectional shape of a spheroid is a circle along the azimuthal angle ($\varphi$), the proposed model is independent to $\varphi$. An ellipse (or a spheroid) has a curved surface without a facet or flat surface. That is, there is no missing orientation when constructing the wulff shape of a particle. Thus, the interfacial energies can be computed for all interface orientations corresponding to all the points on the surface of an ellipse from an elliptic function (one-to-one correspondence). Then, we took a discrete cosine transformation (DCT) of the interfacial energies to compute all coefficients ($\epsilon_n$) in our interfacial energy model (Eq. (7.36)). This can be understood by that our proposed interfacial energy model (Eq. (7.36)) can be regarded as a sum of cosine functions with different frequencies ($\epsilon_n$).
Figure 7.2. (a) The polar plot of dimensionless interfacial (σ) energy. The anisotropy of interfacial energy equals to three. The red curve represents the computed interfacial energies from the equation of an ellipse. The blue curve represents the computed interfacial energy based on our energy model (Eq. (7.32)) with 10-coefficients (ε_{2n}). (b) The dimensionless pressure difference (ΔP) vs. the normal angle (θ) to the interface with respect to z-axis by solving Eq. (34) including our proposed energy model (Eq. (36)) with 15-coefficients (ε_{2n}). θ = 0 corresponds the point at the apex of an ellipse. The particle aspect ratio is 3. The computed pressure difference shows a constant along the surface.

Fig. 7.2 (a) represents that the computed interfacial energy based on our proposed energy model (Eq. (7.36)). It is consistent with the computed polar energy (σ) plot from a particle with the shape of an ellipse. In equilibrium, the pressure difference should be a constant along all interface orientations. Thus, we investigated the degree of pressure difference constancy for different orientations by solving Eq. (7.34) including our proposed energy model (Eq. (7.36)) in Fig. 7.2 (b). As the aspect ratio of a particle becomes higher, the required number of coefficients
(\epsilon_{2n}) in our model (Eq. (36)) increases to satisfy the constancy of chemical potential along the surfaces.

We plot the physical shape of a particle from our proposed energy model (Eq. (7.36)) by constructing the Wulff shape. The physical shape also can be described by using Eq. (30) with an assumption that the pressure difference (\Delta P) is a constant.

Figure 7.3. (a) A dimensionless two-dimensional (2D) physical shape from our proposed energy model (the blue curve in Fig. 7.2 (a)) based on the wulff construction and Eq. (7.33) and (7.34) with a constant chemical potential (e.g., \Delta P = 2)[170]. As seen here, the particle shape from our energy model (Eq. (36)) is consistent with a particle with the shape of an ellipse. (b) A dimensionless three-dimensional (3D) shape of a spheroid based on Eq. (7.32).
Fig. 7.3 (a) and (b) represent the physical shape based on our proposed energy model (Eq. (7.32)) by Wulff construction and Eq. (7.33) and (7.34)[170]. As seen here, the induced physical shape is consistent with an ellipse. By setting $\theta = 0$ in Eq. (7.34) for simplicity since the pressure difference must be a constant at all points, we can take one value of the chemical potential for the growth or coarsening studies.

\[
\Delta P = \frac{2\sigma_1}{l} = \frac{2\sigma_0}{l} f_{\sigma_1/\sigma_0} \text{ at } \theta = 0 \tag{7.37}
\]

\[
f_{\sigma_1/\sigma_0} = \left(1 + \sum_{n=1}^{\infty} \epsilon_{2n}\right) \tag{7.38}
\]

Using Eq. (7.16) and (7.22),

\[
\Delta P = \frac{2\sigma_2}{m} = \frac{2\sigma_0}{m} f_{\sigma_2/\sigma_0} \text{ at } \theta = \frac{\pi}{2} \tag{7.39}
\]

\[
f_{\sigma_2/\sigma_0} = \left(1 + \sum_{n=1}^{\infty} (-1)^n \epsilon_{2n}\right) = \frac{f_{\sigma_1/\sigma_0}}{k} \tag{7.40}
\]

\[
\Delta P = \frac{2\sigma_0}{R} f_{\Delta P}(k) \tag{7.41}
\]

\[
f_{\Delta P}(k) = f_{\sigma_2/\sigma_0} \frac{k^3}{3} = \frac{f_{\sigma_1/\sigma_0}}{\frac{2}{3} k^3} \tag{7.42}
\]
Figure 7.4. (a) The dependence of the interfacial energy anisotropy shape factor \( f_{\sigma_1/\sigma_0} \) (Eq. (7.38)) and \( f_{\sigma_2/\sigma_0} \) (Eq. (7.40)) on the aspect ratio. (b) The dependence of the Gibbs-Thomson shape factor \( f_{\Delta p} \) (Eq. (7.42)) on the aspect ratio.

Here, \( f_{\sigma_1/\sigma_0} \) (Eq. (7.38)) and \( f_{\sigma_2/\sigma_0} \) (Eq. (7.40)) and \( f_{\Delta p} \) (Eq. (7.42)) are shape factors for anisotropic interfacial energy and the Gibbs-Thomson effect, respectively. Based on Eq. (7.37) and (7.39), we can get the pressure difference for a spheroid from an interfacial energy along the long axis \( \sigma_1 \) (or \( \sigma_2 \) along the short axis) and a corresponding length \( l \) (or \( m \) along the short axis).

Fig. 7.4 (a) and (b) represent the dependence of the shape factor for interfacial energy anisotropy \( f_{\sigma_1/\sigma_0} \) (Eq. (7.38)) and \( f_{\sigma_2/\sigma_0} \) (Eq. (7.40)), and Gibbs-Thomson shape factor \( f_{\Delta p} \) (Eq. (7.42)) on the aspect ratio. Recently, Holmedal et al.[166] showed the positive dependence of the Gibbs-Thomson shape factor on aspect ratio. They assumed that the interfacial energy is isotropic.

Since anisotropic physical shape of a particle is basically caused by anisotropic interfacial energy, the anisotropic effect of interfacial energy should be included. Also, the constancy of
chemical potential cannot be achieved along surfaces in equilibrium without consideration of interfacial energy anisotropy.

According to the literature[171], the equilibrium morphology of a single fully-faceted crystal is given by the following.

$$\frac{\sigma_1}{h_1} = \frac{\sigma_2}{h_2} = \ldots = \frac{\sigma_N}{h_N} \quad (7.43)$$

Here, $\sigma_N$ is a surface energy of a crystal and $h_N$ is the distance between a center and a face. The pressure difference over the interface for a fully faceted crystal in Laplace-Young equation[171], as shown below.

$$\Delta P = 2 \frac{\sigma_1}{h_1} = \ldots = 2 \frac{\sigma_N}{h_N} \quad (7.44)$$

Eq. (7.37) and (7.39) for a spheroidal particle are similar to Eq. (7.44) for a fully-faceted crystal. Thus, we simply investigate the dependence of the pressure difference for a fully-faceted crystal in two dimension based on Eq. (7.43) and (7.44) in order to validate the negative dependence of Gibbs-Thomson effect on the aspect ratio of a spheroidal particle (Fig. 7.4 (b)). For example, when a two-dimensional square crystal has a length $a$ and a surface energy $\sigma_1$, thus Eq. (7.43) equals to $\sigma_1/a$. For a two-dimensional rectangular crystal, it has two lengths $b, bk$ and surface energies $\sigma_2, \sigma_2 k$. Here, $k$ is an aspect ratio of a rectangle. Under the assumption that a square and a rectangle have a constant surface area and a constant average interfacial energy, we can set $a = bk^{1/2}$ and $2\sigma_1 = \sigma_2(1 + k)$. Based on these conditions, $\sigma_2/b$ equals to $\sigma_1/a$ multiplied by a shape factor $f(k) = 2k^{1/2}/1 + k$, which is a decreasing function with respect to
aspect ratio $k$. Thus, a fully faceted crystal also shows a negative dependence of the Gibbs-Thomson effect.

As discussed in section 7.3.1, the diffusional growth rate (Eq. (7.20)) of a single spheroidal particle in a matrix shows increases with increasing the aspect ratio of a particle due to increased specific surface area. Based on a generalized Gibbs-Thomson equation (Eq. (7.43)), the pressure difference also induces a higher growth rate as the aspect ratio increases.

### 7.2.3. Asymptotic analysis

In the previous sections, we have discussed the situation of a single spheroid growing in a matrix. For a coarsening study, we assume that we have a dispersion of spheroids with a spectrum of equivalent radii embedded in a matrix. We describe the long-term behavior of the average equivalent radius of precipitates, the far-field supersaturations, the number density of precipitates, and the precipitate composition. This work was performed based on the approach for a sphere described in the previous literatures[159, 172]. The shape factors in the following temporal equations for the coarsening law are expressed by the combination of the diffusional shape factors $f_i(k)$ and $f_m(k)$ (Eq. (7.19) and (7.21), described in section 7.3.1, the shape factors for anisotropic interfacial energy $f_{\sigma_1/\sigma_0}$ and $f_{\sigma_2/\sigma_0}$ (Eq. (7.38) and (7.40), described in section 7.4.2), and the particle aspect ratio $k$. The dynamics of the ripening process can be described by a solution to the continuity equation,

$$\frac{\partial f}{\partial t} + \frac{\partial (ft)}{\partial l} = 0$$  \hspace{1cm} (7.45)
where the lengthening rate $l = dl/dt$ is given by Eq. (7.18) and the particle size distribution function is $f = f(l, t)$ (see Appendix). The mass conservation condition is

$$C_0 = C^\infty (1 - \phi) + C^\beta \phi$$  \hspace{1cm} (7.46)

where the vector $C^\infty$ is the far-field supersaturations, $C_0$ is the alloy composition, $C^\beta$ is the precipitate composition, and $\phi$ is the volume fraction of a spheroid.

$$\phi = \frac{4\pi}{3} \int_0^{\infty} \frac{l^3 f(l, t)}{k^2} dl$$  \hspace{1cm} (7.47)

In Eq. (7.47), $k$ is the aspect ratio of a spheroid and $l$ represents the distance from a center of a particle to a surface along the major (long) axis. Based on the assumption of the small deviation in concentration from equilibrium values, we can describe Eq. (7.48) differently,

$$q^0 = q^\infty + \phi[\alpha - 1]$$  \hspace{1cm} (7.48)

where $q^0 = (C_i^0 - \bar{C}_i^\alpha)/\bar{C}_i^\alpha$, $q^\infty = (C_i^\infty - \bar{C}_i^\alpha)/\bar{C}_i^\alpha$ and the vector distribution coefficient $\alpha = \bar{C}_i^\beta/\bar{C}_i^\alpha$ for $i = 2 \ldots N$. In the limit $t \to \infty$, the supersaturation $q^\infty$ becomes zero. In this limit, Eq. (46) becomes the standard lever law for the equilibrium volume fraction of precipitate $\phi^{eq}$.

We describe the precipitate size distribution and the matrix supersaturation from Eq. (7.18), (7.45), (7.47), and (7.48). In the limit $t \to \infty$, we can find that the temporal evolution of the average precipitate length $\bar{l}$ along the long axis (see Appendix).

$$\bar{l}^3 = K_l t$$  \hspace{1cm} (7.49)

Here, $K_l$ is the rate constant as follows.
In Eq. (7.51), \( f_{K_l}(k) \) is a shape factor for the rate constant \( K_l \). It equals to the diffusional shape factor \( f_i(k) \) multiplied by the shape factor for anisotropic interfacial energy \( f_{\sigma_1/\sigma_0} \) described in Eq. (7.19) and (7.38), respectively. Fig. 7.5 (a) shows the computed values of the shape factor \( f_{K_l}(k) \) with increasing aspect ratio. As seen Eq. (7.49), the temporal exponent for the coarsening law is identical to the exponent for a sphere in the PV[159] theory. However, the coarsening rate constant \( K_l \) (Eq. (7.50)) depends on the aspect ratio of a spheroid. We also derive the temporal evolution of the average precipitate length \( \bar{m} \) along the short axis with the rate constant \( K_m \).

\[
K_l = \frac{8V^\beta_m \sigma_1 f_i(k)}{9(\Delta C)^T M^{-1} \Delta C} = \frac{8V^\beta_m \sigma_0 f_{K_l}(k)}{9(\Delta C)^T M^{-1} \Delta C} \tag{7.50}
\]

\[
f_{K_l}(k) = f_i(k)f_{\sigma_1/\sigma_0} \tag{7.51}
\]

In 1991, Lee et. al.[173] proposed the theoretical model of coarsening kinetics of the rod-type M\(_2\)C precipitates, approximated by prolate spheroids. They chose \( 2\sigma_2/m \) for the pressure.
difference, thereby resulting in the coarsening shape factor of $1/ln (2k)$ along the short axis of a spheroid. The simple formula of $1/ln (2k)$ comes from Ham’s solution[167] in the limit eccentricity goes to 1. The numerical results of $f_m(k)$ (Eq. (21)) and $1/ln (2k)$ are same, except for near the region of the spherical particle limit.

In order to investigate the dependence of the coarsening rate on the aspect ratio under a constant equivalent radius of a particle, we derive the temporal evolution of the average equivalent radius $\bar{R}$ with the rate constant $K_R$ including a shape factor $f_{K_R}(k)$.

$$\bar{R}^3 = K_R t \quad (7.55)$$

$$K_R = \frac{8V_m^0 \sigma_0 f_{K_R}(k)}{9(\Delta \bar{C}) T M^{-1} \Delta \bar{C}} \quad (7.56)$$

$$f_{K_R}(k) = \frac{f_{K_i}(k)}{k^2} = k f_{K_m}(k) \quad (7.57)$$
Figure 7.5. The shape factor (a) $f_{Ki}(k)$ in Eq. (7.51), (b) $f_{Km}(k)$ and $f_{KR}(k)$ in Eq. (7.54) and (7.57), (c) $f_{Nv(t)}$ in Eq. (7.59), (d) $f_{C(t)\infty}$ in Eq. (7.61), $f_{(C^{\phi}\gamma)(t)}$ in Eq. (7.63), and $f_{(C^{\phi}\gamma\gamma)(t)}$ in Eq. (7.65) (= $f_{\Delta P}$ (Eq. (7.42))).

Fig. 7.5 (b) represents the computed values of the shape factor $f_{KR}(k)$. As seen here, the dependence on the aspect ratio shows negative. This means that a spherical particle shows a higher coarsening rate compared to a spheroidal particle.
We can find the number density $N_v(t)$ of precipitates per unit volume integrating numerically the precipitate size distribution (see Appendix), followed by the literatures[159, 172, 174].

$$N_v(t) \equiv 0.21 f_{N_v(t)}(k) \frac{\Phi^{eq}}{K} t^{-1}, \quad K = \frac{8 V_m \sigma_0}{9(\Delta C) M^{-1} \Delta C}$$ (7.58)

$$f_{N_v(t)}(k) = \frac{1}{f_{K_R}(k)}$$ (7.59)

Here, $f_{N_v(t)}(k)$ is the shape factor for the number density, which is inverse of the shape factor for the average equivalent radius $f_{K_R}(k)$ (Eq. (7.57)) as shown in Fig. 7.5 (c). The exponent for the decay is identical to the exponent of a sphere in the PV[159] theory.

The supersaturations can be described as follows.

$$C^\alpha(t) = \bar{C}^\alpha + f_{C^\infty(t)}(k) \left(3 \sigma_0 V_m^{\beta/3} \frac{2}{3} \bar{C} \left[\frac{(\Delta C)^T M^{-1} \Delta C}{(\Delta C)^T G^\alpha \Delta C}\right]^{1/3} t^{-1/3}\right)$$ (7.60)

$$f_{C^\infty(t)}(k) = \frac{f_{\alpha/\sigma_0}^{2/3}}{f_{i}(k)^{2/3}} = \frac{f_{\sigma_2/\sigma_0}^{2/3}}{f_{m}(k)^{2/3}}$$ (7.61)

Here, $f_{C^\infty(t)}(k)$ is a shape factor for the matrix supersaturations, which shows negative dependence on the aspect ratio, shown in Fig. 7.5 (d). As explained in the PV[159] theory, the matrix supersaturations coincide with the tie line representing the equilibrium between the matrix and the precipitate. For a spheroidal particle, it is found that the shape factor does not influence the directional vector information of the matrix supersaturations as shown in Fig. 7.6 (a).
There are two opposite effects on precipitate coarsening (competitive growth) rate due to the anisotropic shape of a particle. One is positive, resulting from the diffusional growth rate due to increased specific surface area as discussed in section 7.3.1. The other is the negative dependence of the Gibbs-Thomson effect on the aspect ratio as discussed in section 7.3.2, and the corresponding reduced matrix supersaturations as shown in Fig. 7.5 (d). As shown by the diffusional shape factor \( f_R(k) \) curve in Fig. 7.1 (b), a spheroidal particle has a diffusional growth rate that is more than three times faster than a spherical particle when the aspect ratio is 50. However, the Gibbs-Thomson shape factor \( f_{\Delta \rho}(k) \) shows a factor of \(~0.12\) at an aspect ratio of 50 in Fig. 7.4 (b). Also, the supersaturation shape factor \( f_{c^\infty(t)}(k) \) shows a factor of \(~0.17\) in Fig. 7.5 (c). Thus, the resulting coarsening shape factor \( f_{K^R}(k) \) shows a negative dependence on the aspect ratio as shown in Fig. 7.5 (b). However, the coarsening rate constant to the one-third \( K^R \) \(^{1/3}\) corresponds to \(~0.7\) when the aspect ratio is 50. That is, the equivalent radius of a spheroid with 50 aspect ratio shows a \(~0.7\) percent of radius for a sphere. Thus, the anisotropic shape of a particle does not significantly influence the coarsening rate.

The time-dependence form of the precipitate composition at the interface during coarsening can be described by letting \( l = \bar{l} \) and replacing the average precipitate length and the supersaturations by their time-dependence forms in Eq. (7.31).

\[
\langle C^\beta \rangle(t) = \bar{C}^\beta + f_{\langle C^\beta \rangle(t)}(k)(3\sigma_0 V^\beta_m \bar{C})^2 \left[ (\Delta \bar{C}) M^{-1} \Delta \bar{C} \right]^{1/3} \left\{ \frac{G^{\beta-1} G\Delta \bar{C}}{(\Delta \bar{C}) G^\alpha \Delta \bar{C}} - \frac{G^{\beta-1} \Delta \bar{V}}{V^\beta_m} \right\}^{-1/3} t^{-1/3} \tag{7.62}
\]
Here, $f_{(\bar{c}^\beta)(t)}$ represents the shape factor for the interfacial composition of the average precipitate, which equals to $f_{c^\infty(t)}(k)$ described in Eq. (7.61). Eq. (7.62) gives the temporal evolution of the precipitate composition during coarsening. According the PV[159] theory for a spherical particle, the vector representing the departure of the precipitate composition from equilibrium values does not coincide with the equilibrium tie-line since the operator $G^{\beta-1}G^\alpha$ is applied to $\Delta\bar{c}$ and rotates the vector. The shape factor $f_{(\bar{c}^\beta)(t)}$ affects the magnitude of the departure of the precipitate compositions from their equilibrium values (similar to the mobility tensor), but it does not influence the direction of the vector as shown in Fig. 7.6 (a).

We can describe the composition profiles inside the particle based on the assumption that no diffusion occurs in the particle. That is, the inside composition profiles can be regarded as the continuing values of the interfacial compositions for smaller particles. The difference in interfacial compositions for a spheroid can be expressed by mean equivalent radius $\bar{R}$ using Eqs. (7.55)-(7.57) in Eq. (7.64). For the equivalent radius $r \leq \bar{R}$, the particle composition profile is

$$\langle \bar{c}^\beta \rangle(r) = \bar{c}^\beta + f_{(\bar{c}^\beta)(r)}(k) \left(3\sigma_0 V_m^{\beta} \right)^{\frac{2}{3}} \left[(\Delta\bar{c}) M^{-1} \Delta\bar{c}] \right)^{\frac{1}{3}} \left\{ \frac{G^{\beta-1}G^\alpha \Delta\bar{c}}{(\Delta\bar{c})^T G^\alpha \Delta\bar{c}} - \frac{G^{\beta-1} V}{V_m^\beta} \right\} \frac{1}{k^\frac{1}{3}} r \right\} \right)$$

$$f_{(\bar{c}^\beta)(r)}(k) = f_{\Delta p}(k) = \frac{f_{\sigma_1/\sigma_0}}{2} = f_{\sigma_2/\sigma_0} \frac{1}{k^\frac{1}{3}}$$
where \( f_{(c^\beta_j)}(k) \) is a shape factor, which equals to the Gibbs-Thomson shape factor \( f_{\Delta \rho}(k) \) (Eq. (7.42)) described in section 7.3.2. Fig 7.6 (b) represents a graphical representation of the composition profile of the \( j \)th component for a particle with mean equivalent radius \( \bar{R} \). The deviation from the equilibrium composition becomes smaller with increasing the aspect ratio of a particle. As explained in the PV[159] theory, the composition at the core of the particle depends on the composition of the nucleating particles, not predicted by the present theory.

Figure 7.6. (a) The Gibbs tetrahedron of a two-phase equilibrium in a quaternary system. The vectors representing the far-field composition and the departure of the precipitate composition from equilibrium are represented by red arrows. The shape factors (Eq. (7.63) and (7.65)) do not influence the directional information, but magnitude similar to the mobility tensor. The lengths of the red arrows become shorter with increasing the aspect ratio of a spheroid. (b) A graphical representation of a composition profile of component \( j \) as a function of equivalent radius \( r \). The profile can be regarded as the
inside composition with assumption of zero diffusivity in the particle. The deviation from the equilibrium composition becomes smaller with increasing the aspect ratio of a particle.

7.3. Conclusions

A general theory of Ostwald ripening for a spheroidal particle has been developed based on past work for a spherical particle in a multicomponent alloy. The analysis is valid for a non-ideal and non-dilute solution. Two correction factors are introduced to account for anisotropic interfacial energy and physical geometry. The growth rate increases with an increase in the aspect ratio of a particle under a constant equivalent radius due to an increased specific surface area under an assumption of fully diffusion-controlled growth. Based on the Gibbs-Thomson equation, including interfacial energy anisotropy, the pressure difference (or chemical potential under a constant molar volume) decreases with an increasing aspect ratio of a particle under a constant equivalent radius. This is consistent with a fully-faceted crystal based on the Laplace-Young equation. Asymptotic analysis shows that the temporal exponents for the coarsening law of a spheroid are identical to exponents in sphere theory. However, the amplitudes depend on the aspect ratio of a particle. The coarsening rate constant was found to decrease as the aspect ratio increases. This can be understood by that the negative dependence of the Gibbs-Thomson effect and matrix supersaturations on the aspect ratio are larger than the positive dependence of diffusional growth rate on the aspect ratio. The particle composition has a negative dependence on the aspect ratio, but the shape factor does not influence the directional vector information, and thus is similar to a mobility tensor.
7.4. Appendix.

The asymptotic analysis is based on the previous literatures [159, 172, 174]. A difference is that the distribution is expressed by a length $l$ of precipitate along the long axis instead of radius $r$. A solution to the equation governing the dynamics of the particle size distribution can be written in powers of time when the distribution is expressed in terms of scaled particle length $z = l\tau^{-x}$ (the distance from a center to a surface along the long axis), where $x$ will be determined. The distribution function is

$$f(l,t) = \tau^{-y}[f_0(z) + \tau^{-y_1}f_1(z) + \cdots]$$  \hspace{1cm} (7.4.1)

where $y > y_1$, and the time has been scaled,

$$\tau = \frac{2V_m\sigma_1 f_1(k)}{(\Delta\bar{C})^T M^{-1} \Delta\bar{C}} t$$  \hspace{1cm} (7.4.2)

In the limit $\tau \to \infty$, the vector far-field supersaturations $q^\infty \to 0$, substituting Eq. (7.47) into Eq. (7.48) and using Eq. (7.4.1) yields

$$q^0 = \frac{4\pi}{3} (\alpha - 1) \tau^{4x-y} \int_0^\infty \frac{z^3 f_0(z)}{k^2} dz$$  \hspace{1cm} (7.4.3)

As $y_1 > 0$. To set Eq. (A3) time-independent, $y = 4x$. This leads to

$$q^0 = \frac{4\pi}{3} (\alpha - 1) \int_0^\infty \frac{z^3 f_0(z)}{k^2} dz$$  \hspace{1cm} (7.4.4)

Substituting this result into Eq. (7.48) yields

$$q^\infty = (\alpha - 1) q_1 \tau^{-y_1}$$  \hspace{1cm} (7.4.5)
where

\[ q_1 = -\frac{4\pi}{3} \int_0^\infty \frac{z f_1(z)}{k^2} \, dz \quad (7.46) \]

Thus,

\[ f(l, t) = \tau^{-4x} [ f_0(z) + \tau^{-y_1} f_1(z) + \cdots ] \quad (7.47) \]

Differentiating Eq. (7.48) with respect to time, using the continuity equation (Eq. (7.45)) in the integrand, integrating by parts,

\[ \frac{d\mathbf{q}^\infty}{d\tau} = -8\pi(\alpha - 1) \int_0^\infty \frac{f l l^2}{k^2} \, dl \quad (7.48) \]

We assume that \( f(0, \tau) = 0 \) and \( f(l, \tau) = 0 \) for \( l \to \infty \). Substituting Eq. (7.45) into Eq. (7.48) yields

\[ q_1 \tau^{-y_1 - 1} = 8\pi \int_0^\infty \frac{f l l^2}{k^2} \, dl \quad (7.49) \]

Using Eq. (7.45) and \( z = \tau^{-x} \) in Eq. (7.18) yields

\[ \dot{l} = \frac{\tau^{-x}}{z} \left[ B q_1 \tau^{-y_1} - \frac{\tau^{-x}}{z} \right] \quad (7.50) \]

where

\[ B = \frac{(\Delta \mathbf{C})^T \mathbf{G}^\alpha \Delta \mathbf{C}}{2\nu_{\infty}^\beta \sigma_1} \quad (7.51) \]

Eq. (7.50) is expressed to lowest order in \( \tau \), as \( \dot{l} = \tau^{-\eta} V(z)[159, 172] \), where
\[ \eta = 2x \quad V(z) = -1/z^2 \quad y_1 > x \]
\[ \eta = 2x \quad V(z) = 1/z(Bq_1 - 1/z) \quad y_1 = x \quad (7.A12) \]
\[ \eta = x - 1 \quad V(z) = Bq_1/z \quad y_1 < x \]

Using the continuity equation (Eq. (7.45)),

\[ \tau^{-4x-1} \left[ xz \frac{\partial f_0}{\partial z} + 4xf_0 \right] = \tau^{-\eta-5x} \frac{\partial (f_0 V)}{\partial z} \quad (7.A13) \]

Balancing the powers of time, \( x = -\eta + 1 \). Thus

\[ q_1y_1\tau^{-y_1} \sim 8\pi \int_0^\infty z^2V(z)f_0(z)dz \quad (7.A14) \]

When \( \tau \to \infty \), the left term becomes zero and thus \( V(z) \) must have a sign change with \( z \) over the interval of integration because \( f_0(z) \) is positive. This is only possible if \( y_1 = x \) as proposed in the literatures\[159,172\]. Thus, \( \eta = 2x \) and \( Bq_1 > 0 \), and this leads to \( y_1 = 1/3 \). Therefore, we get the followings in the long-term limit.

\[ q^\infty = (\alpha - 1)q_1\tau^{-\frac{1}{3}} \quad (7.A15) \]

\[ \tilde{l} = \frac{\int_0^\infty zf_0(z)dz}{\int_0^\infty f_0(z)dz} \quad (7.A16) \]

\[ N_0 = \tau^{-1} \int_0^\infty f_0(z)dz \quad (7.A17) \]

The continuity equation is expressed as

\[ \frac{d}{dz} \left[ f_0 \left\{ \frac{1}{z} \left( Bq_1 - \frac{1}{z} \right) - \frac{z}{3} \right\} \right] - f_0 = 0 \quad (7.A18) \]
As explained in the literatures\cite{159,172,174}, $f_0$ must be zero above $z = z_0$, $z_0 > 0$. Also, $f$ and its derivative must be zero at $z_0$. This gives $z_0 = (3/2)^{1/3}$, $q_1 = (9/4)^{1/3}/B$, and $\bar{l} = (4/9)^{1/3} \tau^{1/3}$. The time-independent scaled precipitate length distribution is obtained integrating Eq. (A18) satisfying Eq. (7.A15) with $q^0 = \phi_{eq}[\alpha - 1]$.

$$f_0 = \frac{3\phi_{eq}g(z)}{4\pi \int_0^{z_0} z^2 g(z) \frac{dz}{k^2}}$$

with

$$g(z) = z^2 \left( \frac{2z_0}{2z_0 + z} \right)^3 \left( \frac{z}{z - z_0} \right)^{11/3} e^{z_0/z}$$

From Eq. (A17), (A19) and (A20), the number density of precipitates per unit volume is shown in Eq. (7.60) with a shape factor (Eq. (7.61)). For the limit of spheres (i.e., $k = 1$), Eq. (7.60) recovers to Eq. (7.44) for spherical particles in the PV\cite{159} theory.
8.1. Summary

We have investigated the phase stability and growth/coarsening mechanism of various Al-based strengthening precipitates on atomic and micro length scales based on thermodynamic and kinetic studies. In Chapter 4, we have investigated thermodynamic stability of the coherent (001)\textsubscript{\theta r}//(001)\textsubscript{Al} and semi-coherent (010)\textsubscript{\theta r}//(010)\textsubscript{Al} interfaces for future nucleation and growth studies. Based on our DFT calculations, the occupancy of interstitial Cu atoms, recently proposed by Bourgeois et al.[33], decreases the stability of the coherent (001)\textsubscript{\theta r}//(001)\textsubscript{Al} interface. Thus, the coherent (001)\textsubscript{\theta r}//(001)\textsubscript{Al} interface without interstitial Cu atoms correspond to the equilibrium state. Also, it is found that the semi-coherent (010)\textsubscript{\theta r}//(010)\textsubscript{Al} interfacial stability does not particularly depend on the semi-coherent interfacial configurations (misfit strains). In Chapter 5, we solve a long-standing controversial problem regarding the T\textsubscript{1} crystal structure in Al-Li-Cu alloys by DFT energetic calculations. Based on our DFT calculations, all five experimental models with disordered Al-Cu layers have energies that are not on the lowest-energy convex hull (at T = 0K). By cluster expansion (CE) method, we found a new, lower-energy structure of T\textsubscript{1} (Al\textsubscript{6}Cu\textsubscript{4}Li\textsubscript{3}) corresponding to a stable phase in experimental phase diagram. The new finding phase still does not have a tie-line with Al, but the formation energy of the phase is very close to the energy (0.013 eV/atom) required to make a tie-line with Al. Thus,
the finite temperature properties (i.e., entropic contribution) should be investigated in the future. In Chapter 6, we investigated native defect energies, solute partitioning, and interfacial stability of $Q$-phase in a quaternary Al-Cu-Mg-Si alloy. By using native defect analysis, the experimentally observed off-stoichiometry of $Q$-phase can be partially explained as being the result of native defects in the $Q$-phase. Based on our predictions by solute-partitioning energies, we determined general rules for site-preference of a solute in the $Q$-phase in terms of electronic structure and atomic radius. The atom probe tomography (APT) experiments for six different elements (Zn, Ni, Mn, Ti, V, and Zr) show that the partitioning behavior of Ni, Zn, and Mn solutes are consistent with DFT predictions. However, the slow diffusing transition elements (Ti, V, and Zr) in Al partitioned to the $Q$-phase precipitates, which is inconsistent with DFT predictions. We surmise that the discrepancy is caused either by trapping in the $Q$-phase leading to a non-equilibrium partitioning like effect due to slow diffusivity, or due to not accounting for finite temperature effects in the DFT calculations. For future coarsening studies, we searched various terminations and orientations and derived a low-energy structure (0.52 J/m$^2$) of the coherent $(11\bar{2}0)_{Q}//(510)_{Al}$ interface. We find Cu is the nearest atom to the interface, which is in agreement with previous literature on Cu interfacial segregation at the $Q'//\alpha$-Al interface. In Chapter 7, we performed phase field modeling with the parameters supplied by first-principles DFT to investigate the underlying physics governing the high aspect ratio of equilibrium $\theta'$ precipitates in Al-Cu alloys. Our phase-field method allows for the high anisotropic interfacial energy needed to describe the shape of $\theta'$ precipitates. Specifically, the model allows for missing orientations and corners on the Wulff shape, and can thus can be used to describe the faceted coherent interfaces of $\theta'$ precipitates. The misfit strain anisotropy is the most important factor in
deciding \( \theta' \) morphology among various elastic energy contributions to \( \theta' \) morphology. Based on our computation, we found that the computed aspect ratio of the equilibrium precipitate morphology is significantly smaller than the equilibrium aspect ratio observed in the experiment. Therefore, we conclude that the experimentally measured \( \theta' \) morphology is strongly influenced by the anisotropic interfacial kinetics. It is also found that the aspect ratio of the equilibrium shape of the precipitate decreases with size due to the face that the misfit strain anisotropy becomes negligible during the growth of \( \theta' \). Finally, in Chapter 8, we develop a general theory of Ostwald ripening for a spheroidal particle to understand anisotropic shape effects in growth and coarsening law. We introduced two correction factors, accounting for anisotropic interfacial energy and physical geometry. Our results show that the growth rate increases with an increase in the aspect ratio of a particle under a constant equivalent radius. This is due to an increased specific surface area under the assumption of fully diffusion-controlled growth. We also found that the chemical potential decreases with an increasing particle aspect ratio under a constant equivalent radius on the Gibbs-Thomson equation. Asymptotic analysis shows that the temporal exponents for the coarsening law of a spheroid are identical to exponents in sphere theory. However, the amplitudes depend on the aspect ratio of a particle. The coarsening rate constant was found to decrease as the aspect ratio increases. The matrix supersaturations and the particle composition also have a negative dependence on the aspect ratio. The shape factor does not influence the directional vector information of the particle composition, and thus is similar to a mobility tensor.
8.2. Outlook

Information for future studies was already discussed in each chapter. In this section, we will briefly refer to the gaps and limitations between linking first-principles calculations and phase-field methods. Chapter 7 shows that we could perform only one-particle-simulation due to small grid spacing based on thermodynamic input variables by DFT calculations. That is, high computational expenses will be needed in order to perform multi-particle simulation given thermodynamic inputs. This is one of the examples of the limitations in modeling across length scales. Additionally, we utilized DFT interfacial energies at sharp interfaces when performing the diffuse interface approach in phase-field modeling. For more accurate linkage across length scales, the finite temperature interface properties (i.e., energy and width) in DFT should be investigated. The properties will be possibly achieved from a low temperature expansion technique (LTE) by utilizing single-flip energies at interfaces. To design a thermally stable microstructure, one of potential methods is to utilize low diffusivity solutes to reduce the coarsening rate of strengthening phases in multicomponent alloys. It is difficult to obtain thermodynamic inputs directly (e.g. free energy) by DFT calculations in multicomponent systems, so the CALPHAD method will need to be incorporated into phase-field method. However, phase-field calculations are inefficient when implemented with CALPHAD via existing application program interfaces. Moreover, there is a major limitation of CALPHAD models, as complex conditions (e.g. anisotropic strain, facet geometry, or anisotropic diffusion) are not considered. Thus, the development of an efficient computing strategy that is able to link CALPHAD with PFM will be needed in the future.
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