Early stage phase separation in ternary alloys: A test of continuum simulations

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Abstract

Phase separation in the $\gamma - \gamma'$ alloy 5.2%Al-14.2%Cr-Ni at 873.15K has been investigated by three-dimensional phase-field simulations, employing a model where both thermodynamic and kinetic parameters were experimentally verified. 510 individual nuclei corresponding to a density of 10^{24}m^{-3} were introduced in accordance with classical nucleation theory, and the microstructural evolution was simulated up to a time of 32h. The microstructural evolution was characterized, and regimes were identified according to the dominant mechanisms for microstructural evolution, where the final regime was found to be a coarsening regime obeying well-known power laws for the particle density and the average γ' particle radius. The evolution of the volume-averaged composition of the particles was found to follow a complicated trajectory, while the composition of individual particles were found to depart significantly from the average. The simulations were compared to experimental results from the literature based on atom probe tomography, and in general good qualitative correspondence was found, albeit with quantitative differences. These are discussed in terms of the assumptions inherent to the phase-field model, and by extension to most common continuum models of diffusive phase transformations.

Keywords: Phase field modeling, Ni-Al-Cr, Phase separation, Coalescence, Coarsening

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1. Introduction

It is well-known that the microstructure of metals and alloys are intimately linked with the mechanical performance of these materials. In the case of Ni-based superalloys which are used extensively in high-temperature conditions such as in gas turbine engines, the beneficial properties are mainly derived from L1₂-ordered γ' particles that are nearly coherent with the disordered γ matrix phase [1]. Predicting and controlling the dual-phase microstructure of Ni-based superalloys through the alloy composition and the processing path is therefore of great technological importance.

Such a dual-phase microstructure may be precipitated from solid solution by quenching a homogenized γ phase ingot into the $\gamma - \gamma'$ phase field and aging, during which γ' particles nucleate, grow into the supersaturated matrix, and eventually coarsen.

This process has been extensively studied experimentally by Atom Probe Tomography (APT), which is a destructive three-dimensional method, so dynamics must be inferred from "snapshots" of microstructures at different aging times. Quantitative simulations of the dynamics of the phase separation process is therefore an attractive tool to rationalize and interpret experimental results, and ultimately to guide future experiments as part of the Integrated Computational Materials Engineering (ICME) approach to materials development [2, 3].

Several studies combining experimental investigations with simulations, especially Lattice Kinetic Monte Carlo (LKMC) methods, may be found in the literature, e.g. [4, 5, 6]. The LKMC framework is particularly suited to investigations of $\gamma - \gamma'$ phase separation in Al-Cr-Ni alloys due to the negligible misfit between small γ' particles and the γ matrix. In this inherently atomistic method, vacancy-mediated diffusion is governed by short-range atomic interactions. Therefore the scales of the problems that may be solved with LKMC is independent of the feature size of the microstructure.

On the other hand, early-stage precipitation dynamics are commonly pre-
dicted with classical models, employing classical nucleation theory combined
with diffusion equations in the continuum limit, e.g. using the popular soft-
ware packages *PrecipiCalc* by QuesTek Innovations LLC, or *TC-PRISMA* by
Thermo-Calc Software AB. These approaches rely on the validity of classical
nucleation theory and certain assumptions in going to the continuum limit, the
most notable being a permanent equilibrium distribution of vacancies through-
out the material, and these assumptions are rarely questioned.

In this paper, we investigate phase separation dynamics in the Ni-based
 $\gamma-\gamma'$ alloy 5.2%Al-14.2%Cr-Ni during aging at 873.15K with three-dimensional
phase-field simulations. The phase-field model was coupled to a CALPHAD-
optimized thermodynamics database, and CALPHAD-style optimized atomic
mobility assessments. Thus, both thermodynamics and kinetics are considered
experimentally verified in the continuum limit. 510 identical nuclei chosen in
accordance with the predictions of classical nucleation theory corresponding to
an initial γ' particle density of 10^{24}m^{-3} were introduced (thus corresponding
to the case of site saturated nucleation) in a random spatial arrangement, and
the microstructural evolution was simulated up to a time of 32h. We take the
investigated alloy to be an appropriate model system for Ni-based superalloys,
as it contains the most common alloying elements of these.

We present our findings, and compare these to the experimental results pub-
lished by Booth-Morrison et al. [7] produced by APT on a comparable alloy
(6.5%Al-9.5%Cr-Ni) aged at the same temperature. As the phase-field simu-
lations are based on a continuum model, we may examine the validity of the
assumptions inherent to these models, and we discuss the similarities and dif-
ferences between experiment and simulation in terms of the limitations of the
model employed.

2. Phase-field model description

2.1. Phase-field variables and energetics

In phase-field models of microstructural evolution, the microstructural features of interest are described by sets of phase-field variables. These variables are defined in the entire system, and are required to vary smoothly in both time and space. Bulk regions are characterized by the phase-field variables attaining some set of equilibrium values, and interfacial regions are characterized by intermediate values, which occur over a specific non-zero width. The reader is referred to e.g. the text by Provatas and Elder [8], and the reviews by Chen [9], Moelans et al. [10], and Steinbach [11] for comprehensive introductions to the phase-field method.

In the present work, we describe the local composition of the Al-Cr-Ni alloy by the two molar fraction variables $\vec{x} = (x_{\text{Al}}, x_{\text{Cr}})$ and so $x_{\text{Ni}} = 1 - x_{\text{Al}} - x_{\text{Cr}}$. The phase structure is described by two phase-field variables $\vec{\eta} = (\eta_{\gamma}, \eta_{\gamma'})$. As we do not require these to sum to unity, we cannot interpret these unambiguously as phase fractions, however, we employ the re-scaling of the original phase-field variables introduced by Moelans [12]

$$\vec{\phi} = (\phi_{\gamma}, \phi_{\gamma'}) = \left(\frac{\eta_{\gamma}^2}{\eta_{\gamma}^2 + \eta_{\gamma'}^2}, \frac{\eta_{\gamma'}^2}{\eta_{\gamma}^2 + \eta_{\gamma'}^2} \right) \quad (1)$$

which sums to unity everywhere, and may thus be regarded as phase fractions. The phase-field variables $\vec{\eta}$ are mathematical constructs, with no intrinsic physical interpretation. Note that using only one phase-field variable for the γ' phase means that $\gamma' - \gamma'$ anti-phase boundaries are not possible.

Furthermore, we employ four phase composition variables $\vec{x}_{\gamma} = (x_{\text{Al}}^{\gamma}, x_{\text{Cr}}^{\gamma})$ and $\vec{x}_{\gamma'} = (x_{\text{Al}}^{\gamma'}, x_{\text{Cr}}^{\gamma'})$, which may be interpreted as describing the local composition in the respective phases, and the weighted sum of these are therefore required to equal the local composition [13]

$$\vec{x} = \sum_{\rho=\gamma, \gamma'} \phi_{\rho} \vec{x}_{\rho} \quad (2)$$

These quantities will be elaborated on in Sec. 2.2. For an isothermal, isobaric system, the convenient thermodynamic potential is the Gibbs free energy F , which we take to be given by

$$F = \int (f_{\text{int}} + f_{\text{bulk}}) dV \quad (3)$$

where f_{int} is the contribution from interfaces

$$f_{\text{int}} = m f_0 + \frac{\kappa}{2} \sum_{\rho=\gamma, \gamma'} |\nabla \eta_\rho|^2 \quad (4)$$

where m is a model parameter, κ is the gradient energy coefficient, and f_0 is the double-well

$$f_0 = \sum_{\rho=\gamma, \gamma'} \left[\frac{\eta_\rho^4}{4} - \frac{\eta_\rho^2}{2} \right] + \frac{\delta}{2} \eta_\gamma^2 \eta_{\gamma'}^2 + \frac{1}{4} \quad (5)$$

with δ being a model parameter. The functional f_{bulk} of Eq. (3) is the contribution of the chemical composition to the Gibbs free energy F , which we take to be given by the expression by Eiken et al. [13]

$$f_{\text{bulk}} = \sum_{\rho=\gamma, \gamma'} \phi_\rho f_\rho(\vec{x}_\rho) + \sum_{k=\text{Al, Cr}} \tilde{\mu}_k \left(x_k - \sum_{\rho=\gamma, \gamma'} \phi_\rho x_{\rho k} \right) \quad (6)$$

where the f_ρ are the free energy densities of the individual bulk phases, and the quantities $\vec{\mu} = (\tilde{\mu}_{\text{Al}}, \tilde{\mu}_{\text{Cr}})$ are Lagrange multipliers which enforce Eq. (2). The model neglects elastic energy, and is therefore limited to small particle sizes, where this effect is negligible, and the precipitates remain unfaceted, as is observed to be the case for particle sizes up to at least $R \sim 10\text{nm}$ by experiment [7].

2.2. Phase composition

The phase compositions $\vec{x}_\rho$ and Lagrange multipliers $\vec{\mu}$ are determined from the local microstructural configuration by minimization of the bulk free energy Eq. (6), with respect to $\vec{x}_\rho$ and $\vec{\mu}$. The minimal energy configuration will be a stationary point of Eq. (6), and will therefore fulfill

$$\frac{\partial f_\gamma}{\partial x_k} = \frac{\partial f_{\gamma'}}{\partial x_k} = \tilde{\mu}_k \quad (k = \text{Al, Cr}) \quad (7)$$

which is the well-known parallel tangent assumption. We can identify $\vec{\mu}$ as interdiffusion potentials, which in the present case of Ni considered the dependent component are related to the chemical potentials through $\vec{\mu} = (\mu_{\text{Al}} - \mu_{\text{Ni}}, \mu_{\text{Cr}} - \mu_{\text{Ni}})$ and so the requirement of minimal bulk free energy is equivalent to requiring equal interdiffusion potentials in the interfacial regions of the two phases. The equality of the diffusion potentials is commonly referred to as quasi-equilibrium [13], since it does not imply thermodynamic equilibrium, but only local equilibrium of the phase compositions of the coexisting phases.

For an equilibrium interface, the Gibbs free energy F will also be minimized with respect to the phase structure variables $\vec{\eta}$, and therefore the phase fractions $\vec{\phi}$. The conditions for this minimum are mathematically identical to the well-known common tangent plane construction, as employed during construction of phase diagrams [14]. So for an equilibrium interface, the phase compositions of the locally coexisting phases $\vec{x}_\rho$ will be constant, and equal to their respective tie line compositions, while the local composition $\vec{x}$ will trace the tie line through the interface.

The quasi-equilibrium condition complicates calculations, since the phase compositions and diffusion potentials must be determined in all interfacial regions in the system, however, the quasi-equilibrium condition is chosen to cause the decoupling of bulk and interfacial energies, and so allows the interfacial widths to be chosen as convenient to the problem at hand, independent of the free energy functions f_ρ [13, 12], which may be a great convenience.

2.3. Kinetic equations

The rate of change of the composition is taken to obey an "Onsager-like" relationship with the driving force for diffusion given by the diffusion potential [12]

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left(\sum_{l=\text{Al, Cr}} \mathbf{M}_{kl} \nabla \tilde{\mu}_l \right) \quad (k = \text{Al, Cr}) \quad (8)$$

where $\mathbf{M}$ is a matrix of interdiffusion mobilities in the volume-centered frame of reference, which we assume may be approximated by interpolation

$$\mathbf{M} = \phi_\gamma \mathbf{M}^\gamma(\vec{x}) + \phi_{\gamma'} \mathbf{M}^{\gamma'}(\vec{x}) \quad (9)$$

and so the mobility matrices are evaluated at the local composition, rather than the phase composition.

The rate of change of the phase structure is taken to obey a time-dependent Ginzburg-Landau equation

$$\frac{\partial \eta_\rho}{\partial t} = -L \left(m \frac{\partial f_0}{\partial \eta_\rho} - \kappa \nabla^2 \eta_\rho + \frac{\partial f_{\text{bulk}}}{\partial \eta_\rho} \right) \quad (\rho = \gamma, \gamma') \quad (10)$$

Here, L is a mobility parameter, which in the case of bulk diffusion controlled transformations is related to the chemical mobility at the interface, as shown by Kim [15]

$$L = L_0 \left(\sum_{k=\text{Al,Cr}} \left(x_{\gamma k}^{\text{eq}} - x_{\gamma' k}^{\text{eq}} \right) \sum_{l=\text{Al,Cr}} [\mathbf{M}^{-1}]_{kl} \left(x_{\gamma l}^{\text{eq}} - x_{\gamma' l}^{\text{eq}} \right) \right)^{-1} \quad (11)$$

L_0 is a model parameter, the superscript eq denotes the tie line compositions of the interface, and $\mathbf{M}^{-1}$ is the inverse of the mobility matrix $\mathbf{M} = \frac{1}{2} (\mathbf{M}^\gamma + \mathbf{M}^{\gamma'})$, which has been shown by Moelans [12] to result in negligible solute trapping at the relatively slowly migrating interfaces occurring during growth and coarsening in the solid state.

2.4. Free energies and mobility parameters

It is common in the literature to employ parabolic free energy densities, which may have been fitted to CALPHAD-optimized free energy functions. This is desirable as parabolic free energy functions result in models that are easily analyzed and computationally simple, but depending on the problem, the parabolic approximation may not be sufficiently precise.

In the present work, we have chosen a more general approach, namely directly employing CALPHAD-optimized free energy densities as assessed by Saunders [16]. This assessment employs a two-sublattice model for the ordered

γ' phase [17], so the free energy density is a function of the *a priori* unknown site fractions. In a recent work, Zhang et al. [18] describes a method to directly incorporate sublattice models into phase-field simulations, where the sublattices exchange mass locally at a finite rate. However, the benefits of adopting this method for the current problem were not clear, so an infinite rate of exchange between the sublattices was assumed in the current work so the sublattice occupation is chosen everywhere as the minimal energy configuration. Details on the numeric implementation are presented in Sec. 2.6.

For the required interdiffusional mobilities, we employ the CALPHAD-style optimized assessments by Engström and Ågren for the γ phase [19], and by Campbell for the γ' phase [20], which gives diagonal atomic mobility matrices in the lattice-fixed frame of reference. The atomic mobilities in the respective phases are converted to interdiffusion mobilities in the volume-fixed frame of reference by the transformation [21]

$$M_{kl}^\rho = V_m \sum_{n=\text{Al,Cr,Ni}} (\delta_{ln} - x_l) (\delta_{kn} - x_k) x_n \Omega_n^\rho \quad (12)$$

where V_m is the molar volume, which must be taken equal in the two phases, Ω_m^ρ is the atomic mobility of species m in phase ρ , and δ_{ij} is the Kronecker delta with the property $\delta_{ij} = 0$ for $i \neq j$, and $\delta_{ij} = 1$ for $i = j$ for integers i and j . Even though the atomic mobility matrix is diagonal, the interdiffusion mobility matrix $\mathbf{M}$ is in general non-diagonal due to above transformation.

2.5. Model parameters and numeric details

We choose a molar volume of $V_m = 6.81 \times 10^{-6} \text{m}^3 \text{mol}^{-1}$ for both phases, a $\gamma - \gamma'$ interfacial free energy of $\sigma = 20 \times 10^{-3} \text{Jm}^{-2}$ in accordance with the magnitudes given by Booth-Morrison et al. [22], and an interfacial width of $W = 4.4 \text{\AA}$ (see [23] for the definition of the interface width), by which the remaining model parameters are fixed by the relations given by Moelans [12] to $m = 2.727 \times 10^8 \text{Jm}^{-3}$, $\kappa = 6.600 \times 10^{-12} \text{Jm}^{-1}$, $\delta = 3.000$, and $L_0 = 5.510 \times 10^{19} \text{m}^{-2}$.

The spatial differential operators were discretized with five-point central finite-difference stencils, and the temporal differential operator was discretized
140 with the forward Euler method.

The grid spacing was chosen to be $h = 1.1\text{\AA}$ (the choice of this specific value will be explained in Sec. 3) and the time step was chosen to be $\Delta t = 10^{-2}\text{s}$.

Periodic boundary conditions were imposed, and the simulations were executed in parallel on 200 cores of Northwestern University’s Quest High Performance Computing Cluster.
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2.6. Computational implementation and validation

Prior to simulation, the free energy densities are determined on a fine (in this case 1000x1000) grid over the range $x_{\text{Al}} + x_{\text{Cr}} \leq 1$. In the case of the ordered γ' phase, this requires constrained numeric optimization to determine
150 site fractions as functions of local composition. Parabolas are fitted to a local neighborhood of all grid points, and the polynomial coefficients are stored for both phases, which allows the local morphology (functional value, gradient and Hessian matrix) of the free energy densities to be determined by interpolation of the polynomial coefficients. This allows solution of the quasi-equilibrium
155 condition iteratively by Newton’s method for constrained optimization, which is elaborated upon in the appendix.

We note that 1) this approach may give inaccurate results for systems with very low concentrations of one or more components (which is irrelevant for current work), as the parabolic fit cannot accurately reproduce the divergence
160 of the derivatives of the free energy density due to the entropic contribution [24], and 2) the memory requirements for this scheme scales linearly with the number of phases, but exponentially with the number of chemical components, thus for simulating higher-order systems i.e. quaternary or higher, other schemes should be considered, such as the one recently proposed by Larsson and Höglund [25].

165 Solution of the quasi-equilibrium condition is the main computational bottleneck. Efficiency has been increased by 1) applying knowledge about the structure of the linear system of equations that must be solved in every itera-

tion of Newton's method, and 2) only solving the quasi-equilibrium condition at positions where the local cumulative change over time (sum of the absolute values of all phase-field variables) exceeded a value ϵ . For the current work, a value of $\epsilon = 10^{-5}$ was found to introduce negligible error by comparison to simulations with a value of $\epsilon = 0$, while providing a significant speed up.

The interdiffusional mobilities were fully dependent on composition, and in the case of the γ' phase on the site fraction. The mobilities were determined on a grid, as was the case for the polynomial coefficients for the free energy functions, and retrieved by interpolation during simulation.

The computational implementation and the chosen parameters was validated by simulating growth of a planar interface, the position of which was found to follow the well-known $t^{1/2}$ law, and by simulating coarsening of two γ' particles in a γ matrix, where the particle radii were found to be parabolic in time as expected [26]. No grid-oriented anisotropy due to poor spatial discretization was observed.

3. Initial conditions

We generate initial conditions for the simulations by introducing a random spatial arrangement of identical γ' nuclei into a γ matrix of uniform composition, thus modeling a site saturated nucleation process. For a classical model such as the one employed in current work, the critical nucleus of classical nucleation theory gives the nucleus size below which the nucleus will dissolve, and above which the nucleus will grow into the supersaturated matrix. The nucleus radius R^* and composition $\vec{x}_{\gamma'}$ is determined by

$$\mu_k^{\gamma}(\vec{x}_{\gamma}) = \mu_k^{\gamma'}(\vec{x}_{\gamma'}) + \frac{2\sigma V_m}{R^*}, \quad (k = \text{Al, Cr, Ni}) \quad (13)$$

As this introduces a non-zero volume fraction of γ' into the γ matrix, we further require that

$$\vec{x}_{\text{alloy}} = \phi_{\gamma'} \vec{x}_{\gamma'} + (1 - \phi_{\gamma'}) \vec{x}_{\gamma} \quad (14)$$

where $\phi_{\gamma'} = nV^*$ is the volume fraction of γ' particles, n is the desired number density, and V^* is the volume of the critical nucleus. Eqs. (13) and (14)

was solved iteratively by relaxation to determine the critical radius R^* , and compositions of the matrix and nuclei, $\vec{x}_\gamma$ and $\vec{x}_{\gamma'}$.

For the alloy composition 5.2%Al-14.2%Cr-Ni, and a number density of $1.02 \times 10^{24} \text{m}^{-3}$, we find a critical radius of $R^* = 5.77 \text{\AA}$, a nucleus composition of 17.36%Al-7.728%Cr-Ni and a matrix composition of 5.190%Al-14.21%Cr-Ni by employing the CALPHAD-optimized free energies to determine the required chemical potentials. These (excluding the initial matrix composition which is virtually indistinguishable from the alloy composition) are indicated on a partial phase diagram in Fig. 1. We note that the composition of the critical nucleus is not on the tie line, as predicted by Philippe et al. [27].

The critical nucleus size R^* represents the smallest length scale of interest in the system, and so to resolve this, the $\gamma - \gamma'$ interface width W must be chosen no greater. Additionally, the smallest value of the grid spacing which was found to not introduce numeric artifacts was chosen. A result of this is that the critical nucleus size R^* marks the size below which γ' particles will dissolve into the matrix independent of the matrix composition.

We introduce the nuclei with constant composition and sharp interfaces, with the smallest size greater than R^* allowed by the spatial discretization.

A recent approach to nucleation in phase-field models by Jokisaari et al. [28] introduces nuclei into a system by introducing a seed exclusively in the order parameter of the nucleating phase, which then provides a driving force for "self-assembly" of precipitates in the usual kinetic equations of the system, resulting in a nucleation current that respects the global conservation laws. Such an approach is not applicable in the current system, as the γ' phase is found to be unstable at the matrix composition in the current work. Therefore, a seed introduced in the order parameter in the current $\gamma - \gamma'$ system will not lead to "self-assembly" of precipitates, but will rather rapidly transform to the matrix phase. We note that this complication may be avoided by using parabolic approximations to the free energy, as the thermodynamic stability is then constant in composition.

Figure 1: Partial phase diagram of the $\gamma - \gamma'$ system with the alloy composition, resulting tie line, and composition of the critical nucleus indicated.

4. Simulation results

Three sets of simulations were executed on a grid with 500^3 grid points corresponding to a cube with side length 55nm, with a total of 520 γ' particles for times up to 32h at a temperature of 873.15K. In the following, the presented average quantities are the average of the three simulations, and an initial transient related to the sharp interface initial conditions of 10min is omitted.

4.1. Characterization of microstructural evolution

An example of a simulated microstructure at three different times is shown in Fig. 2. At the earliest time shown (a, 1h10min), the γ' particles are largely identical, due to the choice of initial conditions. For the middle time (b, 3h32min), some particles exhibit non-spherical shapes due to coalescence with one or more other particles. No particles smaller than the particles in the earliest time shown are observed. At the latest time shown (c, 19h00min) the non-spherical particles from the middle time have largely regained a spherical shape, and several particles smaller than the particles observed at the earliest time may be seen.

The volume fraction of γ' particles shown in Fig 3 increases monotonically towards the thermodynamic equilibrium volume fraction of $\phi_0 = 12.6\%$ consistent with the CALPHAD-optimized free energies applied in current work. The

Figure 2: Simulated evolution of γ' particles in a γ matrix for the alloy 5.2%Al-14.2%Cr-Ni (at.%) aged at 873.15K at aging times a) 1h10min. b) 3h32min. c) 19h00min. Visualized by the $\phi_{\gamma'} = \frac{1}{2}$ surfaces. Particles intersecting the periodic boundaries not shown. Colors are arbitrary.

Figure 3: γ' volume fraction, equilibrium volume fraction ϕ_0 , and quasi-equilibrium volume fraction ϕ_{qe} .

transformation is seen to slow down significantly when the volume fraction is
 235 $\sim 2\%$ lower than ϕ_0 .

This discrepancy is found to be a result of capillarity: Assuming the system
 is undergoing diffusive coarsening, the critical radius R_c below which particles
 shrink and above which particles grow, is equal to the average particle size,
 $R_c = \langle R \rangle$ [26], and the critical particle fulfills Eqs. (13) (with $R_c = R^*$).
 240 These equations have been solved numerically subject to Eq. (14), to give the
 relationship between quasi-equilibrium volume fraction ϕ_{qe} and critical radius
 R_c . We then relate ϕ_{qe} to time by assuming that $R_c = \langle R \rangle$, and using the values
 of $\langle R(t) \rangle$ from the simulations to determine the predicted $\phi_{qe}(t)$. This is shown

in Fig. 3. The good agreement after a time of $t \approx 8$ h implies that growth has
 245 ceased, and the microstructural evolution is dominated by coarsening. Further
 increases in volume fraction towards the thermodynamic equilibrium value are
 therefore the result of an increasing average particle size, rather than growth
 into a supersaturated matrix, which is seen to progress at a much slower rate.

Figure 4: a) Density of γ' particles. b) Particle elimination events decomposed into coalescence – and dissolution events (red and blue lines, right axis) and relative density of γ' particles overlaid for convenience (black line, left axis).

Fig. 4a shows the time evolution of the γ' particle density. The particle den-
 250 sity begins decreasing at a time of $t \approx \frac{1}{2}$ h, slows down considerably at a time of
 $t \approx 3$ h, before speeding up around $t \approx 12$ h, and finally reaching the well-known
 power law relationship $n \propto t^m$ at $t \approx 22$ h37m, where $m = -0.992 \approx -1$ is de-
 termined by least-squares. The characteristic shape of the particle density curve
 may be understood when considering the two mechanisms which may be respon-
 255 sible for particle elimination in the current model: Coalescence, where particles
 in contact join to form a single larger particle, and dissolution of small particles
 into the matrix. The cumulative number of events relative to the initial particle
 number are shown in Fig. 4b, where it is seen that the first decrease in the
 particle density ($t \approx \frac{1}{2}$ h) is due to coalescence events, and the subsequent speed
 260 up ($t \approx 12$ h) is largely due to the onset of dissolution events. This is consistent
 with the early microstructural evolution dominated by growth into the supersat-
 urated matrix (average interparticle distance is decreasing, high probability of

coalescence) and the late stages dominated by coarsening (large particles grow, small particles shrink so average interparticle distance is increasing, thus low probability of coalescence.)

Figure 5: a) Average particle radius. Red line indicates negative growth rate. b) Particle size distributions (PSDs) at various times. Also shown is the Marqusee-Ross PSD for an equilibrium volume fraction $\phi_0 = 12.6\%$ [29]. The number of bins is chosen by the method of Shimazaki and Shinomoto [30] to reduce bias in each instance.

The average γ' particle radius is shown in Fig. 5a. It is seen to largely resemble the evolution of the γ' volume fraction shown in Fig. 3 until a time of $t \approx 4$ h. However, in contrast to the non-decreasing γ' volume fraction, the average particle radius is seen to decrease between times $t = 7$ h24min and $t = 12$ h52min, before again increasing, and reaching the power law relationship $\langle R \rangle \propto t^m$ at $t \approx 22$ h37m, with $m = 0.349 \approx 1/3$ determined by least-squares. Furthermore, the theory for coarsening in multicomponent alloys by Morral and Purdy [31] gives an expression for the rate constant K of the relationship $\langle R \rangle^3 \propto Kt$ which for the current system is evaluated to be $K = 2.10 \times 10^{-31} \text{ m}^3 \text{ s}^{-1}$ (Morral and Purdy) while the power law fit to the simulation results gives $K = 2.04 \times 10^{-31} \text{ m}^3 \text{ s}^{-1}$ (current work) giving a deviation of less than 3%, thus verifying that the phase-field model is accurately reproducing the predictions of a model based upon a sharp interface analysis.

The counterintuitive reduction in average γ' particle radius as a function of
 280 aging time may be understood after considering the time evolution of the γ'
 particle size distribution (PSD), shown in Fig. 5b:

At $t = 2\text{h}$ the PSD is sharply peaked close to $R = \langle R \rangle$ with smaller peaks on
 both the smaller-than- $\langle R \rangle$ side (particles for which growth has been hindered by
 competition) and the larger-than- $\langle R \rangle$ side (particles undergone single/multiple
 285 coalescence events). The trend in going to $t = 4\text{h}$ is to retain a peak close to
 $R = \langle R \rangle$ while the PSD is broadening, which continues to $t = 8\text{h}$ (coinciding
 with the onset of particle dissolution events shown in Fig. 4b), where the PSD
 shows a small but non-zero number of particles approaching the size where
 dissolution occurs, i.e. $R^* = 5.77\text{\AA}$. Continuing to $t = 32\text{h}$, the PSD has
 290 developed significant tails on both sides, but is seen to be less centered than the
 Marqusee-Ross distribution [29], and the discrepancy is not explained by the γ'
 volume fraction being lower than the thermodynamic equilibrium value. It is
 likely that the PSD at $t = 32\text{h}$ represents a transient state, but a statistical basis
 larger than the present simulations would be required to state this conclusively.

We can now interpret the shrinking average γ' particle radius as the result of
 295 coarsening, i.e. diffusive mass transfer between particles: As a smaller particle
 transfers mass to a larger particle, the radial decrease of the smaller particle
 will be of a greater magnitude than the radial increase of the larger particle
 (since $dV \propto R^2 dR$) and as a result the average particle size decreases. However,
 300 during steady state coarsening a concurrent decrease in the particle density
 due to dissolution of small particles results in a non-decreasing average particle
 radius [26]. In the current case, growth into the supersaturated matrix at early
 times results in a narrow PSD, and so dissolution of particles is not observed
 before the PSD has broadened sufficiently to include particles with sizes $R \approx$
 305 $R^* = 5.77\text{\AA}$. We note, however, that a continuous nucleation process, rather
 than the site saturated nucleation process simulated in current work, might
 decrease or altogether eliminate this effect, as smaller particles nucleated late
 in the growth stage would dissolve more readily.

We may now summarize the observed microstructural evolution by subdivi-

310 sion into following six dominant regimes in chronological order. Stated times indicate estimated onset of regime.

1. Growth, $t = 0$.
2. Growth and coalescence, $t = 28\text{min}$. Time corresponds to first observed coalescence event.
- 315 3. Growth with decreased coalescence, $t = 3\text{h}08\text{min}$.
4. Coarsening without γ' particle dissolution, $t = 7\text{h}24\text{min}$
5. Coarsening, $t = 12\text{h}52\text{min}$. Time corresponds to first observed dissolution event.
6. Coarsening following steady state power law, $t \approx 22\text{h}37\text{min}$

320 The above regimes are somewhat overlapping in some cases, e.g. particle coalescence occurs with some frequency in the coarsening regime (cf. Fig. 4b), so the specific subdivision chosen is arbitrary to a degree. In regime 6, "following steady state power law" should not necessarily be taken to mean that the system is undergoing steady state coarsening (i.e. self-similarity which also
 325 requires time-invariant PSDs), but only that the particle density, and average γ' particle radius with good approximation follow $n \propto t^{-1}$ and $\langle R \rangle \propto t^{1/3}$.

On a sidenote, simulations have also been performed in two dimensions, as these are often taken to be an approximation for more computationally demanding three-dimensional calculations. In the current system, using initial conditions chosen so the average edge-to-edge interparticle distance corresponded to
 330 the three-dimensional case (while remembering that the critical radius for nucleation in a two-dimensional system is half that of the three-dimensional system) gave results that were both quantitatively and qualitatively different from the three-dimensional results: The transformation occurs at a much increased rate
 335 (likely due to the longer reaching logarithmic diffusion fields around particles in two dimensions compared to the r^{-1} fields in three dimensions), and the microstructural evolution does not follow the six regimes characterized above. Thus, we conclude that for systems with diffusional interactions, conclusions about the microstructural evolution of three-dimensional systems drawn on the

Figure 6: Trajectories of volume-averaged matrix composition and volume-averaged particle composition minus corresponding equilibrium (tie line) value. Gray lines are straight lines least-squares fitted to points for times $t \geq 8h$.

340 basis of two-dimensional calculations must be scrutinized carefully.

4.2. Evolution of particle and matrix composition

In order to examine the composition of the γ' particles and the γ matrix, we take points as belonging to a particle if $\phi_{\gamma'} \geq 0.995$, belonging to the matrix if $\phi_{\gamma} \geq 0.995$, and consequently belonging to an interfacial region elsewhere. The specific threshold was chosen based on inspection of the simulation results to minimize the volume of the interfacial regions while not introducing significant bias in the composition averaged over individual particles.

Fig. 6 shows the trajectory of the volume-averaged composition of the particles and the matrix, as the difference between the composition and the corresponding equilibrium (tie line) compositions. The gray lines shown are straight lines fitted to points for times $t \geq 8h$, and both are found to approach the tie line value, and so it is possible that the gray lines would provide accurate extrapolation for times $t > 32h$. The trajectories become well-described by straight lines around the time when coarsening becomes the dominant mechanism for microstructural evolution, consistent with the theory by Philippe and Voorhees [32]. Before 8h the evolution of the matrix composition is well-approximated by a straight line, which is almost parallel to the extrapolated line, while the tra-

jectory of the volume-averaged particle composition is more complicated with a non-monotonic Cr content, and a kink in the curve at a time of 8h.

Figure 7: Volume-averaged composition of individual γ' particles minus equilibrium (tie line) value. a) As a function of normalized particle radius for various times. Also shown is a power law fit to x_{Al} for time $t = 32h$. b) Cr content of individual γ' particles as function of Al content. Gray lines are straight lines least-squares fitted to times $t = 1h, 2h,$ and $32h$ (parameters in text body).

Turning attention to the volume-averaged composition of individual γ' particles, Fig. 7a shows composition as a function of normalized particle radius for various times. For $t = \frac{1}{6}h$, the particles are virtually identical due to the initial conditions of the simulations. At $t = 1h$, the particles are found in three clusters, reflecting the number of coalescence events undergone (zero, one or two), and this clustering is still evident at $t = 2h$, but not at the later times shown. At $t = 8h$ and $t = 32h$, the composition of the particles resemble a continuum. During coarsening, the theory by Philippe and Voorhees [32] predicts a R^{-1} dependence in the particle composition, however, although the distribution of particle compositions at $t = 32h$ visually resemble a R^{-1} dependence, and least-squares fitting a power law relationships $\Delta x \propto R^m$ finds $m = -1.042$ (shown on Fig. 7a), but this is found to be inaccurate for particles smaller than approximately $R < 0.4\langle R \rangle$. This is explained by the finite diffusivity in the γ' particles, that above-mentioned theory does not account for: The small

particles are shrinking at high radial rates, and therefore are unable to maintain
 375 constant equilibrium between their internal composition and the time-varying
 composition on the interface as given by the Gibbs-Thomson condition. As a
 result, internal gradients in the composition develop, which cause the volume-
 averaged compositions of these particles to "lag behind" the composition at the
 particle interfaces.

380 Another feature to note in the relationship between the composition of in-
 dividual particles and their size, Fig. 7a, is that while the late times (8h and
 32h) show the particle composition approaching the equilibrium composition
 with increasing size, this is not the case for all particles at early times ($t = 1$
 and $t = 2$ h) where the cluster of the smallest particles, i.e. the particles that
 385 have not experienced coalescence, show the opposite relationship. This slight,
 but consistent relationship is caused by the finite diffusivity in the γ' particles:
 During growth, gradients develop in the internal compositions when the radial
 growth rates are sufficiently high compared to the γ' diffusivity that constant
 equilibrium cannot be maintained. Higher growth rates result in gradients in
 390 composition of greater magnitude. Additionally, as the gradients in composition
 are reduced by diffusion of mass through the particle, larger particles equilibrate
 slower.

Despite the complexities in the relationship between composition and parti-
 cle size, we find the relationship between two components of the composition of
 395 individual particles, Fig. 7b, to be well-approximated by nearly parallel straight
 lines at all times: The three lines shown are fitted to times $t = 1, 2$, and 32h
 with the form $\Delta x_{Cr} = c_1 \Delta x_{Al} + c_2$, with $c_1 = -1.08, -1.10$, and -1.11 , and
 $c_2 = 1.2 \times 10^{-3}, 8.8 \times 10^{-4}$, and 9.4×10^{-5} , respectively. So while the slope is
 nearly constant in time, the point of intersection tends to zero, which is required
 400 to allow $\Delta \vec{x} \rightarrow 0$ for particles where $R \rightarrow \infty$, assuming that the relationship
 between two components of the composition of individual particles remain well-
 described by a straight line. This finding is in agreement with the theory of
 Philippe and Voorhees [32].

Finally, Fig. 8 shows the evolution of the composition of five individual

Figure 8: Composition of five individual γ' particles minus equilibrium (tie line) composition. a and c) As a function of aging time. b and d) As a function of particle radius. Gray lines are the volume-averaged particle composition, in Figs. 8b and 8d as a function of average particle radius $\langle R \rangle$. Note that particles 4 and 5 experienced coalescence events, which results in discontinuities in their composition.

particles with the volume-averaged particle composition shown in gray for comparison as a function of time (Figs. 8a and 8c) and as a function of particle radius (Figs. 8b and 8d). If the system was a binary alloy, the compositions would only be functions of the particle size. Since this is not necessarily the case in a ternary alloy we therefore investigate the magnitude of this effect of Al-Cr-Ni alloys at the early stages of precipitation.

Particle 1 (black curves in Figs. 8a and 8b) reaches its maximal size at a time of $t = 17\text{h}40\text{min}$ before shrinking, however its composition is found to approach its equilibrium value until a time of $t = 20\text{h}52\text{min}$ where the particles compo-

sition (all components simultaneously) begins departing from the equilibrium
415 value.

Particles 2 and 3 (red and blue curves in Figs. 8a and 8b) are found to
increase in size until times $t = 5\text{h}00\text{min}$ and $t = 4\text{h}04\text{min}$ before shrinking and
eventually dissolving. As opposed to particle 1, their extrema in composition
do not occur simultaneously: For particle 2, the Al composition approaches its
420 equilibrium value until a time of $t = 3\text{h}36\text{min}$ before departing, while this oc-
curs for the Cr composition at $t = 3\text{h}08\text{min}$, and for particle 3 the corresponding
times are $t = 3\text{h}16\text{min}$ and $t = 2\text{h}50\text{min}$. This results in compositional trajec-
tories vs. particle size that loops so the curves crosses themselves. These loops
are smaller in the case of Al than in the case of Cr, and we note that this is not
425 possible in a binary alloy, since then concentration $\propto 1/R$.

Particles 1-3 initially follow the volume-averaged particle composition (gray
curves) before monotonically departing away from the equilibrium composition.

Particle 4 (green curves in Figs. 8c and 8d) experiences a coalescence event at
 $t = 1\text{h}40\text{min}$. This does not alter the composition appreciably, as the coalescing
430 particles are found to be almost identical in both size and composition: Parti-
cle size increases by a factor of $\Delta R = 1.27$ compared to $\Delta R = 2^{1/3} = 1.26$
as expected for identical particles, and the composition changes by factors
 $\Delta x_{\text{Al}} = 0.96$ and $\Delta x_{\text{Cr}} = 0.95$. The particle size increases monotonically, but
the composition shows local extrema: A locally closest approach to the equilib-
435 rium value is found at $t = 3\text{h}32\text{min}$ for Al and $t = 2\text{h}52\text{min}$ for Cr, while the
locally furthest departure is found at $t = 11\text{h}00\text{min}$ for Al and $t = 11\text{h}32\text{min}$
for Cr. The composition of this particle crosses the volume-averaged particle
composition (gray curves) once when viewed as a function of time, and twice
when viewed as a function of particle size.

440 Particle 5 (cyan curves in Figs. 8c and 8d) experiences two coalescence events
at $t = 1\text{h}16\text{min}$ and $t = 2\text{h}56\text{min}$, respectively. The earlier event does not alter
the composition significantly: Particle size changes by factor $\Delta R = 1.28$, and
composition by factors $\Delta x_{\text{Al}} = 0.94$ and $\Delta x_{\text{Cr}} = 0.92$, the later event changes
particle size by a factor $\Delta R = 1.18$ and composition by $\Delta x_{\text{Al}} = 1.16$ and $\Delta x_{\text{Cr}} =$

1.28. The composition of particle 5 also show multiple extrema: For Al, a locally
 closest approach to the equilibrium value is found at $t = 3\text{h}36\text{min}$, and a locally
 farthest departure at $t = 6\text{h}52\text{min}$, while for Cr, locally closest approaches to
 equilibrium are found at $t = 2\text{h}32\text{min}$ and $t = 3\text{h}24\text{min}$ (before and after the
 second coalescence event), and a locally furthest departure from equilibrium
 at $t = 7\text{h}32\text{min}$. The composition of this particle remain closer to equilibrium
 than the volume-averaged particle composition following its departure from this
 curve at the first coalescence event, but crosses the volume-averaged particle
 composition once when viewed as a function of particle size.

5. Discussion

Extensive experimental investigations of phase separation in comparable Al-
 Cr-Ni alloys have been carried out with atom probe tomography (APT) e.g. by
 Mao et al. [6], and by Booth-Morrison et al. [22, 7]. Figure 3 in the latter
 publication shows γ' volume fraction, particle density, and average γ' particle
 radius for the comparable alloy 6.5%Al-9.5%Cr-Ni aged at 873K, which may be
 compared with Figs. 3, 4a, and 5a in the present work on which we shall base
 this discussion.

Discounting the regime dominated by nucleation, both the γ' volume frac-
 tion, and the particle density are qualitatively similar. For the particle density,
 the simulations qualitatively correctly predict the rapid early decrease, the in-
 termediate slowdown, and the final $n \propto t^{-1}$ phase. As the early decrease in
 particle density in the simulations was found to be due to coalescence, this is
 taken as evidence that coalescence is an important mechanism for microstruc-
 tural evolution in the early stages of phase separation in this $\gamma - \gamma'$ Al-Cr-Ni
 alloy. Earlier studies have consistently found a high probability for γ' particles
 to form anti-phase boundaries rather than coalescing upon contact, dependent
 on their order parameter mismatch, which would reduce the importance of co-
 alescence as a mechanism for microstructural evolution. However, Mao et al.
 [5] have shown that small γ' particles in proximity become interconnected by

L1₂ ordered "necks" which facilitate coalescence for contacting particles. This
 475 observation thus rationalizes the importance of coalescence during early stage
 phase separation in these $\gamma - \gamma'$ alloys.

The intermediate slowdown was found to be characterized by decreased co-
 alescence, and an absence of particle dissolution events as growth into the su-
 persaturated matrix had resulted in a PSD without a tail of small particles that
 480 could readily dissolve into the matrix, before reaching the well-known classical
 coarsening regime. While the particle density becomes nearly constant in the
 simulations, a slight decrease is seen in the equivalent regime in the experimen-
 tal data. This discrepancy is likely due to the initial conditions applied in the
 simulations: We introduce a random spatial arrangement of identical particles
 485 at one time (i.e. site saturated nucleation), while nucleation in the experimental
 system is known to be a continuous process resulting in nuclei which may fea-
 ture a continuum of sizes. So it is likely that experimentally determined PSDs
 in this transient regime would be skewed towards larger sizes, but still feature
 small (likely the most recently nucleated) particles, which may dissolve without
 490 a long delay required for the reconfiguration of the PSD towards smaller particle
 sizes, as was the case in the simulations.

It is more difficult to find the correspondence between the simulated and the
 experimental average particle radius: The simulated average particle radius in-
 creases, becomes constant and even slightly negative as growth and coalescence
 495 cease, before finally increasing following the well-known $\langle R \rangle \propto t^{1/3}$ dynamics,
 while the experimental result appears to be increasing monotonically. This may
 possibly again be explained by the initial conditions of the simulations: The ran-
 dom spatial arrangement of nuclei results in relatively easily delineated growth
 and coarsening regimes, however if nucleation in the experimental alloy shows a
 500 tendency towards clustering, i.e. spatially preferred nucleation sites, the result
 might be microstructural evolution that is simultaneously dominated by growth
 at some spatial locations, and by coarsening at other spatial locations. Thus, a
 coarsening regime as was observed in the simulations where mass is transported
 from smaller particles to larger particles with few particle dissolution events

505 may be occurring in the experimental system, but be masked by an increasing average particle radius due to concurrent growth at other spatial locations.

However, there is a marked discrepancy between the time scales of the experiment and the simulations, e.g. the $n \propto t^{-1}$ regime sets in around $t \approx 22\text{h}37\text{min}$ in the simulations, while it seems to set in no earlier than $t \approx 256\text{h}$ in the
510 experiment. Contrary to the previous discrepancies between simulation and experiment, this is not believed to be related to the initial conditions for the simulations, but rather to the atomic mobilities employed in the simulations. Firstly, the atomic mobility matrices employed in the simulations are diagonal in the lattice-fixed frame of reference, which means that they do not admit
515 correlations between the diffusive fluxes of different species, which is argued to be an important factor in the kinetic pathway for early-stage phase separation for comparable alloys [6]. As such, we would expect the system to choose quantitatively different pathways during phase separation, but it is not clear that inclusion of the diffusional flux couplings would result in microstructural
520 evolution retarded by at least an order of magnitude. However, in the phase-field model applied in the current work, the phase transformation is required to be volume conserving, and thus the atomic mobilities must be transformed from the lattice-fixed frame of reference to the volume-fixed frame of reference [21], which therefore assumes that the vacancy distribution remains at equilibrium, or equivalently assumes a dense concentration of vacancy sinks and
525 sources, i.e. dislocations, since the coherent particle-matrix interfaces do not act as sinks or sources for vacancies. For the range of particle densities reported by Booth-Morrison et al. [7] of $n = 9.84 \times 10^{23} - 3 \times 10^{21}\text{m}^{-3}$ we estimate a center-to-center interparticle distance via the Wigner-Seitz radius to
530 be $d_{\text{p-p}} \approx 2(3/4\pi n)^{1/3} = 12 - 86\text{nm}$, while the average distance between dislocations with a density of $\rho = 10^{12} - 10^{10}\text{m}^{-2}$ (typical values for well-annealed metals) is estimated as $d_{\text{d-d}} \approx \sqrt{1/2\rho} = 0.7 - 7\mu\text{m}$ [33], and so typical diffusional interactions (particle-matrix or particle-particle) in those experiments occur "far" from the dislocations required to equilibrate the vacancy concentration, which may thus explain the violation of the assumption of equilibrium of
535

the vacancy concentration.

Another possible explanation for the difference between the time scales of the experiment and the simulations are unphysically large diffusivities caused by the uncertainty in the assessment of the atomic mobilities and the uncertainty
540 in the Hessian matrix of the CALPHAD-optimized free energy functions. This is not believed to be the case, as all employed assessments are based on multiple experiments, however, for completeness, diffusion matrices and diffusion eigenmodes for the matrix phase which dominate the long-range diffusive behavior of the system are presented for inspection in the appendix.

545 Considerable progress in the understanding of the phase separation behavior in Al-Cr-Ni alloys has been made by Lattice Kinetic Monte Carlo (LKMC) simulations coupled with interaction energies from density functional theory [4, 5, 6]. LKMC is an atomistic method allowing simulations of vacancy-mediated diffusion in coherent phases, conserving the number of vacancies. However, the
550 high computational demands for simulations with a realistically low vacancy concentration currently limits the time scales which may be probed, and so alternative simulation frameworks are desirable. To the best of the authors knowledge, no phase-field model has been presented to incorporate time-evolving vacancy distributions. Developing such a model would likely present a significant
555 challenge, but would enable extension of quantitative phase-field methods into near-atomic length scales.

Finally, there are several different schemes for incorporating nucleation events into phase-field simulations, see e.g. [34] and references therein, however doing so at diffusive time scales in a computationally efficient, physically consistent
560 manner must of this writing be considered challenging [35].

6. Conclusions

We have performed simulations of $\gamma-\gamma'$ phase separation in 5.2%Al-14.2%Cr-Ni at 873.15K with a phase-field model where the free energy functions were given by CALPHAD expressions [16], and the atomic mobilities were given

565 by CALPHAD-style optimized assessments [19, 20]. Thus, both free energy
functions and atomic mobilities were considered experimentally validated. Mi-
crostructural evolution was simulated up to a time of 32h for 510 individual
 γ' particles corresponding to a γ' particle density of 10^{24}m^{-3} introduced as a
spatially random distribution of identical particles chosen in accordance with
570 classical nucleation theory.

The microstructural evolution was broadly characterized as consisting of
1) a regime dominated by growth and particle coalescence events, 2) growth
with few particle coalescence events, 3) coarsening without particle dissolution
events, and finally 4) "classical" coarsening, i.e. coarsening including particle
575 dissolution events, following the well-known $\langle R \rangle^3 \propto Kt$, with the time constant
 K agreeing well with the theoretical prediction by Morral and Purdy [31].

The microstructural evolution was found to agree qualitatively well with
experimental evidence [7], but with considerable quantitative differences. This
was argued to likely be due to the violation of the common assumption of the
580 vacancy distribution being at permanent equilibrium caused by the large average
distance between dislocations compared to the length scales of interest in the
simulations.

The volume-averaged γ' particle composition was found to follow a com-
plicated trajectory with a kink, which coincided with the transition from mi-
585 crostructural evolution dominated by growth to microstructural evolution dom-
inated by coarsening. The compositional trajectories of individual γ' particles
were found to depart significantly from the volume-averaged composition when
particle interactions and competition for supersaturation sets in, and showed
complexities inherent to non-binary alloys.

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Appendices

γ diffusivity

In this section, we present diffusivities of the γ matrix phase which is expected to dominate the long-range diffusive behavior. The diffusivity matrices
600 are given by the product of the chemical mobilities matrix in the volume-fixed frame of reference, and the Hessian matrix of the free energy density. Both are non-diagonal, and fully dependent on composition. The basis is (Al, Cr).

At the alloy composition $\vec{x}_{\text{alloy}} = (0.052, 0.142)$ we have

$$D_{\text{alloy}} = \begin{bmatrix} 24.6 & 11.8 \\ 11.8 & 9.43 \end{bmatrix} \times 10^{-21} \text{m}^2/\text{s}$$

with corresponding fast and slow diffusion eigenvalue and vector pairs

$$\lambda_{\text{alloy}}^{\text{fast}} = 31.0 \times 10^{-21} \text{m}^2/\text{s}, \quad \vec{V}_{\text{alloy}}^{\text{fast}} = (0.878, 0.479)$$

$$\lambda_{\text{alloy}}^{\text{slow}} = 3.00 \times 10^{-21} \text{m}^2/\text{s}, \quad \vec{V}_{\text{alloy}}^{\text{slow}} = (-0.479, 0.878)$$

While for the equilibrium (tie line) composition $\vec{x}_{\text{eq}} = (0.036, 0.150)$ we have

$$D_{\text{eq}} = \begin{bmatrix} 16.3 & 6.74 \\ 9.22 & 7.59 \end{bmatrix} \times 10^{-21} \text{m}^2/\text{s} \quad (15)$$

$$\lambda_{\text{eq}}^{\text{fast}} = 21.0 \times 10^{-21} \text{m}^2/\text{s}, \quad \vec{V}_{\text{eq}}^{\text{fast}} = (0.823, 0.568)$$

$$\lambda_{\text{eq}}^{\text{slow}} = 3.00 \times 10^{-21} \text{m}^2/\text{s}, \quad \vec{V}_{\text{eq}}^{\text{slow}} = (-0.450, 0.893)$$

So $\lambda_{\text{alloy}}^{\text{fast}}/\lambda_{\text{eq}}^{\text{fast}} = 1.48$ and $\lambda_{\text{alloy}}^{\text{slow}}/\lambda_{\text{eq}}^{\text{slow}} = 1.00$. The fast modes align the fluxes of Al and Cr, while the slow modes opposes the flux of Al and Cr.

The local phase compositions $\vec{x}_\gamma$ and $\vec{x}_{\gamma'}$ and diffusion potentials $\tilde{\mu}_{\text{Al}}$ and $\tilde{\mu}_{\text{Cr}}$ must be determined in all interfacial regions at all times, as the evolution of the system depends on these quantities, as explained in Sec. 2. Due to the quasi-equilibrium assumption, these quantities are taken to be minimizers of the bulk free energy functional as given by Eq. (6).

If the current work had employed parabolic approximations to the free energies of the γ and γ' phases, then Eq. (7) would reduce to a system of linear equations, which would thus be easily solved. However, as current work employs fully non-linear CALPHAD free energy functions, a more complex solution method is required, and Newton's method was chosen due to its fast convergence. Newton's method is an iterative method, where a vector of initial guesses is propagated towards an extremum by solving the system of linear equations

$$\mathbf{H}[\vec{z}_{n+1} - \vec{z}_n] = -\lambda \nabla f_{\text{bulk}}^{\vec{z}_n} \quad (16)$$

where $\mathbf{H}$ is the Hessian matrix of f_{bulk} , λ is a relaxation parameter to ensure convergence ($\lambda = 0.25$ in current work) and $\vec{z}$ is the vector of parameters to be determined, here chosen as $\vec{z} = (x_{\text{Al}}^\gamma, x_{\text{Cr}}^\gamma, x_{\text{Al}}^{\gamma'}, x_{\text{Cr}}^{\gamma'}, \tilde{\mu}_{\text{Al}}, \tilde{\mu}_{\text{Cr}})$. This system of linear equations are transformed into triangular form by Gauss-Jordan elimination, and solved by back substitution, and the process is repeated until convergence, here taken to be when the sum of the magnitude of the elements of $\vec{z}_{n+1} - \vec{z}_n$ becomes less than 10^{-5} . The elements of the Hessian matrix $\mathbf{H}$ and gradient ∇f_{bulk} are evaluated numerically with high precision as described in Sec. 2.6.

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