PHASE-FIELD MODELING OF PRECIPITATION IN METALLIC ALLOYS: MORPHOLOGY, KINETICS AND HARDENING EFFECTS

A Dissertation in
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ABSTRACT

Precipitation hardening is an important strengthening mechanism in metallic alloys, which is realized by impeding the dislocation motions in the matrix via stress field due to the precipitate/matrix lattice mismatch. The precipitation hardening effect is largely determined by a series of inter-correlated factors including the feature and evolution of precipitate morphologies, e.g., the size, shape, volume fraction and spatial distribution of the precipitate and their evolution; the coherency state of the precipitate; and the detailed precipitate-dislocation interaction mechanisms. Therefore, understanding and quantifying the morphology and kinetics of precipitation is an important step towards the estimation of precipitation hardening effects, as well as the proper design of alloys and the optimization of thermo-mechanical processing routes.

The phase-field approach, as a powerful meso-scale simulation method, has been successfully applied to understand the precipitation phenomena. However, there are still several remaining challenges for precipitation phase-field models. In this thesis work, the precipitation phase-field models have been further extended and applied to deal with precipitate phases with different thermodynamic descriptions, to predict the morphology evolution and kinetics of fully coherent and semi-coherent precipitates with the help of first-principles calculations, to predict the possible dislocation evolution pathway and morphology evolution during the sequential coherency loss of an initially coherent or semi-coherent precipitate, to understand the competitions between the diffusional and diffusionless transformation mechanisms, and to provide necessary information for theoretical precipitation hardening models.

The precipitate phase, depending on the specific materials systems, can be treated using solid solution model, sublattice model, or stoichiometric compounds (line compounds). To deal with these different treatments, we use the Kim-Kim-Suzuki model for the solid solution and
sublattice cases, where the equal diffusion chemical potential of alloying elements is assumed to remove the extra potential at the interface. An internal equilibrium is assumed for the sublattice model within different sublattices which converts the sublattice site fractions to alloy compositions. To deal with the precipitation of line compounds, we develop a phase-field model for chemical reactions, which can capture both the solute diffusion in the matrix phase and the linear chemical reaction kinetics.

The phase-field model is then applied to investigate the precipitate morphology, kinetics and hardening effect of the fully coherent $\beta'$-Mg$_7$Nd in Mg-Nd alloys. The necessary input parameters, including the formation energies, lattice constants and elastic constants of both the Mg matrix and the $\beta'$ phase, as well as the anisotropic interfacial energies, are all obtained from first-principles calculations. Especially, the formation energies of the slightly off-stoichiometric Mg$_7$Nd compound are also calculated, which are used to fit the formation energies of $\beta'$ into a parabolic function of solute composition. The interplay between the anisotropies in misfit strain energy and interfacial energy is discussed in detail, showing their dominance in determining the precipitate morphology at different aging stages. The simulated $\beta'$ morphology, with both anisotropies considered, is consistent with experimental observations. Theoretical models based on Orowan’s equation is used to predict the hardening effect of $\beta'$-Mg$_7$Nd.

The phase-field model, with similar thermodynamic treatment of the precipitate phase to that of $\beta'$-Mg$_7$Nd, is further applied to the semi-coherent $\theta'$-Al$_2$Cu in Al-Cu-based alloys. To more accurately simulate the precipitation kinetics, a temperature-dependent nucleation model, with necessary input from experimental observations, and a more accurate parameterization of interface kinetic coefficient, are considered in the model. The phase-field simulations, with materials parameters from validated sources, are performed for isothermal aging at 463 K, 503 K and 533 K. The simulated $\theta'$ is of disk shape under the anisotropies of misfit strain energy, interfacial energy and interface mobility. The predicted $\theta'$ precipitation kinetics, including the
evolution of mean diameters, mean thicknesses and volume fractions, show acceptable agreement with experimental measurements. Possible model improvements and extensions to minimize the discrepancies are discussed.

Coherency loss of the initially coherent or semi-coherent precipitate during continued precipitate growth is a manifestation of energy minimization, which relaxes the misfit strain energy at the expense of increasing the interfacial energy by creating line defects at the matrix/precipitate interface. To understand the kinetics of coherency loss, as well as its effect on precipitate morphology, kinetics and hardening effects, we equivalently consider the effect of line defects, as well as the evolution of their average spacings, on the formulation of misfit strain energies and interfacial energies in the phase-field model. We apply this model to $\gamma''$-Ni$_3$Nb in IN718, where $\gamma''$ is treated using the sublattice model, to predict the critical $\gamma''$ size to trigger the coherency loss under different criteria and a known dislocation configuration at interfaces. We further apply the model to predict the sequential loss of coherency in $\theta'$-Al$_2$Cu, which predicts a coherency loss pathway with the minimum energy cost.

Diffusional precipitation transformation can change its transformation mechanism with the change of alloy composition, temperature and cooling rates. For example, in Ti-6Al-4V, start from $\beta$ phase, the $\alpha$ phase can be a diffusional product during isothermal aging or slow cooling, while becomes diffusionless product during fast cooling. To understand this competition, we combine the graphical thermodynamic approach to predict the possible transformation pathways, and the phase-field simulation to predict the microstructure evolution during continuous cooling of Ti-6Al-4V. The simulated (\alpha+\beta) morphologies are attributed to the interplay between the diffusional and diffusionless mechanisms, as well as that between the nucleation and growth of $\alpha$ phase.
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<td>$p$</td>
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<td>$\mu_i$</td>
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</tr>
<tr>
<td>$J_i$</td>
<td>Diffusion flux of species $i$</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Extent of chemical reaction</td>
</tr>
<tr>
<td>$\Delta E_f$</td>
<td>Formation enthalpy (or formation energy at 0 K)</td>
</tr>
<tr>
<td>$E_{\text{int}}^{\text{el},pq}$</td>
<td>Elastic interaction energy between the pre-existing stress field of phase (or variant) $p$ and the phase (or variant) $q$</td>
</tr>
<tr>
<td>$\Delta \tau$</td>
<td>Increment of the critical resolved shear stress</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Poisson’s ratio</td>
</tr>
<tr>
<td>$b$ or $\mathbf{b}$</td>
<td>Burgers vector</td>
</tr>
<tr>
<td>$f$</td>
<td>Volume fraction of precipitate phases</td>
</tr>
<tr>
<td>$j$</td>
<td>Nucleation rate</td>
</tr>
<tr>
<td>$Z$</td>
<td>Zeldovich factor</td>
</tr>
<tr>
<td>$N_0$</td>
<td>Number of atoms per unit volume</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro’s number</td>
</tr>
<tr>
<td>$\beta'$</td>
<td>Atomic attachment rate</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$\Delta G_{\text{hom}}^*$</td>
<td>Homogeneous nucleation barrier</td>
</tr>
<tr>
<td>$\sigma_Y$</td>
<td>Yield strength</td>
</tr>
<tr>
<td>$\sigma_{\text{ppt}}$</td>
<td>Contribution of precipitation hardening to yield strength</td>
</tr>
<tr>
<td>$\sigma_{ss}$</td>
<td>Contribution of solid solution hardening to yield strength</td>
</tr>
<tr>
<td>$M_T$</td>
<td>Taylor factor</td>
</tr>
<tr>
<td>$d_i$</td>
<td>Diameter of the precipitate</td>
</tr>
<tr>
<td>$t_i$</td>
<td>Thickness of the precipitate</td>
</tr>
<tr>
<td>$r_0$</td>
<td>Inner cut-off radius of dislocation cores</td>
</tr>
<tr>
<td>$H$</td>
<td>Modulus of solid solution hardening</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>Intrinsic strength</td>
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<tr>
<td>$F$</td>
<td>Deformation gradient</td>
</tr>
<tr>
<td>$I$</td>
<td>Identity matrix</td>
</tr>
<tr>
<td>$\lambda_i$</td>
<td>Average spacing of $i$-th dislocation loop</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Anisotropy factor for elasticity</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Incubation time of nucleation</td>
</tr>
<tr>
<td>$p_n$</td>
<td>Nucleation probability</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy</td>
</tr>
<tr>
<td>$l_0$</td>
<td>Length scale</td>
</tr>
<tr>
<td>$\mathbf{r}$</td>
<td>Base vector in real space</td>
</tr>
<tr>
<td>$\mathbf{k}$</td>
<td>Base vector in reciprocal space</td>
</tr>
<tr>
<td>$\theta_i$</td>
<td>The angle characterizing the interface normal of the $i$-th variant of a precipitate phase</td>
</tr>
<tr>
<td>$B_{\text{het}}$</td>
<td>Heterogeneous nucleation factor in nucleation model</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$r^<em>$, $h^</em>$</td>
<td>Critical nucleus radius ($r^<em>$) and thickness ($h^</em>$)</td>
</tr>
<tr>
<td>$\Delta G_n$</td>
<td>Nucleation driving force</td>
</tr>
<tr>
<td>$\alpha, \beta$</td>
<td>Anisotropy factor for interfacial energy ($\alpha$) and interface mobility ($\beta$), Chapter 4</td>
</tr>
<tr>
<td>$d_c$</td>
<td>Critical precipitate diameter for coherency loss, based on stability criterion</td>
</tr>
<tr>
<td>$d_e$</td>
<td>Critical precipitate diameter for coherency loss, based on energy criterion</td>
</tr>
<tr>
<td>$\mathbf{n}_0$</td>
<td>Habit plane normal</td>
</tr>
<tr>
<td>bcc</td>
<td>Body-centered cubic crystal structure</td>
</tr>
<tr>
<td>fcc</td>
<td>Face-centered cubic crystal structure</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal close packed crystal structure</td>
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</tbody>
</table>
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Chapter 1: Introduction

Precipitation is a common phenomenon in a variety of materials systems. It typically forms in liquid or solid solutions with excess solutes, i.e., when the solution is supersaturated at given temperature and pressure. The precipitates usually have different solute compositions and crystal structures from the solution phase, leading to the change of related materials properties of the system. Understanding the formation and evolution mechanisms of the precipitates, in terms of both thermodynamics and kinetics, as well as the correlation between the precipitates and the materials properties of interest, are important prerequisites for optimizing the related materials properties.

1.1 Precipitation in metallic alloys

In this dissertation, we focus our discussions on solid state precipitations in metallic alloys. Since the precipitate phase has different crystal structures from the matrix phase, it causes not only the discontinuity of the slip systems, but also the misfit strains at the precipitate/matrix interface, both of which impede the dislocation motion in the matrix, leading to the enhancement of the strength of the material, i.e., precipitation hardening [1]. Besides, precipitates can act as pinning particles that impede the motion of grain boundaries, which can further contribute to the strength of the material through grain refinement [2]. Therefore, precipitation hardening has been extensively utilized in both fundamental scientific researches and industries as an effective method to improve the strength of alloys, including not only the light-weight Al-, Mg-, and Ti-alloys in automotive and aircraft frameworks, but also steels in many industrial applications and Ni-based alloys for energy generators such as engines and gas turbines.

The further improvement of the strength of alloys through precipitate hardening requires the fundamental understanding of the mechanisms and governing factors of both precipitation itself
and precipitation hardening, i.e., the interaction between precipitates and defects such as dislocations. Over the past decades, extensive experimental research efforts have been devoted to the understanding of various aspects of precipitation in metallic alloys, including the basic thermodynamic properties of the precipitates including the phase stabilities, phase boundaries and phase diagrams; the precipitation kinetics including the nucleation, growth and coarsening kinetics as well as solute diffusivities; the crystal structure of the precipitate and its possible orientation relationship (OR) and lattice correspondence (LC) with the matrix; the precipitate/matrix interface structure, energy and mobility; the interaction of dislocations and other defects such as vacancies, twins, stacking faults, grain boundaries and cracks with precipitates. Based on these investigations, qualitative, semi-quantitative and quantitative theoretical models have been developed to understand these different aspects of precipitation. For example, based on existing experimental data for thermo-chemical properties of the phases and phase boundaries, combining with first-principles calculations for lattice stabilities [3], formation enthalpies and entropies of the phases, the CALPHAD-based thermodynamic approach [4, 5] can predict the related thermodynamic properties at the matrix-precipitate two-phase equilibrium; the nucleation, growth and coarsening kinetics of precipitates can be predicted by the classical nucleation theory [6, 7], the diffusion-controlled growth and the Lifshitz-Slyozov-Wagner (LSW) theory [8], respectively, and the overall precipitation kinetics can be predicted by the John-Mehl-Avrami-Kolmogorov (JMAK) equation [9-11], which can then be applied to predict the time-temperature-transformation (TTT) or continuous cooling transformation (CCT) diagrams of the precipitates [12]; the OR, LC and possible interface structures can be investigated by the O-lattice theory [13, 14]; the equilibrium shape of the precipitates can be predicted by the Wulff construction [15-17] on the γ-plot of angle-dependent precipitate/matrix interfacial energies; the habit plane of the precipitates can be predicted by Khachaturyan’s microelasticity theory [18] or Eshelby’s inclusion theory [19, 20] of minimizing the coherency strain energy; the hardening effect of the precipitates can be predicted by the Orowan equation [21, 22] if the dislocations loop
around the precipitates rather than cut through them, given the volume fraction, aspect ratio, number density and inter-particle spacing of the precipitates in the matrix. As a result, the thermodynamics, kinetics and hardening effects of precipitates can be relatively accurately estimated, which provide useful guidance for the proper heat treatment and thermo-mechanical processing of alloys to maximize the precipitate hardening effect in real applications.

Although our knowledge basis for precipitation in metallic alloys have been well established based on the above-mentioned theories, there are still large rooms for improving our understandings. Firstly, new knowledge about precipitation is continuously developed with the help of advanced experimental techniques and new materials theories. For example, even for the well-known θ’ precipitate in Al-Cu-based alloys, which has been widely used in fundamental materials science textbooks as a typical example for precipitation [1, 6, 23, 24], the detailed solute segregation behavior at both coherent and semi-coherent interfaces [25-27], the detailed semi-coherent interface structures [28], as well as the atomistic mechanisms for lengthening and thickening [28, 29] have only recently been elucidated, with the help of three-dimensional atomic probes (3DAP), high-resolution transmission electron microscopy (HRTEM), high-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM), and first-principles calculations. Secondly, the above-mentioned theories have their own limitations and respective ranges of applicability, which need to be further developed for general precipitation cases. For example, the CALPHAD approach works well for stable precipitate phases (e.g., θ in Al-Cu alloys) while remains challenging for metastable phases (e.g., θ” and θ’ in Al-Cu alloys); the existing precipitate kinetic theory works well for a single type of precipitate with known shapes, while remains challenging for the interactions among different possible precipitates (e.g., the G.P. zone→θ”→θ’→θ precipitation sequence in Al-Cu alloys); the O-lattice theory can predict the final dislocation configurations on infinitely large precipitate/matrix interfaces (i.e., when the precipitate becomes fully incoherent), while could not predict the dislocation nucleation and evolution during precipitate growth; the microelasticity theory does not consider the
interfacial energy contribution to the precipitate shapes and remains difficult in dealing with geometrically nonlinear cases (i.e., when the stretch and/or rotation part of the deformation is large). Thirdly, the precipitate phenomenon, especially its detailed morphology, kinetics and hardening effects, are affected by various governing factors, which are usually correlated and difficult to investigate. Therefore, the fundamental aspects of precipitation in metallic alloys, together with the fine tuning of processing condition of these alloys to maximize the precipitation hardening effect, are still active research topics deserving rigorous considerations and thorough investigations.

1.2 Precipitate morphology, kinetics and hardening effects

In this dissertation, we are particularly interested in the morphology evolution, kinetics and hardening effects of precipitates in metallic alloys. Based on existing investigations, we briefly summarize the governing factors, their possible competitions/interactions, as well as the remaining challenges in research.

1.2.1 Governing factors of precipitate morphology and kinetics

The morphology of a precipitate is largely determined by the anisotropic precipitate/matrix interfacial energy and misfit strains. As mentioned above, if the interfacial energy is the only governing factor, the equilibrium shape of the precipitate can be obtained by the Wulff’s construction [15-17] on the interfacial energy vs. interface index (or orientation) plot, i.e., the $\gamma$-plot, as shown in Figure 1.1(a). This is consistent with the requirement of minimizing the total interfacial energy of the system, and is most applicable for systems with fully incoherent precipitates or precipitates with isotropic elastic stiffness and misfit strains. On the other hand, if the misfit strain is the only governing factor, the precipitate tends to form a thin plate on the plane with the minimum coherency strain energy, which is applicable for systems with isotropic precipitate/matrix interfacial energy, as illustrated by the example in Figure 1.1(b). In most
realistic cases, the precipitate morphology is governed by the competition of these two types of anisotropies, which may become dominant at different precipitation stages, leading to different precipitate morphologies [30]. Typically, for fully coherent precipitates, since the interfacial energy scales with interface area of the precipitates while the misfit strain energy scales with the volume of the precipitates, the contribution of interfacial energy to the total energy of the system is larger than that of the misfit strain energy when the precipitate is small (usually several nanometers), and the anisotropy in interfacial energies plays a dominant role in the precipitate shape; on the other hand, the anisotropy in misfit strains plays a dominant role in the precipitate shape when the precipitate size becomes large [31]. However, when the precipitate size becomes sufficiently large, the coherency of the precipitate/matrix interface becomes difficult to maintain, inducing the formation of defects such as dislocations and structure ledges on the interface, which further decreases the misfit strain energy at the expense of increasing the interfacial energy [32]. The interfacial energy anisotropy may become dominant again for precipitate morphology, especially when the coherency is fully lost. The precipitate can then change its morphology from the relatively smooth spherical, cuboidal, needle or plate shapes to relatively irregular shapes with facets due to the appearance of cusps on the $\gamma$-plot. In addition to the anisotropies in interfacial energy and misfit strains, the anisotropy in interface mobility can be another governing factor for precipitate morphology, especially during the growth of the precipitate [33]. This is due to the fact that the activation energies for atomic movement are different due to the different atomic arrangement of the different interfaces. For example, the large diameter-to-thickness ratio of $\theta'$ precipitates is critically related to the large interface mobility difference between the semi-coherent and the coherent interface: the thickening of $\theta'$ is controlled by Cu diffusion and the nucleation of ledges [29] while the lengthening of $\theta'$ can be greatly facilitated by forming a diffuse interface containing an intermediate $\theta''$ region at the semi-coherent interface [28], which potentially reduces the activation energy for atomic movement during lengthening. However, the detailed atomistic scale interface moving mechanisms for most of the other precipitates have not
yet been fully investigated. In summary, the precipitate morphology is mainly governed by the anisotropies in interfacial energy, misfit strains and interface mobility, which are correlated and affected by lattice matching, coherency state and atomistic interface moving mechanisms.

![Figure 1.1](image)

**Figure 1.1** Illustration of governing factors for precipitate morphology. (a) Determination of the equilibrium shape of a bcc precipitate from an fcc matrix using the Wulff construction on the $\gamma$-plot. “OLI” indicates the O-line interface predicted by the O-lattice theory. $\Delta g$ is the difference between two low-index reciprocal vectors of the two phases. Adapted from [13] with permission. (b) Determination of the habit plane of the $\alpha$ precipitate in Ti-alloys using the microelasticity theory. The black and red dots in the polar plot represent the orientation-dependent elastic strain energies for the fully coherent and semi-coherent $\alpha$ precipitates, respectively. The black and red arrows indicate the habit plane orientation with the lowest elastic strain energy for the two cases, respectively. Adapted from [34] with permission.

The precipitation kinetics are mainly controlled by the activation energy and related rate coefficient of the kinetic processes. For most of the precipitation process in metallic alloys, the precipitation is realized by a nucleation-and-growth mechanism, unless the matrix itself contains compositional instabilities, which can lead to spinodal (or pseudo-spinodal [35, 36]) decompositions. The nucleation rate of precipitates is governed by the energy barrier and the atomic attachment rate for forming a critical nucleus that can decrease the total free energy of the system once it grows larger while becomes energetically unfavorable when it shrinks. In classical nucleation theory [6, 7], this atomic attachment rate is closely related to the solute diffusion while the nucleation energy barrier is governed by the bulk energy difference (nucleation driving force, $\Delta G_n$ in Figure 1.2(a)), interfacial energy and contact angles between the precipitate and the
possible heterogeneous nucleation site. The nucleation barrier and the critical nucleus size can be obtained by finding the saddle point on the landscape of the Gibbs free energy difference w.r.t. nucleus geometry, as illustrated in Figure 1.2(b). This theory assumes the critical nucleus already possesses the equilibrium solute composition and crystal structures of the precipitate phase, while in realistic cases, multiple transition or intermediate states are possible along the nucleation path, and the nucleation path with the lowest nucleation barrier is the most likely one to happen. The growth rate of the precipitates is mainly governed by the growth driving force ($\Delta G_g$ in Figure 1.2(a)), and the energy barriers of atomic diffusion and interface migration, which, as discussed above, can be anisotropic and depending on the detailed interface structures.

![Diagram](image)

Figure 1.2 (a) Illustration for the bulk thermodynamic driving force for nucleation ($\Delta G_n$) and growth ($\Delta G_g$) of precipitates. $X_m$ and $X_p$ are the equilibrium solute composition in the matrix and precipitate phase, respectively, obtained by finding the common tangent line of the free energy curves; $X_0$ is the initial composition in the supersaturated matrix. (b) Illustration of the estimation of the nucleation barrier and critical nucleus size of a disk-shaped $\theta'$ precipitate. The red point is the saddle point of the free energy landscape, indicating the nucleation barrier and the critical nucleus size.

### 1.2.2 Governing factors of precipitate hardening effects

The hardening effects of precipitates are related to the possible dislocation-precipitation interaction mechanisms, which are closely related to the morphology and kinetics of precipitates, and are governed by several inter-correlated factors. Imagine a set of dislocation lines passing through a “forest” of precipitates under applied shear stress on the slip plane. Without considering
other defects such as grain boundaries or microcracks, the critical resolved shear stress (CRSS), which is an indicator for the yield strength of the material, can be estimated by the critical shear stress that allows the dislocation lines to fully percolate through the precipitates [37]. Therefore, a series of factors, including the size, shape, volume fraction, spatial distribution, coherency state, and deformation modes of the precipitates, are responsible for the precipitate hardening effects. Below we give a summary of these factors, with focuses on how they affect the precipitation hardening effect and how they are determined by other factors.

(1) The size of the precipitate determines the possible percolating mechanisms of the dislocations: cutting or looping (bowing), as illustrated in Figure 1.3(a-b). According to the classical theory of precipitate hardening [21, 38], the contribution of cutting is proportional to the square root of precipitate radius while that of bowing is inversely proportional to the precipitate radius. Therefore, for smaller precipitates, the bowing effect is dominant; while for larger precipitates, the cutting effect is dominant. A critical precipitate radius may exist to achieve the maximum strength considering the overall effect of these two mechanisms.

The size of precipitates is largely affected by the type and time of the heat treatment. For isothermal aging, the precipitation will undergo nucleation, growth and coarsening, leading to the increase of precipitate size and decrease of number density. The methods to control the precipitate size include controlling the heterogeneous nucleation sites, controlling the heat treatment temperature and time.

(2) The shape, volume fraction and spatial distribution of the precipitate determine its effectiveness in blocking the dislocation motion on the slip plane. Specifically, if the precipitate maximizes its area, e.g., forming a thin plate, on the plane that is perpendicular to the slip plane, the blocking effect is greatly improved [22]. The higher the precipitate volume fraction is, the higher the hardening effect can become. The optimum precipitate spatial distribution should be the one that can trap the dislocations within a closed region to prevent them from passing through the whole precipitation region [22].
The precipitate shape, as discussed above, is affected by the anisotropies in interfacial energy, misfit strains and interface mobility. The volume fraction of the precipitate is not only affected by its phase stability (which indicates its possibility to be replaced by other more stable precipitates) and the initial solute composition (which gives the upper limit of volume fraction according to the lever rule), but also the heat treatment time and temperature. The spatial distribution of the precipitate is affected by the initial distribution of the heterogeneous sites, the initial solute distribution, as well as the interactions among different variants of the precipitate.

The coherency state of the precipitate determines the efficacy of precipitate hardening. The precipitate hardening effect is high when the precipitate remains coherent with the matrix. With the loss of coherency of the precipitate, its resistivity to dislocation motion is impaired due to the increase of precipitate size and change of precipitate shape (usually decreasing the diameter-to-thickness aspect ratio). Moreover, due to the formation of defects at the precipitate/matrix interface, the precipitate itself can become the source of dislocations, which is also detrimental for impeding the dislocation motion.

The coherency state of the precipitate is determined by several factors. Firstly, the lattice matching between the precipitate and the matrix phase determines the initial coherency state of the precipitates. For example, $\gamma'$ precipitates in Ni-Al-based alloys have well-defined OR and LC with the Ni-matrix, and is initially coherent; $\theta'$ precipitates in Al-Cu-based alloys have well-defined lattice matching with Al-matrix on the (001) plane, while the lattice matching along [001] direction is poor, and the precipitate is initially semi-coherent. Secondly, the coherency state of a precipitate typically changes with the size of the precipitate, while the critical precipitate size of the coherency state change is related to the magnitudes of misfit strains, interfacial energies, as well as the configurations of defects (e.g., Burgers vector and spacing of the dislocations) developed at the precipitate/matrix interface [32], since the defect configuration should become energetically favorable, or at least kinetically possible, for the change of coherency state. Thirdly, the detailed coherency loss mechanisms of precipitates in metallic alloys include punching of
dislocation loops, climbing of matrix dislocations and nucleation of dislocation loops inside precipitates [32]. The punching mechanism requires the satisfaction of both the “energy criterion” and the “stress criterion”, both of which depend on the misfit strain values [32]. The climbing mechanism indicates the interaction between the stress fields generated by the precipitate and that generated by the matrix dislocations, which is not only affected by the misfit strain of the precipitate, but also the type and configuration of dislocations [32]. The nucleation mechanism depends on the thermodynamics and crystal structures of the precipitate, since this mechanism is usually realized by the formation of vacancies (i.e., off-stoichiometry) or stacking faults [32].

The deformation modes of the precipitate determine the detailed dislocation reactions or interaction mechanisms when the dislocation interacts with the precipitate. As discussed above, for coherent precipitates, their interaction with dislocations include the cutting and bowing effects. Bowing of dislocations, or Orowan strengthening [21, 38], occurs for strong precipitates that can resist the dislocation penetration (Figure 1.3(b)). The bowing effect is closely related to the precipitate size and works best for small precipitates. On the other hand, the dislocation cutting mechanism (Figure 1.3(a)) has several types [21, 38]: coherency or order hardening, in which the cutting of precipitates by dislocations will lead to the formation of different types of antiphase boundaries; modulus hardening, in which the shear modulus of the precipitate is larger than that of the matrix; chemical hardening, in which more precipitate-matrix interfaces are introduced by the dislocation cutting through the precipitate. For all these cutting mechanisms, the hardening effects are proportional to the square root of precipitate radius [21].

The dislocation-precipitate interaction modes are affected not only by the precipitate size, but also by the specific materials system, the crystal structure of the precipitate and the precipitate/matrix interface structures, which determines the possible types of matrix dislocation, the precipitate/matrix interfacial energy, antiphase boundary energy in the precipitate, the difference between the shear modulus of the precipitate and the matrix, and the resistivity of the precipitate for dislocation penetration.
In summary, considering all these factors, the requirement for achieving optimum precipitation hardening effect includes medium precipitate size (to maximize the overall effect of dislocation bowing and cutting), thin-plate precipitate morphology with the habit plane perpendicular to the slip plane, large precipitate volume fraction, spatial distribution of precipitates that can trap the dislocations into closed regions, and fully coherent precipitates, as summarized in Figure 1.3(c). However, the quantitative evaluation of precipitate hardening effect for a given precipitate microstructure is still lacking, due to the difficulty in accurately considering all these factors in a theoretical model, and the fact that the precipitate microstructure is evolving with time. Therefore, a prerequisite for hardening effect predictions is the accurate prediction of the morphology evolution and kinetics of precipitation.

1.3 Simulations on precipitation

Over the past several decades, experimental investigations have accumulated different aspects of the precipitation “facts” while the more accurate, including quantitative and in situ characterizations of precipitate morphology, kinetics and interaction with dislocations require the advanced characterization techniques, which is usually time-consuming, financially expensive
and technically challenging. On the other hand, with the development of materials theories and corresponding computational frameworks at different time and length scales, the computational methods have become not only the powerful tool for explaining and understanding experimentally observed precipitate phenomena, but also the alternatives of experimental methods for materials properties optimization and alloy design. These computation methods have significantly advanced the scientific research for precipitation.

1.3.1 Atomistic calculations

For example, at atomistic scale, with the help of the first-principles calculations, the formation energy, lattice parameters, elastic constants, surface and interfacial energies of the mechanically stable (no negative phonon modes) precipitate phases can be evaluated at 0 K [40]; these parameters, together with other thermodynamic properties (e.g., thermal expansion, heat capacity, entropy and Helmholtz free energy) can even be calculated at finite temperatures with the help of the Debye model [41], the supercell phonon calculations [42], or with the help of the Monte Carlo simulations [43, 44]. These calculations provide necessary parameters for CALPHAD-based thermodynamic modeling of the metastable precipitate phases, which are usually difficult to evaluate from experiments. These calculations can also provide accurate information for estimating the precipitate morphology, kinetics and hardening effects. In addition, the calculation of stacking fault energy and generalized stacking fault (GSF) energy surface [45, 46] can provide useful guidance for understanding the dislocation-precipitate interactions as well as the possible deformation modes of precipitates under applied external stress. The self- and impurity diffusivities of alloying elements in the matrix phase [47, 48] can also be achieved using first-principles calculations, combining the related frequency models to consider the correlations of atom jump frequencies and the nudged elastic band (NEB) density functional theory (DFT) calculations to estimate the energy barrier for diffusion, which provide useful information for precipitation kinetics. Recently, with the development of data science and machine learning
technologies [49, 50], high throughput DFT calculations have been performed to calculate the energetics of the possible precipitate phases, search for the strengthening precipitates in multicomponent alloys, and find the correlations among solute segregation behaviors at matrix/precipitate interfaces and the potential governing factors, which become powerful tools aiding the understanding of precipitation mechanisms and materials design [51].

Combined with first-principles calculations, the molecular dynamics (MD) method can simulate the nano-scale precipitate-dislocation interactions, evaluate the possible nucleus size and nucleation barrier, and capture the atomic fluctuations during the growth of the precipitate[52]. The kinetic Monte Carlo (KMC) method can predict the formation and evolution of ordered precipitates such as the Guinier-Preston zones (G.P. zone) [53]. The phase-field-crystal (PFC) model [54-56] describes the phase transformation dynamics through an atomically varying order parameter which is related to the atomic density field. It can capture the atomistic scale microstructure features and evolution dynamics, within diffusional time scales. Recently, the PFC model has been extended to realistic materials systems and the early stage clustering during precipitation [57-61].

### 1.3.2 Phase-field simulations

The morphology evolution, kinetics and hardening effects of precipitates typically take place at mesoscale, which, however, is closely related to atomistic scale phenomena. To study the mesoscale precipitation behavior, the phase-field approach [56, 62-67] is a powerful and versatile method. In the phase-field context, a set of phase-field variables are typically used to describe the precipitation microstructure, i.e., to distinguish the matrix phase and the precipitate phase. These phase-field variables can be of conserved nature, such as solute compositions, or non-conserved nature, such as order parameters, which can be related to physical quantities during the phase transformation (e.g., magnitudes of ordering, atomic shuffle, etc.) or just a phase parameter (e.g., phase variables during solidification) [65]. The total free energy of the whole system, including the bulk free energy of each constituent phase, the interfacial energy, and energies related to long-
range interactions such as elastic, dipole and magnetic interactions [65]. The evolution of the phase-field variables is governed by reducing the total free energy of the system until equilibrium (i.e., uniform temperature, pressure, stress and chemical potentials within the system), e.g., Cahn-Hilliard equations [68] for solute compositions due to energy minimization and mass conservation, Allen-Cahn equations [69] for order parameters which assumes a linear relation between the evolution rate and the driving force. A prominent feature of the phase-field approach is that it introduces a “diffuse-interface” description in which the phase-field variables are allowed to vary smoothly across the interfaces, which contribute to the interfacial energy [65]. In contrast to the sharp-interface models where the governing equations of the bulk phases and the interfaces are treated separately, the diffuse-interface phase-field model unifies them into one set of equations. Therefore, in the numerical solutions, the interface positions do not need to be timely tracked in phase-field models, which greatly reduces the computation cost for sharp-interface models. In addition, the phase-field solutions can well converge to the sharp-interface solutions when the thickness of the diffuse interface approaches zero.

![Figure 1.4 Phase-field simulation for θ’ morphology evolution under the effect of different combinations of anisotropies. (a) No anisotropies; (b) only interfacial energy anisotropy; (c) only misfit strain energy anisotropy; (d) the combination of the anisotropies in interfacial energy and misfit strain energy; (e) all anisotropies are considered, including the anisotropies in interfacial energy, misfit strain energy and interface mobility anisotropy; (f) comparison with experimental observations. Adapted from [43] with permission.](image-url)
The phase-field models were independently developed for solidification and solid-state phase transformations. Here we briefly review the phase-field model development for precipitations. Cahn and his co-workers were the first to introduce the phase-field concept into solid state transformations including phase separation and ordering, developing the well-known Cahn-Hilliard [68] and Allen-Cahn equations [69]. Khachaturyan developed the concentration wave theory [18], which later develops into microscopic phase-field models for ordering by solving the Onsager microscopic diffusion equations [18, 70]. Khachaturyan also developed the microelasticity theory [18], which becomes a powerful tool in evaluating the coherency strain energy in phase transformations and is included in phase-field precipitation models. The microscopic phase-field models with a discrete nature were applied to ordered precipitates including $\gamma'$ ($L_1_2$-ordered) in Ni-Al alloys [71], $\gamma''$ ($D_022$-ordered) in Ni-V-X alloys [72], and $D_019$-Ti$_3$Al in Ti-alloys [73]. Although quite a few precipitates are of ordered crystal structures in alloys, there are more precipitates with complicated crystal structures that are distinct from the matrix phase; meanwhile, the simulation size scale of the microscopic phase-field model is rather limited since the atomistic ordered structure needs to be resolved in the simulation; the atomic interaction parameters are also difficult to obtain in real materials systems. To extend the applicability of the phase-field approach in precipitation, Chen et al. [74] introduced the continuous phase-field variables in precipitation [75] and other solid state transformations [76, 77], replaced the Onsager equation with the Cahn-Hilliard and Allen-Cahn equations, and considered the elastic energy contribution according to the microelasticity theory. The precipitate morphology and kinetics during isothermal aging or under applied stress in a series of materials systems have been investigated, including $\delta'$-Al$_3$Li [78-80], Ti$_{11}$Ni$_{14}$ [81-83], $\gamma$'-Ni$_3$Al [84-88], $\gamma$-TiAl [89], O-phase in Ti-Al-Nb [90], $\theta'$-Al$_2$Cu [43, 44, 91-94] and $\gamma$-hydrides in Zr-alloys [95, 96]. To improve the capability of the phase-field approach in modeling precipitate morphology and kinetics in realistic materials systems, Chen’s group was the first to incorporate the CALPHAD-type thermodynamic databases [85] and use first-principles calculations to obtain
necessary input parameters in phase-field simulations [43, 44]. Specifically, experimentally observed $\theta'$ morphology was well reconstructed in phase-field simulations by using first-principles-calculated anisotropic interfacial energies and misfit strains, together with the adjustment of interface mobility [43, 44], as shown in Figure 1.4. The growth kinetics and precipitate interactions of $\theta'$ were thoroughly investigated [92, 97]. The coarsening kinetics of $\gamma'$ was also investigated by three-dimensional (3D) phase-field simulations in Ni-Al and Ni-Al-Mo systems [87, 88]. The nucleation and growth of precipitates under the effect of static dislocations have also been investigated [98, 99]. Recently, Chen’s group also investigated the precipitate morphology and evolution of the metastable $\beta'$ precipitate in Mg-Nd [31] and $\gamma''$ precipitate in IN718 [100] in 3D, with the incorporation of the thermodynamic database and first-principles calculations. The simulation results were in good agreement with experimental observations. In addition to Chen’s group, Wang’s group, is another pioneering group in precipitation modeling. The nucleation, growth and splitting of $\gamma'$ precipitate in Ni-based alloys under different heat treatments [101-103], the co-precipitation of $\gamma'$, $\gamma''$ and $\delta$ in IN718 [104, 105], the precipitation kinetics, habit plane and variant selection of $\alpha$ precipitates in single- and poly-crystalline Ti-alloys with mixed coherency [34, 35, 106-113], the Ni$_4$Ti$_3$ [114] and P-phase [115] precipitation and their effect on martensitic transformations in Ni-Ti-based shape memory alloys and the $\beta'$ and $\beta_1$ precipitation morphology and heterogeneous nucleation on dislocations in Mg-RE alloys [116-119], have been systematically investigated. Wang’s group has also improved the precipitation phase-field models by incorporating the nucleation events [120, 121], investigating the elastic interactions on nucleation [122, 123], increasing the simulation length scales [124], implementing the high interfacial energy anisotropies [125], and considering the heterogeneous nucleation at grain boundaries [126, 127]. In addition, there are increasing research groups focusing on precipitation morphology and kinetics in metallic alloys. The multi-phase-field approach has also been applied to precipitations in different alloy systems [128-131]. Precipitation morphology and kinetics have also been investigated in other alloy systems such as
carbide, bainite and other precipitates in iron and steels [132-141], β-Mg$_{17}$Al$_{12}$ precipitates in Mg-Al-based alloys [142-144], and γ hydrides in Zr-alloys [145-148]. Recently, research efforts have also been devoted to the improvement of the precipitation phase-field model itself, as well as the prediction of precipitation kinetics or the precipitation model. For example, even for the classical θ' precipitates, Liu et al. [149] improved the estimation of Al/θ' misfit strain energy by considering the detailed lattice deformation pathway, and investigated the heterogeneous nucleation of θ' at dislocations; Kim et al. [150] introduced a 4th rank gradient energy tensor and evaluated its values by first-principles calculations to more accurately describe the interfacial energy anisotropy of θ’. DeWitt et al. [151] combined first-principles calculations and phase-field simulations to investigate the misfit-driven β''' precipitate composition and morphology in Mg-Nd alloys, in which β''' is an ordered hierarchy combining β” and β’, with a wide composition range [151, 152].

![Figure 1.5 Phase-field simulations for dislocation-precipitate interactions of γ” in IN718. (a) DFT calculations of the GSF surface of the equivalent (111) plane in γ”. The Burgers vectors of different faults are given. ISF: intrinsic stacking fault; CSF: complex stacking fault; APB: anti-phase boundary; SISF: superlattice intrinsic stacking fault. (b) Phase-field simulation of the interaction between an AC+AB dislocation pair and a γ” variant, under an applied shear stress of 400 MPa along the direction of AC+AB. The dislocation notations in the figure follow the Thompson tetrahedra. Adapted from [153] with permission.](image)

The hardening effects of precipitates can be instantaneously predicted by plugging the phase-field-simulated precipitate volume fractions, number densities and aspect ratios into existing theoretical or analytical strengthening models of given alloys. Although this simple
approach can provide useful estimations for precipitate hardening, the precipitate-dislocation interaction is not explicitly considered, which, however, is a key research topic for understanding and evaluating precipitate hardening effect. To simulate this interaction in phase-field simulations, the first step is to construct a phase-field model for dislocation dynamics [6, 98, 99, 154-157]. The total free energy of dislocations includes the crystalline energy, which is the γ-surface for displacing the atoms with different displacements along different crystalline directions [155]; the gradient energy, which is related to the dislocation core energy and size; the elastic strain energy, in which the misfit strain caused by dislocations is constructed in such a way that the habit plane of the dislocation loops is the slip plane that the dislocation is on [157]. The dislocation dynamics can then be simulated by solving the governing Allen-Cahn equation. With the dislocation phase-field model, not only the effect of static dislocations on solute segregation and precipitate nucleation [98, 154], but also the interaction between the dynamic dislocation and the precipitate under applied stress, can be investigated using phase-field simulations [153]. Wang’s group has actively investigated these micro-deformation mechanisms. For example, rafting of γ’ precipitates under applied loading have been thoroughly investigated in single-crystal Ni-based alloys [158]. The Orowan strengthening of θ’ was investigated in phase-field simulations under different aspect ratio, number density and distributions of the precipitate, with the help of first-principles calculations for the GSF energy of θ’ [37]. The sophisticated deformation mechanisms of γ” in Ni-based superalloys have also been thoroughly investigated combining first-principles calculations and phase-field modeling [153]. The first-principles calculations were used to obtain the detailed GSF potential energy surface on the (111) slip plane in γ” (Figure 1.5(a)), indicating the possible deformation mechanisms including dislocation generation, formation of complicated stacking fault ribbons and dislocations, intrinsic stacking fault shearing and Orowan looping, which were further investigated in phase-field simulations to capture the whole interaction process (Figure 1.5(b)) [153].
1.3.3 Remaining challenges for phase-field precipitation models

The existing phase-field investigations have outlined the basic framework for precipitation modeling, with the necessary input from first-principles calculations or other atomistic scale calculations, the CALPHAD-type thermodynamic and diffusion mobility databases, and sometimes the experimental calibrations. The phase-field simulations have been successful in semi-quantitatively or even quantitatively predicting the precipitate morphology, kinetics and hardening effects, and have been accepted as standard tools for the mesoscale understanding of precipitation phenomena. However, there are still several outstanding issues. (i) The accuracy of the precipitate kinetics prediction is largely dependent on the accuracy of the related kinetic coefficient, including the solute diffusivity and interface mobility, as well as their possible anisotropy. These values, however, are difficult to obtain both experimentally and using computational methods. (ii) A large portion of precipitates in metallic alloys are stoichiometric compounds (i.e., line compounds), with free energy data available only at certain solute compositions, making it difficult to model using the phase-field approach. Although the solubility of these compounds can be considered (i.e., off-stoichiometry), their thermodynamic treatment in phase-field models is still challenging. (iii) Current phase-field precipitation models work well for initially coherent precipitates, while remain challenging for modeling coherency loss, precipitates with limited coherency with matrix, and the precipitate hardening effect of these semi-coherent precipitates. This is due to the complicated precipitate crystal structures, the corresponding poor-defined lattice matching with the matrix, and the complex, irregular precipitate morphology with not only the habit planes but also several facets. (iv) The nucleation kinetics of precipitates, especially the heterogeneous nucleation mechanisms, are difficult to estimate due to the difficulty in estimating the number of heterogeneous nucleation sites in the system, estimation of their respective nucleation barrier, and the difficulty in finding the saddle-point in the free energy-precipitate morphology landscape. (v) The more sophisticated solute-precipitation (i.e., solute segregation at interfaces) and precipitate-dislocation interactions, as well
as the interactions among different types of precipitates in multi-component alloy systems have not been fully understood. (vi) Most of the current phase-field precipitation models evaluate the lattice deformation under small strains and piecewise elasticity, which may not be accurate enough when the deformation (stretch or rotation) is large, where the geometrically nonlinear elasticity theory and plastic deformations should be considered. Therefore, the further improvement and development of the phase-field approach are necessary to resolve these outstanding issues.

1.4 Overview of thesis work

The current thesis work focuses on the derivation of phase-field precipitation models for different thermodynamic descriptions of the precipitate phases, and apply the developed phase-field models to investigate the precipitate morphology evolution, kinetics and hardening effects in a variety of alloy systems, with the aim of improving the capability and accuracy of phase-field models in predicting the precipitation behavior, and providing insights into further development of the phase-field precipitation models. Specifically, we develop a phase-field model for dealing with stoichiometric compounds, which would partially resolve the technical challenge (ii) listed in Section 1.3.3; we also develop and apply a phase-field model for the sequential coherency loss and interface defects development of initially coherent precipitates, which can be considered as a preliminary attempt for resolving the technical challenge (iii) in Section 1.3.3. In addition, the worked examples and related discussions in this thesis work can also provide guidance for resolving the technical challenges (i), (iv) and (v).

The organization of the thesis work is detailed as follows. Chapter 2 gives the detailed derivation of phase-field models, from basic thermodynamic principles, for different thermodynamic descriptions of the precipitate phases including solid solutions, line compounds, parabolic approximations and sub-lattice models, together with the corresponding numerical
algorithms. Applications of these treatments are also given. In Chapter 3 and 4, we apply the phase-field model for predicting precipitate morphology evolution, kinetics and hardening effects of $\beta'$ in Mg-Nd and $\theta'$ in Al-Cu-based alloys, with necessary input information from first-principles calculations, respectively; the simulation results show acceptable agreement with experimental observations. In Chapter 5, we extend the phase-field model for predicting coherency loss and the corresponding dislocation evolution at interfaces, with the application to $\theta'$ in Al-Cu and $\gamma''$ in IN718 alloys. The effect of coherency loss on precipitate hardening is also estimated. In Chapter 6, we apply the phase-field model to investigate the formation of $\alpha$ products during continuous cooling of Ti-6Al-4V alloys under different cooling rates, which show a competition between the diffusional (precipitation) and diffusionless (martensitic transformation) transformation mechanisms. In Chapter 7, we summarize the thesis work with an outlook into future research in precipitation simulations using the phase-field approach.
Chapter 2: Details of the Phase-Field Model for Precipitation

The phase-field approach deals with the evolution of a microstructure, i.e., structural and compositional inhomogeneities, from an initially non-equilibrium state to its thermodynamic equilibrium state under given conditions. The equilibrium condition for second phase precipitations from the supersaturated solid solution matrix phase, under given temperature and pressure, is the uniform distribution of potentials (or intensive thermodynamic variables) including temperature ($T$), pressure ($p$), chemical potential ($\mu$) and stress ($\sigma$) within the whole system. In this chapter, we provide the details of the formulation of phase-field precipitation models.

2.1 General procedures to construct a phase-field model

To describe the precipitation process and the microstructure evolution process to reach the corresponding equilibrium condition, the following general procedure should be considered:

(1) The physical variables describing the different phases and the precipitation microstructures should be identified. These physical variables typically include the solute compositions and structural/ordering order parameters, since the precipitate phases usually have different compositions and crystal structures from the matrix phase.

(2) The governing thermodynamic and kinetic rules/mechanisms of the precipitation process and the related physical variables should be identified. These include the identification of the type of thermodynamic free energies to describe the precipitation process (e.g., Gibbs free energy for given temperature, pressure and composition), the thermodynamic models describing the matrix and precipitate phases and the corresponding expressions for thermodynamic equilibrium; the governing kinetic pathways of the precipitation process and the kinetic rules for the related physical variables, i.e., minimization (for order parameters) or constrained minimization (for
solute composition, under the constraint of mass conservation) of the total free energy of the system. In this work, we consider the precipitation under given $T$ and $p$, and we select the Gibbs free energy to describe the precipitation process.

(3) The related free energies (or extended chemical potentials) should be formulated as functionals of the related physical variables. The free energy includes the contributions from the bulk chemical free energy of each phase, the interfacial energy and the elastic strain energy. In particular, based on the diffuse-interface assumption, a double-well potential of the order parameters and gradient energy terms of order parameters and compositions are introduced to describe the interfacial energy. Through 1-D analytical solutions, the height of the double well and the gradient coefficients can be related to the energy and thickness of the interface. The elastic strain energy is typically formulated to account for the matrix/precipitate misfit strains.

(4) The governing kinetic equations of the physical variables should be formulated according to the identified kinetic rules. Specifically, the Allen-Cahn equation, or the time-dependent Ginzburg-Landau (TDGL) equation, is used to describe the evolution of the order parameters, which are generally non-conserved phase-field variables [69]. The Allen-Cahn equation assumes a linear relation between the evolution rate of the order parameter and the driving force of the precipitation transformation, which is basically an energy minimizer. The Cahn-Hilliard equation, which is an extended version of the diffusion equation, is used to describe the evolution of the solute compositions, under the constraint of mass conservation [68]. This equation ensures the conservation of solute composition by equalizing the composition evolution rate to the divergence of the diffusion flux, whereas the diffusion flux is assumed to be linearly proportional to the driving force of solute diffusion, i.e., the gradient of chemical potential (or chemical potential divided by $T$). The extended chemical potential, which includes the gradient terms of composition, is formulated in the phase-field context. The Cahn-Hilliard equation ensures the uniform chemical potential of each solute at equilibrium, i.e., $\nabla (\mu / T) = 0$. 

In addition of these evolution equations, the mechanical equilibrium is also solved at each evolution time step, under the assumption that the mechanical equilibrium is established much faster than the diffusion-controlled precipitation process.

The specific phase-field formulations depend on the detailed thermodynamic models of the matrix and precipitate phases. The matrix phase is usually treated as a solid solution, and its molar Gibbs free energy, as well as the related chemical potentials of the various alloying elements, is usually formulated according to the regular solution (or extended regular solution) model. There are also occasions where its free energy is formulated according to the sublattice model [159]; for example, in the solid solution of Fe, large atoms such as Cr can substitute the Fe atoms while smaller atoms such as C usually locate in the interstitial sites of the Fe crystal structures: they possess different lattice sites of the crystal, and they are treated in different sublattices. On the other hand, the thermodynamic treatment of the precipitate phase is more complicated, leading to different variations of the corresponding phase-field model. These treatments can be classified into three different types: (i) The precipitate phase also has extensive solubility of the alloying elements, and is also treated as solid solutions using the (extended) regular solution model. This is the case for the α phase in Ti-alloys. (ii) The precipitate phase has limited solubilities on different types of the lattice sites. In this case, its free energy is formulated based on the sublattice model, as a function of site fractions of alloying elements on each sublattice. This case can be converted to the regular solution model if the sublattice is simple and there exists one-to-one relations between the sublattice site fractions and solute compositions. For example, θ-Al₂Cu in Al-Cu alloys is treated using the sublattice model Al₀,₆₆₇(Al,Cu)₀,₃₃₃ [160] where the site fraction of Cu in the second sublattice can be directly converted to the composition of Cu. However, more generally, no direct one-to-one relation exists between sublattice site fractions and solute compositions. In this case, more constraints are required to obtain the equilibrium compositions and site fractions. (iii) The precipitate phase is treated as a stoichiometric compound or line compound, without any solubility beyond the stoichiometry of
the compound. In this case, since the chemical potential of alloying elements in the compound is not defined, the equilibrium condition is the balance of the chemical potentials of the different species in the related precipitation reaction, rather than the uniform distribution of chemical potentials in the system for the above-mentioned two cases. The phase-field model for chemical reactions is more suitable for this case.

In the following sections, we discuss in detail about the related phase-field models for these three different treatments of precipitate phases. For illustration purposes, we give the detailed derivation procedures for binary (solvent A and solute B), two-phase systems (matrix \( \alpha \) and precipitate \( \beta \)) while give the extension results for general multi-component, multi-phase systems.

### 2.2 Precipitate phases treated as solid solutions

We start our discussions for the case where both the matrix and the precipitate phases are treated as solid solutions. We use \( X_A \) and \( X_B \) (in molar ratio, between 0 and 1) to describe the composition variation and an order parameter \( \eta \) to describe the matrix (\( \eta = 0 \)) and precipitate phase (\( \eta = 1 \)). The total free energy of the system \( G \) includes the contribution from the bulk chemical free energy of each phase (i.e., the free energy of a homogeneous phase), the interfacial energy and the elastic strain energy, which is a functional of compositions and order parameters, and can be written as

\[
G = \int \left( g_{ch} + g_{int} + e_{el} \right) dV \tag{2.1}
\]

where \( g_{ch} \), \( g_{int} \) and \( e_{el} \) are the energy densities of bulk chemical free energy, interfacial energy and elastic strain energy, respectively. The chemical free energy density includes the contribution from each phase, which is mixed together by an interpolation function of the phase order parameters. The interfacial energy density includes the double-well-type potential and the gradient energy to account for the inhomogeneous distribution of compositions and order parameters near the phase interfaces and boundaries of domains of the different variants of the
same phase. The elastic energy density considers the effect of applied stress/strain and the effect of a mismatched inclusion, which is formulated according to the microelasticity theory [18] and evaluated under stress equilibrium. Below we provide details for the formulations of these energetics, with an emphasis on the bulk chemical free energies.

2.2.1 Bulk chemical free energy

The bulk chemical free energy density is typically formulated as

$$g_{ch}(X_B, \eta) = \frac{1}{V_m} \left( g^\alpha(X_B) \cdot (1 - h(\eta)) + g^\beta(X_B) \cdot h(\eta) \right)$$

(2.2)

where $V_m$ is the molar volume, $g^\alpha$ and $g^\beta$ are molar Gibbs free energies of the two phases, respectively, which can be written as $g^\phi = \sum_i X_i^\phi \mu_i^\phi$ ($i=A, B; \phi=\alpha, \beta$ in this case) with $X_i^\phi$ being the solute compositions and $\mu_i^\phi$ the chemical potentials of the solutes in each phase, respectively.

If we further write $g_{ch}$ as $g_{ch}(X_B, \eta) = \frac{1}{V_m} \sum_i X_i \mu_i$, we can have two different thermodynamic treatments at the interface: one is the Wheeler-Boettinger-McFadden (WBM) model [161, 162] where $X_i = X_i^\alpha = X_i^\beta$ and $\mu_i = (1 - h(\eta)) \cdot \mu_i^\alpha + h(\eta) \cdot \mu_i^\beta$, i.e., equal solute composition, is assumed, and the other is the Kim-Kim-Suzuki (KKS) model [163, 164] where $X_i = (1 - h(\eta)) \cdot X_i^\alpha + h(\eta) \cdot X_i^\beta$ and $\mu_i = \mu_i^\alpha = \mu_i^\beta$, i.e., equal chemical potential, is assumed. The KKS model can remove the extra potential at the interface and avoid the related issues when the thickness of the interface in the phase-field context is increased, which is more suitable for large-scale calculations. On the other hand, the WBM model works for smaller scale simulations where solute segregation is significant and the quasi-equilibrium condition is not achieved at interfaces.

We specifically focus on the formulations and solutions of the KKS model in this work, since the free energy formulation of the WBM model is quite straight-forward and we aim to extend the simulation size scales. The KKS model requires [164]
\[ X_i = (1 - h(\eta)) \cdot X_i^\alpha + h(\eta) \cdot X_i^\beta \]  

(2.3a)

\[ \bar{\mu}_i = \frac{\partial g^\alpha}{\partial X_i^\alpha} = \frac{\partial g^\beta}{\partial X_i^\beta} \]

(2.3b)

where \( \bar{\mu}_i \) is the diffusion chemical potential for species \( i \), \( X_i^\alpha \) and \( X_i^\beta \) are the solute compositions in each phase, respectively. These constraints require the solution of \( X_i^\alpha \) and \( X_i^\beta \) for given values of \( X_i \) and \( \eta \). The molar Gibbs free energy of a solid solution phase is usually formulated by an extended regular solution model using the Redlich-Kister polynomial [165] to model the excess Gibbs free energy

\[ g^\alpha (X_B^\alpha) = (1 - X_B^\alpha) \cdot \mu_A^{\alpha 0} + X_B^\alpha \cdot \mu_B^{\alpha 0} + RT \left( X_B^\alpha \ln X_B^\alpha + (1 - X_B^\alpha) \ln(1 - X_B^\alpha) \right) 
+ X_B^\alpha (1 - X_B^\alpha) \sum_{j=0}^{d} L_{ij}^\alpha \left( 1 - 2 X_B^\alpha \right)^k \]

(2.4)

where \( \mu_A^{\alpha 0} \) and \( \mu_B^{\alpha 0} \) are the molar Gibbs free energy, or chemical potential, of pure elements A and B with the \( \alpha \) crystal structure, \( L_{ij}^\alpha \) are interaction parameters between A and B in \( \alpha \) solid solution, which measure the deviation of the solid solution to ideal solution. Since Eq. (2.4) is very nonlinear, it is difficult to find analytical solutions to Eq. (2.3). Therefore, we propose to use the Newton-Raphson iterative method to solve Eq. (2.3), via

\[
\begin{pmatrix} X_B^\alpha \\ X_B^\beta \end{pmatrix}^{(n)} = \begin{pmatrix} X_B^\alpha \\ X_B^\beta \end{pmatrix}^{(n-1)} - \begin{pmatrix} \frac{\partial F_1}{\partial X_B^\alpha} & \frac{\partial F_2}{\partial X_B^\alpha} \\ \frac{\partial F_1}{\partial X_B^\beta} & \frac{\partial F_2}{\partial X_B^\beta} \end{pmatrix}^{-1} \begin{pmatrix} F_1^{(n-1)} \\ F_2^{(n-1)} \end{pmatrix}
\]

(2.5)

where \( (n) \) represents the \( n \)-th iteration, \( F_1 = (1 - h(\eta)) \cdot X_B^\alpha + h(\eta) \cdot X_B^\beta - X_B \) and \( F_2 = \frac{\partial g^\alpha}{\partial X_i^\alpha} - \frac{\partial g^\beta}{\partial X_i^\beta} \).

Notably, when Eq. (2.4) is approximated using parabolic functions, i.e., Taylor expansion at the equilibrium compositions under given \( T \) and \( p \) to the 2\(^{nd}\) order, Eq. (2.3) can be solved analytically. The fitted parabolic function \( g^\alpha \) can be expressed as
\[ g_e^\alpha (X_B^\alpha) = A^\alpha + B^\alpha (X_B^\alpha - X_B^{\alpha e}) + \frac{1}{2} C^\alpha (X_B^\alpha - X_B^{\alpha e})^2 \]  

(2.6)

where \( X_B^{\alpha e} \) is the equilibrium composition of B in \( \alpha \) phase, \( A^\alpha = g_e^\alpha (X_B^{\alpha e}) \), \( B^\alpha = \frac{\partial g^\alpha}{\partial X_B^\alpha} \bigg|_{X_B^\alpha=X_B^{\alpha e}} \) and \( C^\alpha = \frac{\partial^2 g^\alpha}{\partial (X_B^\alpha)^2} \bigg|_{X_B^\alpha=X_B^{\alpha e}} \) are the values of \( g^\alpha \), the first derivative and the second derivative of \( g^\alpha \) w.r.t. solute compositions at the equilibrium compositions. Eq. (2.3) can then be analytically solved by

\[
\begin{pmatrix}
X_B^\alpha \\
X_B^\beta
\end{pmatrix} = 
\begin{pmatrix}
1 - h(\eta) & h(\eta)
\end{pmatrix}^{-1} \begin{pmatrix}
X_B \\
C^\alpha & -C^\beta
\end{pmatrix} \begin{pmatrix}
B^\beta - B^\alpha + C^\alpha X_B^{\alpha e} - C^\beta X_B^{\beta e}
\end{pmatrix}
\]

(2.7)

Similar treatment can be extended to general multi-component, multi-phase systems where all the phases are treated as solid solution phases. Considering a system with \( N \) alloying elements and \( M \) precipitate phases. We use \( \{ \eta_j \} \ (j=1, 2, \ldots, M) \) to distinguish the different precipitate phases, and \( X_i^{(j)} \) to represent the solute composition of the \( i \)-th alloying element \((i=1, 2, \ldots, N)\) in the \( j \)-th phase \((j=0, 1, 2, \ldots, M)\), where we use \( j=0 \) to represent the matrix phase. The KKS constraints now become

\[
X_i = \left( 1 - \sum_{j=1}^{M} h(\eta_j) \right) \cdot X_i^{(0)} + \sum_{j=1}^{M} h(\eta_j) \cdot X_i^{(j)}
\]

(2.8a)

\[
\tilde{\mu}_i = \frac{\partial g^{(0)}}{\partial X_i^{(0)}} = \frac{\partial g^{(1)}}{\partial X_i^{(1)}} = \cdots = \frac{\partial g^{(M)}}{\partial X_i^{(M)}}
\]

(2.8b)

with \((M+1)\times N\) unknowns and the same numbers of equations. The iterative solution strategy, extended from Eq. (2.5), now becomes
\[
\begin{pmatrix}
X_1^{(0)} \\
\vdots \\
X_N^{(0)} \\
X_1^{(j)} \\
\vdots \\
X_N^{(j)} \\
X_1^{(M)} \\
\vdots \\
X_N^{(M)}
\end{pmatrix} = 
\begin{pmatrix}
\frac{\partial \tilde{F}_1^{(0)}}{\partial X_1^{(0)}} & \cdots & \frac{\partial \tilde{F}_1^{(0)}}{\partial X_1^{(M)}} & \cdots & \frac{\partial \tilde{F}_1^{(0)}}{\partial X_N^{(M)}} \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
\frac{\partial \tilde{F}_N^{(0)}}{\partial X_1^{(0)}} & \cdots & \frac{\partial \tilde{F}_N^{(0)}}{\partial X_1^{(M)}} & \cdots & \frac{\partial \tilde{F}_N^{(0)}}{\partial X_N^{(M)}} \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
\frac{\partial \tilde{F}_1^{(j)}}{\partial X_1^{(0)}} & \cdots & \frac{\partial \tilde{F}_1^{(j)}}{\partial X_1^{(M)}} & \cdots & \frac{\partial \tilde{F}_1^{(j)}}{\partial X_N^{(M)}} \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
\frac{\partial \tilde{F}_N^{(j)}}{\partial X_1^{(0)}} & \cdots & \frac{\partial \tilde{F}_N^{(j)}}{\partial X_1^{(M)}} & \cdots & \frac{\partial \tilde{F}_N^{(j)}}{\partial X_N^{(M)}} \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
\frac{\partial \tilde{F}_1^{(M)}}{\partial X_1^{(0)}} & \cdots & \frac{\partial \tilde{F}_1^{(M)}}{\partial X_1^{(M)}} & \cdots & \frac{\partial \tilde{F}_1^{(M)}}{\partial X_N^{(M)}} \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
\frac{\partial \tilde{F}_N^{(M)}}{\partial X_1^{(0)}} & \cdots & \frac{\partial \tilde{F}_N^{(M)}}{\partial X_1^{(M)}} & \cdots & \frac{\partial \tilde{F}_N^{(M)}}{\partial X_N^{(M)}}
\end{pmatrix}^{-1}
\begin{pmatrix}
\tilde{F}_1^{(0)} \\
\vdots \\
\tilde{F}_N^{(0)} \\
\tilde{F}_1^{(j)} \\
\vdots \\
\tilde{F}_N^{(j)} \\
\tilde{F}_1^{(M)} \\
\vdots \\
\tilde{F}_N^{(M)}
\end{pmatrix}^{(n-1)}
\]

where \( \tilde{F}_i^{(0)} = \left(1 - \sum_{j=1}^{M} h(\eta_j)\right) \cdot X_i^{(0)} + \sum_{j=1}^{M} h(\eta_j) \cdot X_i^{(j)} - X_i \) and \( \tilde{F}_i^{(j)} = \frac{\partial g_i^{(0)}}{\partial X_i^{(0)}} - \frac{\partial g_i^{(j)}}{\partial X_i^{(j)}} \) (for \( j>0 \)). The analytical solutions to parabolic approximations of \( g_p \) can be obtained similar to Eq. (2.7) The detailed derivation is shown in Appendix A.

### 2.2.2 Interfacial energy

The total interfacial energy \( G_{\text{int}} \) of the system can be written as \( G_{\text{int}} = \gamma \cdot A = \int g_{\text{int}} dV \), where \( \gamma = \int_{-\lambda}^{\lambda} g_{\text{int}} dx \) is the interfacial energy (per unit area, J/m²), \( (2\lambda) \) is the interface thickness and \( A \) is the total area of the interface. The interfacial free energy density \( g_{\text{int}} \) can be formulated according to the diffuse-interface description and the Ginzburg-Landau theory:

\[
g_{\text{int}} = w \cdot \eta^2 (1 - \eta)^2 + \frac{1}{2} \kappa_\eta (\nabla \eta)^2 + \frac{1}{2} \kappa_X (\nabla X) \] ^2
\]

The formulation contains two parts, one is the bulk contributions, which is typically formulated by a double-well potential with a barrier height \( w \); the other is the gradient term of the phase-field variables (compositions and order parameters), which is the energy penalty due to the inhomogeneous distribution of these phase-field variables near interfaces. \( \kappa_\eta \) and \( \kappa_X \) are the gradient coefficients for the order parameter and the composition, respectively. Note that if the system contains multiple compositions and order parameters, the double-well potential should
contain the interaction terms of the order parameters to ensure energy minima in each phase or phase variant; the gradient energy should be the sum of the gradient energies of each composition and order parameter.

The barrier height and gradient coefficients can be related to physical quantities including the interfacial energy $\gamma$ and interface thickness $(2\lambda)$ through 1-D analytical solutions to $\frac{\delta \gamma}{\delta X_B} = 0$, and $\frac{\delta \gamma}{\delta \eta} = 0$, respectively. Specifically, for order parameters,

$$\gamma = \frac{\kappa_{ij} \cdot w}{3\sqrt{2}}$$  \hspace{1cm} (2.11a)

$$\lambda = 2 \sqrt{\frac{\kappa_{\eta}}{w}}$$  \hspace{1cm} (2.11b)

where $\alpha$ is a parameter determining the interface regions. For example, if the interface region is defined as $0.1 \leq \eta \leq 0.9$, $\alpha = 2.2$. For compositions, similar relations can be obtained. Note that since the KKS model removes the excess chemical potential at interfaces, $\kappa_X = 0$, and the gradient terms of compositions are neglected.

The precipitate/matrix interfacial energies can be quite anisotropic depending on the materials systems. To consider this anisotropy, two typical methods are usually adopted. (1) The gradient coefficient is treated as second-order or fourth-order tensors, i.e., $\kappa_{n,ij}$ or $\kappa_{n,ijkl}$, with its component determined by Eq. (2.11) for different interfacial energy values. In this treatment, the interfacial energy is formulated as a smooth, ellipsoidal shape function of the interface orientations without cusps or sharp corners [150]. This treatment works best for coherent precipitates. (2) The gradient coefficient is formulated as a function of the local interface directions, and the function can include sharp corners or cusps [94]. This treatment works best for precipitates with partial coherency.
2.2.3 Elastic strain energy

The elastic strain energy is formulated based on the microelasticity theory [18], which can capture the effect of a misfitted inclusion:

\[ e_{el} = \frac{1}{2} C_{ijkl}(r)(\varepsilon_{ij} + \delta \varepsilon_{ij} - \varepsilon_{ij}^0)(\varepsilon_{kl} + \delta \varepsilon_{kl} - \varepsilon_{kl}^0) \]  

(2.12)

where \( C_{ijkl}(r) \) is a position-dependent elastic stiffness tensor, \( \varepsilon_{ij} \) is the homogeneous strain depending on the applied stress/strain and boundary conditions, \( \delta \varepsilon_{ij} \) is the heterogeneous strain due to local displacement gradient, satisfying \( \int_V \delta \varepsilon_{ij} dV = 0 \), and \( \varepsilon_{ij}^0 \) is the stress-free transformation strain (SFTS), or eigenstrain, due to the lattice mismatch between the precipitate and matrix phases. Given the lattice parameters of each phase, the LC and OR between the crystal structures of the precipitate and matrix phases, \( \varepsilon_{ij}^0 \) can be obtained. The heterogeneous strain \( \delta \varepsilon_{ij} \), defined as

\[ \delta \varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \]

where \( u_i (i=1,2,3) \) are the components of local displacement vector, can then be solved from the mechanical equilibrium condition, \( \sigma_{ij} = 0 \), where

\[ \sigma_{ij} = C_{ijkl}(r)(\varepsilon_{ij} + \delta \varepsilon_{ij} - \varepsilon_{ij}^0) \]

is the local elastic stress.

Specifically, under periodic boundary condition and homogeneous elasticity, the mechanical equilibrium equation can be analytically solved, and the total elastic strain energy \( E_{el} \) can be written as [18]

\[ E_{el} = \int_V e_{el} dV = \frac{V}{2} C_{ijkl} \varepsilon_{ij}^0 \varepsilon_{kl}^0 - V_p C_{ijkl} \varepsilon_{ij}^0 \varepsilon_{kl}^0 + \frac{V_p}{2} C_{ijkl} \varepsilon_{ij}^0 \varepsilon_{kl}^0 - \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} n_i \sigma_{ij}^0 \Omega_{ik} \sigma_{kj}^0 n_i |\theta(k)|^2 \]  

(2.13)

Where \( V \) is the volume of the system, \( V_p \) is the volume of the precipitate phase, \( k \) is the base vector in reciprocal space, \( n_i (i=1,2,3) \) are the component of the unit vectors of the reciprocal space, \( \sigma_{ij}^0 = C_{ijkl} \varepsilon_{kl}^0 \) is the “eigenstress”, \( \Omega_{ik} = (C_{ijkl} n_j n_i)^{-1} \) is the inverse of the Green’s function.
in reciprocal space, and \( \theta(\mathbf{k}) \) is the Fourier transform of the shape function of the precipitate, which satisfies \( V \int_V \theta(\mathbf{r}) \, dV = V_p \). Based on Eq. (2.13), we can further define an elastic interaction potential

\[
B(n) = C_{ijkl} \varepsilon_{ij}^0 \varepsilon_{kl}^0 - n_i \sigma_{ij}^\Omega \sigma_{kl}^\Omega n_l
\]

which is an anisotropic function and indicates the effect of the anisotropies in elastic stiffness and misfit strains on the morphology of the precipitate. For inhomogeneous elasticity cases, the mechanical equilibrium condition can be solved using the iterative-perturbation Fourier spectral method [166-169].

### 2.2.4 Governing kinetic equations

With these energetics and the corresponding driving forces \( \left( \frac{\delta G}{\delta X_B} \right. \) and \( \frac{\delta G}{\delta \eta} \) formulated, the evolution of the phase-field variables can be obtained by solving the governing kinetic equations. Specifically, the Cahn-Hilliard equation is derived from the diffusion equation with an extended chemical potential containing the gradient terms of the composition. Therefore, it is a 4th order partial differential equation in the WBM model (Eq. (2.15a)) while remains 2nd order in the KKS model (Eq. (2.15b)):

\[
\frac{\partial X_B}{\partial t} = \nabla \cdot \left( M \nabla \frac{\delta G}{\delta X_B} \right) = \nabla \cdot \left( M \nabla \left( \frac{1}{V_m} \frac{\partial g_{ch}}{\partial X_B} - \kappa_X \nabla^2 X_B \right) \right)
\]  

\[
\frac{\partial X_B}{\partial t} = \nabla \cdot \left( M \nabla \frac{\delta G}{\delta X_B} \right) = \nabla \cdot \left( M \nabla \left( \frac{1}{V_m} \frac{\partial g_{ch}}{\partial X_B} \right) \right)
\]

where \( M \) is the interdiffusion mobility, which is related to the interdiffusivity \( D \) by

\[
D = M \left( \frac{\partial^2 g_{ch}}{\partial (X_B)} \right)^2
\]

Note that the elastic strain energy density is also a function of composition if
the compositional mismatch strain is considered, which will contribute to an additional \( \frac{\partial e_d}{\partial X_B} \) term in the equations.

The Allen-Cahn equation is used to simulate the evolution of order parameters by assuming a linear relationship between the evolution rate and the driving force. Below is the general form of the Allen-Cahn equation:

\[
\frac{\partial \eta}{\partial t} = -L \frac{\delta G}{\delta \eta} = -L \left( \frac{1}{V_m} \frac{\partial g_{ch}}{\partial \eta} + \frac{\partial g_{int}}{\partial \eta} - \kappa \nabla^2 \eta + \frac{\partial e_d}{\partial \eta} \right)
\]

(2.16)

where \( L \) is a kinetic coefficient related to the interface mobility. Since precipitation is usually a diffusion-controlled process, the value of \( L \) can be estimated using thin-interface analysis under the assumption of infinite interface mobility. Both governing equations can be solved efficiently using the semi-implicit Fourier spectral method [170, 171].

### 2.3 Precipitate phases treated using sublattice models

Now we move to the phase-field model in which the precipitation phase is treated using the sublattice model. This is the case when the precipitate phase has a distinct crystal structure from the matrix phase, with different equivalent lattice sites, and has limited solubility range. The sublattice model reduces to the solid solution model if there exist one-to-one relationships between solute compositions and site fractions of sublattices. However, for general cases, no such relation exists and the Gibbs free energy of the precipitate phase is formulated as a function of site fractions, which adds additional degrees of freedom to the phase-field model. To deal with this situation, either additional order parameters [85] and governing equations [172] should be introduced in the phase-field model, or the free energy should be converted to the function of solute compositions through internal constraints. Within the KKS context, we assume that an internal quasi-equilibrium condition is achieved for alloying elements in each sublattice. In this section, we give the details of this treatment followed by a worked example.
2.3.1 Derivation of the treatment

We illustrate this treatment by considering a precipitate phase $\beta$ with the sublattice model $(A, B)_k(A, B)_l$, with $k+l=1$. The molar Gibbs free energy of the phase has the similar form with Eq. (2.4), but it becomes a function of sublattice site fractions rather than solute compositions. Therefore, the relationship between the solute composition and site fractions in the $\beta$ phase is

$$X_B^\beta = k y_B^I + l y_B^{II} \quad (2.17)$$

where $y_B^I$ and $y_B^{II}$ are site fraction $B$ in the first (I) and the second (II) sublattice, respectively.

Taking derivatives of $X_B^\beta$ on both sides, we obtain

$$k \frac{\partial y_B^I}{\partial X_B^\beta} + l \frac{\partial y_B^{II}}{\partial X_B^\beta} = 1 \quad (2.18)$$

The diffusion chemical potential of $B$ in $\beta$, by considering the relation in Eq. (2.18), is written as

$$\bar{\mu}_B^\beta = \frac{\partial g^\beta}{\partial X_B^\beta} = \frac{\partial g^\beta}{\partial X_B^\beta} \frac{\partial y_B^I}{\partial y_B^\beta} + \frac{\partial g^\beta}{\partial y_B^{II}} \frac{\partial y_B^{II}}{\partial X_B^\beta} = \frac{1}{k} \frac{\partial g^\beta}{\partial y_B^I} + l \frac{\partial g^\beta}{\partial y_B^{II}} \left( \frac{k}{l} \frac{\partial g^\beta}{\partial y_B^{II}} \right) \quad (2.19)$$

At the internal quasi-equilibrium condition, we have $\bar{\mu}_B^\beta = \frac{\partial g^\beta}{\partial X_B^\beta} = \frac{1}{k} \frac{\partial g^\beta}{\partial y_B^I} - \frac{1}{l} \frac{\partial g^\beta}{\partial y_B^{II}}$. Therefore, the KKS constraint becomes

$$X_B = (1-h(\eta)) \cdot X_B^\alpha + h(\eta) \cdot \left( k y_B^I + l y_B^{II} \right) \quad (2.20a)$$

$$\frac{\partial g^\alpha}{\partial X_B^\alpha} = \frac{1}{k} \frac{\partial g^\beta}{\partial y_B^I} - \frac{1}{l} \frac{\partial g^\beta}{\partial y_B^{II}} \quad (2.20b)$$

which can be solved using a similar iterative scheme to Eq. (2.5):
\[
\begin{pmatrix}
X_B^a \\
y_B^l \\
y_B^H
\end{pmatrix}^{(n)}
= 
\begin{pmatrix}
X_B^a \\
y_B^l \\
y_B^H
\end{pmatrix}^{(n-1)}
- 
\begin{pmatrix}
\frac{\partial \tilde{F}_1}{\partial X_B^a} & \frac{\partial \tilde{F}_1}{\partial y_B^l} & \frac{\partial \tilde{F}_1}{\partial y_B^H} \\
\frac{\partial \tilde{F}_2}{\partial X_B^a} & \frac{\partial \tilde{F}_2}{\partial y_B^l} & \frac{\partial \tilde{F}_2}{\partial y_B^H} \\
\frac{\partial \tilde{F}_3}{\partial X_B^a} & \frac{\partial \tilde{F}_3}{\partial y_B^l} & \frac{\partial \tilde{F}_3}{\partial y_B^H}
\end{pmatrix}^{-1}
\begin{pmatrix}
\tilde{F}_1 \\
\tilde{F}_2 \\
\tilde{F}_3
\end{pmatrix}^{(n-1)}.
\]

with \( \tilde{F}_1 = (1-h(\eta)) \cdot X_B^a + h(\eta) \cdot (k y_B^l + l y_B^H) \). The treatment can be extended to multi-phase, multi-component, multi-sublattice cases. We consider \( N \) alloying elements, \( M \) precipitate phases, \( ns(l) \) sublattices for each phase \((l=1,2,...,M)\), each with the stoichiometry of \( k(j,l) \) \((j=1,2,...,ns(l)), l=1,2,...,M)\), and the sum of \( k(j,l) \) equals 1 for each \( l \). Assuming all elements exist in each sublattice, and we denote the site fraction of the \( i \)-th alloying element in the \( j \)-th sublattice of the \( l \)-th phase as \( y_{i(j,l)} \), the corresponding iterative scheme can be obtained, which is provided in detail in Appendix A.

With this treatment, the solute compositions within each phase and site fractions within each sublattice can be obtained, and the formulation of other energetics and evolution equations is the same with that in the solid solution model.

### 2.3.2 Worked examples

In this section, we apply the developed sublattice treatment for \( \beta \)-Mg\(_{17}\)Al\(_{12}\) in Mg-10at.%Al and AZ91 alloys. According to existing thermodynamic optimizations [173], \( \beta \)-Mg\(_{17}\)Al\(_{12}\) in the binary Mg-Al system is treated by the sublattice model Mg\(_5\)(Mg,Al)\(_{12}\)(Mg,Al)\(_{12}\), with

\[
X_{Al}^\beta = \frac{12}{29}(y_{Al}^l + y_{Al}^H)
\]

The molar Gibbs free energies of the \( \alpha \)-Mg matrix \((g_m^a)\) and the \( \beta \) precipitate \((g_m^\beta)\) are given as follows:

\[
g_m^a = \delta_{Al}^{hcp} \cdot X_{Al}^a + \delta_{Al}^{hpb} \cdot (1 - X_{Al}^a) + RT(X_{Al}^a \ln X_{Al}^a + (1 - X_{Al}^a) \ln(1 - X_{Al}^a)) + X_{Al}^a (1 - X_{Al}^a) \left( \delta_{Al,Mg}^L + \delta_{Al,Mg}^{L''} (2X_{Al}^a - 1) + \delta_{Al,Mg}^{L'''} (2X_{Al}^a - 1)^2 \right)
\]

\[
g_m^\beta = \delta_{Al}^p \cdot X_{Al}^\beta + \delta_{Al}^{pb} \cdot (1 - X_{Al}^\beta) + RT(X_{Al}^\beta \ln X_{Al}^\beta + (1 - X_{Al}^\beta) \ln(1 - X_{Al}^\beta)) + X_{Al}^\beta (1 - X_{Al}^\beta) \left( \delta_{Al,Mg}^L + \delta_{Al,Mg}^{L''} (2X_{Al}^\beta - 1) + \delta_{Al,Mg}^{L'''} (2X_{Al}^\beta - 1)^2 \right)
\]
\[ 29g_\beta = y_{Al}\beta y_{Al}\beta ^0 G_{Mg:Al:Al}^\beta + y_{Al}\beta (1-y_{Al}\beta )^0 G_{Mg:Al:Mg}^\beta + (1-y_{Al}\beta ) y_{Al}\beta ^0 G_{Mg:Mg:Al}^\beta + (1-y_{Al}\beta )(1-y_{Al}\beta ) y_{Al}\beta ^0 G_{Mg:Mg:Mg}^\beta \] (2.22b)

\[ +12RT \left( y_{Al}\beta ^0 \ln y_{Al}\beta + (1-y_{Al}\beta ) \ln (1-y_{Al}\beta ) + y_{Al}\beta ^0 \ln y_{Al}\beta + (1-y_{Al}\beta ) \ln (1-y_{Al}\beta ) \right) \]

\[ + (1-y_{Al}\beta ) y_{Al}\beta L_{Mg:Al:Al:Mg}^\beta + (1-y_{Al}\beta ) y_{Al}\beta L_{Mg:Mg:Al:Mg}^\beta \]

where the temperature-dependent lattice stability of the pure elements \((^0 G_{Al}^{hcp}, ^0 G_{Mg}^{hcp})\) and end members \((^0 G_{Mg:Al:Al}^\beta, ^0 G_{Mg:Al:Mg}^\beta, ^0 G_{Mg:Mg:Al}^\beta, ^0 G_{Mg:Mg:Mg}^\beta\)\), as well as the interaction parameters \((^0 L_{Al:Mg}^\alpha, ^1 L_{Al:Mg}^\alpha, ^2 L_{Al:Mg}^\alpha, ^0 L_{Mg:Al:Al:Mg}^\beta, ^0 L_{Mg:Mg:Al:Mg}^\beta\)\), are taken from [173].

Figure 2.11 - D phase-field simulations of the growth of \(\beta-Mg_{17}Al_{12}\) in \(Mg-10at.\%Al\), using the developed sublattice treatment. (a) Composition profile; (b) profile of the sublattice site fractions. The numbers on the right-hand-side of the figure are equilibrium values from thermodynamic calculations. The black-dashed-line indicates the approximated interface position.

To validate the developed treatment in Section 2.3.1, we perform 1-D simulations for an \(Mg-10at.\%Al\) alloy at \(T=500\) K. The whole system is discretized into 1024 grids with a uniform grid size of 1nm. Periodic boundary condition is used so that the governing equations can be solved using semi-implicit Fourier spectral method. We assume there is a small \(\beta\) nuclei (8 nm in length) at the center of the system \((\eta=1, X_{Al}=12/29)\) while the rest of the system is the \(\alpha\) phase \((\eta=0, X_{Al}=0.1)\). The iterative scheme Eq. (2.21) is used at each evolution step to obtain the Al composition in each phase, together with the site fractions of Al in each sublattice of the precipitate phase. The simulated composition profiles are given in Figure 2.1, together with the
corresponding equilibrium values from thermodynamic calculations. As shown in Figure 2.1 (a),
the overall Al composition, which is the mixture of the composition of the two phases via Eq.
(2.20a), shows the typical diffusional profile, whereas the composition profile for each phase,
$X_{\alpha}^\alpha$ and $X_{\beta}^\beta$, first reach the equilibrium values (0.03347 and 0.41363, respectively) inside the
precipitate phase; these profiles will finally reach their respective equilibrium values in both
phases at equilibrium, when the precipitate phase reaches its equilibrium volume fraction
predicted by the lever rule. Similarly, in Figure 2.1 (b), the sublattice site fractions of Al will first
reach the equilibrium values inside the precipitate phase. The thermodynamic calculations and
phase-field simulations both indicate that Al is preferred to stay in the third sublattice with a
much higher equilibrium site fraction (0.98155). The example shows the good agreement of the
developed phase-field sublattice treatment with thermodynamic calculations, indicating its
accuracy in predicting the final equilibrium state.

2.4 Precipitate phases as line compounds

We now consider another interesting case, where the precipitate phase is treated as a line
compound or stoichiometric compound, where the Gibbs free energy of the precipitate phase only
exist at a fixed composition, i.e., its stoichiometry. Since the chemical potential of alloying
elements is not defined in the line compound, and the free energy of the line compound is not a
continuous function of composition, this case is difficult to deal with using the conventional
phase-field model for precipitation. As a compromise, the free energy of the line compound is
usually extended to other compositions by extrapolation, assumption or fitting [92]. For example,
the free energy of the stoichiometric precipitate phase can be approximated by a parabolic
function according to Eq. (2.6), with $X_{B}^{\beta\alpha}$ being its stoichiometry, $A$ being its Gibbs free energy
value while $B$ and $C$ are taken from the corresponding values of the matrix phase. To more
accurately construct the free energy, DFT calculations have been performed to calculate the
energetics of the slightly off-stoichiometric compounds with the same crystal structure as the line
compound, and fit the calculation results into a narrow parabolic function [31]. Although strictly speaking, any compounds can become off-stoichiometric, the line compound model is still widely used due to the rather limited solubility range in the compound, and the difficulty in experimentally or computationally determine the solubility range. Therefore, a phase-field model capable of dealing with the line compound can be quite useful, and can be extended to other similar problems.

### 2.4.1 Model derivation

We consider the precipitation of a line compound as a chemical reaction [174]. Rather than obtaining uniform chemical potential of alloying elements within the system under given $T$ and $p$ at equilibrium, the thermodynamic equilibrium condition involving chemical reactions is the balance of chemical potentials according to the stoichiometry. For illustration purposes, we consider the precipitation of a line compound $A_aB_b$ (β phase) from the supersaturated binary solid solution of B in A (α phase). The chemical reaction proceeds as

$$
\frac{a}{a+b} A + \frac{b}{a+b} B \rightarrow \frac{1}{a+b} A_aB_b,
$$

and the corresponding equilibrium condition becomes

$$
\frac{a}{a+b} \mu_A^\alpha + \frac{b}{a+b} \mu_B^\alpha = \frac{1}{a+b} \mu_{A_aB_b}^\beta.
$$

The precipitation process involves the chemical reaction to form the stoichiometric compound and the diffusion of alloying elements in the solid solution phase. To figure out the interactions between these two processes, we derive the evolution equations by considering an infinitesimal region in the system involving both phases, and track the change of species in this region within an infinitesimal time period $dt$, as illustrated in Figure 2.2.
Figure 2.2 Illustration of the system with both the chemical reaction to form line compounds ($\beta$) and the solute diffusion in the matrix phase ($\alpha$). An infinitesimal representative volume is selected, with length $dx$ along the x-axis and surface area $S$ perpendicular to the x-axis. $J_A^{in}$ and $J_B^{in}$ are the x-components of diffusion fluxes of A and B elements into the representative volume; $J_A^{out}$ and $J_B^{out}$ are the x-components of diffusion fluxes of A and B elements out of the representative volume.

Here, the length of the region is $dx$, the area of the surface where fluxes come in is $S$, the fluxes of the two elements come into the region are $J_A^{in}$ and $J_B^{in}$, respectively, while the fluxes of the two elements come out of the region are $J_A^{out}$ and $J_B^{out}$, respectively. Assuming at $t=0$, the total amount of element A and B in the system is $N_A^0$ and $N_B^0$, while the total amount of the stoichiometric $\theta'$ phase is $N_{A_0B_0}^0$ (all in mol, here we do not consider the amount of A and B inside $\theta'$ at $t=0$). Within the time period $dt$, the net change of each species includes the change due to both chemical reactions and diffusion fluxes. Assuming the reaction always follow the stoichiometry, then for every newly formed $n$ mol $A_aB_b$, there are $a\times n$ mol A and $b\times n$ mol B consumed. Therefore, at $t=dt$, the total amounts of A atoms, B atoms and $A_aB_b$ compounds within the system are calculated respectively as:

$$N_A = N_A^0 - a \cdot d\xi - (J_A^{out} - J_A^{in}) \cdot dt \cdot S \quad (2.23a)$$

$$N_B = N_B^0 - b \cdot d\xi - (J_B^{out} - J_B^{in}) \cdot dt \cdot S \quad (2.23b)$$
\[ N_{A_B} = N^0_{A_B} + d\xi \]  

(2.23c)

where \( \xi \) is the extent of chemical reactions (in mol) and \( d\xi \) is the amount of the newly formed A\textsubscript{s}B\textsubscript{s} phase. Applying the differential operator of the equations on both sides, we obtain:

\[ dN_A = -a \cdot d\xi - dJ_A \cdot dt \cdot S \]  

(2.24a)

\[ dN_B = -b \cdot d\xi - dJ_B \cdot dt \cdot S \]  

(2.24b)

Dividing both sides by the volume of the region \( S \cdot dx \), we obtain the change rates of the concentration \( c_A, c_B \) of each species:

\[ \frac{\partial c_A}{\partial t} = -a \cdot \frac{\partial \xi}{\partial t} - \nabla \cdot J_A \]  

(2.25a)

\[ \frac{\partial c_B}{\partial t} = -b \cdot \frac{\partial \xi}{\partial t} - \nabla \cdot J_B \]  

(2.25b)

Assuming a linear chemical reaction kinetics, i.e., the chemical reaction rate is linearly proportional to the driving force of chemical reaction, through a kinetic coefficient \( L_R \), we further have:

\[ \frac{\partial \xi}{\partial t} = L_R \frac{a}{a+b} \frac{\mu_A}{a+b} \frac{b}{a+b} \frac{\mu_B}{a+b} - \frac{1}{T} \mu_{A_B} \]  

(2.26)

Now we extend the governing kinetic equations Eq. (2.25) and Eq. (2.26) into phase-field models since these equations do not contain the diffuse-interface description and is of sharp-interface nature [175-177]. Assuming the molar volume of atoms in A, B and A\textsubscript{s}B\textsubscript{s} are the same, \( V_m \), then \( c_A = X_A/V_m, c_B = X_B/V_m \), where \( X_A \) and \( X_B \) are the atomic ratio of A and B, respectively; we further define an order parameter, \( \eta \), ranging from 0 (matrix phase) to 1 (precipitate phase), to be the normalized extent of the chemical reaction, so that \( \xi = \eta / (a+b) V_m \). To describe the diffuse matrix/precipitate interface, we formulate the interfacial energy according to Eq. (2.10). The
driving force of the chemical reaction, i.e., the chemical affinity \( \frac{a}{a+b} \mu_A + \frac{b}{a+b} \mu_B - \frac{1}{a+b} \mu_{A_2B_3}, \)
is multiplied by an interpolation function \( h(\eta) \). Therefore, the Allen-Cahn equation can be formulated according to Eq. (2.26):

\[
\frac{\partial \eta}{\partial t} = -L_r \left( \frac{\partial h}{\partial \eta} \left( \frac{a}{a+b} \mu_A + \frac{b}{a+b} \mu_B - \frac{1}{a+b} \mu_{A_2B_3} \right) + \frac{\partial g_{\text{int}}}{\partial \eta} - \kappa \eta \nabla^2 \eta \right)
\]  

(2.27)

Here we select \( h(\eta)=6\eta^5-15\eta^4-10\eta^3 \) according to the thin-interface analysis. The kinetic coefficient \( L_r \) is related to \( L_R \). We further convert the diffusion equations Eq. (2.25) into lab reference frame, and consider the fact that \( X_A+X_B=1 \). Therefore, we have the Cahn-Hilliard equation

\[
\frac{\partial X_B}{\partial t} = -\frac{a}{a+b} \frac{\partial \eta}{\partial t} + \frac{1}{V_m} \nabla \cdot M \nabla \tilde{\mu}
\]  

(2.28)

where \( M \) is the interdiffusion mobility and \( \tilde{\mu} \) is an extended diffusion chemical potential, \( \tilde{\mu} = \mu_B - \mu_A - \kappa \chi \nabla^2 X_B \). Note Eq. (2.28) contains a source term \( -\frac{a}{a+b} \frac{\partial \eta}{\partial t} \) compared with conventional Cahn-Hilliard equations, which is the effect of chemical reaction. The effect of elastic strain energy can also be considered into the equations according to the formulations in previous sections.

### 2.4.2 Worked examples

In this section, we apply the line compound model to \( \theta'\)-Al\(_2\)Cu, with the consideration of the chemical reaction \( \frac{2}{3} Al(\alpha) + \frac{1}{3} Cu(\alpha) \rightarrow \frac{1}{3} Al_2Cu(\theta') \), i.e., \( a=2 \) and \( b=1 \) in Eq. (2.27) and Eq. (2.28).

We start our simulation by obtaining the necessary chemical potentials of the species (Al, Cu and \( \theta'\)-Al\(_2\)Cu) from existing thermodynamic databases, as listed below (in J/mol):

\[
\mu_{Al}^{\alpha} = RT \ln(1-x_{Cu})
\]

(2.29a)
\[
\mu_{Cu}^e = RT \ln x_{Cu} + (1-x_{Cu}) \left\{ (-24085-18.19T) + (40399.8-3.91T)(1-2x_{Cu}) \right\} +(-19683+16.07T)(-1+3(1-2x_{Cu})^2)/2
\] (2.29b)

\[
\mu_{Al,Cu} = -10245.8 + 0.0579T
\] (2.29c)

We then perform 1-D simulations for an Al-10at.%Cu alloy to validate the equilibrium state and analyze the precipitate growth kinetics, without considering the elastic effect. The whole system is discretized into 1024 grids with a uniform grid size of 1nm. Periodic boundary condition is used so that the governing equations can be solved using semi-implicit Fourier spectral method. We assume there is a small \(\theta'\) nuclei (4 nm in length) at the center of the system \(\eta=1\) while the rest of the system is the \(\alpha\) phase \(\eta=0, X_{Cu}=0.1\). We first perform the simulation at \(T=463\ K\) for the semi-coherent interface to investigate the growth kinetics of \(\theta'\). As shown in Figure 2.3, start from a sharp Al/\(\theta'\) interface, the diffuse-interface profile can be achieved and maintained during the growth of \(\theta'\). The evolution of the \(\theta'\) volume fraction (Figure 2.3(b)) indicates the diffusion-controlled growth kinetics, and the final equilibrium volume fraction is quite consistent with the lever rule prediction. The Cu composition evolution shown in Figure 2.3(a) indicates that the equilibrium Cu composition, consistent with that directly calculated from the balance of chemical potentials, is firstly achieved inside \(\theta'\) and finally achieved throughout the system at equilibrium. This indicates that the solution to Eq. (2.28) itself could not maintain the conservation of Cu composition since it only represents the Cu composition in the matrix; on the other hand, \((X_{Cu}+1/3\eta)\) is conserved throughout the simulation since it represents the realistic Cu distribution during the chemical reaction.
Figure 2.3 Precipitation growth kinetics of θ’ predicted from the phase-field model for precipitation of line compounds at T=463 K. (a) Evolution of Cu composition; (b) evolution of order parameter; (c) evolution of θ’ volume fraction. The red-dashed-line in (c) indicates the equilibrium volume fraction from lever rule predictions.

Figure 2.4 Dissolution kinetics of θ’ predicted from the phase-field model for precipitation of line compounds at T=800 K. (a) Evolution of Cu composition; (b) evolution of order parameter; (c) evolution of θ’ volume fraction. The arrow in (b) indicates the interface moving direction. The red-dashed-line in (c) indicates the equilibrium volume fraction from lever rule predictions.

With these findings, we further perform the 1-D simulations for the dissolution of θ’. We start our simulation from the final equilibrium profile of \( X_{Cu} \) and \( \eta \) obtained at \( T=463 \) K, and “heat up” the system by setting the simulation temperature at \( T=800 \) K. As obtained from thermodynamic calculation, this change of temperature will increase the Cu solubility in the matrix from 0.173% (463 K) to 4.49% (800 K), leading to a 10.5% decrease in equilibrium volume fraction of θ’. This decrease is verified by the simulation results in Figure 2.4. Therefore, the line compound model can capture both the growth and dissolution of the precipitates.
2.5 List of general assumptions

In this section we list all the assumptions we made, together with related rationale, for the phase-field models and related simulations on precipitation in this dissertation.

(1) Stress equilibrium is assumed to be established much faster than any phase transformation process. Therefore, at each evolution time step of the Allen-Cahn and Cahn-Hilliard equations, we solve the mechanical equilibrium equation.

(2) Although the STFS or eigenstrains caused by precipitation are plastic strains, we still assume a linear elastic constitutive relation, and the elastic strain is calculated by $\varepsilon_{ij} = \delta_{ij} - \varepsilon_{ij}^0$. Meanwhile, although the finite strain theory is sometimes used in calculating the SFTS tensor, the simulation mesh is assumed undeformed. The consideration of the elasto-plastic constitutive relation and full geometric nonlinearity (i.e., large deformation) caused by precipitation will be investigated in our future work.

(3) Although the temperature-dependent bulk free energies and diffusivities are generally considered based on existing thermodynamic and diffusion mobility databases, we assume the interfacial energies, elastic constants and misfit strains (except in Chapter 6) are temperature-independent, since the temperature dependence of these physical quantities are usually lacking. Meanwhile, we assume homogeneous elasticity, i.e., the matrix and precipitate phases have the same elastic moduli. This is based on the fact that the volume fractions of precipitates we are investigating are relatively low while the iterative elastic solver to the mechanical equilibrium equation is rather time-consuming.

(4) The phase transformation kinetics is assumed linear. For example, the Allen-Cahn equation assumes a linear relationship between the rate of change of the order parameters and the driving force for phase transformation; the Cahn-Hilliard equation assumes a linear relationship between the diffusion flux and the driving force for diffusion. This linear kinetics is acceptable for phase transformations not too far away from the equilibrium points.
We assume equal diffusion chemical potential at interfaces (i.e., the KKS model). This is because for diffusion-controlled precipitation process, the kinetics near interfaces are much faster so that the quasi-equilibrium condition is satisfied faster near interfaces than in the bulk.

2.6 Summary

In summary, we provide the detailed formulations of precipitation phase-field models for different thermodynamic treatments of the precipitate phase. The table below (Table 2.1) summarizes the corresponding treatments, as well as the corresponding examples to be provided in the following chapters.

<table>
<thead>
<tr>
<th>Thermodynamic model of the precipitate phase</th>
<th>Corresponding treatments in the phase-field model</th>
<th>Worked examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid solution model</td>
<td>KKS model, Eq. (2.9)</td>
<td>α in Ti-6Al-4V, Chapter 6</td>
</tr>
<tr>
<td>Line compounds</td>
<td>Chemical reaction model, Eq. (2.26) and Eq. (2.27)</td>
<td>θ’ in Al-Cu, Chapter 2</td>
</tr>
<tr>
<td></td>
<td>Parabolic fit according to DFT calculations of the energetics of the off-stoichiometric compounds</td>
<td>β’ in Mg-RE, Chapter 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>θ’ in Al-Cu-Si, Chapter 4</td>
</tr>
<tr>
<td>Sublattice model</td>
<td>KKS model, Eq. (2.21)</td>
<td>γ’ and γ” in IN718, Chapter 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>β in Mg-Al, Chapter 2</td>
</tr>
</tbody>
</table>
Chapter 3: Predicting Precipitate Morphology, Kinetics and Hardening Effects in Mg-RE Alloys

3.1 Introduction

Magnesium alloys have attracted broad interests and applications for aerospace and automobile industries due to their light weight [21, 178-180]. However, to meet the requirement of high strength and creep resistance in real applications, the strengthening mechanisms and effects should be thoroughly investigated. The poor yield strength and creep resistance of Mg-alloys can be related to the ease of dislocation motions on the (0001) basal planes [21, 22, 178-181]. To overcome this issue, increasing efforts have been made during the past decades to introduce multiple strengthening mechanisms through alloying [21, 179, 180]. Among the different alloying elements, the rare earths (RE) can be ideal candidates due to the formation of plate-shaped Mg$_x$RE$_y$ precipitates on $\{10\overline{1}0\}$ and/or $\{11\overline{2}0\}$ prismatic planes of the Mg matrix [21, 22, 178, 181-187], which can effectively block the dislocation motion on basal planes. Figure 3.1(a) shows the aging curves of different types of Mg-alloys[21]. It is clearly shown that the hardening effects of Mg-RE alloys are significant even with relatively small amounts of alloying elements. Figure 3.1(b) illustrates the contribution of different strengthening mechanisms in Mg-alloys, estimated from a theoretical model [188], showing the dominance of precipitate hardening in the overall hardening effect of Mg-alloys.
Figure 3.1 Precipitate hardening effect in Mg-alloys. (a) Aging curves of multiple Mg-alloys; (b) theoretically calculated individual contribution to yield strength in AZ91, showing the significant of precipitate hardening of Mg17Al12. Adapted from [188] with permission.

There have been extensive experimental studies on the microstructure-mechanical properties relationships of Mg-RE alloys, since the precipitate hardening effect is critically related to the precipitate microstructures. The influence of precipitate size, morphology, orientation, and spatial distribution on precipitate hardening has been explored [21, 116-119, 178, 189]. The precipitate morphologies in different types of Mg-RE alloys (RE=Y, La, Ce, Nd, Sm, Gd and Dy) have been carefully characterized using the state-to-art HAADF-STEM. Typically, G.P. zones (or β”/β’’, Mg,RE), metastable β’ (Mg,RE), β1 (Mg,RE) and stable β (Mg41RE5, varies for different systems) precipitates form at different stages during isothermal aging of Mg-light RE (La, Ce, Nd, Sm) alloys, while the G. P. zones are generally replaced by atomic clusters in Mg-heavy RE (Gd, Tb, Dy, Y) alloys [190]. The crystal structures of G. P. zones, β’, β1 and β are identified to be D019-ordered structure (hexagonal), base-centered orthorhombic, face-centered cubic, and tetragonal structures, respectively. Note the crystal structure of β’ in Mg-light RE alloys are two times shorter than that in Mg-heavy RE alloys, and we use β’-short and β’-long to distinguish them, as shown in Figure 3.2. These different structures are also identified as β’F and β’ in some other works [119]. Recent investigations also show that β”-D019 and β’ belong to the same ordering group and are identified as β’’’[151, 152]. The inherent correlation among these different precipitate phases have been investigated using first-principles calculations [40, 119, 152, 190-
The experimental observations indicate that these metastable precipitates generally have prismatic plane habits, and maintain relatively good coherency with Mg matrix. Specifically, $\beta''$ and $\beta_1$ phases form $\{10\overline{1}0\}$ plates or laths, while $\beta'$ forms $\{11\overline{2}0\}$ plates [193]. All these precipitates display prismatic orientations, which can effectively block the dislocation motion on basal planes. The age-hardening response of Mg-RE alloys indicates that $\beta''$ and $\beta'$ are the key strengthening precipitates since they are both present at the peak aging point [193]. To tailor the precipitate microstructures for the desired yield strength, it is critical to identify the governing factors of the precipitate morphology and to understand the structure-property relationship. This process can be achieved through integrated computational approaches, which can not only provide quantitative and fundamental understanding of microstructure evolution, but also simplify the alloy design procedure and reduce the manufacturing cost.

![Figure 3.2](image)

Figure 3.2 $\beta'$-long precipitate in Mg-Gd (a) system and $\beta'$ precipitate Mg-Nd (b) system. The Mg-Gd ($\beta'$-long) precipitate is twice as long as its Mg-Nd ($\beta'$) counterpart. Atoms are colored according to species and whether they lie in the A ($z=0$) or B ($z=0.5$) basal planes.

The mechanical properties of alloys are largely determined by their structure at different length scales, ranging from atomistic-scale crystal structures to nano-scale precipitate morphologies and micro-scale grain structures. Especially, the precipitate hardening effect is
critically related to nano- to micro-scale precipitate structures, which is also related to the atomistic-scale crystal structures and properties of the precipitate phase, the matrix/precipitate interfacial properties and precipitate-dislocation interactions [21]. Therefore, a multi-scale framework, based on the combination of first-principles calculations and phase-field simulations [31, 43, 44] has been proposed to simulate microstructure evolution, in order to understand the structure-property relationship. Specifically, first-principles calculations have already been used to investigate the phase and interface stabilities of β” and β’ phases in Mg-RE systems [31, 40, 190, 192], the solute-vacancy binding [194-196], stability of long-period-stacking-ordered structures [197-199], dislocations and solid-solution strengthening [200-202], impurity diffusivities [48] and Mg/Mg,RE, interfacial energies [6, 31, 117, 190]. The phase-field approach [65], which is a powerful tool in predicting microstructure evolution during phase transformations, has been applied in predicting the precipitate morphologies in Mg-alloys including β’ and β’’’ in Mg-Nd [6, 31, 119, 151], Mg-Y, Mg-Gd [117], β’F in Mg-Nd [119], β₁ in Mg-Nd [118] and Mg-Y-Nd [116], and Mg₁₇Al₁₂ in Mg-Al alloys [142-144].

In this work, we provide the first theoretical investigations on the three-dimensional (3-D) morphologies of β’-Mg-RE precipitates, using a Mg-Nd alloy as a representative for the Mg-light RE alloy systems. The first-principles calculations provide the following fundamental parameters: (i) the formation energy of β’; (ii) the lattice parameters of β’; (iii) the elastic constants for β’ and α-matrix; (iv) the formation energy of the disordered Mg-Nd solid solution using the special quasi-random structure (SQS) approach[203, 204]. 3-D phase-field simulations are then performed to predict the morphology and kinetics of β’ precipitates. The calculated precipitate diameter, thickness and volume fraction are used to predict the precipitate hardening effect due to Orowan looping [205].
3.2 Methodology

3.2.1 First-principles calculations

DFT is used to predict all the necessary inputs for phase-field simulations, as listed in Section 3.1, at 0 K. All DFT calculations are performed using the Vienna Ab-initio Simulation Package (VASP) [206, 207]. Projector augmented wave potentials [208] in the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parameterization [209] is used. All compounds are relaxed with respect to all internal and external degrees of freedom with an energy cutoff of 350 eV and a Γ-centered k-point mesh equivalent to at least 10,000 k-points per reciprocal atom, i.e., a mesh of 9×6×12 for Mg7Nd. A finite-temperature smearing method of first-order Methfessel-Paxton is used, with a smearing width of 0.1 eV and energy convergence criteria of 1 meV/atom. The “f-core potential” is used for the Nd atoms, where the f-electrons are restricted to the core, which can accurately predict the ground state, energetic stability and elastic constants for RE intermetallic compounds[6, 192, 210-215]. The 0 K formation enthalpy per atom is calculated as

\[
\Delta E_f [Mg_x RE_{1-x}] = E[Mg_x RE_{1-x}] - (x \cdot E[Mg] + (1-x) \cdot E[RE])
\]  

(3.1)

where \(x\) is the fraction of Nd in the compound. The calculated formation energies are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg7Nd (β')</td>
<td>-60meV/atom (-5.77kJ/mol-atom)</td>
</tr>
<tr>
<td>Mg7.47Nd (β', slightly Mg-rich)</td>
<td>-52meV/atom (-5.03kJ/mol-atom)</td>
</tr>
<tr>
<td>Mg6.94Nd (β', slightly Nd-rich)</td>
<td>-55meV/atom (-5.34kJ/mol-atom)</td>
</tr>
<tr>
<td>Mg7Nd (hcp SQS)</td>
<td>-16meV/atom (-1.50kJ/mol-atom)</td>
</tr>
<tr>
<td>MgNd (hcp SQS)</td>
<td>-25meV/atom (-2.46kJ/mol-atom)</td>
</tr>
<tr>
<td>MgNd3 (hcp SQS)</td>
<td>-30meV/atom (-2.90kJ/mol-atom)</td>
</tr>
<tr>
<td>Nd (hcp)</td>
<td>+27meV/atom (+2.61kJ/mol-atom)</td>
</tr>
</tbody>
</table>
The calculated lattice parameters of both pure Mg and β'-Mg7Nd, together with available experimental values, are shown in Table 3.2. Specifically, since the orthorhombic β’ crystal structure is a simple decoration of the hcp structure, we use the dimensions of Mg in the orthorhombic unit cell using the experimentally determined OR and LC between these two phases:

\[ a_{Mg} (\text{orthorhombic cell}) = 2a_{Mg}. \]

<table>
<thead>
<tr>
<th>Lattice Constant (Å)</th>
<th>Mg (exp.)</th>
<th>Mg7Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>6.36 (6.4)</td>
<td>7.17</td>
</tr>
<tr>
<td>b</td>
<td>11.05 (11.08)</td>
<td>10.89</td>
</tr>
<tr>
<td>c</td>
<td>5.20 (5.21)</td>
<td>5.11</td>
</tr>
</tbody>
</table>

Finite lattice distortions are performed on each structure to calculate the elastic constants \( C_{ijkl} \), with the corresponding energies calculated using VASP [6, 216, 217]. For each elastic constant, 5 equally spaced deformations are calculated, with two compressive and two tensile, at a step-size of 1.5%. The elastic constants are then calculated according to the fact that the elastic constants are second derivatives of energies with respect to displacements. The calculated elastic constants are used for both the phase-field simulations and the subtraction of misfit strain contributions to interfacial energies in DFT, as shown in Table 3.3. The calculated elastic constants of Mg are used in the phase-field simulations assuming the homogeneous elastic moduli, since the volume fraction of β’ is rather small (<5%).

<table>
<thead>
<tr>
<th>Elastic Constants (GPa)</th>
<th>Mg (exp.)</th>
<th>Mg7Nd (β’)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{11} )</td>
<td>62.6 (63.5)</td>
<td>46.7</td>
</tr>
<tr>
<td>( C_{22} )</td>
<td>62.6 (63.5)</td>
<td>60.5</td>
</tr>
<tr>
<td>( C_{33} )</td>
<td>64.9 (66.4)</td>
<td>72.7</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>26.0 (25.9)</td>
<td>30.7</td>
</tr>
<tr>
<td>( C_{13} )</td>
<td>20.9 (21.7)</td>
<td>28.7</td>
</tr>
<tr>
<td>( C_{23} )</td>
<td>20.9 (21.7)</td>
<td>14.5</td>
</tr>
<tr>
<td>( C_{44} )</td>
<td>13.3 (18.4)</td>
<td>16.4</td>
</tr>
<tr>
<td>( C_{55} )</td>
<td>13.3 (18.4)</td>
<td>33.4</td>
</tr>
<tr>
<td>( C_{66} )</td>
<td>18.3 (18.8)</td>
<td>28.9</td>
</tr>
</tbody>
</table>
The contribution of the coherency strain energy at the precipitate/matrix interface, $\Delta E_{CS}(k, x)$, can be calculated as a function of direction and composition [218],

$$\Delta E_{CS}(k, x) = \min_{a_i} [(1 - x) \cdot \Delta E_{\text{epi}}^{\text{Mg}}(k, a_i) + x \cdot \Delta E_{\text{epi}}^{\beta'}(k, a_i)]$$

(3.2)

where $x$ is the fraction of $\beta'$, $\Delta E_{\text{epi}}^{\text{Mg}}$ is the energy to biaxially deform the material. The coherency strain energy is calculated by minimizing over the composition-weighted sum of the epitaxial strain energy curve to find the common lattice constant $a_i$ at the interface of the two mismatched phases. This minimization is performed over the complete composition range for each interface of interest, (100), (010) and (001) in this work.

The supercells containing slabs of Mg and $\beta'$, with the interfaces of interest, are constructed to calculate the pure chemical contribution of the Mg/$\beta'$ coherent interfacial energies. The constructed supercells are relaxed with respect to all degrees of freedom. The formation energy of the supercell with respect to bulk Mg and $\beta'$ is calculated as:

$$\Delta E_f[\text{supercell}] = E[\text{supercell}] - (E[\text{Mg}_{\text{bulk}}] + E[\beta'_{\text{bulk}}])$$

(3.3)

where $E[X]$ is the total energy of $X$. This formation energy can be further decomposed into two parts: the coherency strain energy and the interfacial energy penalty of the two phases forming bonds across the interface,

$$\Delta E_f[\text{supercell}] = N\Delta E_{CS}(k, x) + 2A\gamma$$

(3.4)

where $N$ is the total number of atoms in the supercell, $\Delta E_{CS}$ is the coherency strain energy per atom, $x$ is the fraction of $\beta'$, $A$ is the area of the interface, and $\gamma$ is the interfacial energy. Figure 3.3 illustrates the 160-atom supercell containing 80 atoms of Mg and 80 atoms of $\beta'$ for calculating the (001) interfacial energy.
Figure 3.3 The Mg and β’ [001] 160 atom interfacial supercell. The dashed lines indicate the two interfaces between the Mg and β’ phases. Atoms are colored according to species and whether they lie in the A (x=0) or B (x=0.5) prismatic planes.

The calculated Mg/β’ interfacial energies are listed in Table 3.4. Based on the results, we find that the (001) interface has the smallest interfacial energy and that (010) interfacial energy is about twice that of (100). We also include the total number of in-basal-plane Mg-RE bonds in β’ that changed to Mg-Mg bonds with the introduction of an interface, since it indicates a linear trend of increasing interfacial energy with increasing number of broken in-basal-plane Mg-RE bonds. This finding highlights the crucial effect of the change of such bonds on the Mg/β’ interfacial energy.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Supercell size</th>
<th>Interfacial Energy (mJ/m²)</th>
<th>In-basal-plane Mg-RE bonds changed into Mg-Mg bond with introduction of interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>160 atoms</td>
<td>64.1</td>
<td>1</td>
</tr>
<tr>
<td>(010)</td>
<td>96 atoms</td>
<td>130.9</td>
<td>2</td>
</tr>
<tr>
<td>(001)</td>
<td>160 atoms</td>
<td>8.5</td>
<td>0</td>
</tr>
</tbody>
</table>

3.2.2 Phase-field model

We consider the isothermal aging of a Mg-0.6at.%Nd alloy at 0 K. The precipitation of the intermetallic β’ from a disordered, supersaturated Mg solid solution is a diffusional process accompanied by structure change. To describe the microstructure, one composition field ($X_{Nd}$)
and three order parameters ($\eta_1$, $\eta_2$, $\eta_3$) are used, where the three order parameters are used to distinguish the three energetically degenerated and crystallographically equivalent $\beta'$ variants. The Kim-Kim-Suzuki (KKS) model is employed to remove the extra interface potential [164]. Following Chapter 2, the total free energy of the system contains the energy contributions from local free energy, gradient energy and elastic strain energy.

The local free energy includes the bulk chemical free energy of each phase and the double-well potential of the order parameters. The bulk free energy of the $\alpha$-Mg solid solution is obtained by fitting the DFT-calculated formation energies of the 16-atom SQS with 0%, 25%, 50%, 75% and 100% Nd into a parabolic function (in kJ/mol):

$$g^\alpha(X_{Nd}^\alpha) = 4.2497(X_{Nd}^\alpha - 0.8292)^2 - 2.9226$$

(3.5)

The bulk free energy of the $\beta'$ phase is obtained by fitting the DFT-calculated formation energies of the stoichiometric and off-stoichiometric $\beta'$ structures into a parabolic function (in kJ/mol):

$$g^{\beta'}(X_{Nd}^{\beta'}) = 12298(X_{Nd}^{\beta'} - 0.1259)^2 - 5.7959$$

(3.6)

The DFT calculation points of formation energies and parabolic fitting are shown in Figure 3.4. The complete form of the bulk chemical free energy density is expressed as:

$$g_A(X_{Nd}, \{\eta_1, \eta_2, \eta_3\}) = \frac{1}{V_m}\left(g^\alpha(X_{Nd}^\alpha) \cdot (1 - \sum_{i=1}^{3} h(\eta_i)) + g^{\beta'}(X_{Nd}^{\beta'}) \cdot \sum_{i=1}^{3} h(\eta_i)\right)$$

(3.7)

where $h(\eta) = 3\eta^2 - 2\eta^3$ is an interpolation function, $V_m = 10^{-5}$ m$^3$/mol is the molar volume. The parabolic approximation of formation energies allows for the analytical solution of the Nd compositions in each phase according to Eq. (2.7).
Figure 3.4 DFT-calculated formation energy and fitted formation energy functions for Mg and β’

The Mg/β’ interfacial energy can be modeled by a gradient term describing the part of interfacial energies related to the inhomogeneous distribution of phase-field variables near interfaces, and the double-well potential $g_{dw} (\{\eta_i\}) = w \cdot \left( \sum_{i=1}^{3} \eta_i^2 (\eta_i - 1)^2 + \sum_{i \neq j} 5 \eta_i^2 \eta_j^2 \right)$, where $w$ is the height of the double well. Based on 1-D analytical solutions of the phase-field equations, the anisotropic gradient coefficients and the double-well barrier height can be obtained from the interfacial energy ($\gamma$) and interface thickness ($2\lambda$) values, according to Eq. (2.11). Due to the highly anisotropic interfacial energies (Table 3.4), we use anisotropic gradient coefficients, which are represented in tensor form, $\kappa_{ij}$. Based on the DFT-calculated interfacial energies of the (100), (010) and (001) interfaces, as well as the estimated interface thickness for the (001) interface (0.25nm), the anisotropic gradient coefficient tensor can be obtained (unit: $2 \times 10^{-9}$ J/m):

$\kappa_{ij} (1) = \begin{pmatrix} 0.062 \\ 0.257 \\ 0.001 \end{pmatrix}, \kappa_{ij} (2) = \begin{pmatrix} 0.208 & -0.084 \\ -0.084 & 0.111 \\ 0.001 \end{pmatrix}, \kappa_{ij} (3) = \begin{pmatrix} 0.208 & 0.084 \\ 0.084 & 0.111 \\ 0.001 \end{pmatrix}$
The elastic strain energy is evaluated based on Khachaturyan’s microelasticity theory\cite{18}, as given in Eq. (2.12). As a key factor governing the precipitate morphology, the stress-free transformation strain (SFTS) \( \varepsilon_{ij}^0 \) is caused by the lattice mismatch between the precipitate and matrix phases. According to the experimentally observed OR (100)\( _{\beta'} \parallel (11\overline{2}0)\_a \), [001]\( _{\beta'} \parallel [0001]_a \) and LC \( a_{\beta'} \sim 2a_a, b_{\beta'} \sim 2\sqrt{3}a_a, c_{\beta'} \sim c_a \) \cite{193}, under the assumption that the Mg/\( \beta' \) interface is fully coherent \cite{193}, the deformation gradient tensor can be obtained by

\[
F = \begin{pmatrix}
\frac{a_{\beta'}}{2a_a} & 0 & 0 \\
0 & \frac{b_{\beta'}}{2\sqrt{3}a_a} & 0 \\
0 & 0 & \frac{c_{\beta'}}{c_a}
\end{pmatrix}
\]  

The SFTS of variant 1 of \( \beta' \), \( \varepsilon_{ij}^{00}(1) \), is then calculated by \( \varepsilon_{ij}^{00}(1) = \frac{F^T F - I}{2} \); the SFTS for the other two variants can be achieved by the 3-fold rotational symmetry operations:

\[
\varepsilon_{ij}^{00}(1) = \begin{pmatrix} 0.1355 \\ -0.0144 \\ -0.0172 \end{pmatrix}, \varepsilon_{ij}^{00}(2) = \begin{pmatrix} 0.0231 & -0.0649 & 0.098 \\ -0.0649 & 0.098 & -0.0172 \\ 0.0231 & 0.0649 & -0.0172 \end{pmatrix}, \varepsilon_{ij}^{00}(3) = \begin{pmatrix} 0.0231 & 0.0649 & -0.0172 \\ -0.0649 & 0.098 & -0.0172 \\ 0.0231 & 0.0649 & -0.0172 \end{pmatrix}
\]

The evolution of the precipitate microstructures is achieved by solving the governing Cahn-Hilliard (for the conserved composition field \( X_{\text{Nd}} \))\cite{68} and Allen-Cahn (for the non-conserved order parameters)\cite{69} equations. The inter-diffusion mobility \( M \) is estimated from the impurity diffusivity of Nd in Mg. The kinetic coefficient \( L \) is estimated under the assumption that the precipitation is diffusion-controlled. The equations are solved using the semi-implicit Fourier spectral method \cite{170, 171} in reduced units, with normalization factors of \( E=2 \) GPa and \( l_0=1 \)nm. Since the value of Nd diffusivity has not yet been reported, we use reduced time scales in the
simulation. Note this reduced time scale \( (\Delta t^*) \) can be converted to real time scale \( (\Delta t) \) by 
\[
\Delta t = \frac{t_0}{D_{\text{Nd}}} \cdot \Delta t^*
\]
once \( D_{\text{Nd}} \) becomes available. The system size for simulation is 128×128×128 grids for 3-D single particle simulations and 200×200×200 grids for multi-particle simulations, with grid spacing of 0.25 nm.

### 3.3 Phase-field simulations of precipitate morphology

We start our simulations with one spherical \( \beta' \) precipitate with a radius of 3 nm to investigate the effect of the different energy anisotropies and related energy values on the precipitate morphology evolution. The interfacial energy and elastic strain energy have different effects on \( \beta' \) morphologies. If interfacial energy is the only governing factor, the resulting \( \beta' \) morphology would be a plate on \( (001) \) plane according to the Wulff construction\[16, 17, 219\], since the \( (001) \) plane has the lowest interfacial energy. However, if the elastic strain energy is the only governing factor, the precipitate would form a thin plate on the plane that can minimize the elastic interaction potential \( B(n) \)[18] in Eq. (2.14). Using the DFT-calculated elastic constants of pure Mg and the SFTS of a \( \beta' \) variant, this habit plane can be one of the following four options: 

\[
(0.93, 0.08, 0.36), (0.93, 0.08, -0.36), (0.93, -0.08, 0.36), (-0.93, 0.08, 0.36)
\]

The situation becomes rather complicated when these two factors coexist. Therefore, we design a series of controlled phase-field simulations, each with a spherical \( \beta' \) variant in the middle of the system: (i) only the anisotropic elastic strain energy is considered, with an isotropic interfacial energy of 50 mJ/m²; (ii) only the anisotropic interfacial energy is considered, neglecting the misfit strains; (iii) both the elastic and interfacial anisotropies are considered. Meanwhile, in these sets of simulations, the total interfacial energy \( E_{\text{int}} \) and elastic strain energy \( E_{\text{el}} \) within the system are also calculated. Specifically, \( E_{\text{int}} \) is calculated according to:

\[
E_{\text{int}} = \int_V \left( g_{\text{local}}(X_{\text{Nd}}, \{1,0,0\}) - g_{\text{local}}(X_{\text{Nd}}, \{0,0,0\}) + \frac{K_{ij}^d}{2} (\nabla \eta_i)(\nabla \eta_j) \right) dV \tag{3.9}
\]
Note that both the gradient energy and the local free energy contribute to the interfacial energy.

The length of $\beta'$ along the major axial directions, i.e., $l_{[100]}$, $l_{[010]}$ and $l_{[001]}$, are also measured.

Figure 3.5 Phase-field simulation of a single $\beta'$ particle, with different combinations of anisotropies: (a) $\beta'$ morphology at $t' = 60000\Delta t$, considering interfacial anisotropy only; (b) $\beta'$ morphology at $t' = 60000\Delta t$, considering elastic strain anisotropy only; (c) $\beta'$ morphology at $t' = 60000\Delta t$, considering both anisotropies; (d) evolution of $l_{[010]}/l_{[100]}$ aspect ratio of $\beta'$ precipitate under different anisotropy conditions; (e) evolution of ratio of total elastic strain energy to total interfacial energy, under different anisotropy conditions.

The simulation results are shown in Figure 3.5, including the precipitate morphology, as well as the change of $E_{el}/E_{int}$ and $l_{[010]}/l_{[100]}$ ratios with time. The findings according to the simulation results can be summarized as follows. (i) With only the elastic strain energy anisotropy, the $\beta'$ will form a thin plate on the (100) prismatic plane, rather than the (001) habit plane predicted by the Wulff construction, or the four possible habit planes predicted from Eq. (2.14). We find that although (100) is not the global minimum of the elastic interaction potential, it is a local extreme point, and the corresponding value of the elastic interaction potential is rather close to the global minimum values. Since we start from a spherical particle, and the particle size is small, i.e., the
elastic energy contribution is low, the (100) habit plane is selected without much energy penalty. The $l_{(0\text{0}10)/l_{(1\text{0}00)}$ ratio continuously increase with time while the $E_{el}/E_{int}$ ratio will become larger than 1. (ii) With only the interfacial energy anisotropy, the β’ will gradually develop into a plate on (001), with the $l_{(0\text{1}0\text{1})}/l_{(1\text{0}0\text{0})}$ ratio approaching a critical value of $\gamma_{(0\text{1}0\text{0})}/\gamma_{(1\text{0}0\text{0})} = 2.03$, consistent with the Wulff construction. (iii) With both energy anisotropies, the interfacial energy contribution is initially higher since it scales with precipitate area (i.e., when $E_{el}/E_{int} < 1$), and the minimization of interfacial energy is dominating the precipitate morphology, forming a faceted lenticular shape on the (001) plane; as the precipitate growths larger (i.e., when $E_{el}/E_{int} > 1$), the elastic energy contribution becomes dominant, and the requirement of minimizing elastic strain energy will lead to the formation of the (100) habit plane. Note that since the (001) interfacial energy is rather small, the (001) interface is rather sharp and less mobile during the precipitation growth. Therefore, the final precipitate morphology would be the faceted lenticular shape with (100) habit plane and (001) facets.

The simulation results also reflect that both the interfacial energy anisotropy and the elastic strain anisotropy tend to increase the $l_{(0\text{1}0\text{0})}/l_{(1\text{0}0\text{0})}$ aspect ratio, which is different from existing investigations on Mg-Y and Mg-Gd alloys, where the two energy anisotropies play different roles[117]. In Mg-Nd, the anisotropic SFTS ratio along [010] and [100] is 0.116, indicating a higher $l_{(0\text{1}0\text{0})}/l_{(1\text{0}0\text{0})}$ ratio would help minimize the elastic strain energy of the system. On the other hand, $\gamma_{(0\text{1}0\text{0})}/\gamma_{(1\text{0}0\text{0})} = 2.03$ indicates that the increase of (100) plane area and decrease of the (010) plane area will minimize the interfacial energy of the system. These are compared with the anisotropy factors in Mg-Y and Mg-Gd in Table 3.5, showing that the $\gamma_{(0\text{1}0\text{0})}/\gamma_{(1\text{0}0\text{0})}$ ratio tends to decrease the $l_{(0\text{1}0\text{0})}/l_{(1\text{0}0\text{0})}$ ratio while the large $\left| \varepsilon_{22}^{00}(1)/\varepsilon_{11}^{00}(1) \right|$ ratio in Mg-Nd can further increase the $l_{(0\text{1}0\text{0})}/l_{(1\text{0}0\text{0})}$ ratio. Therefore, considering only the precipitate shape, β’ in Mg-Nd is more like a thin plate, which can potentially provide higher hardening effect than β’ in Mg-Y and Mg-Gd[117].
Table 3.5 Anisotropic factors in Mg-Nd, Mg-Gd and Mg-Y

<table>
<thead>
<tr>
<th>Anisotropy Factor</th>
<th>Mg-Nd (this work)</th>
<th>Mg-Gd [117]</th>
<th>Mg-Y [117]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{22}^{00}$ / $\epsilon_{11}^{00}$ (L)</td>
<td>0.1163</td>
<td>0.5376</td>
<td>0.6135</td>
</tr>
<tr>
<td>$\gamma_{(010)} / \gamma_{(100)}$</td>
<td>2.03</td>
<td>0.1333</td>
<td>0.1456</td>
</tr>
</tbody>
</table>

3.4 Phase-field simulations of inter-precipitate interactions

To investigate the 3-D multi-particle precipitate morphology and interactions among different precipitates, we perform 3-D simulations with the presence of all the three $\beta'$ variants. The site-saturated nucleation is assumed due to the large initial nucleation driving force. The initial nuclei are spherical with a radius of 3nm. As shown in Figure 3.6, the $\beta'$ precipitates all form faceted lenticular shapes, which is in good agreement with the reported HAADF-STEM image (Figure 3.7 (b))[193]. Although the full 3-D morphology of $\beta'$ has not been achieved, the observed $\beta'$ morphology along [001] shows similar morphology compared with the current simulations.

The neighboring $\beta'$ precipitates usually connect with each other in Mg-RE alloys, even forming new phases in their connecting regions[116, 117, 119, 193, 220]. This can be attributed to the elastic interactions among different $\beta'$ variants. To explain this phenomenon, the elastic interaction energy among different $\beta'$ particles is calculated as[123]

$$E_{\text{int}}^{\epsilon_{ij}, \rho} = -\sigma_{ij}(\rho) : \epsilon_{ij}^{00}(q)$$  \hspace{1cm} (3.10)

where $\sigma_{ij}(\rho)$ is the elastic stress field generated by the $\rho$-th variant of $\beta'$ precipitates. As an example, the elastic interaction energy of different $\beta'$ variants around variant 1 is calculated in Figure 3.8. The (001) facets and the [100] tips are the places where the elastic interaction energy is the most negative, i.e., forming inter-precipitate connections at these places are energetically favored. Moreover, it is also revealed that the elastic interaction energy becomes more negative when the $\beta'$ variant interacts with the same variant itself. Therefore, the facet-facet connection
between (001) facets of the same variant is the most energetically favored connection type, followed by tip-tip connection between the same and different variants. The 3-D phase-field simulation results in Figure 3.6(a) do show these two kinds of connections, as indicated by the dashed circles. This is also consistent with HAADF-STEM observations in [193].

Figure 3.6 Phase-field simulation of multi-particles at \( t' = 20000\Delta t \): (a) 3D morphology; (b) 2D morphology on (001) plane; (c) 2D morphology on (010) plane; (d) 2D morphology in (100) plane. Dashed white circle in (a): facet-facet connection of the same variant; dashed black ellipse in (a): tip-tip connection of the same variant.
Figure 3.7 Phase-field simulation of β’ morphology on (001) basal plane (a) and comparison with experimental HAADF-STEM images (b). The red, green and blue colors in (a) represent the three β’ variants. The triad sets of arrows in (a) and (b) indicate the three [100]-type directions on the basal plane. Adapted from [193] with permission.

Figure 3.8 Calculation of elastic interaction energy of variant 1 with other variants. (001) cross section of elastic interaction energy distribution: (a) variant 1 with variant 1; (b) variant 1 with variant 2; (c) variant 1 with variant 3. (100) cross section of elastic interaction energy distribution: (d) variant 1 with variant 1; (e) variant 1 with variant 2; (f) variant 1 with variant 3. Elastic interaction energy isosurface (-1.377kJ/mol, in yellow) around variant 1 of a β’ precipitate (in red): (g) variant 1 with variant 1; (h) variant 1 with variant 2; (f) variant 1 with variant 3.
3.5 Prediction of precipitate hardening effect

The three variants of β’, with (100) prismatic habit planes, can form triangular arrays on the basal plane to effectively block the dislocation motion. To evaluate the precipitate hardening effect of the phase-field simulated precipitate microstructures, we assume the precipitates are shear-resistant and the dominant precipitate hardening mechanism is Orowan looping. This assumption is supported by the relatively higher shear modulus of the precipitate phase than the Mg matrix. Therefore, we use the following analytical model to estimate the increment of the CRSS by triangular arrays of β’ [205]:

\[
\Delta \tau = \frac{C_{44} b}{2\pi\sqrt{1-\nu}} \ln \left(0.866 \sqrt{\frac{d_t}{f}} - 0.393 d_t - 0.866 f_t \right) \left(3.11\right)
\]

The parameters and related values for this estimation are listed in Table 3.6. To investigate the effect of precipitate morphology on hardening effect, we also estimate the hardening effect (CRSS values) of the following precipitates: (a) artificial spherical precipitates; (b) artificial plate-shaped precipitates with (001) habit plane; (c) β’ precipitate in Mg-Gd with equilibrium shape [117]. These precipitate cases are all assumed to have the same average diameter and volume fraction with the simulated β’ precipitates in Mg-Nd. Note that the Orowan equation for triangular arrays of spherical particles [205] are used for these precipitates until the average \( l_{[010]} / l_{[100]} \) ratio becomes higher than 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Explanations</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{44} )</td>
<td>Shear modulus of Mg matrix</td>
<td>17GPa</td>
</tr>
<tr>
<td>( b )</td>
<td>Magnitude of the Burgers vector of dislocations</td>
<td>0.32nm</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Poisson’s ratio</td>
<td>0.29</td>
</tr>
<tr>
<td>( f )</td>
<td>Volume fractions of β’ precipitates</td>
<td>Taken from phase-field simulations</td>
</tr>
<tr>
<td>( d_t )</td>
<td>Uniform diameter of prismatic plates</td>
<td>Average [100] length, from phase-field simulations</td>
</tr>
<tr>
<td>( t_t )</td>
<td>Mean planar thickness of prismatic plates</td>
<td>Average [010] length, from phase-field simulations</td>
</tr>
</tbody>
</table>
The calculated CRSS increments for these precipitates during isothermal aging are shown in Figure 3.9. With the increase of volume fractions and average aspect ratios of β’ precipitates, the CRSS increments for real β’ precipitates (in Mg-Nd and Mg-Gd) become larger than the spherical precipitates and the precipitates with basal plane habit. This trend holds until the volume fraction of β’ in Mg-Nd reaches its equilibrium value (about 4.8%), which is the peak aging point. The further increase of aging time will decay the hardening effect due to the coarsening of β’, i.e., further increase of the average diameter and thickness while the volume fraction is kept constant. Compared with β’ in Mg-Gd, under the same volume fractions, β’ in Mg-Nd can provide more hardening effect due to the much higher $l_{[010]} / l_{[100]}$ aspect ratio.

Figure 3.9 Evolution of CRSS for systems containing β’ precipitates with different shapes. The volume fraction of β’ precipitates reach equilibrium (4.8%) at about $t^* = 55000 \Delta t$.

3.6 Summary

In this work, we combine first-principles calculations and phase-field simulations to investigate the 3-D morphology of β’ precipitates in Mg-Nd under the interplay between the
anisotropies in interfacial energies and elastic strain energies. A theoretical model is used to predict the precipitate hardening effect due to Orowan looping. The following conclusion can be made according to our simulation results.

1. The β’ precipitates display a faceted lenticular shape with {100} prismatic habit plane and small facets on {001} basal plane, which is generally consistent with experimental observations. The β’ morphology is the result of the interplay between the interfacial energies and elastic strain energies. Both the relative values and the anisotropies of these energetics affect the precipitate shape, as shown from the simulated β’ morphology evolution and the corresponding $E_{\text{el}}/E_{\text{int}}$ and $l_{[010]}/l_{[100]}$ ratios.

2. The hardening effect of β’ predicted by the theoretical model shows that under the same volume fraction and mean diameter, the high $l_{[010]}/l_{[100]}$ ratio of β’ in Mg-Nd can significantly increase the CRSS value, indicating the higher precipitate hardening effect of β’ in Mg-Nd under this situation. The more detailed precipitate hardening estimation would rely on the more careful analysis on the dislocation-β’ interaction mechanisms through a combination of first-principles calculations and phase-field simulations in the future work.

3. This study again demonstrates the usefulness of the multi-scale modeling approach, integrating the first-principles calculations, phase-field simulations and theoretical mechanical models, to elucidate the governing factors for microstructure morphology development and predict the structure-property relation of the materials. This approach can be applicable to a variety of microstructure phenomena in a variety of alloy systems.
Chapter 4: Predicting $\theta'$ Precipitation Kinetics in 319 Aluminum Alloys

4.1 Introduction

Aluminum alloys are light weight alloys that have been widely applied in practical applications. Compared with Mg-alloys, Al-alloys usually have better strength, ductility, creep- and crack-resistance and oxidation resistance, and precipitation hardening is also a very important strengthening mechanism in Al-alloys. For example, the metastable $\theta'$-Al$_2$Cu is the key strengthening precipitate in Al-Cu-based alloys, which has attracted extensive research interest and has been used as a typical model material for mechanistic studies of precipitation. Based on these existing investigations, it has been well-established that $\theta'$ is a metastable precipitate phase [221], has a tetragonal crystal structure [222], maintaining partial coherency with the Al matrix [222, 223], and form plate- or disk-shaped morphology [6, 223, 224] due to the anisotropic interfacial energy and misfit strains. The hardening effect of $\theta'$ is attributed to its impedance of dislocation motions on the slip planes of the Al matrix, usually through an Orowan mechanism[37].

In industrial applications, the optimization of the precipitation hardening effect of $\theta'$ requires the proper design of heat treatment strategy, so that relatively large amount of $\theta'$, rather than the more stable $\theta$ phase, with large diameter-to-thickness aspect ratios can be obtained within the microstructures of the materials parts during service temperatures. This is typically achieved by a combination of homogenization or solution treatment at high temperatures (> precipitate solvus temperatures, typically close to 500 °C) to reach the $\alpha$-single phase field in the phase diagram for the as-cast samples, isothermal aging at certain temperatures (usually near 200 °C) for certain time to enable precipitation, and quenching to room temperatures [225]. The temperature and duration of the isothermal aging are the key processing parameters since they are related to the
size, number density and growth speed of the precipitates. The proper control of these processing parameters relies on the fundamental understanding of the thermodynamic and kinetic aspects of θ’ precipitation, as well as the hardening mechanisms. However, since the θ’ characteristics related to hardening effects, including the size, morphology, volume fraction, number density and spatial distributions, are very sensitive to the change of the processing parameters as well as the alloy compositions, they are still hard to control in experiments. On the other hand, theoretical analysis and/or computer modeling [43, 44, 52, 92, 93, 226] have become a reliable alternative to the trial-and-error based experimental investigations, which can not only elucidate the fundamental aspects about precipitation and precipitation hardening, but also reduce the time and cost for alloy development and property optimization. For example, phase-field methods [65], with the help of first-principles calculations for necessary input parameters, have already been extensively applied for θ’ precipitates. For example, the pioneering work by Vaithyanathan et al. [43, 44] used atomistic scale calculations to provide the necessary input information for phase-field simulations including finite-temperature bulk free energies, lattice constants, elastic constants for the matrix and precipitate phases, as well as the anisotropic Al/θ’ interfacial energies. The experimentally observed θ’ morphology was qualitatively reproduced by combining the anisotropies in interfacial energy, misfit strain and interface mobility. Hu et al. [92] applied the KKS model and proposed an approach for dealing with the stoichiometric compounds in phase-field models, with detailed analysis of growth kinetics of θ’. Liu et al. [149] considered the detailed lattice deformation pathway from Al to θ’, and investigated the heterogeneous nucleation behavior of θ’ on different types of dislocations, as well as the growth kinetics, which were verified by experimental measurements. Liu et al. [37] also combined DFT calculation and phase-field simulations to investigate the detailed deformation mechanism of θ’ and the precipitate hardening effects, by considering the precipitate-dislocation interactions. Kim et al. [150] improved the description of interfacial energy anisotropy by introducing a 4th rank gradient tensor, which was parameterized by DFT calculations.
However, most of these existing investigations focus solely on the precipitate growth behaviors without quantification of nucleation behavior; meanwhile, the comprehensive experimental validations of $\theta'$ precipitation kinetics, in terms of precipitate size, aspect ratio and volume fractions, are still lacking. In this study, we develop a 3-D phase-field framework to predict $\theta'$ morphology and kinetics under different isothermal aging temperatures, in a 319 Al-alloy (Al-3.5wt.%Cu-6.0wt.%Si). The time-dependent nucleation behavior and diffusion-controlled growth kinetics are more accurately considered. The input parameters are taken from validated experimental or theoretical investigations. The simulated mean diameter, mean thickness and volume fractions of $\theta'$ at different aging time are compared with experimental observations. The possible sources for the disagreement are thoroughly discussed. The yield strength of the alloy is predicted using an analytical model with the simulated $\theta'$ characteristics.

### 4.2 Methodology

The phase-field model used in this study is similar to the one we proposed in Chapter 2. Specifically, we apply the KKS model [164], and use parabolic approximations for the bulk free energies. The microelasticity theory [18] is used to calculate the elastic strain energy, while the Al/$\theta'$ misfit strain is taken from [44]. One of the main features of the current model is the introduction of an angle-dependent description of the anisotropic interfacial energies and interface mobility, the others being the determination of interface kinetics coefficients using thin-interface analysis and the introduction of a nucleation model based on classical nucleation theory. Therefore, we briefly describe the phase-field model in this section.

The major alloying elements in 319 alloys include both Cu and Si. However, since the thermodynamic description of $\theta'$ containing Si has not yet been investigated, we still focus on Cu since it is the most responsible for $\theta'$ precipitation. The Si effect is implicitly considered in other parameters, as will be discussed later. The alloy system is then simplified into an Al-1.5at.%Cu binary system. We use $X_{Cu}$ to describe the composition change while using $\{\eta_i\}$ ($i=1,2,3$) to
describe the three structural variants. The bulk free energies of $\alpha$-Al solid solution and $\theta'$ are taken from existing database. To facilitate the solution to KKS equations, these nonlinear free energy functions $g^\phi (\phi=\alpha, \theta')$ are approximated by parabolic functions according to Eq. (2.6) at the given temperature. The equilibrium Cu compositions in the phases of interest, the values of the molar Gibbs free energy, its 1st derivative and 2nd derivative w.r.t. Cu composition, at the equilibrium Cu composition, respectively, are obtained from the thermodynamic database [92] (given in Table 4.3). Since $\theta'$ is treated as a line compound in the database, only $g^\theta (X_{Cu}^{\theta'})$ is available, where $X_{Cu}^{\theta'} = 1/3$ is the equilibrium Cu composition in $\theta'$. Therefore, we assume $\frac{dg^\theta}{dX_{Cu}^{\theta'}} = \frac{dg^\alpha}{dX_{Cu}^{\alpha}}$, and further use DFT to calculate the formation energies of the stoichiometric ($\theta'$-Al$_2$Cu, or Al$_{0.667}$Cu$_{0.333}$) and two slightly off-stoichiometric compounds at 0 K, Al$_{0.6875}$Cu$_{0.3125}$ and Al$_{0.6458}$Cu$_{0.3542}$ (similar to what we have done for Mg$_7$Nd [31]), fit the calculated formation energies into a parabolic function, and assume the curvature (second derivative of the Gibbs free energy with respect to composition) of the free energy does not change with temperature, obtaining a value of $\frac{d^2 g^\theta}{d(X_{Cu}^{\theta'})^2} = 4.11 \times 10^6$ J/mol.

The plate-shaped $\theta'$ morphology is a result of the cusps on the $\gamma$-plot. To accurately describe this feature, the angle-dependent interfacial energy and mobility are useful methods. In this work, following Hu et al. [92], we use the following angle-dependent functions for interfacial energy $\gamma(\theta)$ and interface mobility $L(\theta)$:

$$\gamma(\theta) = \frac{\gamma_{\text{semi}}}{1 + \alpha} \begin{cases} 1 + \frac{\alpha}{\sin \phi_0} + \frac{\alpha \cos \phi_0}{\sin \phi_0} \sin \theta, & -\frac{\pi}{2} \leq \theta \leq -\frac{\pi}{2} + \phi_0 \\ 1 + \alpha \cos \theta, & -\frac{\pi}{2} + \phi_0 \leq \theta \leq \frac{\pi}{2} - \phi_0 \\ 1 + \frac{\alpha}{\sin \phi_0} - \frac{\alpha \cos \phi_0}{\sin \phi_0} \sin \theta, & \frac{\pi}{2} - \phi_0 \leq \theta \leq \frac{\pi}{2} \end{cases} \quad (4.1a)$$
\[
L(\theta) = \frac{L_{\text{semi}}}{1 + \beta} \begin{cases} 
1 + \frac{\beta}{\sin \phi_0} \sin \theta, & -\frac{\pi}{2} \leq \theta \leq -\frac{\pi}{2} + \phi_0 \\
1 + \beta \cos \theta, & -\frac{\pi}{2} + \phi_0 \leq \theta \leq \frac{\pi}{2} - \phi_0 \\
1 - \frac{\beta}{\sin \phi_0} \sin \theta, & \frac{\pi}{2} - \phi_0 \leq \theta \leq \frac{\pi}{2} 
\end{cases}
\] (4.1b)

where \( \theta = \arccos \left( \frac{\partial \eta_i / \partial x}{\sqrt{(\partial \eta_i / \partial x)^2 + (\partial \eta_i / \partial y)^2 + (\partial \eta_i / \partial z)^2}} \right) - \frac{\pi}{2} \) is the angle between the interface normal of the precipitate and the x-axis, \( \phi_0 = \pi/10000 \) is a small regularization angle, \( \gamma_{\text{semi}} \) and \( L_{\text{semi}} \) are the interfacial energy and mobility coefficient for the semi-coherent interface, respectively and \( \alpha \) and \( \beta \) are anisotropy factors for interfacial energy and interface mobility coefficients, respectively. We obtain the interfacial energies of the coherent and semi-coherent interfacial energies from DFT calculations, using the VASP package [206, 207]. The supercells contain the interfaces of interest are similar to previous works [28], but with larger sizes and a basis-set cutoff energy of 300 eV. The supercell is relaxed with respect to all internal and external degrees of freedom. The formation energy of each supercell contains the contribution from the bulk Al and \( \theta' \) constituents, the interfacial energy due to chemical bonding, and the coherency strain energy at the interface. To estimate the coherency strain energy contributions, more calculations are performed, replacing the Al or \( \theta' \) constituent with vacuum. The interfacial energy caused by purely chemical bonding is then estimated. We obtain the semi-coherent interfacial energy \( \gamma_{\text{semi}} = 0.49 \) J/m² and the coherent interfacial energy \( \gamma_{\text{coh}} = \frac{\gamma_{\text{semi}}}{1 + \alpha} = 0.24 \) J/m² with \( \alpha = 1.04 \).

To solve the governing Cahn-Hilliard and Allen-Cahn equations, we take the value of \( D_{\text{Cu}} \) from existing investigations about Cu impurity diffusivity in Al [227]. The angle-dependent kinetic coefficient \( L(\theta_i) \) in the Allen-Cahn equations is assumed to follow the same angle-dependence as the interfacial energy, but with a different anisotropy factor \( \beta \). We estimate the kinetic coefficient for the semi-coherent interface from the thin-interface analysis [97]:
\[ L_{\text{semi}} = \frac{\gamma_{\text{semi}}}{\kappa_{\text{semi}} M_0} \left( 1 + \frac{\kappa_{\text{semi}} \zeta^*}{D_{\text{Cu}} \sqrt{2w}} \right) \]  

where \( w \) is the double-well potential height for the local free energy, \( \kappa_{\text{semi}} \) is the gradient coefficient of the semi-coherent interface, both of which can be calculated using known interfacial energy and interface thickness \((2\lambda)\), following Eq. (2.11). \( M_0 \) is the interface mobility and

\[ \zeta^* = \frac{1}{V_m} g_{\alpha}^{\text{Cu}} x_{\alpha}^{\text{Cu}} (X_{\text{Cu}}^{\alpha}) \cdot g_{\theta'}^{\text{Cu}} x_{\theta'}^{\text{Cu}} (X_{\text{Cu}}^{\theta'}) \cdot (X_{\text{Cu}}^{\alpha} - X_{\text{Cu}}^{\theta'})^2 \int h(\eta) \cdot (1 - h(\eta)) \cdot g_{\alpha}^{\text{Cu}} x_{\alpha}^{\text{Cu}} (X_{\text{Cu}}^{\alpha}) \cdot g_{\theta'}^{\text{Cu}} x_{\theta'}^{\text{Cu}} (X_{\text{Cu}}^{\theta'}) \cdot d\eta, \]

where \( X_{\text{Cu}}^{\alpha} \) and \( X_{\text{Cu}}^{\theta'} \) are the equilibrium Cu compositions in the two phases at a given temperature, \( V_m \) is the molar volume, \( h(\eta) \) is the interpolation function, \( g^{\alpha} \) and \( g^{\theta'} \) are the molar Gibbs free energies of the \( \alpha \) and \( \theta' \) phases, respectively, and \( g_{\alpha}^{\text{Cu}} x_{\alpha}^{\text{Cu}} \) and \( g_{\theta'}^{\text{Cu}} x_{\theta'}^{\text{Cu}} \) are their second derivatives, obtained from thermodynamic database[92]. For the diffusion-controlled process, the interface mobility is much faster, i.e., \( M_0 \rightarrow \infty \); therefore, the value of \( L_{\text{semi}} \) can be readily estimated. On the other hand, since the thickening process is much slower than lengthening while the interface mobility value is difficult to obtain, a very large value \( \beta=1000 \) is assumed.

The nucleation kinetics of \( \theta' \) is assumed to follow the following modified classical nucleation theory[6]:

\[ j = Z N_0 \beta^* \exp \left( - \frac{B_{\text{het}} \cdot \Delta G_{\text{hom}}^*}{k_B T} \right) \]  

where \( j \) is the nucleation rate, \( Z \) is the Zeldovich factor, \( N_0 \) is the number of atoms per unit volume, \( \beta^* \) is the atomic attachment rate, \( \Delta G_{\text{hom}}^* \) is the energy barrier for homogeneous nucleation, \( T \) is temperature (in K) and \( k_B \) is the Boltzmann constant; \( B_{\text{het}} \) is a phenomenological parameter describing the extent of heterogeneity in nucleation behavior. The values of \( B_{\text{het}} \) at different aging temperatures are estimated based on experimentally measured precipitate number densities, as
shown in Figure 4.1 and listed in Table 4.1. Specifically, a larger value of $B_{\text{het}}$ leads to slower nucleation rate and lower number density, but the mean precipitate size can be larger since $B_{\text{het}}$ will not affect the equilibrium volume fraction of the precipitates. As shown in Figure 4.1, since the experimentally measured number densities have very large error bars, it is difficult to find a consistent trend vs. time for all the three temperatures. Therefore, a uniform number density at each temperature is assumed, which is used to estimate the value of $B_{\text{het}}$. As seen in Table 4.1, the high number density and $B_{\text{het}}$ value at the lower temperature are consistent with the expectation that the nucleation driving force is high, nucleation barrier is low and the amount of heterogeneous nucleation sites is high. The values of the parameters in Eq. (4.3) are given in Table 4.2 based on the expressions given in [228], assuming a plate-shaped $\theta'$ precipitate. Note the more accurate way to estimate the heterogeneous nucleation behavior is to explicitly consider the effect of the possible heterogeneous nucleation sites such as dislocations, grain boundaries and pre-existing precipitates (such as $\theta''$ and Q/Q’ in [319]). This has been partially done in [149] which considers the effect of dislocations. However, the quantification of heterogeneous nucleation behaviors under the influence of these nucleation sites remains difficult due to the lack of information about the amount of these pre-existing nucleation sites.

![Figure 4.1](image.png)

Figure 4.1 The experimentally measured number density values at different aging temperatures: (a) 463 K, (b) 503 K, and (c) 533 K. The data points in the figure show the average number density at each aging time. The number beside the error bar indicates the number of measured TEM foils for the data point.
### Table 4.1 Mean number density and fitted $B_{het}$ values

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mean number density (/m$^3$)</th>
<th>$B_{het}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>463 K (190 °C)</td>
<td>2.04×10$^{21}$</td>
<td>0.00644</td>
</tr>
<tr>
<td>503 K (230 °C)</td>
<td>1.21×10$^{21}$</td>
<td>0.00456</td>
</tr>
<tr>
<td>533 K (260 °C)</td>
<td>7.07×10$^{20}$</td>
<td>0.0033</td>
</tr>
</tbody>
</table>

### Table 4.2 Evaluation of parameters in the nucleation model [228]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Explanations</th>
<th>Expressions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z$</td>
<td>Zeldovich factor</td>
<td>$Z = \frac{a_{el}^3 \Delta G_n^2}{16\pi \sqrt{6k_B T \gamma_{semi} \gamma_{coh}}}$</td>
</tr>
<tr>
<td>$N_0$</td>
<td>Number of atoms per unit volume</td>
<td>$N_0 = N_A / V_m$</td>
</tr>
<tr>
<td>$\beta^*$</td>
<td>atomic attachment rate</td>
<td>$\beta^* = \frac{2\pi r^* (r^* + h^*) D_{Cu}}{a_{el}^3 (X_{Cu}^{ee} - X_{Cu}^{ee})^2}$</td>
</tr>
<tr>
<td>$r^<em>, h^</em>$</td>
<td>Critical nucleus radius ($r^<em>$) and thickness ($h^</em>$)</td>
<td>$r^* = \frac{-2\gamma_{semi}}{\Delta G_n}, h^* = \frac{-\gamma_{coh}}{\Delta G_n}$</td>
</tr>
<tr>
<td>$\Delta G_{hom}^*$</td>
<td>Homogeneous nucleation barrier</td>
<td>$\Delta G_{hom}^* = \frac{8\pi \gamma_{semi}^2 \gamma_{coh}}{\Delta G_n^2}$</td>
</tr>
<tr>
<td>$\Delta G_n$</td>
<td>Nucleation driving force</td>
<td>$\Delta G_n(X_{Cu}) = \frac{1}{V_m} \left( g^{ee}(X_{Cu}^{ee}) - g^{ee}(X_{Cu}) - \frac{dg^{ee}}{dX_{Cu}^{ee}}</td>
</tr>
</tbody>
</table>

Note: $a_{el} = 4.05$ Å is the lattice parameter of the Al-matrix, $N_A$ is the Avogadro constant and $k_B$ is the Boltzmann constant.

### 4.3 Simulation results

The kinetic characteristics of $\theta'$, including the evolution of its number density, mean diameter, mean thickness and volume fraction, are experimentally measured to provide necessary validation for the phase-field simulations. These characteristics are measured from the transmission electron microscopy (TEM) images of a cast 319 alloy taken in a previous work[225], which contains the detailed description of alloy compositions, casting and heat
treatment procedures, and TEM characterizations. Since TEM images are taken for very thin foils, based on descriptions in [225], a foil thickness of 100 nm is assumed, which allows for the estimation of the 3-D precipitate number densities. The precipitate volume fractions are then calculated form the diameter, thickness and number density data, assuming the precipitate is of plate shape.

3-D phase-field simulations are performed at the three temperatures in a 160×160×160 nm³ simulation box, with grid size Δx=1 nm. θ’ nuclei with critical diameters and thicknesses calculated according to Table 4.2 are sequentially introduced into the simulation box following Eq. (4.3), and the total number of nuclei introduced into the system are 9, 5, and 3 for the three aging temperatures, respectively. Every time a nucleus is determined to be introduced into the system, its spatial center and variant number are randomly selected. The model parameters for phase-field simulations are listed in Table 4.3. The parameters used in the model are normalized using $C_{44}$, $D_{Cu}$ and $l_0$, which are characteristic parameters for energy, time and length scales, respectively. We convert the discretization time step size in the simulation to real time step in order to make a direct comparison with experimental measurements. To reduce the statistical errors, we perform 5 simulations with different random numbers for each simulation case, and take the average of these simulation results.

Table 4.3 Parameters for phase-field simulations

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Explanations</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_m$</td>
<td>Molar volume</td>
<td>$1.06 \times 10^{-5}$ m³/mol</td>
</tr>
<tr>
<td>$D_{Cu}$</td>
<td>Cu impurity diffusivity in Al</td>
<td>$8.88 \times 10^{-5} \exp(-133900/R/T)$ m²/s</td>
</tr>
<tr>
<td>$\gamma_{semi}, \gamma_{coh}$</td>
<td>Interfacial energies</td>
<td>$\gamma_{semi}=0.49$ J/m², $\gamma_{coh}=0.24$ J/m²</td>
</tr>
<tr>
<td>$(2\lambda)_{semi}$</td>
<td>Interface thickness for the semi-coherent interface</td>
<td>2 nm</td>
</tr>
<tr>
<td>$C_{11}, C_{12}, C_{44}$</td>
<td>Elastic constants</td>
<td>$C_{11}=108$ GPa, $C_{12}=61$ GPa, $C_{44}=29$ GPa</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Formula</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>---------</td>
</tr>
</tbody>
</table>
| $\epsilon_{ij}^0$ | Misfit strain tensor | \[
\begin{pmatrix}
0.0075 \\ 0.0075 \\ -0.051
\end{pmatrix} \cdot h(\{\eta_i\})
\] |
| $X_{Cu}^{eq}$ | Equilibrium Cu composition in Al-matrix (calculated from the thermodynamic database in [92]) | 0.00173 at $T=463$ K (190 °C) 
0.00314 at $T=503$ K (230 °C) 
0.00447 at $T=533$ K (260 °C) |
| $X_{Cu}^{\theta'}$ | Equilibrium Cu composition in $\theta'$ | 1/3 |
| $g^\alpha(X_{Cu}^{eq})$ | Values of the $\alpha$-phase molar Gibbs free energy at equilibrium Cu compositions | -59.7 J/mol at $T=463$ K (190 °C) 
-106.6 J/mol at $T=503$ K (230 °C) 
-156.3 J/mol at $T=533$ K (260 °C) |
| $g^\alpha_{X_{Cu}^{eq}}(X_{Cu}^{eq})$ | First derivative values of the $\alpha$-phase molar Gibbs free energy at equilibrium Cu compositions | -30637 J/mol at $T=463$ K (190 °C) 
-30612 J/mol at $T=503$ K (230 °C) 
-30586 J/mol at $T=533$ K (260 °C) |
| $g^\alpha_{X_{Cu}^{eq},X_{Cu}}(X_{Cu}^{eq})$ | Second derivative values of the $\alpha$-phase molar Gibbs free energy at equilibrium Cu compositions | 2.24×10^6 J/mol at $T=463$ K (190 °C) 
1.37×10^6 J/mol at $T=503$ K (230 °C) 
9.9×10^5 J/mol at $T=533$ K (260 °C) |
| $g^\theta(X_{Cu}^{\theta'})$ | Values of the $\theta'$-phase molar Gibbs free energy at equilibrium Cu compositions | -10219 J/mol at $T=463$ K (190 °C) 
-10217 J/mol at $T=503$ K (230 °C) 
-10215 J/mol at $T=533$ K (260 °C) |
| $g^\theta_{X_{Cu}^{\theta'}},X_{Cu}$ | Second derivative values of the $\theta'$-phase molar Gibbs free energy at equilibrium Cu compositions | 4.11×10^6 J/mol |
| $L_{semi}$ | Interface kinetic coefficient for the semi-coherent interface (from Eq. (4.2)) | 3.87×10^{-12} m^3/(Js) at $T=463$ K (190 °C) 
1.01×10^{-10} m^3/(Js) at $T=503$ K (230 °C) 
8.53×10^{-10} m^3/(Js) at $T=533$ K (260 °C) |
| $\alpha, \beta$ | Anisotropy factor for interfacial energy ($\alpha$) and interface mobility ($\beta$) | $\alpha=1.04, \beta=1000$ |

Note $R$ is the gas constant. $h(\{\eta_i\}) = \sum_{i=1}^3 (3\eta_i^2 - 2\eta_i^3)$. The simulated $\theta'$ precipitate morphology at different aging temperatures and times are shown in Figure 4.2, together with the corresponding TEM images at the same temperature and time for fair comparisons. With the consideration of the anisotropies in interfacial energy, misfit strain and interface mobility, the plate- or disk-shaped $\theta'$ precipitates observed from TEM images are well reproduced.
Figure 4.2 Simulated $\theta'$ morphologies and comparison with TEM observations. Phase-field simulations are performed in a $160 \times 160 \times 160$ nm$^3$ volume and are shown in (a) 463K, after 10 h, (c) 503K, after 3 h, and (e) 533K, after 0.5h; the corresponding TEM images with [001] zone axis at the same aging temperatures and times are shown in (b), (d) and (f), respectively. The different colors represent different variants of $\theta'$. The white dashed regions in TEM images have the same size as the simulation volume. The x-, y-, and z-axis represent [100], [010] and [001] directions, respectively.
To quantify the precipitation kinetics, the average diameter, thickness and volume fraction of the precipitates are measured from phase-field simulations, and compared with available
experimental data at different aging times, as presented in Figure 4.3~Figure 4.5. These simulation results are the best agreement we obtain between simulation and experiments, using the validated model parameters. Specifically, since there are very large error bars in experimental measurements, we do not include them in these figures. Instead, we evaluate the error bars of the mean diameters and thicknesses from simulations by calculating their standard deviations. The error bars in the simulated volume fractions are estimated based on the standard deviations in both the mean diameters and thicknesses. From Figure 4.3~Figure 4.5, it is shown that the simulated precipitate diameters and volume fractions agree well with experimental calibrations at both 503 K and 533 K, while for 463 K, both predictions are higher than experimental measurements. The simulated precipitate thicknesses are almost constant for all the three aging temperatures, and the precipitate kinetics at early aging stages are generally underestimated. To overcome these deviations, we further discuss their possible causes and solutions.

4.4 Discussions

The comparisons in Figure 4.3~Figure 4.5 indicate that the deviations mainly include the following three aspects: (I) volume fraction; (II) thickness; and (III) early-stage kinetics. In this section, we discuss in detail the possible sources and corresponding solutions.

4.4.1 Precipitate volume fraction

The available thermodynamic databases for Al-Cu and Al-Cu-Si systems allows for the estimation of the equilibrium volume fraction of θ’ at a given temperature via the lever rule, which is the upper limit for the volume fraction of θ’ since only the bulk chemical free energies are considered while the interfacial energy and elastic strain energy contributions are ignored, assuming an infinitely long aging time. We use this lever rule prediction as a benchmark, compare it with both the simulation results and experimental measurements, to discuss the possible ways to improve the thermodynamic database, the experimental measurements, as well as the phase-field models. However, it should be noted that the interfacial and misfit strain
energies can all shift the free energy of the precipitate phase upward, leading to a decrease in precipitate volume fractions in real cases.

<Lever rule vs. experimental results>

We collect different thermodynamic databases of Al-Cu-based alloys containing θ’, and use the lever rule to estimate the equilibrium θ’ volume fractions at the three aging temperatures, as listed in Table 4.4, along with the “stable” θ’ volume fractions from experimental measurements. Compared with the lever rule predictions, the experimental measurements show much less variations with the change of temperature. This difference can be attributed to the following reasons.

Table 4.4 Comparison of θ’ volume fractions from lever rule predictions and the current experimental measurements

<table>
<thead>
<tr>
<th></th>
<th>Lever rule predictions from different thermodynamic databases</th>
<th>Experimentally measured “stable” volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hu [92]</td>
<td>Ravi [229]</td>
</tr>
<tr>
<td>463 K (190 ºC)</td>
<td>4%</td>
<td>3.4%</td>
</tr>
<tr>
<td>503 K (230 ºC)</td>
<td>3.6%</td>
<td>3.1%</td>
</tr>
<tr>
<td>533 K (260 ºC)</td>
<td>3.2%</td>
<td>2.6%</td>
</tr>
</tbody>
</table>

(1) The approximation of 319 alloy as a binary or even ternary alloy is an over-simplification. In the TEM images in Figure 4.2(b) (d) (f), there are small black dots which are confirmed to be the metastable Q’ or stable Q phase, containing Al, Cu, Si and Mg. These Q’/Q particles are different from the disk-shaped θ’ precipitates which display line segments in TEM images. As reported from literature[231, 232], the composition and stoichiometry of Q’/Q phases have significant variations, making it difficult to be evaluated using thermodynamic theory and included in existing thermodynamic databases. The Q’/Q phases are reported to form prior to the formation of θ’[231, 232], which can be heterogeneous nucleation sites for θ’. Moreover, according to a previous study, the Q’/Q phase can consume certain amount of Cu, and coexist
with θ’ during aging[232]. The decreasing trend of Q’/Q number densities with increasing aging temperatures is consistent with the experimentally measured trend of θ’ volume fractions in Table 4.4. Therefore, the neglect of Q’/Q phase in existing thermodynamic databases could be a possible cause for the difference of θ’ volume fraction between experimental measurements and the lever rule predictions. Recently, DFT calculations have shed new light on the stoichiometry, formation energies and interfacial properties of the Q phase [233], making it possible to simulate the co-precipitation of Q and θ’, which can be a potential work in the future.

(2) The experimental quantification of θ’ volume fractions may need further improvement. For example, the TEM foil thickness was not measured for each foil, which may cause uncertainties in the precipitate number density measurements and therefore volume fractions. Moreover, although several TEM images have been measured to calibrate the precipitate diameter, thickness, estimate the number density and calculate the volume fraction, the amount of measurements may not be sufficient enough to represent the precipitation kinetics in the whole macroscopic sample. In practice, it is difficult to maintain the homogeneity of composition distribution for the whole sample before isothermal aging in the whole sample, even after long time of homogenization heat treatment. Therefore, in selected microscopic zones where the TEM images are taken, the initial Cu composition may be very different from the nominal composition of the alloy. Many more TEM images should be taken for different microscopic zones at different positions of the macroscopic sample, and compositional analysis should be conducted for each microscopic region.

(3) The existing thermodynamic description of θ’, especially the predictions of the θ’ solvus boundary, still need further improvement. Since θ’ is metastable and can be replaced by the more stable θ during aging, it is not easy to experimentally identify the θ’ solvus boundary. However, these data points are useful inputs for CALPHAD-type thermodynamic modeling and optimization of θ’. In almost all the existing database containing θ’, the θ’ solvus boundary is fitted from the experimental results collected by Murray [221], as adapted in Figure 4.6, which
also shows the predicted θ’ solvus boundary from all existing thermodynamic databases. Among them, the prediction by Ravi et al. [229] has the least-square deviation from the experimental data points. However, within the temperature range we are interested in (463 K–533 K), the experimental solvus line is steeper, which agrees with the volume fraction trend from our current experimental measurements, but is not well captured by the predicted solvus boundary in Figure 4.6. Due to the limited data points and corresponding confidence for solvus lines from experiments, more experimental measurements should be conducted for θ’ solvus lines.

![Figure 4.6 Summary of existing experimental investigations (adapted from Murray[221]) and thermodynamic databases (Hu [92], Ravi [229], Al-Cu-Si ternary [230]) for θ’ solvus boundaries in Al-Cu.](image)

<Lever rule vs. phase-field simulations>

As mentioned, the lever rule prediction neglects the interfacial and misfit strain energy contributions, which leads to the discrepancies between the experimentally measured precipitate volume fractions and that from lever rule predictions. On the other hand, the phase-field approach, with these energetics included in the free energy functional of the system, can more quantitatively predict the precipitate volume fractions than the lever rule predictions. Since the interfacial energies and misfit strain energies are not temperature-dependent, it is expected that the
deviations of the simulated “stable” precipitate volume fractions from lever rule predictions should be similar for these three temperatures. However, as shown in Table 4.4, this deviation increases with temperature, and even reach about 50% at 533 K. Therefore, we perform a set of phase-field tests to figure out the reason, as illustrated in Figure 4.7.

![Figure 4.7](image)

Figure 4.7 Effect of interface thickness on phase-field simulation results. (a) $\theta'$ volume fractions with $(2\lambda)_{\text{semi}}=2$ nm at $T=533$ K; (b) $\theta'$ volume fractions with $(2\lambda)_{\text{semi}}=4$ nm at $T=533$ K; (c) $\theta'$ volume fractions with $(2\lambda)_{\text{semi}}=2$ nm at $T=463$ K; (d) $\theta'$ mean diameters with $(2\lambda)_{\text{semi}}=4$ nm at $T=533$ K. The red dotted lines indicate the lever rule predictions of equilibrium $\theta'$ volume fractions.

We specifically consider the different combinations of the anisotropies, at $T=533$ K, in Figure 4.7(a): (1) all anisotropies are considered; (2) anisotropies in interfacial energy and interface mobility are considered, while elastic energy is excluded, i.e., the misfit strain is assumed to be zero; (3) only interfacial energy anisotropy is considered, with misfit strain set as
zero and an isotropic interface mobility coefficient \( L(\theta) = L_{semi} \); (4) only interface mobility anisotropy is considered, with misfit strain set as zero and an isotropic interfacial energy \( \gamma(\theta) = \gamma_{semi} \); (5) all anisotropies are excluded. Based on the simulation results, when all the anisotropies are turned off (case (5)), the simulated stable volume fraction is much closer to the lever rule prediction. The effects of misfit strains and interface mobility anisotropies are minor, while the effect of interfacial energy anisotropy is significant, as shown from the comparison between case (1) and (3).

The significant effect of interfacial energy anisotropy may be attributed to a numerical pinning effect, since a constant barrier height \( w \) implies the same angle-dependence of interfacial thickness with interfacial energies. By using an interface thickness of 2 nm for the semi-coherent interface and a grid size of 1 nm, the interface thickness for the coherent interface is about only one grid point, which may cause the numerical pinning issue. In this case, the mobility of the coherent interface becomes rather limited in the simulations, reducing the volume fraction of the precipitates. This numerical pinning issue is confirmed by the almost constant precipitate thickness, especially at higher temperatures. To further confirm this issue, we perform the same set of simulations at 533 K with a larger interface thickness, i.e., 4 nm for the semi-coherent interface. The results in Figure 4.7(b) reflects a much less deviation from lever rule predictions for all simulation cases, indicating that the numerical pinning effect is reduced.

We also perform simulations at 463 K with the interface thickness of 2 nm for the same cases, as shown in Figure 4.7(c). This set of simulations show much less numerical pinning effect since the variations for the different simulation cases are rather small compared to those at 533 K. Since the anisotropy factors for these two different temperatures are the same, the different variations among the different cases are attributed to the different precipitation growth driving forces. The growth driving force at 463 K is larger than that at 533 K, which can overcome the numerical pinning force. Therefore, to evaluate the numerical pinning effect during phase-field
simulations, a set of test simulations with different interface thicknesses should be performed, in order to select a proper interface thickness value. There are also other methods to overcome the numerical pinning effect. For example, the adaptive mesh algorithm [234, 235] uses finer mesh sizes at interface regions, which can resolve the correct interface kinetics. Alternatively, rather than making the barrier height $w$ constant, it can be made angle-dependent so that the interface thickness becomes constant for different interfaces[125, 236]. Recently, another method is proposed to realize the sharp phase-field model with only one grid point at the interface while maintaining the desired interface kinetics, which is realized by choosing a proper double-well function [237]. We will investigate the effect of these methods in our future work.

4.4.2 Precipitate thicknesses

As discussed above, the increase of interface thickness in the simulation can reduce the numerical pinning effect and obtain better agreement of the precipitate volume fraction predictions between the phase-field simulations and lever rule predictions. However, the predictions for precipitate diameters and thicknesses become worse, in which the lengthening is slowed down while the thickening is accelerated, and the change of the interface mobility anisotropy factor $\beta$ could not effectively resolve this issue (Figure 4.7(d)). This may be due to the fact that the number of simulation grids is limited, and the further increase in $\beta$ could not be effectively captured in the simulations. In this sense, the numerical pinning effect, although unfavorable for volume fraction predictions, can assist the control of precipitate thickening. For example, if we still use the smaller interface thickness value (2 nm), while calculating the nucleation rate and critical diameter of a new ledge layer of 1 nm thick according to Eq. (4.3), and manually introduce this new ledge layer of already-nucleated $\theta'$ particles, the overall agreement of precipitate kinetics can be improved. Note in this case we nucleate both the $\theta'$ particles and the ledge layers of already-nucleated $\theta'$, which we call “controlled-thickening”. This is actually consistent with the generally accepted lengthening kinetics, which involves the
nucleation of new atomically thin ledges of $\theta'$ along the thickness directions. As shown in Figure 4.8, at 533 K, with the improved thickening kinetics (Figure 4.8(b)), the agreement of mean diameters also gets improved, and a higher stable volume fraction is obtained compared with the simulations where the precipitate thickness remains constant.

![Figure 4.8](image)

Figure 4.8 Phase-field simulations with controlled thickening at 533 K (260 °C). (a) Mean precipitate diameter. (b) Mean precipitate thickness. (c) Precipitate volume fraction.

In practice, as observed by HRTEM images, the semi-coherent Al/$\theta'$ interface is more diffuse than the coherent one[28], and the mobility of the coherent interface is rather limited, since the kinetic mechanism of thickening includes the nucleation of ledges, which is much slower than lengthening. This acts as a real lattice pinning effect[29], which, to some extent, can be represented by the numerical pinning effect in phase-field simulations.

### 4.4.3 Early-stage kinetics

The underestimation of the early-stage kinetics mainly manifests itself in two aspects: (1) the underestimation of the nucleation behavior and (2) the underestimation of kinetic coefficients. In this section, we discuss these two aspects in detail.

**<Nucleation behavior>**

The experimentally observed nucleation behavior of $\theta'$ in 319 shows obvious heterogeneity. Firstly, during isothermal aging, defects such as dislocations can act as heterogeneous nucleation
sites. For example, experimental observations both in the current study and elsewhere [223] show that small $\theta'$ precipitates can form zig-zag arrays, implying its nucleation along certain matrix dislocation lines. As discussed in [149], the elastic interactions between matrix dislocations and precipitates can provide additional nucleation driving force at certain positions of the dislocation lines or loops where the elastic interaction energy is highly negative, i.e., where the formation of precipitation is energetically favored.

Secondly, the metastable precipitates or clusters, such as G. P. zones, $\theta''$ and Q'/Q phases may precipitate before the formation of $\theta'$ during isothermal aging, which can serve as heterogeneous nucleation sites or even precursors for $\theta'$. In the present study, the formation of G. P. zones and $\theta''$ is not experimentally observed due to the limited inspections of the aged samples at early aging stages, while the effect of Q'/Q particles/rods is evident. According to a recent study [232], within the temperature ranges of interest ($463 \text{ K} - 533 \text{ K}$), Q'/Q can be an important precursor for $\theta'$. However, careful quantification about its effect would not become available until an improved thermodynamic description of Q'/Q and more experimental characterizations are established.

Moreover, since 319 alloys contain large amount of Si, the effect of Si should be considered. Although there is no Si partition inside $\theta'$ reported, they can segregate at the Al side of the Al/$\theta'$ interface, which, according to [26], can reduce the interfacial energies of both the coherent and the semi-coherent interfaces. This can lead to the reduction of nucleation barrier and the acceleration of nucleation rates. Based on existing quantitative analysis on the interfacial energy reduction due to Si segregation, the nucleation barrier can be 1.4 times lower, and the critical nucleus radius of $\theta'$ can be only 87% of that without Si. Therefore, the Si segregation can lead to larger numbers of finer $\theta'$ nuclei at early aging stages. In addition, as reported in [28], the semi-coherent interface of $\theta'$ can be more diffuse than expected, consisting of a $\theta''$ front, especially at lower aging temperatures. This can lead to an increase of the semi-coherent interfacial energy,
which can be \( \sim 0.9 \text{ J/m}^2 \) according to [28], together with an increased lengthening kinetics. This would result in higher nucleation barrier while the critical nucleus size can be increased. To estimate these two possible effects, we perform two sets of simulations at 463 K: (i) site-saturated nucleation of \( \theta' \) with decreased interfacial energy, which corresponds to an upper limit for the Si segregation effect; (ii) nucleation with larger semi-coherent interfacial energy and critical nucleus size, but no change in nucleation rates, which is an upper limit for the effect of the diffusive semi-coherent interface. The predicted mean diameter evolution is shown in Figure 4.9, which shows slight improvements of early-stage precipitation kinetics while the deviation with experimental measurements persists. More careful considerations for these two effects are needed. For example, in the following chapters, the solute segregation effects will be explicitly considered and thoroughly investigated in the phase-field model.

![Figure 4.9 Investigations on possible improvements for early-stage precipitate kinetics at 463 K: (a) site-saturated nucleation with decreased interfacial energy due to Si segregation; (b) increased interfacial energy and critical nuclei size due to the diffuse nature of the semi-coherent interface.](image)

<Kinetic coefficients>

Quantification of kinetic coefficients, including diffusion coefficients and interface mobilities, are important for the accurate prediction of precipitate kinetics. In the current study, due to the lack of interface mobility data, we assume the lengthening of \( \theta' \) is diffusion-controlled.
The diffusivity of Cu in α-Al matrix is therefore an important quantity for the time scale estimation of the precipitation process.

Figure 4.10 Summary of existing investigations on Cu diffusivity in α-Al. Fitted lines are from Du et al. [227], Zhang et al. [238], Cao et al. [239] and Liu et al. [240]; experimental data points from Doig et al. [241].

The experimental investigations on Cu diffusivity in α-Al has been collected in [221], while the diffusion mobility databases for Al-Cu-based alloys have been developed. The fitted Cu diffusivities in α-Al, within the temperature range we are interested in, are summarized in Figure 4.10, together with the experimental data points. The fitted lines are in good agreement with experimental data; nevertheless, the quality of existing fittings need further verification due to the lack of sufficient experimental data points within this low temperature range. In the current phase-field simulations, rather than directly use the reported $D_{Cu}$ values, we use a value that is twice of that in [227], to better reproduce the experimental precipitation kinetics, within acceptable range. This treatment is supported by the facts that (1) most of the collected
experimental $D_{Cu}$ data at low temperatures are out of the range shown in Figure 4.10, spanning a region between 0.5 and 2 times of the fitted diffusivity, and the low temperature measurements tend to be underestimated by this fitting; (2) the average of all the diffusivity data in Figure 4.10 indicates that the factor of 2 is a reasonable estimate; (3) Si has been reported to have catalytic effects on Cu diffusion and $\theta'$ precipitation[25], while without further experimental quantifications of this effect, the modification of diffusivity can be a possible approximation for this effect. This discrepancy points out the demand for more accurate experimental investigations for Cu and Si diffusivities in $\alpha$-Al especially at low temperatures.

4.5 Mechanical property predictions

With the phase-field simulated kinetic characteristics of $\theta'$ precipitates, it is possible to predict the precipitate hardening effect and the overall yield strength of the alloy using existing mechanical property models. For $\theta'$, there have been several such models developed [37, 225, 242] assuming $\theta'$ is non-shearable and an Orowan mechanism (i.e., dislocations looping around the precipitates) for precipitation hardening. This can be justified from ab-initio calculations in [37], which predicts that, in order for a matrix dislocation to shear through $\theta'$, an applied stress (1.06 GPa) much higher than the CRSS of the alloy system is required. Among these models, we consider the model by Weakley-Bollin et al.[225] in this study. The total yield strength $\sigma_Y$ of the material contains the contributions from precipitation hardening $\sigma_{ppt}$, solid solution (and G.P. zones) strengthening $\sigma_{ss}$, as well as the intrinsic strength of the material $\sigma_i$. Specifically, the mechanical models are formulated as[225]

$$\sigma_{ppt} = M_Y \left(0.13 \left( \frac{C_{4b}}{\sqrt{d' \cdot t_i}} \right) \left( \sqrt{f + 0.75 \frac{d}{t_i}} + f + 0.14 \frac{d}{t_i} f^{3/2} \right) \ln \frac{0.87 \sqrt{d' \cdot t_i}}{r_0} \right)$$

(4.4a)

$$\sigma_{ss} = H \left( X_0 - f / 3 \right)^{2/3}$$

(4.4b)

The physical meaning and values of the parameters in Eq. (4.4) are given in Table 4.5.
Table 4.5 Physical meaning and values of parameters in Eq. (4.4)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Physical Meaning</th>
<th>Values (unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_T$</td>
<td>Taylor factor</td>
<td>3.06</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>Shear modulus</td>
<td>29 (GPa)</td>
</tr>
<tr>
<td>$b$</td>
<td>Magnitude of Burgers vector of matrix dislocations</td>
<td>0.286 (nm)</td>
</tr>
<tr>
<td>$d_o$, $t_o$, $f_o$</td>
<td>Mean diameter, mean thickness and volume fractions of $\theta'$</td>
<td>From phase-field simulations</td>
</tr>
<tr>
<td>$r_0$</td>
<td>Inner cut-off radius of dislocation cores</td>
<td>0.286 (nm)</td>
</tr>
<tr>
<td>$H$</td>
<td>Modulus of solid solution hardening</td>
<td>2000 (MPa), $T=463$ K</td>
</tr>
<tr>
<td>$X_0$</td>
<td>Initial composition of Cu (atomic ratio)</td>
<td>0.015</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>Intrinsic strength</td>
<td>70 (MPa)</td>
</tr>
</tbody>
</table>

With these parameters, together with the simulated precipitate diameters, thicknesses and volume fractions (Figure 4.3~Figure 4.5), the yield strength of the alloy can be predicted at the three aging temperatures and compared with corresponding experimental values, as shown in Figure 4.11.

![Figure 4.11 Predicted yield strength of the 319 alloy at different aging temperatures using the precipitation kinetics from phase-field simulations, with experimental comparison. (a) Using typical phase-field simulations; (b) considering controlled thickening.](image)

The yield strength predictions are quite consistent with experimental values for the two higher temperatures (503 K and 533 K) up to the peak aging point, since the predicted
precipitation kinetics at these two temperatures have better agreement with experimental measurements (Figure 4.3–Figure 4.5). However, the experimental yield strength begins to decrease beyond the peak aging point (0.3 h at 533 K and 1 h at 503 K) due to the decreased diameter/thickness aspect ratio (i.e., mean diameter remains almost the same while the mean thickness increases) while in phase-field simulations, the precipitate thicknesses remain almost constant (Figure 4.4(b) and Figure 4.5(b)), leading to the continuous increase of the diameter/thickness aspect ratio and the predicted yield strength. This can be improved by considering the controlled thickening, i.e., using the thickness results in Figure 4.8(b), as shown in Figure 4.11(b). The predictions at 463 K need further improvement especially in terms of the early-stage kinetics. Therefore, the accurate prediction of the precipitation kinetics plays a vital role in the accurate prediction of the mechanical properties of the material. The suggestions in Section 4.4 should be considered to improve the yield strength predictions.

The yield strength model itself can also be improved since the current model does not explicitly consider the detailed precipitate-dislocation interaction mechanisms (e.g., interaction mechanisms as a function of precipitate size), as well as the spatial distribution of the precipitates. These possible improvements will be discussed in our future work.

**4.6 Summary**

We extend the existing phase-field models of θ’ precipitates, with the integration of a nucleation model and more careful growth kinetics treatments, to provide quantitative analysis for the precipitation kinetics in 319 alloys. We perform systematic phase-field simulations and comprehensive comparison with experimental measurements in terms of the evolution of the mean diameter, mean thickness and volume fraction of the precipitates, using validated model parameters from reliable sources, at different aging temperatures. The simulated growth kinetics show acceptable agreement with experimental observations. In view of existing deviations,
possible sources of the disagreement and corresponding solutions are thoroughly discussed and proposed. Specifically,

(1) More accurate experimental efforts are demanded to improve the existing thermodynamic descriptions of $\theta'$, and to elucidate the atomistic and microscopic mechanisms of precipitation kinetics. These include the more accurate measurements of the evolution of the precipitate number density, diameters, thickness and volume fraction, the more accurate calibration of $\theta'$ solvus line and related diffusion coefficients and interface mobility, and the more quantitative analysis of the microscopic factors affecting the $\theta'$ precipitation, such as the role of $\theta''$, $Q'/Q$, pre-existing dislocations, as well as the role of solute segregation.

(2) The phase-field model, especially its numerical accuracy in dealing with relatively sharp interfaces (to avoid numerical pinning) and resolving the different anisotropies and the high aspect ratio of $\theta'$, needs further improvement. Besides, more microscopic mechanisms related to the nucleation and growth of $\theta'$ should be considered.

We believe the current study can lay the foundation of applying the phase-field approach to investigate the precipitation kinetics and hardening effects of commercial alloys during heat treatment processes.
Chapter 5: Predicting Coherency Loss of Precipitates

5.1 Introduction

The coherency state of precipitates is an important factor for the precipitation hardening effects in metallic alloys. When the precipitate is coherent with the matrix, i.e., when there are well-defined OR and LC between the crystal structures of the precipitate and the matrix phases, and the misfit strains between the two phases are within the elastic range, the precipitation hardening effect is the most effective. This is because the elastic stress field generated by the misfit strains of the coherent precipitate can interact the stress field of the matrix dislocations, which can impede the dislocation motion on the slip planes[1]. In contrast, when the precipitate has limited coherency with the matrix phase, line defects such as dislocations and structure ledges can develop at the precipitate/matrix phase, which do not only decrease the impedance of dislocation motion through decreasing the misfit strains, but also become the sources or generators of dislocations, hampering the precipitation hardening effect.

An initially coherent precipitate can gradually lose its coherency with the matrix during the continuous growth of the precipitate, even without the presence of the applied stress/strains [32]. This is because the elastic strain energy due to the precipitate/matrix lattice mismatch scales with the volume while the interfacial energy scales with interface area; both of these energy contributions are energy penalty terms for precipitation. With the continuous growth of the precipitate, the elastic strain energy contributions will possess a large portion of the energy penalty terms, making the further growth of the precipitate energetically unfavorable. To minimize the total free energy of the system, the precipitate may choose to develop line defects on the initially coherent precipitate/matrix interface, relaxing the misfit strains and elastic strain energy distributions at the expense of increasing the interfacial energies, i.e., the precipitate
undergoes coherency loss. There is typically a critical precipitate size where the further growth of
the precipitate will make the coherency state energetically or kinetically unfavorable.
Understanding the coherency loss process and predicting this critical precipitate size is important
in controlling the precipitate size during realistic heat treatment process.

Coherency loss of precipitates is a manifestation of the requirement for minimizing the total
free energy within the system. However, there are different possible kinetic mechanisms for the
development of line defects on the precipitate/matrix interface. These possible mechanisms have
been summarized by Weatherly et al. [32]: (i) the punching of dislocation loops near the
precipitate/matrix interface due to the coherency stresses in the matrix; (ii) the climbing of
dislocations from the matrix; and (iii) the nucleation of dislocation loops inside the precipitate.
For each of the three proposed mechanisms, the amount of dislocations at the interface is closely
related to the precipitate size, and a critical size exists where there is no energy barrier for
creating new dislocations at the interface. These detailed coherency loss mechanisms have been
verified by experimental observations on dislocation types and distributions at the interface, for γ’
precipitates in Ni-based alloys, β’ precipitates in Al-Mg-Si alloys and θ’ precipitates in Al-Cu
alloys, respectively [32]. Following similar theoretical framework, the coherency loss of lamellar
Ti-Al [243], γ’ in superalloy CMSX-4 during creep [244], Al3Sc in Al-Sc alloys [245], and α
precipitate in Ti-6Al-4V [246] has been analyzed and discussed.

Although the basic theoretical framework of coherency loss of precipitates has been
established, there are still several remaining issues. For example, coherency loss is a kinetic
process, starting from a coherent precipitate to the final state where one or more types of line
defects can develop on different precipitate/matrix interfaces and the coherency of the precipitate
can be fully lost; the kinetic pathway or sequence for the development and evolution of the line
defects is difficult to capture from experimental observations. Moreover, coherency loss is
accompanied by the modifications in the anisotropies of misfit strains, interfacial energies and
interface mobilities, which can lead to the change of precipitate morphology; while this process has not been thoroughly investigated. In addition, coherency loss will further complicate the precipitate-dislocation interactions, leading to the change of the hardening effect, which has also been under-investigated. Recently, the development of computational tools makes it possible to resolve these long-standing problems. For example, Le Bouar [247] applied a 3-D atomistic static approach to investigate the coherency loss during the bcc→9R transformation of Cu precipitates in ferrite steels, showing that the coherency loss is caused by the formation of dislocation loops inside the precipitate, with the detailed interface structures, properties and critical radius for coherency loss predicted. Shim et al.[248] applied molecular dynamics (MD) to investigate the coherency loss of a Cu precipitate in bcc Fe due to interactions with screw dislocations in the matrix. Quek et al. [249] performed 3-D level-set dislocation dynamic simulations to investigate the interactions between the dislocation-precipitate interactions and the coherency loss of a misfitting spherical particle, showing the change of dislocation bypassing mechanisms due to coherency loss. Geslin et al. [250] proposed and applied a nonlinear elastic model for coherency loss of a misfitting precipitate, which can capture the nucleation, glide and cross-slip of dislocations. Geslin et al. [251] implemented the nudged elastic band method in a dislocation dynamics model to investigate the coherency loss due to homogeneous nucleation of partial dislocation loops. Oum et al. [252] proposed a 3-D crystal plasticity model for coherency loss during precipitation. In addition, the meso-scale phase-field approach has also been actively applied in predicting coherency loss of misfitting precipitates. Minami et al. [253] formulated a phase-field model for dislocation formation in two-phase alloys, which considers the elastic energy density as a period function of the shear and tetragonal strains, allowing for the formation of multiple dislocations; the dynamic equation was also considered due to the loss of mechanical equilibrium around the cores of the moving dislocations. Shi et al. [34] applied the phase-field approach to predict the critical size of α precipitates in Ti-alloys for coherency loss with known configurations of line defects on the α/β interface. Goerler et al. [254] applied the multi-phase-
field approach to investigate the γ’ morphology during long-term thermal exposure of CMSX-4, considering the coherency loss by reducing the misfit strains and strength of the wetting condition. Louchez et al. [255] applied a microscopic phase-field model for dislocation dynamics and coherency loss of an hcp/fcc interface.

However, the simulation of the full coherency loss process remains a challenging task due to the size scale change during the continuous growth of precipitates and the multi-scale nature of the problem: the size of the initially coherent precipitate is usually within nano-scales while the size of the precipitate when the coherency is fully lost is usually on the μm scale or even larger; the size of dislocation cores is usually within atomistic scales, while the spacing of adjacent dislocation loops is within nano-scales and the length of dislocation lines/loops is comparable to the size of the precipitate. In this sense, the atomistic scale models can capture the dislocation nucleation and interaction only when the precipitate size is small, while the mesoscale or continuum models are capable of simulating the whole coherency loss process using mean-field approximations or homogenization methods to take the dislocation effect into consideration.

In this work, we propose and apply a phase-field model, capable of predicting the gradual coherency loss of an initially coherent precipitate due to the sequential development of dislocation loops and the evolution of their average spacing (rather than their detailed interactions), based on the energy criteria. The modification of the misfit strain and interfacial energy due to the coherency loss, as well as the resulting change of precipitate morphology until the full coherency loss, is also predicted. The precipitation hardening effects of the precipitates before and after coherency loss are estimated using analytical models. As a preliminary attempt, we apply the model to the coherency loss of γ” in IN718 and θ’ in Al-Cu alloys. The more challenging cases where the precipitate phase only has limited coherency with the matrix, which may result in complicated precipitate shape (e.g., including one or several side facets) and configurations of line defects, such as α precipitate in Ti-alloys (considering not only the habit
planes but also the side facets) [256] and β-Mg17Al12 precipitate in AZ91 [257], will be left for our future work.

5.2 Model description

The key points to the construction of the phase-field coherency loss include the description of the line defects in the model and the formulation of free energies under the effect of the generation and evolution of the defects. However, since the problem is of multi-scale nature, it is numerically challenging to include both the precipitate growth and dislocation dynamics in an integrated model. Therefore, in the current work, rather than explicitly consider the dynamics and interactions of the line defects, we consider their effective modifications to the energetics of the system. Specifically, we identify the configuration of line defects when the precipitate fully loses its coherency (this can be done either by existing experimental investigations or crystallographic models such as the O-lattice theory [13, 14]), and effectively consider their modifications to the precipitate/matrix interfacial energies through the Read-Shockley equation [258] and modifications to the precipitate/matrix misfit strains by formulating their deformation gradients. The sequential formation and evolution of the line defects will be determined through an energy criterion, i.e., the new configuration of the line defects can form when it becomes energetically favorable. We assume the evolution of these line defects follows an evolution rule similar to the Allen-Cahn equation[69], while the kinetic coefficient is related to the mobility of the line defects, which will be determined through atomistic scale calculations in our future work. The simulation results following these treatments can be qualitative or even semi-quantitative.

The formulation of elastic strain energy follows the microelasticity theory [18]. The key point here is the consideration of the effect of line defects on the SFTS of the precipitate. If we know the configuration of the line defects, their deformation gradients can be obtained. For example, if we know the Burgers vector and average spacing of a set of dislocation loops developed at the precipitate/matrix interface, their deformation gradient $F_{d1}$ can be evaluated by:
\[
F_{dl} = I + \frac{1}{\lambda} b \otimes n
\]  

(5.1)

where \( I \) is the identity matrix, \( b \) is the Burgers vector of the dislocation loops, \( n \) is the normal of the plane the dislocation loops are on, and \( \lambda \) is the average spacing of the dislocation loops. The total deformation gradient of the system, \( F_{tot} \), including the contributions from both the line defects at the interfaces and the precipitate/matrix lattice mismatch, can be calculated according to the multiplicity rule:

\[
F_{tot} = F_{dl} \cdots F_{dl} F_0
\]  

(5.2)

Where \( F_{dl} \), \( \ldots \), \( F_{dl} \) are the deformation gradient tensors for the possible \( n \) types of line defects at the interfaces, and \( F_0 \) is the deformation gradient tensor due to lattice mismatch. The corresponding SFTS tensor can be calculated as \( \varepsilon^{00} = \frac{1}{2} (F_{tot} + F_{tot}^T) - I \) under small-strain approximations and \( \varepsilon^{00} = \frac{1}{2} (F_{tot}^T F_{tot} - I) \) under finite-strain approximations.

The increase in interfacial energy due to the formation of line defects can be estimated using the Read-Shockley equation [258] under the assumption that the line defects are equivalent to the formation of low-angle grain boundaries. Therefore, this increase in interfacial energy, \( \gamma_{dis} \), can be calculated by

\[
\gamma_{dis} = \gamma_0 \theta(A - \ln \theta)
\]  

(5.3)

where \( \gamma_0 \) is a materials-specific pre-factor, \( \theta = b/\lambda \) is equivalent to the misorientation angle between the two grains, which is related to the configurations of the line defects, and \( A = 1 + \ln \frac{b}{2\pi r_0} \) is related to the dislocation core radius \( r_0 \). The pre-factor can be expressed as

\[
\gamma_0 = \frac{C_{44} b}{4\pi(1-\nu)}
\]  

for elastically isotropic materials [258], with \( C_{44} \) being the shear modulus, \( b \) the
amplitude of the Burgers vector, and $\nu$ the Poisson ratio; or $\gamma_0 = \frac{C_{44}b}{4\pi(1-\nu)} \sqrt{\frac{2(1-\nu)}{\varsigma(1+\varsigma(1-2\nu))}}$ for materials with cubic anisotropy, where $C_{44}$ is the shear modulus and $\varsigma = \frac{2C_{44}}{C_{11} - C_{12}}$ is the anisotropy factor for elasticity [258]. The interfacial energy contribution due to chemical bonding, $\gamma_{chem}$, can be calculated from DFT. Therefore, the total interfacial energy can be calculated by $\gamma_{tot} = \gamma_{chem} + \gamma_{dis}$. The interfacial energy can be anisotropic due to not only the different chemical bonds, but also the different configurations of the line defects. The interfacial energies and thicknesses are used to calculate the gradient energy coefficients and double-well potential barrier height in the phase-field model through 1-D analytical solutions. The gradient coefficients can be of tensor form, or even angle-dependent, to describe the anisotropies in interfacial energy.

The phase-field simulations start from a critical nucleus of the precipitate (estimated by the classical nucleation theory) which is fully-coherent or semi-coherent with the matrix. The governing equations for the growth of the precipitate include the Cahn-Hilliard equations for the composition fields and Allen-Cahn equations for order parameters, which have been described in detail in previous chapters. Assume we know there are $n$ types of line defects on the precipitate/matrix interfaces when the coherency of the precipitate is fully lost, there are $(C_{n}^{1} + C_{n}^{2} + \cdots + C_{n}^{n})$ types of their combinations in total, which, of course, can be reduced according to the symmetry of the material. The initiation of the line defects or their combinations is predicted by comparing their respective energy values and the energy values for the fully coherent state assuming the line defects have already been developed, finding the line defect configurations or their combinations with the lowest energy. Note that we assume the precipitate retain its morphology at the moment of coherency loss and/or the change of line defect configurations/combinations, since we assume the development and evolution of the line defects are much faster than the diffusion-controlled growth process of the precipitate. Once the line
defects are developed, we use the following equation to predict the evolution of their average spacings \( \{ \lambda_i \} \), under the requirement of minimizing the total free energy within the system:

\[
\frac{\partial \lambda_i}{\partial t} = -L_i \lambda_i \frac{\delta G}{\delta \lambda_i} = -L_i \left( \frac{\partial g_{\text{int}}}{\partial \lambda_i} + \frac{\partial e_{\text{el}}}{\partial \lambda_i} \right)
\]  

(5.4)

The flow chart of this solution procedure is shown in Figure 5.6(a). Starting from the initially coherent state, the evolution of the precipitate will be governed by the Cahn-Hilliard (for solute composition) and Allen-Cahn (for order parameters) equations; at the end of each time step, the size of the precipitate along different directions will be measured (by the “size measurer” module) and the total energies of the systems containing the fully coherent precipitate and the semi-coherent precipitates with different types of line defect configurations will be calculated and compared (by the “energy calculator” module, based on Eq. (2.13) and Eq. (3.9)). If the energy of any semi-coherent configurations is lower than the coherent precipitate, coherency loss is initiated, with modifications to the gradient coefficients and misfit strains. The initial spacing of the line defects is assumed to be the same as the precipitate size along related directions. The further evolution of the precipitate is again realized by solving the Cahn-Hilliard and Allen-Cahn equations, while the evolution of line defects is realized by solving Eq. (5.4). At the end of each evolution step, the energy comparisons are also performed to identify the possibility of further coherency loss. These iteration loops continue until the fully incoherent state is achieved. Here we define the “ideal” fully incoherent state to be the situation where the precipitate/matrix misfit strains are fully compensated by the line defects at the precipitate/matrix interface. However, this state may not be achieved, and in practice, when the average line defect spacings no longer evolve in our simulations, we define the state to be fully incoherent.

### 5.3 Results and discussion

We apply the proposed phase-field model for coherency loss of two different materials systems, one is \( \gamma" \) in IN718, where we only consider one type of line defects with fixed
dislocation spacing determined from experimental observations, the other is $\theta'$ in Al-Cu alloys where we consider the sequential coherency loss and evolution of the spacings of the line defects.

### 5.3.1 γ” precipitate in IN718

Inconel 718 [259], or IN718, is a conventional Ni-based superalloy which is widely used in energy-related applications such as engines, gas turbines and oil field operations due to its excellent comprehensive properties such as high strength, high corrosion and oxidation resistance and good weldability[260]. IN718 has major alloying elements of Fe, Cr, Nb, Al, Ti and Mo, and the major strengthening phase is the metastable, plate-shaped $\gamma''$-Ni$_3$Nb, with an D0$_{22}$-ordered crystal structure and is coherent with the Ni-matrix[261]. The loss of coherency of $\gamma''$ has been reported during prolonged aging, which is attributed to the formation of stacking faults within the precipitate[261]. The metastable $\gamma''$ can be replaced by the more stable $\delta$ phase with the same stoichiometry but much less coherency with the Ni-matrix[262]. Therefore, heat treatment of IN718 needs to be properly controlled to maintain the coherency of $\gamma''$ to maximize the precipitation hardening effect, while avoiding the formation of $\delta$ which is detrimental to the mechanical properties of IN718. Experimental measurements have been conducted to determine the critical size for the coherency loss of $\gamma''$. For example, Slama et al.[263] estimated that the critical diameter for the coherency loss of $\gamma''$ is about 100 nm. Cozar et al. [264] obtained similar results in a Fe-Ni-Ta alloy. Devaux et al.[265] noticed a change of the tangent of the thickness/diameter-diameter relation for $\gamma''$ in IN718, and attributed this change to the coherency loss of $\gamma''$.

Since IN718 is a multi-component, multi-phase system involving complicated interactions of solutes and the different precipitate phases, while our primary focus of the current study is the $\gamma''$ phase, we simplify the alloy into a pseudo-ternary system by classifying the alloying elements into $\gamma'$-forming elements (such as Al and Ti) and $\gamma''$-forming elements (such as Nb and Ta), while other elements are considered as Ni-like [266], since $\gamma'$ and $\gamma''$ usually coexist during early stages
of the heat treatments, e.g., isothermal aging. The simplified system can be denoted as Ni-Alx-Nby, where Alx is the weighted sum of all γ'-forming elements while Nby is the weighted sum of all γ''-forming elements. The overall composition (atomic ratio or molar ratio) of the system is $X_{Al}^0 = 0.023$ and $X_{Nb}^0 = 0.032$. We consider both γ’ and γ” precipitates in the simulation, which are represented by different order parameters. In the Ni-Alx-Nby pseudo-ternary database by CompuTherm LLC[266], the γ matrix is treated as a solid solution phase while the γ’ and γ” precipitates are both treated as the sublattice model $(Ni, Al, Nb)_{0.75}(Ni, Al, Nb)_{0.25}$, with different end-member lattice stabilities and interaction parameters. In the KKS model [164], the sublattice model can be treated using the methodology developed in Section 2.3, Chapter 2, using the iterative numerical scheme to obtain the sublattice site fractions under internal equilibrium. However, since the iterative scheme is time consuming, we fit the molar Gibbs free energies of each phase into parabolic functions at their equilibrium compositions or sublattice site fractions at a given temperature under ambient pressure. The detailed solution strategy follows Eq. (A4) in Appendix A.

The lattice parameters of IN718 at given aging temperatures are calculated based on the DFT-based calculations in [267], with the consideration of the multiple alloying elements and their compositions rather than the consideration of pure Ni, resulting in $a_\gamma = 3.6\,\text{Å}$ at 0 K and $a_\gamma = 3.617\,\text{Å}$ at 300 K, which is generally consistent with existing values [105]. The lattice parameters of γ’ and γ” are calculated by DFT using VASP, under the assumption that these values are insensitive to the temperature change, resulting in $a_{\gamma'} = 3.573\,\text{Å}$ for γ’ while $a_{\gamma'} = 3.649\,\text{Å}$ and $c_{\gamma'} = 7.51\,\text{Å}$ for γ”. The SFTS for both γ’ and γ” phases, under the fully coherent situation, are calculated under their given LCs and ORs with the matrix:
The calculated misfit strain component \( \varepsilon_{ij}^{00,\gamma''} \) is quite consistent with the reported value \( \varepsilon_{11}^{\gamma''} = 0.0089 \) at 1023 K before coherency loss according to the relaxed lattice parameters of \( \gamma \) and \( \gamma'' \) [263]. The component \( \varepsilon_{33}^{00,\gamma''} = 0.0384 \) is close to the reported values at room temperatures[264]. The coherent \( \gamma/\gamma' \) and \( \gamma/\gamma'' \) interfacial energies are estimated to be 50 mJ/m\(^2\) and 100 mJ/m\(^2\), respectively. The elastic constants of IN718 are taken as \( C_{11}=203 \text{ GPa}, C_{12}=150 \text{ GPa} \) and \( C_{44}=135 \text{ GPa} \) [105].

The identification of the line defects configurations is important in determining the critical precipitate dimensions for coherency loss. However, the detailed coherency loss mechanisms can be rather complicated. For example, Sundararaman et al.[262] proposed the stacking-fault-induced coherency loss of \( \gamma'' \), which can be realized by the decomposition of matrix dislocations into partial dislocations. One of the formed partial dislocations can be pinned to the \( \gamma/\gamma'' \) interface while the other partial dislocation passes through the interface to form stacking faults[262]. The interaction between the stacking faults and surrounding dislocations can be rather complicated [268], which may need further atomistic scale calculations and advanced characterization techniques to elucidate. In this study, however, we consider the overall effect of these defects to reduce the misfit strains during and after coherency loss. From experimentally reported misfit strains before and after coherency loss of \( \gamma'' \), the value of \( \varepsilon_{11}^{00,\gamma''} \), rather than that of \( \varepsilon_{33}^{00,\gamma''} \), is further reduced, which may be resulted from the large surface area of (001) of the precipitate phase as well as the high diameter/thickness aspect ratio[263]. Therefore, we assume the coherency loss of \( \gamma'' \) is due to the formation of the matrix dislocation loops \( \mathbf{b} = \frac{a_x}{2} \begin{bmatrix} 1 & 1 & 0 \end{bmatrix} \) on the broad (001) interface of \( \gamma'' \), while the average spacing of the dislocation loops is measured from...
the experimentally observed average stacking fault spacing, $\lambda=30$ nm, from [262]. We assume that the average spacing will not further evolve after the coherency loss. The modifications to SFTS and interfacial energies due to coherency loss can then be calculated, resulting in 

$$
\epsilon_{ij}^{0,\gamma'} = \begin{pmatrix}
0.003 & 0.003 \\
0.003 & 0.0384 \\
\end{pmatrix}
$$

and $\gamma_{dis}=56.3$ mJ/m$^2$. Note the calculated $\epsilon_{11}^{0,\gamma'}=0.003$ after coherency loss is quite consistent with the value at 1023 K[263].

![Figure 5.1 Morphology evolution of $\gamma'$ and $\gamma''$ precipitates. The $\gamma'$ precipitate is in blue color and the $\gamma''$ precipitate is in red color. (a) Initial spherical $\gamma''$ nucleus with a diameter of 6nm at $t=0$ s at $T>1141$K; (b) plate-like morphology of the $\gamma''$ particle at $t=1$ min at $T=1160$K; (c) illustration of the diameter and thickness of the $\gamma''$ particle at $t=1$ min at $T=1160$K; (d) initial spherical $\gamma'$ and $\gamma''$ nucleus at $T<1141$K; (e) plate-like $\gamma''$ precipitate and spherical $\gamma'$ precipitate at $t=3$ min at $T=1120$K; (f) plate-like $\gamma''$ precipitate and spherical $\gamma'$ precipitate at $t=8.5$ h at $T=950$K.](image)

With these parameters, we perform phase-field simulations to estimate the critical precipitate size of coherency loss, and investigate the effect of coherency loss on precipitate morphology and kinetics. We start our simulation with two spherical particles in the system, one is $\gamma'$, the other is $\gamma''$. Simulations are performed at different isothermal aging temperatures ranging from 950 K to
1190 K. The two particles are far away from each other since the $\frac{\text{Al}+\text{Ti}}{\text{Nb}}$ atomic ratio in the current alloy system is only 0.72, which is less than the empirical threshold (~0.9) for the formation of $\gamma'/\gamma''$ compact precipitates[261]. The initial diameters for both precipitates are set as 6 nm. As shown in Figure 5.1, the $\gamma'$ precipitate maintains spherical shape while the $\gamma''$ develops into a plate.

The coherency loss of $\gamma''$ is predicted by comparing the total energy difference between the fully coherent precipitate and the semi-coherent precipitate with given configurations of the line defect. Since we assume the bulk chemical free energies are the same for the coherent and semi-coherent precipitates, the total energy difference mainly comes from the differences in elastic strain energy and interfacial energy. By calculating these energetics during phase-field simulations, the energy difference vs. precipitate diameter relation can be obtained, as illustrated in Figure 5.2, at 1160 K. The results indeed indicate a critical precipitate size beyond which the semi-coherent precipitate becomes energetically favored, i.e., $\Delta E<0$. This diameter, denoted here as $d_c$, is about 140 nm. In addition to this threshold value, we should also pay attention to the precipitate diameter where $\Delta E$ is maximized, since it can be the kinetic or stability threshold for coherency loss. When the precipitate grows to this critical diameter, the development of line defects on its interface is not energetically favored; however, once there are interfacial line defects developed at this diameter, the further growth of the precipitate will lead to an energy decrease, and more importantly, the recovery of the coherency loss, i.e., the dissolution of the line defects, would become energetically unfavorable. This is similar to the critical nucleus size during solid state transformations[6]. Therefore, we denote this diameter as $d_c$, a critical diameter beyond which the precipitate is susceptible to coherency loss. In this set of simulation, $d_c$ is about 91 nm.
Figure 5.2 Energy contributions and difference for coherent and semi-coherent γ” particles at T=1160K. (a) Elastic strain energy $E_{el}$ and gradient energy $E_{grad}$ for semi-coherent and coherent γ” particles with the same given configuration, as a function of precipitate diameter. (b) Energy difference between the semi-coherent and coherent γ” particles with the same given configuration, as a function of precipitate diameter. The critical diameter for coherency loss is given by the diameter with the maximum $\Delta E$: $d_c=91nm$. The diameter $d_e=140nm$ with $\Delta E=0$ is also plotted.

We now further discuss the detailed mechanisms for the development of line defects when the precipitate size is between $d_e$ and $d_c$. These mechanisms include, as mentioned earlier, dislocation punching, climbing, and nucleation inside precipitates[32]. (1) Punching of dislocation loops near the interface is a result of the accumulation of coherency stress in the matrix. This mechanism requires a stress criterion, in which the shear stress on the slip plane should exceed the CRSS of the material. By using the simple analysis by Weatherly et al.[32], and using the shear modulus, transformation strain, as well as the estimation of the CRSS of pure Ni, this criterion can be satisfied for the coherency loss of γ”, indicating the dislocation punching is a possible mechanism for coherency loss. (2) Climbing of matrix dislocations requires the attraction of matrix dislocations by the precipitate via elastic interactions. To evaluate the possibility of this mechanism, we calculate the elastic interaction energies of various edge dislocations in the stress field of γ” according to Eq. (3.10). The results for a full dislocation $b = \frac{d_e}{2} [\bar{1}10]$ on (111) plane are shown in Figure 5.3, indicating the precipitate can attract the
dislocation to its periphery where the elastic interaction energy is negative. (3) Nucleation of 
dislocation loops inside the precipitate can be realized by the possible off-stoichiometry or the 
formation of stacking faults in γ". However, more experimental evidence should be provided to 
support this hypothesis.

![Figure 5.3 Elastic interaction energy between a full dislocation and a single variant of γ" precipitate (diameter=100nm).](image)

Figure 5.3 Elastic interaction energy between a full dislocation \( \mathbf{b} = \frac{a_y}{2} \begin{bmatrix} 1 & 1 & 1 \end{bmatrix} \) on (111) plane and 
a single variant of γ" precipitate (diameter=100nm). (a) The red color shows the precipitate 
morphology and the green color shows the region with elastic interaction energy lower than - 
0.375GPa; (b) elastic interaction energy distribution on (001) intersection; (c) elastic interaction 
energy distribution on (010) intersection; (d) elastic interaction energy distribution on (100) 
intersection.

Coherency loss modifies the anisotropies in misfit strains and interfacial energies, and 
therefore can affect the morphology of the precipitate. To show this effect, we perform two sets 
of simulations: (1) a normal one, in which the γ" precipitate becomes semi-coherent once its 
diameter reaches \( d_c \); (2) a reference one, in which the γ" precipitate maintains its coherency 
throughout the simulation. The diameters and thicknesses of the precipitates are measured during 
the simulation, as shown in Figure 5.4(a). The simulation results indicate that, compared with the
fully coherent counterpart, the precipitate shape becomes more “rounded” after coherency loss, i.e., the growth rate of the precipitate diameter becomes lower while the growth rate of the precipitate thickness becomes higher, leading to a decreased diameter/thickness ratio, as illustrated in the inset image in Figure 5.4(a). This is mainly due to the change in interfacial energy anisotropies since the habit plane (\{100\}) predicted by the microelasticity theory remains the same before and after coherency loss, while the minimization of interfacial energies becomes more urgent after coherency loss. The simulated growth kinetics with the consideration of coherency loss is also consistent with the experimental measurements [262, 263, 265, 269], as shown in Figure 5.4(b). The critical precipitate diameter for coherency loss is usually determined by the break in the $e/L$-$L$ curve, which is generally within the range of 50 to 120 nm for $\gamma''$ [263-265].

Figure 5.4 Growth kinetics of a $\gamma''$ particle. The particle is assumed to be coherent initially and then loses coherency at a critical diameter of 91 nm. (a) The lengthening and thickening kinetics of the particle at $T=1160$ K. After coherency loss, the growth kinetics of the coherent particle is plotted in dashed lines for comparison. The inset image shows the morphologies of the coherent and semi-coherent particles at $t=150$ s. (b) The thickness/diameter ratio (aspect ratio) of the particle vs. the diameter of the particle. Experimentally reported values from Devaux et al. [265], Han et al. [269], Slama et al. [263] and Sundaraman et al. [262] are also plotted.

The prediction of aging time to reach the critical size for coherency loss can be a useful guidance for realistic heat treatment of IN718. In this work, we estimate the time needed to form
a critical $\gamma''$ nucleus from existing TTT diagrams[270]. The time needed for the $\gamma''$ precipitate to reach the critical size from a critical nucleus is estimated by converting the time scales in phase-field simulations ($\Delta t^*$) into real time ($\Delta t$) using the reported diffusivity of Nb ($\bar{D}_{nb}$) in IN718[265]:

$$\Delta t = t_0^* \cdot \frac{\bar{D}_{nb}}{\Delta t^*}.$$ 

The simulation results are shown in Figure 5.5, in which the red dashed line represents the time needed to reach $d_c$ while the purple dashed line represents the time needed to reach $d_e$. The region between these two lines is the intermediate region where the $\gamma''$ precipitate is susceptible to coherency loss.

![Figure 5.5 Time estimation of coherency loss. The solid lines are TTT curves of the initiation (volume fraction ~1%) of grain boundary $\delta$, $\delta$ and $\gamma''$ phases, respectively, as reproduced from [270]. The red dots predict the time when the diameter of a $\gamma''$ particle in the system reaches $d_c=91\text{nm} (\pm 5\text{nm})$; the pink dots predict the time when the diameter of a $\gamma''$ particle in the system reaches $d_e=140\text{nm} (\pm 5\text{nm})$.](image)

### 5.3.2 $\theta'$ precipitate in Al-Cu alloys

$\theta'$, as introduced in previous chapters, is the key hardening precipitate in Al-Cu-based alloys. $\theta'$ is semi-coherent with the Al matrix and form a disk shape due to the anisotropies in interfacial
energy, misfit strain and interface mobility. During prolonged aging, 0' can gradually lose the
coherency with the Al-matrix, developing several types of dislocation loops on both the coherent
and the semi-coherent interfaces, and finally replaced by the more stable 0 phase. According to
TEM observations by Weatherly et al.[32], there can be the following dislocation configurations
and their combinations after coherency loss of 0': (1) dislocation loops $b_1 = a_\alpha[100]$ and
$b_2 = a_\alpha[010]$ on the broad (001) interface of 0' (or alternatively, $b_1 = \frac{a_\alpha}{2}[110]$ and
$b_2 = \frac{a_\alpha}{2}[\overline{1}10]$); (2) dislocation loops $b_3 = a_\alpha[001]$ on the semi-coherent interface. However, no
information was given about the development sequence of these dislocation loops. Therefore, we
consider the following five combinations of the dislocations: i) only $b_1$ or $b_2$ on the initially
coherent broad interface; ii) only $b_3$ on the semi-coherent interface; iii) $b_1$ and $b_2$ on the broad
interface; iv) $b_1$ (or $b_2$) on the broad interface and $b_3$ on the semi-coherent interface; v) $b_1$ and $b_2$
on the broad interface and $b_3$ on the semi-coherent interface. Using the phase-field model
described in Section 5.2, we propose to figure out the sequence of the development of dislocation
loops, the evolution of their average spacings, and the corresponding evolution of precipitate
morphologies.

We start our simulation with a single variant of 0', at 503 K, with the critical nucleus size
(i.e., plate-shaped morphology, with diameter 4 nm and thickness 2 nm) determined by the
classical nucleation theory. The size of the simulation size is $128\Delta x \times 512\Delta x \times 512\Delta x$ ($\Delta x = 1$ nm).
The model parameters before the initial coherency loss of the precipitate are the same with those
given in Chapter 4, except that we use a larger interface thickness, 4 nm, in this case. The
modifications of interfacial energy and deformation gradient due to the emergence and evolution
of dislocation loops follow those described in Section 5.2. To determine the dislocation
configuration for the initial coherency loss of the precipitate, we assume that the initial spacings
of the dislocation loops are identical to the dimensions of the precipitate, i.e., the initial spacing of
$b_1$ or $b_2$ is equal to the diameter of the precipitate while that of $b_3$ is equal to the thickness of the precipitate. The further evolution of the dislocation loop spacings follows Eq. (5.4). We are specifically interested in finding the dislocation sequence with the lowest energy cost.

Figure 5.6 Phase-field simulations for sequential coherency loss of $\theta'$ at $T=503$ K. (a) Flow chart of the phase-field model with the consideration of sequential coherency loss and evolution of the average spacing of interfacial line defects. (b) Possible coherency loss pathways of $\theta'$. The potential pathways are marked by black arrows while the predicted pathway with the lowest energy cost, $b_3 \rightarrow b_1 + b_3 \rightarrow b_1 + b_2 + b_3$, is marked by red arrows. (c) Phase-field simulations of precipitation kinetics during the sequential coherency loss of $\theta'$. The evolution of precipitate diameters, thicknesses and dislocation line spacings are all plotted. Regions with different colors show the different coherency state during the evolution.
The simulation results are shown in Figure 5.6. The dislocation sequence with the lowest energy cost is found to be \( b_3 \rightarrow b_1 + b_3 \rightarrow b_1 + b_2 + b_3 \) among all the possible pathways (Figure 5.6 (b)). The corresponding precipitate kinetics, together with the evolution of dislocation average spacings, are also shown in the figure. From the simulation, we find that the critical precipitate size for the initial coherency loss (emergence of \( b_3 \)) is about 11 nm in thickness and 73 nm in diameter based on the energy criterion, while the emergence of \( b_1 \) takes place at 31 nm in thickness and 152 nm in diameter; finally, the emergence of \( b_2 \) takes place at 37 nm in thickness and 162 nm in diameter. With the continuous growth of the precipitate and the further development of the dislocation loops, the dislocation spacings continue to decrease in order to further reduce the elastic strain energy, until the coherency of the precipitate becomes almost fully lost. The initial coherency loss due to the formation of \( b_3 \) dislocation is consistent with the fact that the out-of-broad-plane component of the Al/\( \theta' \) misfit strain, -0.051, is much larger than the in-broad-plane components, 0.0075, and the development of \( b_3 \) dislocation loops on the edges of \( \theta' \) can largely relax the misfit strain and reduce the elastic strain energy. The development of \( b_3 \) results in an obvious increase of thickening rates of \( \theta' \), since the introduction of \( b_3 \) reduce the anisotropies in misfit strains which is the dominant factor for precipitate morphology at this stage, though it also increases the anisotropies in interfacial energy. Although \( b_3 \) is the first developed interface dislocation, its further evolution is rather slow since the further decrease of \( b_3 \) dislocation spacing (d1 in Figure 5.6(c)) would lead to significant increase in interfacial energy. With the development of \( b_3 \), the elastic strain energy is partially relaxed and the precipitate continuously grow, until it becomes large enough to trigger the further loss of coherency. This time, dislocations will be developed on the broad Al/\( \theta' \) interface to reduce the in-plane misfit strain components. \( b_1 \) will be developed and further evolve, accompanied by the change of the initially isotropic in-plane misfit strains and interfacial energies. From now on, the in-plane shape of \( \theta' \) deviates from the ideal circular shape, forming an elliptic shape, and causing the differences in precipitate diameters along the two in-plane directions ("precipitate diameter1" and
“precipitate diameter2” in Figure 5.6(c)). After a short period (~3 h), the \( b_2 \) dislocation loop will also form on the broad interface. Once developed, its average spacing (d3 in Figure 5.6(c)) will remain constant for about 25 h, until the elastic strain energy becomes large enough to enable the further reduction of its spacing. The inequal spacing of \( b_1 \) and \( b_2 \) will further enlarge the deviation of the in-plane precipitate shape from the ideal circular shape. The dislocation spacings will further decrease until the coherency of the precipitate is fully lost. Note that in this set of simulations, the \( b_1 \) and \( b_3 \) dislocations can fully compensate the corresponding Al/\( \theta' \) misfit strain component, while the \( b_2 \) dislocation spacing will not further evolve at about 75 nm. Compared with the fully coherent case, the diameter/thickness aspect ratio of the precipitate will significantly decrease during coherency loss, and the dominant factors of the precipitate morphology repeatedly change between the anisotropy and minimization of the elastic strain energy and those of the interfacial energy. This change of aspect ratio is consistent with existing experimental observations, where \( \theta' \) precipitates without coherency loss on the broad Al/\( \theta' \) interface (aspect ratio ~ 44) are observed to be much thinner than the ones with coherency loss (aspect ratio ~ 10) [32].

The sequential loss of coherency changes the morphology, especially diameter/thickness aspect ratios of the precipitate, beyond the initial coherency loss point of about 4 h (Figure 5.7(a)). This morphology change will have a prominent impact on the precipitation hardening effect. In this study, under the assumption that the precipitation hardening mechanisms (i.e., precipitate-dislocation interactions) do not change with the loss of coherency, we compare the hardening effect for both the fully coherent and semi-coherent cases, using the hardening model shown in Eq. (4.4a) [225]. The estimation indicates up to 30 MPa (~35%) difference in the hardening effects for these two cases (Figure 5.7(b)), indicating the importance of maintaining the full coherency and high aspect ratio of \( \theta' \) during heat treatment to maximize the precipitate hardening effect. It should be noted that the detailed dislocation-precipitate interactions and the hardening
mechanisms are all subject to change when the coherency of the precipitate is lost, which needs more careful investigations in the future.

Figure 5.7 Precipitation kinetics and hardening effects for the case without coherency loss during precipitate growth and the case with sequential coherency loss. (a) Predicted precipitation kinetics from phase-field simulations. (b) Predicted precipitation hardening effects.

5.4 Summary

In this chapter, we propose a phase-field model which is capable of predicting the critical precipitate size for coherency loss, the possible development sequences and evolution of the average spacings of line defects that lead to the coherency loss of the precipitate, and the corresponding change of precipitate morphology and kinetics after coherency loss. We apply this model to the coherency loss of γ” in IN718 and θ’ in Al-Cu. Based on the investigations, the following conclusion can be reached:

(1) We consider the coherency state change of γ” from the fully coherent state to a given semi-coherent state based on experimental results, without the further evolution of the dislocation spacings. The predicted critical precipitate size for coherency loss lies within dc=91 nm and de=140 nm based on different criteria, which is generally consistent with experimental results.
(2) We investigate the possible development sequences and evolution of the average spacings of the dislocations at Al/θ’ interfaces based on experimental investigations, and identify that the $b_3 \rightarrow b_1 + b_3 \rightarrow b_1 + b_2 + b_3$ path has the lowest energy cost. The effects of sequential coherency loss on the precipitate morphology, kinetics and hardening effects are also predicted.
Chapter 6: Understanding Microstructure Evolution During Continuous Cooling of Ti-6Al-4V Alloys

6.1 Introduction

Titanium (Ti) alloys, with high strength-to-weight ratio and excellent corrosion resistance, have been extensively utilized as structural materials in aerospace related applications [271]. Among the various commercial Ti-alloys, Ti-6Al-4V (in wt.%), with a good balance of strength, ductility, fatigue resistance and fracture properties, as well as its good producibility, is still the most widely used Ti-alloy [271]. The excellent mechanical properties of Ti-6Al-4V is largely attributed to its rich (α+β) microstructure, which is a result of not only the thermodynamic stabilization of both α (hcp crystal structure) and β (bcc crystal structure) phases by different alloying elements, but also the complicated competition between different phase transformation modes under different thermo-mechanical processing conditions. The thermodynamic stabilization effect of alloying elements has been thoroughly understood by investigating the effect of different alloying elements on the β→α transus temperature. Specifically, with both α-stabilizer Al and β-stabilizer V, Ti-6Al-4V has a transus temperature about 1000 °C and thermodynamically enables the (α+β) two-phase mixture within a wide temperature range [272]. On the other hand, the different phase transformation modes in Ti-6Al-4V provide the kinetic details about how the (α+β) two-phase mixture emerges and evolves, giving rise to the various types of (α+β) two-phase microstructures that are distinct in mechanical properties. For example, under different thermo-mechanical processing conditions in the β-phase field, Ti-6Al-4V can undergo various types of phase transformations including β→α_p precipitation through bulk solute diffusion [273], β→α_m massive transformation through short-range diffusion [274], β→α’ martensitic transformation through diffusionless displacive mechanism [275], recrystallization of β grains [276], as well as their combinations. Consequently, a wide spectrum of (α+β)
microstructures, ranging from parallel α colonies, fully laminar structures (or basket-weave and Widmanstätten structure), to bimodal or even fully equi-axed microstructures can be obtained [271, 277].

Understanding the kinetic mechanisms of the various phase transformation modes and their competitions in Ti-6Al-4V, as well as in other similar dual-phase Ti-alloys, is an important prerequisite for controlling the mechanical properties of the alloy systems. Accordingly, a number of experimental investigations have been devoted to the identification of phase transformation modes and the understanding of their correlation with the microstructure patterns through direct observation and calibration. For example, based on experimental observations, it has been generally accepted that the diffusional β→α precipitation takes place under low cooling rate and initiates near grain boundaries, forming colony-type microstructures [273, 278]; with increasing cooling rate, the nucleation of α precipitates can occur inside β grains to form basket-weave microstructures [279], while the martensitic transformation takes place upon fast cooling (>20K/s) to a critical temperature (Ms), forming fine, acicular α’ martensites [275]. However, due to the difficulties of existing experimental techniques in in situ observation of the whole phase transformation processes at high temperatures, it is still challenging to obtain the real-time evolution of microstructures, more precisely evaluate the interplay among the different phase transformation mechanisms and explain the microstructure features. Nevertheless, these in-depth understandings about the microstructure features which is currently lacking, are critically important in the mechanical property control of not only conventional manufacturing processes such as casting but also more advanced manufacturing processes. For example, during additive manufacturing of Ti-6Al-4V alloys, the multiple thermal cycles and complicated thermal history can significantly affect the microstructure morphology and texture in both grain and sub-grain length scales, which in turn will affect the macroscopic mechanical property of the build [280-286].
In addition to the experimental investigations, there have been a series of theoretical frameworks devoted to the understanding of kinetic mechanisms of phase transformations in Ti-alloys. For example, based on existing thermodynamic databases of Ti-alloys, the so-called “graphical thermodynamic approach” [36, 287-290], which analyzes the relevant phase stabilities with respect to compositional and/or structure changes, has been established in Ti-alloys [35, 107, 291-293]. The possible kinetic pathways leading to different types of microstructures in Ti-alloys under different heat treatment conditions have been systematically studied. However, the graphical thermodynamic approach largely relies on bulk thermodynamics while neglects the anisotropic energy contributions such as interfacial energies and coherency strain energies, which determine the microstructure morphology and prominently affect the details of the transformation and microstructure evolution kinetics. In this regard, the phase-field approach [65], which uses the diffuse-interface approximation and can couple thermodynamic and diffusion mobility databases, as well as the microelasticity theory [18] for solid state transformations, is a desirable computational method for investigating such kinetic details. Specifically for Ti-alloys, the phase-field simulations have been performed for understanding the diffusion-controlled precipitate growth behavior[294], the equilibrium shape of α-precipitates as a function of size and coherency[34], the effect of grain boundaries [108, 109, 113, 127] and dislocations [110, 111] on the microstructure evolution, as well as the pseudo-spinodal mechanisms [35, 107]. These models, although well-developed, are focused on isothermal transformations in Ti-alloys, and are not able to capture the microstructure features with temperature variation. Besides, non-isothermal phase-field models of solid state transformations [103] have been attempted in a few alloy systems, which provide useful guidance for developing a non-isothermal phase-field model for simulating \( \beta \rightarrow (\alpha+\beta) \) phase transformations and subsequent microstructure evolutions in Ti-6Al-4V during continuously cooling.
The key challenges of simulating non-isothermal $\beta \rightarrow \alpha$ transformations in Ti-6Al-4V lie not only in the formulation of temperature-dependent free energies and kinetic coefficients, but also the consideration of temperature-dependent nucleation criterion based on the phase transformation kinetic pathway. Accordingly, in our phase-field model, we include temperature-dependent Ti-Al-V thermodynamic database [295], as well as diffusion mobility information from literature [47, 296]; to capture the temperature-dependent nucleation rate, we implement Poisson seeding based on classical nucleation theory [120, 121]. Specifically, we discuss the non-classical nucleation behaviors, especially elastic interactions, on microstructure evolution. We then use the developed phase-field model to simulate the microstructure evolution during continuously cooling of Ti-6Al-4V, under different cooling rates. The interplay between the diffusional and displacive transformation mechanisms is also investigated and discussed.

6.2 Phase transformation kinetic pathway analysis

In this section, we first give the theoretical framework of the graphical thermodynamic approach for general multicomponent, multiphase alloy system involving both compositional variations and structural change. We then apply the method to Ti-6Al-4V under both isothermal and non-isothermal conditions. Possible extension to non-conventional kinetic pathways of Ti-6Al-4V is also discussed.

6.2.1 General framework

The thermodynamic and kinetic features of phase transformations of alloys can be predicted from the variations of the related free energy with respect to its natural variables. Under given temperature ($T$) and pressure ($p$), it is natural to use the Gibbs free energy to evaluate these processes, while the state of a phase can be represented by a specific point on the Gibbs free energy landscape (or hypersurface) with respect to the thermodynamic configurational variables including compositions ($X$) and order parameters ($\eta$). The possible kinetic pathways of a phase transformation are closely related to the local topological features of $G$. These include: (1) the
local variational characteristics of $G$ with respect to infinitesimal perturbations of the variable
(i.e., the second derivatives of $G$ with respect to the variable), which determines whether the
given phase point is stable or unstable, as well as the ranges of the variables within which the
phase point is stable or unstable; (2) the relative value of $G$ on the pathway, which determines the
relative stability of the phase points with each other, i.e., whether the given phase point is stable
or metastable. Note this analysis can be performed under other specific conditions using other
types of free energies. For example, the strain phase separation and strain spinodal in ferroelastic
and ferroelectric systems can be analyzed similarly using the Helmholtz free energy under given
temperature, volume and strain[297].

To enable the graphical thermodynamic analysis, it is critical to construct a free energy
function that can describe the related phase transformation processes. For a general
multicomponent and multiphase system with $N$ alloying elements ($X_1, X_2, \ldots, X_N$) and $M$ product
phases ($\eta_1, \eta_2, \ldots, \eta_M$), we use the following free energy function[161, 162]:

$$g(\{X\},\{\eta\}) = \left[1 - \sum_{i=0}^{M} h(\eta_i)\right] \cdot g^0(\{X\}) + \sum_{i=0}^{M} h(\eta_i) \cdot g'(\{X\}) + g^{\text{Landau}}(\{\eta\}), \quad (6.1)$$

where $g'(\{X\})$ (i=0,1,..,M) are the molar Gibbs free energies of the matrix and product phases,$
h(\eta_i)$ is an interpolation, and $g^{\text{Landau}}(\{\eta\})$ is a Landau-type free energy that describes the
structural transformations. The relative stabilities of the different states are determined by the
above-mentioned criteria:

(1) The positive-definiteness of the Hessian matrices for a given stagnation point:
The positive-definite, negative-definite and indefinite Hessian matrix imply that a state is at local minimum, local maximum or a saddle point, respectively. If located at a local minimum, then the state is stable with respect to any local variations of the configurational variables; if located at a local maximum or a saddle point, then the state is unstable with respect to any local variations of the configurational variables which lead to the negative eigenvalues of the Hessian matrix. Specifically, the compositional instability leads to spinodal decomposition while the structural instability leads to continuous structural transformation or ordering. With these instabilities, even infinitesimal perturbations of the configurational variables can lead to the phase transformation.

(2) The relative values of $G$ for given states on the possible pathways. Under certain conditions, the states of interest can all be stable (local minima), while their relative $G$ values (energy differences) determine the driving force of the phase transformation from a metastable state to the most stable state. The transformation from a local minimum to another local minimum with lower energy requires overcoming an energy barrier, i.e., there exist saddle points between the two points on the landscape of $G$. This means that the transformation, either diffusional or diffusionless, takes place through a nucleation-and-growth mechanism.

6.2.2 Application to isothermal conditions in Ti-6Al-4V

We now formulate the free energy of Ti-6Al-4V based on existing thermodynamic databases [295, 298]. Based on thermodynamic calculations, there are three dominant phases, $\alpha$ (hcp), $\beta$
(bcc) and Ti₃Al (D0₁₉) at temperatures below the β transus temperature in Ti-6Al-4V. Therefore, we formulate the bulk free energy density of the system as follows:

\[
g_{\text{bulk}}(X_{\alpha\beta}, X_{\eta\phi}, T) = (1 - h(\eta) - h(\phi)) \cdot g^\alpha(X_{\alpha\beta}, T) + h(\eta) \cdot g^\beta(X_{\alpha\beta}, T) + h(\phi) \cdot g^{\text{Ti}_3\text{Al}}(X_{\alpha\beta}, T) + w^\alpha \cdot \eta^2 (\eta - 1)^2 + w^{\text{Ti}_3\text{Al}} \cdot \phi^2 (\phi - 1)^2 + w^{\text{int}} \cdot \eta^2 \phi^2
\]

where \(X_{\alpha\beta}\) and \(X_{\eta\phi}\) are the compositions of Al and V, respectively, \(\eta\) is the structural order parameter describing the bcc to hcp crystallographic structural change, \(\phi\) is the long-range order parameter for the ordered D₀₁₉ structure, and \(g^{\text{Landau}}(\eta, \phi) = w^\alpha \cdot \eta^2 (\eta - 1)^2 + w^{\text{Ti}_3\text{Al}} \cdot \phi^2 (\phi - 1)^2 + w^{\text{int}} \cdot \eta^2 \phi^2\) is a Landau-type free energy for structure transformations to \(\alpha\) and D₀₁₉ phases, with \(w^\alpha\), \(w^{\text{Ti}_3\text{Al}}\) and \(w^{\text{int}}\) to be energy humps. For the interpolation function, we chose \(h(x) = 3x^2 - 2x^3\), which ensures the local extremes of the parent phase \((x=0)\) and product phase \((x=1)\), and can capture the transition of parent phase stability with temperature change. The molar Gibbs free energies of \(\alpha\) and \(\beta\) phases are directly taken from the database, both of which are treated as solid solution phases. The molar Gibbs free energy of Ti₃Al is formulated based on the \((\text{Ti,Al,V})_3(\text{Ti,Al,V})_1\) sublattice model in the database [295, 298], which is converted to an explicit function of composition based on the fact that the equilibrium site fractions of Al and V in the first sublattice are negligible. We start the analysis from the homogeneous, single-crystal \(\beta\) phase with initial compositions \((X_{\alpha\beta}^0, X_{\eta\phi}^0) = (0.1019, 0.036)\) in atomic fraction, corresponding to 6wt.%Al and 4wt.%V; and initial order parameters \((\eta, \phi) = (0, 0)\). Note that the \(\alpha\) phase can be of diffusional, massive and martensitic products, while we do not distinguish them in this analysis and use a unified free energy function with possible composition variation, since their crystal structures are all hcp. By analyzing the phase stabilities with respect to changes in \(\{X\}\) and \(\{\eta\}\), the possible kinetic pathways at different isothermal aging temperatures can be obtained.

<Phase stabilities w.r.t. compositional change>
We evaluate the compositional part of the Hessian matrix for $\beta$ phase at $(\eta, \phi)=(0,0)$ at different temperatures, and obtain the phase stability map in compositional space shown in Figure 7.1. Based on the positive-definiteness or the signs of the eigenvalues of the Hessian matrix, the full compositional space can be divided into three regions similar to [299]: I) Hessian matrix is negative-definite, indicating $\beta$ phase is unstable w.r.t. composition variations along all compositional directions; II) Hessian matrix has one positive and one negative value, indicating $\beta$ phase is unstable w.r.t. composition variations along specific compositional directions while stable w.r.t. others; III) Hessian matrix is positive-definite and $\beta$ is stable for all composition directions. The boundaries of these regions are determined by finding the Hessian matrix with zero determinants.

Figure 6.1 Compositional stability analysis for $\beta$ phase in Ti-Al-V system, using thermodynamic database functions. (a) Isothermal section of compositional instability surface at different temperatures. (b) Compositional stability analysis at $T=400K$ for the initial composition of Ti-6Al-4V; the two pink points, linked by the white tie line, represent the equilibrium composition of $\beta$ phase (upper left) and $\alpha$ phase (lower right), respectively; the thick yellow line separates stability region II and III; the two white dashed lines gives the compositional instability directions for $\beta$ phase with the initial composition; the red arrows show the most unstable direction.
For Ti-6Al-4V, the initial composition \((X_{Al}^0, X_{V}^0) = (0.1019,0.036)\) is within the instability regime below \(T_s = 424\) K as shown in Figure 6.1(b), under which the phase separation of \(\beta\) occurs via spinodal decomposition, forming a solute-rich and a solute-lean phase while the bcc crystal structure is maintained, followed by the further evolution into the stable (\(\alpha+\beta+Ti_3Al\)) mixture via nucleation-and-growth mechanisms. For example, at \(T = 400\) K, \(\beta\) phase is unstable w.r.t. certain composition directions since one of the eigenvalues of the Hessian matrix is negative. These unstable compositional directions can be calculated by \((Hv) \cdot v \leq 0\), which lie between the two white dashed lines in Figure 6.1(b). Here \(v = (\cos \theta, \sin \theta)^T\) is a directional unit vector of compositional variation from the initial composition \((X_{Al}^0, X_{V}^0) = (0.1019,0.036)\) with an angle \(\theta\). The most probable decomposition path can be determined by finding the eigenvector of the Hessian matrix corresponding to the negative eigenvalue, which is indicated by the red arrow in Figure 6.1(b). Note the structural instabilities can also take place at this temperature, and the phase separation of \(\beta\) is rarely reported in experiments due to the difficulty to retain \(\beta\) phase at this low temperature. On the other hand, \(\beta\) phase separation is possible in \(\beta\)-Ti alloys with more of \(\beta\)-stabilizers[271].

Above \(T_s\), compositional instabilities of \(\beta\) vanishes and the transformation pathway is determined by the relative stabilities of the possible phases according to the relative values of \(G\) of these phases. This is obtained by finding the critical temperature where the free energies of \(\beta\) and \(\alpha\) phases, under the same composition of \((X_{Al}^0, X_{V}^0) = (0.1019,0.036)\), are equal. We find this temperature to be \(T_f = 1145\) K. Above this temperature and below the \(\beta\) transus \(T_f = 1249\) K, the \(\alpha\) phase with the equilibrium composition that is different from the initial composition can directly nucleate from the \(\beta\) matrix and grow via the diffusional mechanism; while below this temperature, the bcc to hcp structural transformation may first take place through a diffusionless mechanism, followed by the diffusional \(\alpha \rightarrow (\alpha+\beta)\) transformation through nucleation-and-growth mechanisms.
Although the direct nucleation of $\alpha$ with the equilibrium composition is also possible, the diffusionless $\beta \rightarrow \alpha$ transformation, or the direct nucleation of $\alpha$ from $\beta$ without composition change is more likely since the structure change involving local atomic movements or short-range diffusion is usually much faster than the long-range diffusion. It should be noted that, when $T$ is higher than $T_0$ and close to $T_{\beta}$, the driving force for phase transformation is rather small, which leads to extremely high nucleation barrier and low nucleation probability for homogeneous nucleation. Therefore, $\alpha$ product may nucleate at or near structure inhomogeneities such as grain boundaries or dislocations, which can reduce the nucleation barrier. With the decrease of $T$, homogeneous nucleation of $\alpha$ inside $\beta$ grains, or heterogeneous nucleation of $\alpha$ near the already-formed grain boundary $\alpha$ products, becomes possible.

The D0$_{19}$-ordered Ti$_3$Al precipitates can emerge below 895 K from thermodynamic calculations, which has been experimentally reported in Ti-6Al-4V especially when the oxygen composition is about 0.2 wt.% or higher[300]. Therefore, the kinetic pathway of phase transformation becomes diffusionless $\beta \rightarrow \alpha$ through nucleation-and-growth, followed by diffusional $\alpha \rightarrow (\alpha + \beta + \text{Ti}_3\text{Al})$ through nucleation-and-growth below 895 K.

<Phase stabilities w.r.t. structural change>

$\beta$ phase can become dynamically unstable w.r.t. atomic shuffle at low temperatures (e.g., below $T_c=484.4$ K in pure Ti according to DFT calculations[301-303]) since the shear modulus becomes negative. The bcc to hcp transformation is continuous below this critical temperature, while becomes discontinuous above this temperature where the nucleation of $\alpha$ by overcoming an energy barrier is required. However, this critical temperature is difficult to capture and the typical $\beta \rightarrow \alpha$ martensitic transformations are usually characterized by a start temperature $M_s$, which may reflect a critical driving force. From the available TTT diagrams of Ti-6Al-4V[304-307], we know $M_s$ is about 550–650 °C, which lies in the $\beta \rightarrow \alpha \rightarrow (\alpha + \beta)$ regime. Note we use the same thermodynamic function to describe the martensitic phase $\alpha'$ since it also has an hcp structure.
(rather than orthorhombic structure for Ti-alloys with higher contents of β stabilizers) in Ti-6Al-4V. Assuming $M_s$=873 K, we estimate the critical driving force to be about 1200 J/mol. Figure 6.2(a) shows the relative stabilities of β and α phase at various temperatures. Note that β is still metastable w.r.t. $\eta$ at $M_s$ while becomes unstable when $T<T_c$.

Figure 6.2 Stability of β phase with respect to structure change at various temperatures. (a) Isothermal case; (b) rapid cooling (or high undercooling). β phase is at $\eta=0$ and α phase is at $\eta=1$. At $T=M_s$, β phase ($\eta=0$) is still metastable with respect to β→α structure change.

Therefore, when $T<M_s$, discontinuous ($T_c<T<M_s$) or continuous ($T<T_c$) β→α’ transformations take place to form metastable α’ martensites. α’ can then decompose into the equilibrium (α+β+Ti₃Al) mixture by diffusional nucleation-and-growth mechanism. However, this latter process can be rather slow due to the low solute diffusivities at these low temperatures. Therefore, the α’ microstructure is usually maintained.

The possible kinetic pathways from a homogeneous β phase under different isothermal aging temperatures, considering both the compositional and structural variables, are summarized in Table 6.1. The corresponding energy landscapes for each regime are shown in Figure 6.3, using molar Gibbs free energy functions from realistic Ti-Al-V database[295, 298].

Table 6.1 Summary of kinetic pathways in Ti-6Al-4V under isothermal condition

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>Kinetic Pathways</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$ (1145K)&lt;$T_β$</td>
<td>$β\rightarrow$(diffusional nucleation and growth)$\rightarrow(α+β)$</td>
</tr>
</tbody>
</table>
Figure 6.3 The illustration of kinetic pathways in Ti-6Al-4V under isothermal condition for (a) $T_0$ (1145K)<$T<T_β$ (1249K): $β$→(diffusional nucleation and growth)$→α$→(diffusional nucleation and growth)$→(α+β)$; (b) $T_{Ti3Al}$ (895K)<$T<T_0$ (1145K): $β$→(diffusionless nucleation and growth)$→α$ or $α'$ (martensite)$→$ (diffusional nucleation and growth)$→(α+β+Ti_3Al)$; (c) $T_s$ (423K)<$T<T_{Ti3Al}$ (895K): $β$→(diffusionless nucleation and growth)$→α$→(diffusional nucleation and growth)$→(α+β+Ti_3Al)$). The dashed red arrow represents discontinuous transformations (through nucleation-and-growth mechanism).
6.2.3 Application to non-isothermal conditions in Ti-6Al-4V

Continuous cooling is another heat treatment process which is frequently used for Ti-alloys. Compared with isothermal aging, the diffusionless structural transformations have higher probability to happen due to the larger undercooling during rapid cooling. To consider the undercooling effect, we add an additional term to the free energy:

\[
\left( g^\beta(X_{\alpha}^0, X_{\gamma}^0, T^0) - g^\alpha(X_{\alpha}^0, X_{\gamma}^0, T) \right) \cdot h(\eta),
\]

where \( T^0 \) is the initial temperature of cooling. Upon cooling, the \( M_s \) temperature can be higher than the isothermal counterpart, which can reach 800 °C according to experimental reports and existing CCT diagrams for Ti-6Al-4V[308, 309]. This indicates an increased critical driving force for martensitic transformation, which can be as high as 13,000 J/mol. The corresponding \( \beta \) stability under different temperatures during continuous cooling is shown in Figure 6.2(b).

The kinetic pathways during continuous cooling can also be analyzed by the graphical thermodynamic approach. Under slow cooling rates (e.g., <0.1 K/s), the temperature is largely homogenized in the sample, resulting in small undercooling, and the kinetic pathways are quite similar to those under isothermal conditions. In contrast, under fast cooling (e.g., >20 K/s), the temperature homogenization is largely forbidden, resulting in large undercooling. The structural transformation can be dominant in this case. For example, the temperature \( T_o \) where the Gibbs free energy of the two phases are equal is shifted from 1145 K during isothermal aging to 1243 K. The kinetic pathways from a homogeneous \( \beta \) phase during continuous cooling to different temperature ranges are summarized in Table 6.2.

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>Kinetic Pathways</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_0 ) (1243K)&lt;( T &lt; T_{\beta} ) (1249K)</td>
<td>( \beta \rightarrow ) (diffusional nucleation and growth) ( \rightarrow (\alpha+\beta) )</td>
</tr>
<tr>
<td>( T_{Ti3Al} ) (895K)&lt;( T &lt; T_{0} ) (1243K)</td>
<td>( \beta \rightarrow ) (diffusionless nucleation and growth) ( \rightarrow \alpha ) or ( \alpha' ) (martensite) ( \rightarrow ) (diffusional nucleation and growth) ( \rightarrow (\alpha+\beta) )</td>
</tr>
<tr>
<td>( T &lt; T_{Ti3Al} ) (895K)</td>
<td>( \beta \rightarrow ) (diffusionless, discontinuous) ( \rightarrow \alpha' ) (martensite) ( \rightarrow ) (diffusional nucleation and growth) ( \rightarrow (\alpha+\beta+Ti_3Al) )</td>
</tr>
</tbody>
</table>
6.3 Phase-field model

The key feature of the current phase-field model is the consideration of the temperature-dependence for most of the physical parameters. These include free energies, diffusivities, misfit strains, and nucleation rates. For simplicity we only consider the α and β phases. Assuming the transformation follows the Burgers OR, there are 12 possible structural variants for the α products\cite{310}. Therefore, we extend the order parameter in Eq. (6.3) to 12 order parameters. Note a more physical treatment is to consider the atomic process during bcc→hcp transformations, which includes both atomic shuffle and shear deformation, the physical order parameters to describe the transformation. The KKS model is used, with the corresponding constraint equations solved by the Newton-Raphson iterative method. The anisotropic α/β interfacial energies are obtained from existing DFT calculations \cite{311}, which, together with the estimated interface thicknesses, are used to parameterize the gradient energy coefficients and double-well energy barrier height.

The elastic strain energy is again evaluated based on the microelasticity theory\cite{18}. The key is to properly estimate the SFTS tensor during β→α transformations. Based on the OR, we define the following local reference coordinate system:

\[
\begin{bmatrix}
[111]_\beta \\ [2\bar{1}10]_\alpha \\
[11\bar{2}]_\beta \\ [0\bar{1}10]_\alpha \\
[\bar{1}10]_\beta \\ [0001]_\alpha
\end{bmatrix}.
\]

In this local reference frame, we choose three non-planar lattice vectors in each phase, \([111]_\beta, [1\bar{1}1]_\beta, [\bar{1}10]_\beta\) and \([2\bar{1}0]_\alpha, [1\bar{1}2]_\alpha, [0001]_\alpha\), as the column vectors of the lattice vector matrices:

\[
\mathbf{B} = (a_\beta, b_\beta, c_\beta) = \begin{bmatrix}
\frac{\sqrt{3}}{2}a_\beta & \frac{\sqrt{3}}{2}a_\beta \sin \theta_\beta & 0 \\
0 & \frac{\sqrt{3}}{2}a_\beta \cos \theta_\beta & 0 \\
0 & 0 & \sqrt{2}a_\beta
\end{bmatrix}
\]  

(6.4a)
\[ H = (a, b, c) = \begin{pmatrix} a & a \sin \theta & 0 \\ 0 & a \cos \theta & 0 \\ 0 & 0 & c_a \end{pmatrix} \]  

(6.4b)

where \( a_\beta \) is the lattice parameter of \( \beta \) phase, \( a_\alpha \) and \( c_\alpha \) are lattice parameters of \( \alpha \) phase, \( \theta_\beta = 19.47^\circ \) and \( \theta_\alpha = 30^\circ \). If the coherency can be maintained during the shearing process, the deformation gradient \( F_0 \) can be calculated by \( F_0 = H \cdot B^{-1} \). Note that \( F_0 \) is independent of the choices of lattice vectors if the selected three lattice vectors are non-coplanar. Moreover, through polar decomposition, we find that \( F_0 \) contains a pure rotation of 5.26°, which is consistent with [34] and is characteristic of the Burgers OR.

We further calculate the SFTS from \( F_0 \) based on finite strain theory. Specifically, we use the Biot strain measure, which conserves the volumetric strain:

\[ \varepsilon^{00} = \sqrt{F_0^T F_0} - I \]  

(6.5)

Therefore, we obtain the transformation strain tensor for each variant in each local reference frame. The 12 SFTSs can be obtained by transforming the \( \varepsilon_{\text{ref}}^{00} \) tensor in each reference frame to the global coordinate system.

Cahn-Hilliard (C-H) equations are generalized diffusion equations. The typical form of C-H equation, in the context of KKS model, is

\[ \frac{\partial X_i}{\partial t} = \nabla \cdot \left( M_i \nabla \frac{\partial g}{\partial X_i} \right), \quad i = Al, V \]  

(6.6)

where \( M_i \) (\( i = Al, V \)) is the chemical mobility of Al or V. In real Ti-6Al-4V alloys, there are interdiffusions in the system, therefore, to more accurately simulate the evolution of composition, the following C-H equations are used [163]:
\[
\frac{\partial X_{\alpha \ell}}{\partial t} = \nabla \cdot \left( \sum_{p} h(\eta_{p}) \cdot \left( \tilde{D}_{\alpha \ell}^{-} \nabla X_{\alpha \ell}^{a} + \tilde{D}_{\alpha \ell}^{+} \nabla X_{\alpha \ell}^{a} \right) + \left( 1 - \sum_{p} h(\eta_{p}) \right) \cdot \left( \tilde{D}_{\alpha \ell}^{-} \nabla X_{\alpha \ell}^{\beta} + \tilde{D}_{\alpha \ell}^{+} \nabla X_{\alpha \ell}^{\beta} \right) \right) \quad (6.7a)
\]

\[
\frac{\partial X_{\ell}}{\partial t} = \nabla \cdot \left( \sum_{p} h(\eta_{p}) \cdot \left( \tilde{D}_{\ell}^{-} \nabla X_{\ell}^{a} + \tilde{D}_{\ell}^{+} \nabla X_{\ell}^{a} \right) + \left( 1 - \sum_{p} h(\eta_{p}) \right) \cdot \left( \tilde{D}_{\ell}^{-} \nabla X_{\ell}^{\beta} + \tilde{D}_{\ell}^{+} \nabla X_{\ell}^{\beta} \right) \right) \quad (6.7b)
\]

This type of C-H equations can provide couplings with thermodynamic and diffusion mobility databases, if available.

The interdiffusivities of \(\beta\) phase are available from existing databases [296]. However, due to the difficulty of interdiffusivity measurement for the low-temperature \(\alpha\) phase, the diffusion mobility database of \(\alpha\) phase is yet to be developed. Recently, the impurity diffusivities of Al and V in \(\alpha\)-Ti have become available from first-principles calculations[47], which we use in this study to approximate the diagonal terms of the interdiffusivity, i.e., \(\tilde{D}_{\alpha \ell}^{-}\) and \(\tilde{D}_{\alpha \ell}^{+}\), while we neglect the off-diagonal terms \(\tilde{D}_{\alpha \ell}^{-}\) and \(\tilde{D}_{\alpha \ell}^{+}\). It should be noted that due to the crystal anisotropy, the solute diffusivities in \(\alpha\)-Ti have two independent components, characterizing diffusivities in the basal plane and perpendicular to basal plane, respectively. With this consideration, the C-H equations become more complicated, as shown in Appendix B. However, in this study, since the anisotropy in solute diffusivities of \(\alpha\)-Ti is not so strong, we only consider the in-basal-plane diffusivities in \(\alpha\)-Ti.

Unlike the conservative form of C-H equations, the Allen-Cahn (A-C) equations, or time-dependent Ginzburg-Landau equation, deal with non-conservative field variables such as order parameters characterizing the \(\beta\rightarrow\alpha\) structural transformation:

\[
\frac{\partial \eta_{p}}{\partial t} = -L \left( \frac{\partial g_{\text{bulk}}}{\partial \eta_{p}} \cdot \frac{\partial \eta_{p}}{\partial \eta_{p}} \right) - \kappa_{p} \cdot \nabla \cdot \nabla \eta_{p} + \frac{\partial E_{\alpha \ell}}{\partial \eta_{p}} \right) \right) \right) \right) , \; p = 1, 2, \ldots, 12 \quad (6.8)
\]

where \(L\) is a kinetic coefficient related to interface mobility. The completed form of the equation under KKS assumption is given in Chapter 2. Based on thin-interface analysis, the kinetic
coefficient $L$ can be estimated following Eq. (4.2) [312]. This estimation works best for diffusion-
controlled processes where interface mobility $\to \infty$ and otherwise relies on the experimental 
calibration of interface mobility. In this study, since the phase transformations in Ti-6Al-4V may 
also contain diffusionless processes under certain temperatures, we simply assume that $L$ is 
proportional to the diffusion coefficient, as given in Table 6.3.

The classical nucleation theory works best for diffusion-controlled transformations with 
regular-shaped critical nuclei. The nucleation rate $j$ can be determined by

$$j = ZN_0\beta^* \exp\left(-\frac{\Delta G^*}{RT}\right) \exp\left(\frac{t}{\tau}\right)$$

(6.9)

where $Z$ is Zeldovich’s factor, $N_0$ is the number of available nucleation sites in the corresponding 
system (here a simulation cell), $\beta^*$ is atomic attachment rate, $\Delta G^*$ is nucleation barrier, $t$ is 
elapsed time and $\tau$ is incubation time for nucleation. The detailed formulation of these quantities 
can be found in [6, 228], following the same formulations listed in Table 4.2.

With the nucleation rate estimated, the nucleation probability $p_n$ of a corresponding system 
(here a simulation cell) within a given time period $\Delta t$ can be approximated to follow Poisson 
distribution[120, 121]:

$$p_n = 1 - \exp(-j \cdot \Delta t)$$

(6.10)

At each grid point, the nucleation probability is calculated and compared with a random number 
between 0 and 1. If $p_n$ is larger than the random number, an $\alpha$ nucleus is put into the system.

6.4 Results and discussion

In phase-field simulations, all quantities and equations are non-dimensionalized by certain 
quantities in real units, including a characteristic energy $E$, a characteristic length $l_0$ and a 
characteristic time step $\Delta t$. In this study, since we have more reliable diffusivity data than
interface mobility, we use the impurity diffusivity of Al in β phase, $D_{\text{Al}}^\beta$ [296], to determine the value of the characteristic time step through $\Delta t(T) = l_0^2 \cdot \Delta t^* / D_{\text{Al}}^\beta(T)$ where $\Delta t^*=0.01$ is the reduced time step in phase-field simulation. Note that $\Delta t$ changes with temperature and is also related to the choice of the length scale $l_0$. The simulation parameters are listed in Table 6.3.

**Table 6.3 Parameters used in phase-field simulations**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Description</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>Characteristic energy</td>
<td>2 GPa</td>
</tr>
<tr>
<td>$l_0$</td>
<td>Characteristic length, i.e., grid spacing</td>
<td>20 nm</td>
</tr>
<tr>
<td>$C_{11}$, $C_{12}$, $C_{44}$</td>
<td>Elastic constants of β-Ti [313]</td>
<td>97.7 GPa, 82.7 GPa, 37.5 GPa</td>
</tr>
<tr>
<td>$a_\alpha$</td>
<td>Lattice parameter of α-Ti, fitted from [314]</td>
<td>$2.952 \times 10^{-4} T - 4.83 \times 10^{-8} T^2 + 6.36 \times 10^{-10} T^3 - 1.64 \times 10^{-12} T^4 + 1.62 \times 10^{-15} T^5 - 5.43 \times 10^{-19} T^6$ (Å)</td>
</tr>
<tr>
<td>$c_\alpha$</td>
<td>Lattice parameter of α-Ti</td>
<td>$1.5963 \times a_\alpha$ (Å)</td>
</tr>
<tr>
<td>$a_\beta$</td>
<td>Lattice parameter of β-Ti, fitted from [314]</td>
<td>$-2.59 \times 10^{-4} T + 2.64 \times 10^{-2} T - 8.4 \times 10^{-5} T^2 + 1.33 \times 10^{-7} T^3 - 8.4 \times 10^{-10} T^4 + 3.95 \times 10^{-14} T^5 - 4.37 \times 10^{-18} T^6$ (Å)</td>
</tr>
<tr>
<td>$\gamma_{(112)}$</td>
<td>(112)$_\beta \left</td>
<td>(01 \overline{1})_\alpha$ interfacial energy [311]</td>
</tr>
<tr>
<td>$\gamma_{(01\overline{1}T_1)}$</td>
<td>(0111)$_\beta \left</td>
<td>(2 \overline{1} \overline{1}0) \alpha$ interfacial energy [311]</td>
</tr>
<tr>
<td>$\gamma_{(1T0)}$</td>
<td>(110)$_\beta \left</td>
<td>(0001)_\alpha$ interfacial energy</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Molar volume</td>
<td>$1.04384 \times 10^{-5}$ m$^3$/mol</td>
</tr>
<tr>
<td>$L$</td>
<td>Interface kinetic coefficient</td>
<td>$D_{\text{Al}}^\beta / E / l_0^2$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Incubation time for nucleation</td>
<td>$1 / 2 \beta Z^2$</td>
</tr>
</tbody>
</table>

In our phase-field simulations, we assume the uniform distribution of temperatures within the whole simulation region at each simulation time step, while the temperature changes with time. During realistic heat treatments this assumption is valid within the microscopic scale (<1mm), which imposes an upper limit for the value of $l_0$. Moreover, since $\Delta t$ is a function of diffusivities, which may have relatively large values at high temperatures compared with $l_0^2$, to improve the computation efficiency, $l_0$ could not be too small. Based on these considerations, we use $l_0=20$ nm as the discretization grid spacing of the phase-field simulations, and the total
The morphology of \( \alpha \) phase in a \( \beta \) single crystal is determined by the interplay between the anisotropy of interfacial energy and elastic strain energy. If interfacial energy is the only governing factor for the morphology of \( \alpha \) phase, the equilibrium shape of \( \alpha \) phase would be a
plate-like ellipsoidal shape, with an aspect ratio of ~8, and a habit plane of \{11\overline{2}\}, using the interfacial energies from DFT calculations (Table 6.3). If elastic strain energy is the only governing factor for the morphology of \(\alpha\) phase, the morphology of \(\alpha\) phase will be a thin plate (or disk) with habit plane normal determined by minimization of \(B(n)\) according to Eq. (2.14).

In this study, since we use the temperature-dependent lattice constants of both phases[314], we first calculate the SFTSs at different temperatures ranging from room temperature up to the \(\beta\) transus temperature, then predict the habit plane orientation by minimizing \(B(n)\). The predicted habit plane orientations \(n_0\), together with the experimentally reported ones, including \{3 3 4\}[315], \{8 8 11\}[316], \{8 9 12\}[317] and \{11 11 13\}[318, 319], are plotted in Figure 6.5(a). The predicted values are quite close to the reported ones even with the change of temperature. The change of \(n_0\) when the temperature changes from room temperature to \(\beta\) transus temperature is only about 6°. It should be mentioned that compared with the change of \(n_0\), the change of \(B(n_0)\) with temperature is more significant, as shown in Figure 6.5(b), indicating that the elastic effect on microstructure morphology and nucleation barrier of \(\alpha\) products becomes more prominent at lower temperatures.

![Figure 6.5](image_url)

**Figure 6.5** Theoretical analysis and phase-field simulations for the habit plane orientation of \(\alpha\) precipitates. (a) Habit plane orientation \(n_0\) predicted from minimizing \(B(n)\) within the temperature range from room temperature to \(\beta\) transus. Experimentally reported values are also plotted. (b) Change of \(B(n_0)\) with temperature. (c) Phase-field simulations of the morphology of a single \(\alpha\) variant at \(T=900\) K.
To investigate the effect of temperature change in the habit plane orientation of a single $\alpha$ variant, we perform a series of phase-field simulations, including isothermal simulations at different temperatures and non-isothermal simulations under different cooling rates. The initial $\alpha$ nuclei is assumed to be spherical to remove any anisotropic effects. The simulated $\alpha$ morphologies are thin plates due to the anisotropies in interfacial energies and misfit strains, and the habit planes of $\alpha$ plates are consistent with the analytical $\mathbf{n}_0$ by minimizing $B(\mathbf{n})$, which is also close to the experimental values. For example, Figure 6.5(c) shows the morphology of an $\alpha$ plate during isothermal aging at 900 K. The habit plane normal $[0.52 \ 0.52 \ 0.68]$ is only $0.32^\circ$ from $\{3 \ 3 \ 4\}$, $3.08^\circ$ from $\{8 \ 9 \ 12\}$, $1.2^\circ$ from $\{8 \ 8 \ 11\}$ and $3.11^\circ$ from $\{11 \ 11 \ 13\}$. The simulation results, as well as the comparison with experimental results, indicate that the misfit strain energy plays a more dominant role in the morphology of $\alpha$ phase.

We further investigate the phase transformation features during continuously cooling under different cooling rates, i.e., 1 K/s for slow cooling, 10 K/s for moderate cooling and 100 K/s for rapid cooling. Based on the discussions above, the initial simulation temperatures with more than one $\alpha$ nuclei in the simulation region are 1027.3 K, 1023.7 K and 1019.9 K, respectively. According to the kinetic pathway analysis in Section 6.2, the most probable kinetic pathway is $\beta \rightarrow \alpha \rightarrow (\alpha + \beta)$ through nucleation-and-growth mechanism, indicating the possibility of partitionless $\beta \rightarrow \alpha$ transformations. Therefore, rather than putting $\alpha$ nuclei with equilibrium solute compositions, we only set the corresponding order parameter within the nuclei to be 1 while keep the solute composition of the nuclei unchanged. The continuously cooling simulations are performed until the simulation regions are cooled down to room temperature.
Figure 6.6 Phase-field simulation of $\beta \rightarrow \alpha$ transformations under different cooling rates in $\beta$ single crystal and the comparison with experimental observations. (a) Phase-field simulations under cooling rates of 1 K/s, 10 K/s and 100 K/s, system size $2.56\mu m \times 2.56\mu m \times 2.56\mu m$. The different colors in the figures represent the different $\alpha$ variants. (b) Experimental observations. Adapted from [271] with permission.

Figure 6.6 shows the microstructure evolution process for the three cooling rates, together with the experimental observations with similar cooling rates [271]. For slow cooling, the initial simulation temperature is the highest while the total number of nuclei is the lowest, resulting in coarse $\alpha$ laths almost parallel to each other. For moderate cooling, there is an increase in nuclei number and decrease in the size of $\alpha$ laths; meanwhile, the microstructure pattern is more complicated than during slow cooling, forming basket-weave-type microstructures. For rapid cooling, there is a significant increase in nuclei number and decrease in $\alpha$ lath size in the system. As shown in Figure 6.7(a), the $\alpha$ particle number increases significantly with increasing cooling rates, which is a result of the competition between nucleation and growth of $\alpha$ product. During
slow cooling, since the system stays at the high-temperature regime for a longer time period, the nucleation events take place slower due to the lower nucleation driving force and higher nucleation barrier; on the other hand, the growth of the nucleated $\alpha$ products is more sufficient, which results from the higher diffusion and interface mobilities at higher temperatures and the more growth space due to lower nucleation rates. In contrast, during rapid cooling, although the nucleation events take place at lower temperatures compared with that during slow cooling, the nucleation proceeds faster in time due to the faster cooling rates. As a result, the system quickly goes into the low-temperature regime, with a significant increase in nucleation driving force while a decrease in both growth kinetics and growth spaces.

Figure 6.7 Microstructure characteristics for simulation results under different cooling rates. (a) Number of particles in the simulation region. (b) Variation of solute compositions within the simulation region.

In addition to the prominent change in microstructure features due to the competition between the nucleation and growth kinetics of $\alpha$ products, the cooling rate can also affect the phase transformation modes, i.e., the interplay between the diffusional transformation and the partitionless transformation. To investigate the change in transformation modes, we calculate the variations in solute compositions during temperature change in each system, as plotted in Figure 6.7(b). The straight dashed lines represent the initial Al and V solute compositions of the Ti-6Al-4V alloy. The upper and lower data points in the figure show the maximum and minimum solute compositions detected during the simulations with different cooling rates. As shown, the
variations of Al compositions for the three cooling rates are almost consistent; on the other hand, the variations in V compositions decrease significantly with increasing cooling rates. This is primarily due to the low diffusion coefficient of V in β-Ti, resulting in the β→α partitionless of V with the increasing cooling rates. Therefore, the diffusional transformations take place during slow cooling while the rapid cooling enables the partitionless transformations.

6.5 Summary

In this work, we built up a phase-field model to study the microstructure evolution during continuously cooling in Ti-6Al-4V alloys. We incorporated the temperature-dependent thermodynamic database, diffusion mobility information and nucleation probability predictions, as well as the anisotropic interfacial energy and elastic energy effect, to investigate the microstructure features under different cooling rates. We apply the graphical thermodynamic approach to analyze the possible phase transformation kinetic pathways during both isothermal aging and continuous cooling. Based on the simulation results, we make the following conclusions.

(1) The morphology of a single α nucleus is governed by the interplay between interfacial energy anisotropy and elastic strain energy anisotropy. The predicted habit planes of α products agree well with experimentally reported results.

(2) By investigating the microstructure evolution process under different cooling rates, we find that the change of microstructure features with cooling rates comes from the competition between nucleation and growth behaviors of the α products. Meanwhile, the transformation mode changes from diffusion-controlled to partitionless with increasing cooling rates.
Chapter 7: Summary and Future Work

7.1 Summary and conclusions

In this dissertation, the precipitation phase-field model is further developed and applied for precipitate phases with different thermodynamic treatments, different coherency states and different heat treatment conditions. Under these different situations, the phase-field simulations are performed to investigate the governing factors for precipitate morphology and kinetics, with the necessary input materials parameters from first-principles calculations, existing thermodynamic and diffusion mobility databases, or existing literature reports (experimental/theoretical). The simulated precipitate morphologies and kinetic features are used in existing theoretical models to predict the precipitation hardening effect. Based on the simulation results and discussions in each chapter, we can draw the following conclusions in terms of the precipitate morphology, kinetics and hardening effects, as well as the related phase-field model development.

(1) The developed phase-field treatments for different thermodynamic descriptions of the precipitate phase in Chapter 2, including solid solution model, sublattice model and line compounds, can accurately predict the thermodynamic equilibrium state of precipitation, as well as the evolution kinetics towards the equilibrium state. This has been verified by α phase in Ti-6Al-4V (Chapter 6) for the solid solution model, by γ" phase in IN718 (Chapter 5) and β in Mg-Al-based alloys (Chapter 2) for the sublattice model, by β’ in Mg-Nd (Chapter 3) and θ’ in Al-Cu (Chapter 4) where the free energy of the precipitate phase is fitted into a continuous function of composition with the help of first-principles calculations, and by θ’ in Al-Cu (Chapter 2) for the line compound model where the
chemical reactions are explicitly considered. These treatments can be applicable to general multi-component, multi-phase systems.

(2) The phase-field approach can accurately predict the morphology evolution of precipitates, given the values and anisotropies in lattice misfit strain, interfacial energy and interface mobility. The governing factors of precipitate morphologies at different growth stages can be identified. Typically, the interfacial energy and its anisotropy dominate at early growth stages or small precipitates while the misfit strain energy and its anisotropy dominate when the precipitate size becomes large, since the misfit strain energy scales with the volume of the precipitate while the interfacial energy scales with the interface area of the precipitate. This finding has been verified by the morphology evolution of β’ in Mg-Nd (Chapter 3), where the interfacial energy anisotropy alone suggests a plate-shaped precipitate with (001) habit plane while the misfit strain energy anisotropy along suggests a plate-shaped precipitate with (100) habit plane. The simulation results indicate a faceted lenticular precipitate with (100) habit plane and (001) facets, showing the interplay between these two types of energetics. For the semi-coherent θ’ (Chapter 4), the simulated disk-shaped morphology agrees with the predictions from both the misfit strain energy anisotropy and the interfacial energy anisotropy. If the precipitate undergoes coherency loss, the development of line defects at precipitate/matrix interfaces will decrease the effect of the misfit strain energy and anisotropy while increase the effect of the interfacial energy and anisotropy, leading to precipitate morphologies with less anisotropy compared with the fully coherent case (Chapter 5).

(3) The phase-field model developed in Chapter 5 can predict the critical precipitate size to trigger coherency loss, as well as the sequential development of line defects and evolution of their average spacings at the precipitate/matrix interface. By applying the model to γ” in IN718, the critical precipitate diameter for coherency loss is predicted
using both the energy criterion (140 nm) and the stability criterion (91 nm), which agrees with the experimentally observed range (50~120 nm). By applying the model to θ’ in Al-Cu alloys, the possible dislocation pathway, $b_3 \rightarrow b_1 + b_3 \rightarrow b_1 + b_2 + b_3$, is predicted, indicating that the coherency loss firstly takes place at the semi-coherent interface, followed by the development of dislocation loops and further evolution of the dislocation spacings on the broad, coherent interface. For both γ” and θ’, the loss of coherency would lead to impeded lengthening and accelerated thickening of the precipitates, resulting in higher thickness/diameter aspect ratio of the plate- or disk-like precipitates compared with the fully coherent case.

(4) In Chapter 6, the phase-field precipitation model has been successfully extended to non-isothermal situations and both the diffusional and diffusionless transformation mechanisms. The graphical thermodynamic approach has been applied to predict the possible phase transformation kinetic pathways in Ti-6Al-4V within different temperature range and under different heat treatment conditions. The phase-field simulations are then performed for β→α transformations in Ti-6Al-4V, which can well reproduce the experimentally observed habit planes of α products, and qualitatively predict the morphology of α plates under different cooling rates. Simulation results indicate that it is the interplay between the diffusional and diffusionless transformation mechanisms, as well as the interplay between the nucleation and growth of α products, that lead to the different α morphology and distribution under different cooling rates. Specifically, under high cooling rates, the diffusionless mechanism dominates, with high nucleation density and insufficient growth time, leading to refined α plates; under low cooling rates, the diffusional mechanism dominates, with lower nucleation density and sufficient time for diffusional growth, leading to coarse α laths.

(5) The theoretical mechanical models, with the input from phase-field simulation results, can semi-quantitatively predict the precipitate hardening effect. By applying the model
to different precipitate phases ($\beta'$ in Chapter 3, $\theta'$ in Chapter 4 and 5), it is found that the volume fraction and aspect ratio of precipitates play key roles in precipitate hardening. Especially, under the same volume fractions, the diameter/thickness aspect ratio can lead to over 30% differences in precipitate hardening effects, comparing the predicted hardening effects between $\beta'$-Mg$_7$Nd and $\beta'$-Mg$_7$Gd (Chapter 3), or between the $\theta'$ precipitates with and without coherency loss (Chapter 5). These findings provide practical guidance not only for designing the alloy systems or alloying elements with desired precipitate phases, but also for manipulating the thermo-mechanical processing conditions to control the size, aspect ratio and coherency state of the precipitates in real applications.

To conclude, the major findings and conclusions, as well as the contributions to the respective research areas, can be summarized into the following three aspects. (i) Improvement of the phase-field approach for precipitation. This includes the treatments for sublattice model (Chapter 2 and 5) and stoichiometric compounds for general multi-component, multi-phase cases (Chapter 2), the incorporation of chemical reaction kinetics (Chapter 2), the consideration of sequential coherency loss (Chapter 5), the consideration of nucleation kinetics (Chapter 4 and 6), the extension to non-isothermal situations (Chapter 6) and the integration with first-principles calculations (Chapter 3, 4, and 6). (ii) Elucidation of the mechanisms and competing factors related to precipitate morphology, kinetics and hardening effects. This includes the elucidation of the precipitate morphology evolution under the interplay between the elastic strain energy and interfacial energy (Chapter 3, 4, 5 and 6), the prediction of coherency loss pathways and critical precipitate dimensions to trigger coherency loss (Chapter 5), the competition between diffusion and chemical reaction kinetics (Chapter 2), and the competition between diffusional and diffusionless transformation mechanisms, as well as the competition between nucleation and growth, during continuous cooling of Ti-6Al-4V (Chapter 6). (iii) Guidance for design of alloy compositions and processing routes in real applications. This includes the control of the
precipitate size and aspect ratio during aging to optimize the hardening effect (Chapter 3 and 4), and the control of the aging time and precipitate size to minimize the coherency loss of the precipitates (Chapter 5).

7.2 Future work

Although the precipitation phenomena and its effect on mechanical properties of materials have been extensively investigated, as discussed in Chapter 1, there are still several remaining challenges in the related area. Some of these issues can be investigated using the developed phase-field and computational framework in this thesis work. They are discussed in the following sections.

7.2.1 Predicting morphology evolution of precipitates with limited coherency

In the current thesis work, although the phase-field models have been extended from the consideration of the initially coherent or semi-coherent precipitates to the consideration of sequential coherency loss, the precipitates investigated generally have well-defined OR and LC with the crystal structure of the matrix phase. In realistic situations, the OR and LC can be rather complicated, resulting in relatively poor lattice matching between the precipitate and the matrix, and the complicated precipitate morphologies with side facets or irregular shapes. For example, the γ-Mg17Al12 precipitates in AZ91 (Mg-9wt.%Al-1wt.%Zn) typically exhibit a (0001) habit plane and a lozenge shape within the habit plane [21, 188, 189]. Although its morphology has been investigated using phase-field simulations [142-144], there are still controversies about the treatment of the misfit strain tensor and the anisotropies in interfacial energy and interface mobility. The difficulty in accurately predicting the morphology evolution of this type of precipitate lies in the poor lattice matching, and the corresponding lack of data for the anisotropic interfacial energies and mobilities. Moreover, the mechanism and pathway of further coherency loss of these precipitates are more complicated due to the complicated interfacial dislocation structures [257].
Therefore, in our future work, the key to predict the morphology evolution of these complicated precipitates lies in the atomistic calculations to provide the key input information for phase-field simulations. With these data available, the anisotropic interfacial energy and mobility can be fitted into angle-dependent functions similar to Chapter 4, and the phase-field simulations can be performed accordingly.

### 7.2.2 Linking with atomistic kinetic mechanisms of precipitation

In most of existing phase-field simulations for precipitation, the precipitation process is assumed to be diffusion-controlled. In the current work, the effect of chemical reaction kinetics can be considered (Chapter 2) with the help of first-principles calculations for the energy of the possible transient states along the reaction/transformation path. However, in realistic situations, the atomistic kinetic mechanisms and the corresponding transient states can be more complicated than the transient states of the bulk transformations. Therefore, atomistic calculations on the kinetic mechanisms and the transient states should be performed, which can then be implemented in the newly-developed precipitation phase-field model for line compounds in Chapter 2.

For example, even for the well-studied θ’ precipitates, the atomistic lengthening and thickening mechanisms are quite different and complicated. Experimental observations have shown that the thickening of θ’ can be accomplished by the partial occupancy of Cu atoms at the interstitial sites of the θ’ crystal structure, which is critically related to the diffusion of Cu in θ’-Al2Cu [29]. On the other hand, the lengthening of θ’ can be facilitated by forming a diffuse Al/θ’ interface include the θ” front [28]. The consideration of these detailed kinetic mechanisms in the phase-field model of line compounds can improve the accuracy of precipitation kinetics predictions and overcome the discrepancies discussed in Chapter 4.

Moreover, although the nucleation kinetics have been considered based on the classical nucleation theory in the current thesis work, the detailed atomistic nucleation mechanisms and possible intermediate states have not been fully considered. Meanwhile, the pre-existing defects
such as dislocations, grain boundaries and twin boundaries, as well as the pre-existing atomic clusters or other precipitate phases, can serve as heterogeneous nucleation sites of the precipitate of interest. Consideration of these detailed nucleation mechanisms beyond the classical nucleation theory, as well as the development of efficient numerical algorithms for precipitation in the phase-field model, would be a meaningful future work to more accurately predict the nucleation kinetics and the overall kinetic behavior of precipitation.

### 7.2.3 Predicting precipitation hardening effect with detailed precipitate-dislocation interaction mechanisms

In the current thesis work, the precipitation hardening effect is predicted by existing theoretical models using the phase-field simulation results. These theoretical models usually assume certain hardening mechanisms (e.g., dislocation cutting or bowing), with the input information of precipitate size, aspect ratio, volume fractions and/or number densities. However, in realistic situations, the detailed deformation modes, i.e., the dislocation-precipitation mechanisms, can be complicated, which depends on the crystal structure, slip systems, size, morphology and distribution of the precipitate, the energy of forming dislocations in the precipitate phase, and the amplitude of the applied shear stress. These different aspects, together with their interactions, are not fully captured by the theoretical models.

On the other hand, phase-field simulations with the consideration of dislocation dynamics can be a useful tool for this problem. The model will rely on atomistic calculations to provide the GSF energy of both the matrix phase and the precipitate phase on a given slip plane or in 3-D space, which is fitted into the crystalline energy of dislocations in both phases. The calculated GSF surface can provide useful information for the possible deformation modes of the precipitate. Dislocation phase-field models will then be applied to investigate the dislocation-precipitate interaction under applied shear stresses and evaluate the hardening effects. This model has been applied to several systems with fcc matrix, such as Ni- [153] and Al-based alloys [37]. However,
simulations for bcc or hcp matrices have not yet been conducted, which could be an interesting future work for understanding the precipitation deformation modes and hardening effects. Moreover, the simulation results can be useful for constructing the crystal plasticity models of these alloy systems, which could be further applied to investigate the microstructure evolution under plastic deformation, e.g., crack initiation and propagation, with the presence of the precipitate phases.

### 7.2.4 Application of phase-field simulations to realistic manufacturing and processing situations

With the developed phase-field precipitation models for non-isothermal conditions, the morphology evolution and kinetics of precipitate under various heat treatment conditions can be investigated in our future work. For example, additive manufacturing (AM) has become a popular fabrication technique of industry-relevant alloy parts with complicated geometries. The AM process involves multiple heating/cooling cycles to melt and densify the metallic powders. The microstructures of the AM builds are significantly affected by the complicated temperature distribution and thermal history during building, generating microstructure features that are significantly different from those of the conventional cast or wrought samples. The precipitation behavior under these cooling/heating cycles has not yet been fully understood, which, however, is important for the mechanical properties of the build. By applying the non-isothermal phase-field precipitation model to AM, the precipitation kinetics and morphology evolution can be obtained, which can not only elucidate the precipitation kinetic mechanisms under such complicated thermal history, but also provide useful information to predict and further control the mechanical properties of the AM build.
Appendix A: Developed multicomponent, multiphase thermodynamic treatments for precipitate phases in phase-field models

A.1 Precipitate as solid solution phase

Here we give the general expression for analytical solutions to the KKS constraints, in multicomponent, multiphase systems, where the molar Gibbs free energies are approximated using parabolic functions at equilibrium compositions under given $T$ and $p$, and where the precipitate phases are treated as solid solution phases. This is the generalization of Eq. (2.7). To start with, we extend Eq. (2.6) to general multicomponent cases:

$$g_p^\phi(x_i) = A^\phi + \sum_{i=1}^{N} B_i^\phi(X_i - X_i^\phi) + \frac{1}{2} \sum_{i,j} C_{ij}^\phi(X_i - X_i^\phi)(X_j - X_j^\phi)$$ \hspace{1cm} (A1)

where $g_p^\phi$ is the approximated molar Gibbs free energy of a phase, $X_i^\phi$ is the equilibrium composition of the $i$-th alloying element in $\phi$ phase, $A^\phi$, $B_i^\phi$ and $C_{ij}^\phi$ are the values of $g^\alpha$, the first derivative and the second derivative of $g^\alpha$ w.r.t. solute compositions at the equilibrium compositions, respectively. Note $C_{ij}^\phi$ can be written as a symmetric matrix. The analytical solution can be obtained by $x = A^{-1}\tilde{f}$, where $x$ is a vector with $(M+1)\times N$ unknown components, each represent the composition of a certain element in a certain phase, $x = (X_1^{(0)}, X_2^{(0)}, \ldots, X_N^{(0)}, \ldots, X_1^{(M)}, X_2^{(M)}, \ldots, X_N^{(M)})^T$; $\tilde{f}$ is a vector with $(M+1)\times N$ known components, with $\tilde{f}_i = \tilde{f}_i$ for $i \leq N$, and $\tilde{f}_{N+i-j}, j = B_i^{(0)} - B_i^{(j)} + \frac{1}{2} \sum_{k=1}^{N} (C_{ik}^{(j)} - C_{ik}^{(0)}) X_k^{(0)}$ for $1 \leq j \leq N$ and $1 \leq i \leq M$. The matrix $A$ is an $((M+1)\times N) \times ((M+1)\times N)$ matrix, whose components are determined according to $A_{ij} = 1 - \sum_{j=1}^{M} h(\eta_j)$ for $1 \leq i \leq N$; $A_{i+j,N} = h(\eta_j)$ for $1 \leq i \leq N$ and $1 \leq j \leq M$;
\( A_{(N+(i-1)M+j)k} = C_{ik}^{(0)} \) for \( 1 \leq i \leq N, 1 \leq j \leq M \) and \( 1 \leq k \leq N \); and \( A_{(N+(i-1)M+j)(N+j-1)N+k} = -C_{ik}^{(j)} \) for \( 1 \leq i \leq N, 1 \leq j \leq M \) and \( 1 \leq k \leq N \); while all the rest components of \( A \) are zero.

### A.2 Precipitates with sublattices

The KKS constraints for general multicomponent, multiphase and multi-sublattice situations, considering the internal quasi-equilibrium within each sublattice, are

\[
X_i = \left(1 - \sum_{l=1}^{M} h(\eta_l)\right) X_i^{(0)} + \sum_{l=1}^{M} h(\eta_l) \sum_{j=1}^{n_{l}(l)} y_{l}^{(j)(k)} k(j,l) \tag{A2a}
\]

\[
\frac{\partial g^{(0)}}{\partial X_i^{(0)}} = \frac{1}{k(j,l)} \frac{\partial g^{(l)}}{\partial y_{l}^{(j)(k)}} \tag{A2b}
\]

Extended from Eq. (2.21), the general iterative solution scheme to the KKS constraints, under multicomponent, multiphase and multi-sublattice situations can be written as

\[ \hat{x}^n = \hat{x}^{n-1} - J^{-1} \hat{f}^n \], where the subscript \( n \) and \( n-1 \) represent the iteration steps, \( \hat{x} \) is a vector containing all the unknown solute compositions and sublattice site fractions, \( \hat{f} \) is a vector containing the targeted iterative requirements, and \( J \) is the Jacobian matrix of \( \hat{f} \) w.r.t. \( \hat{x} \). The first \( N \) components of \( \hat{x} \) are the unknown solute compositions in the matrix phase, \( X_i^{(0)}, 1 \leq i \leq N \); while the first \( N \) components of \( \hat{f} \) are the compositional constraints of the KKS model,

\[
\left(1 - \sum_{l=1}^{M} h(\eta_l)\right) X_i^{(0)} + \sum_{l=1}^{M} h(\eta_l) \sum_{j=1}^{n_{l}(l)} y_{l}^{(j)(k)} k(j,l) - X_i. \]

The rest components of \( \hat{x} \) are the unknown sublattice site fractions in the precipitate phases, \( y_{l}^{(j)(k)} \), with \( 1 \leq i \leq N, 1 \leq l \leq M \) and \( 1 \leq j \leq n_{l}(l) \); while the rest components of \( \hat{f} \) are the diffusion chemical potential constraints of the KKS model,

\[
\frac{\partial g^{(0)}}{\partial X_i^{(0)}} = \frac{1}{k(j,l)} \frac{\partial g^{(l)}}{\partial y_{l}^{(j)(k)}} , \text{ with } 1 \leq i \leq N, 1 \leq l \leq M \text{ and } 1 \leq j \leq n_{l}(l). \] The treatment can also be generalized
to more complicated cases where some of the precipitate phases are treated as solid solutions while others are treated using sublattice models, while not all alloying elements are present in each sublattice of each phase. However, since the main ideas of these treatments are the same, we will not give the details of the treatment in this study.

Again, if the molar Gibbs free energies of the matrix and precipitate phases are approximated into parabolic functions at their respective equilibrium solute compositions and/or sublattice site fractions, the KKS constraints can be solved analytically. The general procedure is consistent with those discussed in Section A.1. However, since the detailed expressions are very lengthy, rather than giving the general form for multicomponent, multiphase, multi-sublattice cases, we illustrate this treatment method using a specific example, namely the precipitation of $\gamma'$ and $\gamma''$ from $\gamma$ in IN718, as discussed in Chapter 5.

The $\gamma'$ and $\gamma''$ phases are both treated as $(Ni, Al, Nb)_{0.75}(Ni, Al, Nb)_{0.25}$, but with different end-member lattice stabilities and interaction parameters in the pseudo-ternary database, as mentioned in Chapter 5. Therefore, Based on Eq. (A1), if we denote the $\gamma$, $\gamma'$ and $\gamma''$ phases as the 0th, 1st and 2nd phases, Al and Nb as the 1st and 2nd solute compositions, we have $N=2$, $M=2$, $ns(1)=2$, $ns(2)=2$, and $k(1,1)=k(1,2)=0.75$, $k(2,1)=k(2,2)=0.25$. Under given $T$ and $p$, we fit the molar Gibbs free energies of each phase into parabolic functions at their respective equilibrium compositions and sublattice site fractions:

\[
g_{p}^{(0)}(X_{1}^{(0)}, X_{2}^{(0)}) = A^{(0)} + \sum_{i=1}^{2} B_{i}^{(0)} (X_{i}^{(0)} - X_{i}^{(0)e}) + \frac{1}{2} \sum_{i,j=1}^{2} C_{ij}^{(0)} (X_{i}^{(0)} - X_{i}^{(0)e})(X_{j}^{(0)} - X_{j}^{(0)e}) \tag{A3a}
\]

for the $\gamma$ matrix

\[
g_{p}^{(d)}(y_{1}^{(1x,0)}, y_{1}^{(2x,0)}, y_{2}^{(1x,0)}, y_{2}^{(2x,0)}) = A^{(d)} + \sum_{i=1}^{2} \sum_{j=1}^{2} B_{ij}^{(d)} (y_{i}^{(1x,0)} - y_{i}^{(1x,0)e})(y_{j}^{(2x,0)} - y_{j}^{(2x,0)e}) \tag{A3b}
\]

\[
+ \frac{1}{2} \sum_{i,j=1}^{2} \sum_{s=1}^{2} C_{ij}^{(d)} (y_{i}^{(s,0)} - y_{i}^{(s,0)e})(y_{j}^{(s,0)} - y_{j}^{(s,0)e})
\]
for \( \gamma' (\phi=1) \) and \( \gamma'' (\phi=2) \)

Where \( X_i^{(0)e} \) are the equilibrium solute compositions in the matrix phase, \( y_i^{(jK\phi)e} \) are the equilibrium sublattice site fractions in the \( j \)-th sublattice of the \( \phi \)-th phase. The parameters \( A, B \) and \( C \) are the values of the molar Gibbs free energy, its first derivatives and second derivatives w.r.t solute compositions and/or site fractions, which can be obtained from the thermodynamic database.

Therefore, the analytical solution to Eq. (A2) can be obtained from \( x = A^{-1} \tilde{f} \), where \( x \) is a vector for unknown quantities, \( x = \left( X_1^{(0)}, X_2^{(0)}, y_1^{(1K\phi)e}, \ldots, y_2^{(1K\phi)e}, y_1^{(2K\phi)e}, \ldots, y_2^{(2K\phi)e} \right)^T \), \( \tilde{f} \) is a known vector with \( \tilde{f}_i = X_i \) for \( i \leq N \), and

\[
\tilde{f}_{N+\left(l-1\right)\times N+m+\left(l-1\right)\times ns+l} = \frac{1}{k(s,l)} B^{(xK\phi)}_i - B^{(0)}_i - \sum_{j=1}^{N} y_j^{(0)e} - \frac{1}{k(s,l)} \sum_{j=1}^{N} C^{(xK\phi)}_j y_j^{(0)e} \quad \text{for} \quad 1 \leq i \leq N, \quad 1 \leq l \leq M
\]

and \( 1 \leq s \leq ns(l) \). Note here we have \( N=M=ns=2 \). The matrix \( A \) can be expressed as:

\[
A = \begin{pmatrix}
1 - \sum_{j=1}^{2} h_j & 0 & 0.75 h_1 & 0.25 h_1 & 0 & 0 & 0.75 h_2 & 0.25 h_2 & 0 & 0 \\
0 & 1 - \sum_{j=1}^{2} h_j & 0 & 0 & 0.75 h_1 & 0.25 h_1 & 0 & 0 & 0.75 h_2 & 0.25 h_2 \\
C_{11}^{(0)} & C_{12}^{(0)} & -C_{11}^{(2K)} & -C_{12}^{(2K)} & 0 & 0 & 0 & 0 & 0 & 0 \\
C_{11}^{(1)} & C_{12}^{(1)} & -C_{11}^{(2K)} & -C_{12}^{(2K)} & 0 & 0 & 0 & 0 & 0 & 0 \\
C_{12}^{(0)} & C_{12}^{(0)} & 0 & 0 & 0.75 & 0 & 0 & -C_{12}^{(2K)} & 0 & -C_{12}^{(2K)} \\
C_{12}^{(1)} & C_{12}^{(1)} & 0 & 0 & 0 & 0 & 0.75 & -C_{12}^{(2K)} & 0 & -C_{12}^{(2K)} \\
C_{12}^{(2)} & C_{12}^{(2)} & 0 & 0 & 0 & 0 & 0 & 0.25 & 0 & 0.25 \\
C_{12}^{(2)} & C_{12}^{(2)} & 0 & 0 & 0 & 0 & 0 & 0 & 0.25 & 0.25 \\
C_{12}^{(2)} & C_{12}^{(2)} & 0 & 0 & 0 & 0 & 0 & 0 & 0.25 & 0.25 \\
\end{pmatrix}
\]
Appendix B: Coupling with diffusion mobility databases in phase-field models

B.1 Calculation of the interdiffusivity using the diffusion mobility database:

The inter-diffusivity of species $p$ and $q$ in the matrix $n$ can be calculated according to the work by Ågren et al. [320]:

$$ \tilde{D}_{pq}^n = \sum_{i=1}^{n-1} (\delta_{ip} - x_p) x_q M_i \left( \frac{\partial \mu_p}{\partial x_q} - \frac{\partial \mu_q}{\partial x_p} \right) $$  \hspace{1cm} (B1)

Specifically, for the bcc phase of Ti-6Al-4V, we have:

$$ \tilde{D}_{AlAl}^n = (1 - x_{Al}^\beta) x_{Al}^\beta M_{Al} \left( \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} - \frac{\partial \mu_{Al}^\beta}{\partial x_{Ti}} \right) - x_{Al}^\beta x_{Al}^\beta M_{Al} \left( \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} - \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} \right); $$

$$ \tilde{D}_{VAl}^n = (1 - x_{Al}^\beta) x_{Al}^\beta M_{Al} \left( \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} - \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} \right) - x_{Al}^\beta x_{Al}^\beta M_{Al} \left( \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} - \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} \right); $$

$$ \tilde{D}_{VVi}^n = (1 - x_{Al}^\beta) x_{Al}^\beta M_{Al} \left( \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} - \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} \right) - x_{Al}^\beta x_{Al}^\beta M_{Al} \left( \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} - \frac{\partial \mu_{Al}^\beta}{\partial x_{Al}} \right). $$  \hspace{1cm} (B2)

The mobilities can be derived from the existing diffusion mobility database using a CALPHAD type approach [296]:

$$ M_i = \frac{M_i^0}{RT} \exp\left(-\frac{Q_i}{RT}\right) $$  \hspace{1cm} (B3)

Here $M_i^0$ is the frequency factor and $Q_i$ is the activation energy. For simplicity of optimization, the frequency factor and the activation energy are combined into one parameter $Q_i$ with the expression of $Q_i = -Q_i^0 + RT \ln M_i^0$. Therefore $M_i = \frac{1}{RT} \exp\left(\frac{Q_i}{RT}\right)$. The parameter $Q_i$ can be approximated into a Redlich-Kister polynomial:
\[
Q_i = \sum_p x_p Q_i^p + \sum_{p,q,p} x_p x_q \left( \sum_{r=0,1,2,...}^r Q_i^{p,q} (x_p - x_q)^r \right) + \sum_{p,q,p,v,q} x_p x_q x_v [v_{pqv} Q_i^{p,q,v}] 
\]

(B4)

In this system, the mobility parameters are available in the Table 1 of reference [296], while the chemical potentials in Eq. (B2) are evaluated based on the thermodynamic database of Ti-Al-V[295, 298].

**B.2 Cahn-Hilliard equations with anisotropic diffusivities:**

We extend the Cahn-Hilliard equations in Eq. (6.7) for anisotropic diffusivities (Einstein notation for \(j, k\) and \(l\)):

\[
\frac{\partial X_i}{\partial t} = \nabla_k \left( \sum_p h(\eta_p) \cdot \tilde{D}^{\alpha}_{g,kl} \nabla_j X^\beta_j + \left( 1 - \sum_p h(\eta_p) \right) \cdot \tilde{D}^{\beta}_{g,kl} \nabla_j X_j \right) 
\]

(B5)

where \(\nabla_k = \frac{\partial}{\partial x_k}\) \((k=1,2,3)\) is a gradient operator, \(\tilde{D}^{\alpha}_{g,kl}\) and \(\tilde{D}^{\beta}_{g,kl}\) are anisotropic interdiffusivity tensors, with the first two subscripts \((i \text{ and } j)\) representing the \(i\)-th and \(j\)-th alloying elements \((i, j=1,2,...,N)\), while the last two subscripts \((k \text{ and } l)\) representing the \(k\)-th and \(l\)-th special coordinates \((k, l=1,2,3)\). The special anisotropy in \(\tilde{D}^{\alpha}_{g,kl}\) lies in the different components of \(\tilde{D}^{\alpha}_{g,kl}\) for different \(k\) and \(l\) for fixed \(i \text{ and } j\), which is determined by the symmetry operation (point group) of the material.
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