

Understanding coarsening of a post-corrosion microstructure in a molten salt by combining phase-field modeling and in situ tomography

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ABSTRACT

Alloys corroding in molten salt have been observed to form bicontinuous, nanoporous microstructures via dealloying, which subsequently undergo coarsening due to facile transport in high-temperature conditions. In this work, we describe a methodology to elucidate the underlying transport mechanisms during coarsening of a bicontinuous microstructure via quantitative comparisons between phase-field simulations and four-dimensional in situ experiments, in this case X-ray nanotomography of the coarsening of a dealloyed 80 wt% Ni-20 wt% Cr microwire in molten KCl-MgCl₂ at 800°C. We conduct phase-field simulations initialized from experimental data to model coarsening via three different transport mechanisms: surface diffusion, solid bulk diffusion, and liquid bulk diffusion. These simulations reproduce key features of the experiment, such as the densification of the outer layer of the dealloyed wire and the reduction in radius over time. We quantitatively compare different microstructural characteristics between the simulations and experiment and extract temporal scaling factors that optimally match the time scales of the simulations to that of the experiment. This allows us to evaluate morphological similarity between the simulations and experiment and relate the experimental coarsening kinetics to fundamental material properties. We find that surface diffusion is most likely to be the dominant coarsening mechanism, and its kinetics imply a surface diffusivity of $D_s = 8.9 \times 10^{-20} \text{ m}^3/\text{s}$, which is within the range of reported values for Ni-vacuum interfaces at 800°C. However, the difference between the experiment and the surface diffusion simulation increases substantially at late times, suggesting that other mechanisms, such as the dissolution of residual Cr, may be at play.

1. Introduction

Molten salts are materials with versatile applications, ranging from coolant in advanced nuclear reactors [1,2] to electrolytes in batteries [3] to thermal energy storage in concentrated solar power plants [4,5]. These systems require structural materials to safely contain the molten salts, which could lead to corrosion driven by impurities at the elevated temperatures required for operation [6]. Furthermore, alloys in contact with molten salts can undergo dealloying, wherein one alloy component preferentially dissolves and the remaining alloy components form a complex microstructure [7–10]. The mass loss resulting from dealloying can compromise the structural integrity these materials, presenting a

major challenge to the longevity of molten salt reactors and concentrated solar power plants [11]. Several solutions have been proposed, such as coatings [11] and optimizing alloy compositions [12]. In addition, many investigations, experimental and computational, have examined the effects of corrosion [13–15] and dealloying [9,16,17] on the morphological evolution of alloys in molten salts.

Materials development for molten salt applications requires fundamental understanding of the interactions between alloys and the molten salt. These interactions are understood in terms of the thermodynamics, kinetics, and electrochemistry of the corrosion reaction and the transport processes in the metal, in the salt, and at the metal-salt interface. The associated thermodynamic and kinetic parameters can be assessed

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using thermochemical [18–20] and electrochemical [21,22] experiments and atomistic simulations [23,24] and then integrated into continuum-scale models for microstructure evolution [25–27]. Here we focus specifically on phase-field modeling [28–30], which can fully resolve complex bicontinuous morphologies [31,32] and can thus be compared to four-dimensional (4-D, three spatial dimensions plus time) X-ray nanotomography measurements of dealloying. Specifically, we aim to compare our simulation results to experiments by Liu et al. [9] in which a micrometer-scale Ni-20Cr wire is immersed in equimolar KCl-MgCl₂ at 800°C, resulting in a porous Ni-rich dealloyed structure.

Setting up a phase-field simulation to compare directly to molten-salt dealloying experiments is a challenging task. Combining the assessed thermodynamic [18,19] and kinetic [20,22] properties for the metal and salt would lead to a highly complex model, and it is not clear a priori which simplifications are appropriate. Additionally, some important parameters are unavailable. It is not known how the kinetics of surface diffusion at the metal-molten salt interface differ from the metal-vacuum case (which is well studied [33,34]), and surface diffusion is thought to be highly important for evolution during dealloying [35]. It may be possible to determine surface diffusivity by comparing corrosion simulations to 4-D experiments, but this task is complicated by the presence of competing driving forces, namely the reaction potential for oxidation of the less noble metal and capillarity, the tendency of the system to reduce its interfacial area [36].

As a first step toward understanding the microstructural evolution of Ni-Cr alloys in molten salt, we consider post-corrosion coarsening, which was also imaged by Liu et al. [9]. Coarsening, also known as Ostwald ripening, is a process of capillarity-driven microstructure evolution that reduces total interfacial area and increases the length scale of features [37–40]. Coarsening lacks the competition between the oxidation reaction and capillarity that exists earlier in the corrosion process. The driving force due to capillarity also depends on the length scale of the microstructure via the Gibbs-Thomson effect, which relates chemical potential to curvature at interfaces [41]. Due to these characteristics, coarsening via a single transport mechanism possesses a spatiotemporal scaling relationship in the form of $\ell(t) \sim t^{1/n}$, where t is time, ℓ is the length scale, and the exponent n depends on the limiting transport mechanism [42,43]. These scaling relationships for coarsening were first identified by Herring [43], and they appear (with different, geometry-specific prefactors) in analytical solutions for the coarsening of spherical particles in the dilute limit [37,40] and the flattening of a nearly planar surface [44].

In this work, we exploit this scaling relationship to compare coarsening simulations of a complex bicontinuous structure to 4-D experiments and determine the coarsening rate constant. If the simulation is initialized from a microstructure obtained as part of an in situ 4-D experiment, and one assumes that the morphological evolution in the experiment follows the mechanism modeled by the simulation, then the scaling relation implies that there exists a constant ratio between the experimental time and the simulation time that enables the evolution to be matched. We propose that this ratio (hereafter referred to as the scaling time) can be measured and converted into a rate constant that relates to the kinetic and thermodynamic properties of the system using information about the sharp-interface limit of the phase-field model [45, 46]. Prior work by Zhang et al. [47,48] relies on point-by-point comparison between experimental and simulated data to extract kinetic information. However, such comparisons can be made only if there is high-resolution, low-noise 4-D data, which limits the applicability of this approach, such as in complex environments like high temperatures, the liquid phase of molten salts, or when samples are rapidly evolving or radiation-sensitive, where exposure time or dose must be minimized to capture dynamic changes or avoid beam-induced damage. Our approach circumvents this by taking a statistical method to comparing the experimental and simulated datasets.

We first describe the theoretical background for coarsening and the phase-field model. Then, we present the methodologies, including how

the simulated microstructures differ from the experimental data. To obtain the simulated microstructures, we conduct phase-field simulations initialized based on a snapshot from a 4-D X-ray nanotomography dataset obtained by Liu et al. [9]. We investigate coarsening via surface diffusion, which was the most likely coarsening mechanism identified by Liu et al., with the goal of computing the surface diffusivity of Ni at the metal-salt interface. Since our previous works indicate that different coarsening mechanisms can lead to differences in morphology [49,50], we simulate two additional cases: coarsening via vacancies through the metal and diffusion of Ni²⁺ through the molten salt, which we call solid bulk diffusion and liquid bulk diffusion, respectively. By comparing evolution across different mechanisms and identifying the best match to the experiment, we attempt to provide evidence for the underlying mechanism(s) of coarsening and calculate the rate constants. These rate constants are compared to values based on kinetic and thermodynamic properties in literature to further assess the plausibility of these mechanisms.

2. Theory and modeling

2.1. Sharp-interface models for coarsening

Figure 1a illustrates the experimental setup that we seek to capture in our models. The image volume will constitute the computational domain of our simulations, and it contains a section of the microwire (shown in its pre-corrosion state) as well as the molten salt (an equimolar KCl-MgCl₂ mixture). The salt and wire are contained in a quartz capillary that lies outside the image volume and is assumed to be inert. For additional details about the experiments, we refer the readers to Ref. [9].

Figure 1b illustrates diffusional fluxes due to the coarsening mechanisms under consideration. While there is residual Cr in the dealloyed Ni-Cr wire (~12at.%, based on the estimate of 10% dissolved volume in Ref. [9]), we assume that Ni diffusion is rate-limiting for coarsening because Ni is the main component of the solid and Cr typically diffuses more quickly than Ni [20,23]. We define the interface unit normal vector $\mathbf{n}$ to be pointing outward from the solid phase. In this work, mean curvature H refers to the mean of the principal curvatures κ_1 and κ_2 ,

$$H = (\kappa_1 + \kappa_2)/2, \quad (1)$$

and our sign convention for H is such that $H = (1/\text{radius}) > 0$ for a sphere of solid phase surrounded by liquid.

For coarsening via surface diffusion, we consider a model derived by Mullins [51]. This model combines the Gibbs-Thomson effect, mass transport via surface diffusion, and interfacial motion into a single equation:

$$v_n = -D_s^M \nu \frac{\gamma V_M^2}{RT} \nabla_s^2 H = -B_{\text{surf}} \nabla_s^2 H, \quad (2)$$

where v_n is the interfacial velocity in the normal direction, D_s^M is the surface diffusivity from Ref. [51] with dimensions length²/time, ν is the surface concentration with dimensions atoms/length², γ is the interfacial energy, V_M is molar volume of Ni metal, ∇_s^2 denotes the surface Laplacian, T is temperature, and $R = 8.314 \text{ J}/(\text{mol K})$ is the gas constant. The constant $B_{\text{surf}} = D_s^M \nu \gamma V_M^2 / RT$ has been referred to as the Mullins coefficient for surface diffusion [34,44,51]. Recent experimental literature (e.g., Ref. [34]) frequently report surface diffusivity D_s with dimensions length³/time, which is related to D_s^M via $D_s = \nu V_M D_s^M$. Thus, any values discussed here will be of D_s rather than D_s^M . This gives a Mullins coefficient for surface diffusion in the form

$$B_{\text{surf}} = \frac{\gamma V_M D_s}{RT}, \quad (3)$$

which has dimensions length⁴/time.

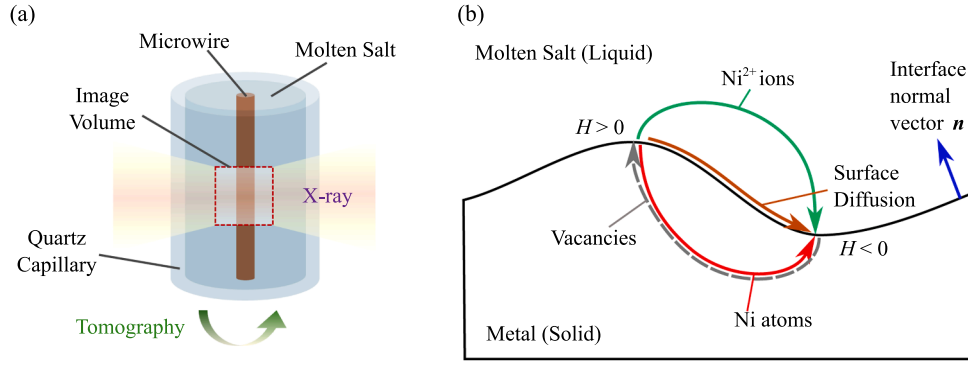


Figure 1. Schematics illustrating (a) the experimental setup (not to scale) and (b) the coarsening mechanisms under consideration. In (b), fluxes of Ni-containing species via different mechanisms (light green for liquid bulk diffusion, brown for surface diffusion, and red for solid bulk diffusion) with arrows indicating that the species flow from higher to lower H , while the flux of vacancies (dashed gray line) is in the opposite direction. The sign conventions for mean curvature H and the interface normal vector $\mathbf{n}$ (blue arrow) are indicated relative to the solid phase.

For the bulk diffusion cases, we simplify our thermodynamic descriptions of the metal and salt by considering coarsening via diffusion of dilute species: vacancies in the metal and Ni^{2+} ions through the molten salt. This approach closely follows Mullins [44], and our expressions will differ from those encountered for concentrated binary alloys (e.g., in Ref. [39]). We expect that electromigration of Ni^{2+} can be neglected since it is a dilute component of a well-supported/highly conductive electrolyte [52,53] and we assume that diffusion is rate limiting rather than the nickel redox reaction at the interface. For both bulk diffusion cases, transport of the dilute species (vacancies and Ni^{2+} ions) in each phase is described by Fick's first and second laws [54],

$$\mathbf{j}_A = -\frac{D_A}{V_M} \nabla X_A, \quad (4)$$

and

$$\frac{\partial X_A}{\partial t} = \nabla \cdot D_A \nabla X_A, \quad (5)$$

where $\mathbf{j}_A$ denotes the flux of species A (Ni^{2+} ions or Ni vacancies), D_A is the diffusivity, V_M is the molar volume of A , and X_A is the mole fraction of species A . In analytical treatments of coarsening, it is assumed that the interface motions are sufficiently slow such that the concentration field is given by the solution to the steady-state Fick's second law [39].

The Gibbs-Thomson effect relates the local equilibrium concentrations at the interface to the interfacial mean curvature H [39–41,55]. For the Ni^{2+} ion mole fraction $X_{\text{Ni}^{2+}}$, this relationship can be expressed as [56]

$$X_{\text{Ni}^{2+}} = X_{\text{Ni}^{2+}}^{\infty} \left(1 + \frac{2H\gamma V_M}{RT} \right), \quad (6)$$

and for the vacancy mole fraction X_V [54],

$$X_V = X_V^{\infty} \left(1 - \frac{2H\gamma V_M}{RT} \right), \quad (7)$$

where $X_{\text{Ni}^{2+}}^{\infty}$ and X_V^{∞} denote the equilibrium mole fractions at a planar interface (i.e., one with $H = 0$). Both equations are linearizations of exponential expressions about $H = 0$ that appear in Refs. [54,56], which should be sufficient to model the micrometer-scale features encountered in this work. The difference in sign between Equations (6) and (7) exists because the oxidation of neutral Ni atoms in the metal to Ni^{2+} ions in the molten salt decreases the volume of the solid phase, while injection of vacancies increases the volume of the solid phase [41]. It is assumed that the molar volume of Ni^{2+} ions in the molten salt does not differ significantly from that of neutral Ni atoms in the metal and remains a constant. Note that Equations (6) and (7) can be written in the form $X_A =$

$X_A^{\infty} \pm H\Gamma_A$, where the quantity $\Gamma_A = X_A^{\infty} 2\gamma V_M / RT$ is known as the capillary length associated with species A [39].

The interface migrates via accumulation of Ni atoms. For liquid bulk diffusion, this can be expressed as [39]

$$v_n = -V_M \mathbf{j}_{\text{Ni}^{2+}} \cdot \mathbf{n}, \quad (8)$$

For solid bulk diffusion, we have

$$v_n = V_M \mathbf{j}_{\text{Ni}} \cdot \mathbf{n}, \quad (9)$$

where the flux of Ni atoms $\mathbf{j}_{\text{Ni}}$ is equal and opposite to that of vacancies, $\mathbf{j}_{\text{Ni}} = -\mathbf{j}_V$. The signs of Equations (8) and (9) differ because a flux of Ni^{2+} ions toward the interface is going in the opposite direction from a flux of Ni atoms toward the interface (see Figure 1). In summary, coarsening via liquid bulk diffusion is described by Equations (4), (5), (6), and (8), while coarsening via solid bulk diffusion is described by Equations (4), (5), (7), and (9). Similarly to surface diffusion, the physical parameters determining kinetics of coarsening via bulk diffusion can be combined into a single coefficient [34,44],

$$B_{\text{bulk}} = D_A X_A^{\infty} \frac{\gamma V_M}{RT} = \frac{D_A \Gamma_A}{2} \quad (10)$$

which will be referred to as the Mullins coefficient for bulk diffusion, with dimensions $\text{length}^3/\text{time}$. The factor of $1/2$ is for consistency with the original Mullins work [44].

2.2. Phase-field model

Phase-field modeling is a powerful tool for examining the evolution of complex microstructures, including the coarsening of precipitates, solidification, and spinodal decomposition and dealloying, which can result in bicontinuous microstructures [27,29,32,57–59]. There have also been fundamental studies examining the kinetics and effects of underlying transport mechanisms on morphological evolution during coarsening [31,60]. Phase-field studies have been employed in concert with experimental techniques to deepen understanding of microstructure evolution [61–63]. For general information regarding phase-field models and their applications, we refer the reader to textbooks [30, 54], other literature (e.g., Ref. [28]) and references therein. The models employed here are similar or identical to those used in our previous studies of coarsening, Refs. [49,50]; we describe these models here to derive the Mullins coefficients that we use to relate the phase-field models to the sharp-interface models and thus the experimental system.

Phase-field models implicitly track (or capture) interfacial motion by solving an order parameter ϕ which smoothly varies between two values, each representing a phase. We base our models for coarsening on the Cahn-Hilliard equation [64,65]. The free energy functional $\mathcal{F}$ for

this model is given by [65]

$$\mathcal{F}[\phi] = \int_{\Omega} \left[f(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right] dV \quad (11)$$

where ϕ ranges from 0 to 1, with 0 and 1 corresponding to the interior of the liquid and solid phases, respectively; $f(\phi)$ is the bulk free energy density; ε is the gradient energy coefficient; and Ω is the system volume over which $\mathcal{F}$ is integrated. The second term, $\frac{\varepsilon^2}{2} |\nabla \phi|^2$, penalizes the gradient between phases, leading to diffuse interface with a finite volume, and both terms in the integral contribute to the interfacial energy. For simplicity, we employ a bulk free energy of the quartic polynomial form

$$f(\phi) = \frac{W}{4} \phi^2 (1 - \phi)^2, \quad (12)$$

where W sets the energy barrier height between the two phases. This results in an interfacial energy of [31,65]

$$\gamma_{\text{PF}} = \frac{\varepsilon}{6} \sqrt{\frac{W}{2}}, \quad (13)$$

an equilibrium planar interface that follows a hyperbolic tangent profile,

$$\phi(x) = \frac{1}{2} \left[1 - \tanh \left(\frac{x}{2\delta_{\text{int}}} \right) \right], \quad (14)$$

where $\delta_{\text{int}} = 4\varepsilon\sqrt{(2/W)}$, and a capillary length [39,45,49] of

$$\Gamma_{\text{PF}} = \frac{2\gamma_{\text{PF}}}{f''(0)} = \frac{\varepsilon}{6} \sqrt{\frac{2}{W}} \quad (15)$$

The chemical potential is given by the variational derivative of the free energy functional:

$$\mu = \frac{\delta \mathcal{F}}{\delta \phi} = f'(\phi) - \varepsilon^2 \nabla^2 \phi. \quad (16)$$

The gradient of the chemical potential drives the evolution of ϕ , and the governing equation for this motion differs between transport mechanism. For bulk diffusion, the Cahn-Hilliard equation [64] is used to describe the dynamics:

$$\frac{\partial \phi}{\partial t} = \nabla \cdot (M_{\text{bulk}}(\phi) \nabla \mu), \quad (17)$$

where the mobility for bulk diffusion $M_{\text{bulk}}(\phi)$ is dependent on the concentration of the phase with the general form [49,66,67]

$$M_{\text{bulk}}(\phi) = (M^+ - M^-)h(\phi) + M^-, \quad (18)$$

where $M^+ = M(\phi = 1)$ and $M^- = M(\phi = 0)$, and $h(\phi)$ is an interpolation function given by

$$h(\phi) = \phi^3 (10 - 15\phi + 6\phi^2). \quad (19)$$

The transition between $h(\phi = 0)$ and $h(\phi = 1)$ is sharper than the transition via hyperbolic tangent in ϕ between $\phi = 0$ and $\phi = 1$. The rationale for the choice of this form of interpolation is detailed in Ref. [49].

To relate the phase-field model to Equation (5) of the sharp-interface model, we note that the Laplacian term in Equation (16) will be negligible in the bulk during coarsening [45] and that by the chain rule $M_{\text{bulk}}(\phi) \nabla f'(\phi) = M_{\text{bulk}}(\phi) f''(\phi) \nabla \phi$. Approximating $f''(\phi)$ and $M_{\text{bulk}}(\phi)$ by their values in the bulk of the phases, $f''(0) = f''(1) = W/2$, and using $M_{\text{bulk}} = M^{\pm}$, we find that within the bulk of a single phase Equation (17) recovers Equation (5) with $D_{\text{PF}} = f''(0)M^{\pm}$. With this expression for diffusivity and the capillary length given in Equation (15), we find the phase-field Mullins coefficient for coarsening via bulk diffusion to be simply

$$B_{\text{bulk}}^{\text{PF}} = \frac{\Gamma_{\text{PF}} D_{\text{PF}}}{2} = \gamma_{\text{PF}} M^{\pm}. \quad (20)$$

For surface diffusion, we employ the model by Rätz, Ribalta, and Voigt (RRV) [46,68], which eliminates the Gibbs-Thomson effect in the bulk [50]:

$$\frac{\partial \phi}{\partial t} = \nabla \cdot M_{\text{surf}}(\phi) \nabla \frac{1}{g(\phi)} \mu, \quad (21)$$

where $g(\phi) = \phi^2 (1 - \phi)^2$ is a stabilizing function proportional to $f(\phi)$. The mobility is confined to the interfacial region, which is expressed as

$$M_{\text{surf}}(\phi) = g(\phi) = \phi^2 (1 - \phi)^2. \quad (22)$$

It is possible to define $M_{\text{surf}}(\phi)$ with a constant prefactor, but it is omitted here, as all scaling factors will be included in the Mullins coefficient in this manner. We relate the phase-field model for surface diffusion to transport in the sharp-interface model by considering the asymptotic behavior of Equation (21) as $\varepsilon \rightarrow 0$, wherein the Mullins coefficient $B_{\text{surf}}^{\text{PF}}$ is related to the phase-field model parameters by [46,50]

$$B_{\text{surf}}^{\text{PF}} = \varepsilon^2 \int_0^1 \frac{\sqrt{2f(\phi)} d\phi}{\int_0^1 g(\phi) d\phi} \int_0^1 \frac{M_{\text{surf}}(\phi)}{\sqrt{2f(\phi)}} d\phi. \quad (23)$$

Evaluating Equation (23) with $M_{\text{surf}}(\phi) = g(\phi)$ given by Equation (22) and $f(\phi)$ given by Equation (12) yields

$$B_{\text{surf}}^{\text{PF}} = \frac{5}{6} \varepsilon^2 \quad (24)$$

for the Mullins coefficient for surface diffusion in the phase-field model.

We note that the RRV model is non-variational in the Cahn-Hilliard free energy in Equation (11), although it retains the equilibrium profile and thermodynamic characteristics of the planar interface given in Equations (13)-(15). Salvalaglio and Wise [68] showed that it is variational for a modified functional. We employ it here because it has consistently been shown to match the sharp-interface dynamics of capillarity-driven surface diffusion [46,60] and because we have found that simulations based on the model converged more rapidly to self-similar evolution than a variational Cahn-Hilliard-based model [50]. Comparisons between phase-field simulations for bulk and surface diffusion and the sharp-interface analytical solution of Mullins [44] are provided in section S1 of the Supplementary Materials to validate these models.

3. Methods

3.1. Simulation methods

Following Refs. [49,50], Equations (17) and (21) were solved with the finite difference method as follows. Forward Euler time stepping was used for all simulations. For the spatial discretization, we employed a uniform grid and used the conventional seven-point stencil to approximate the Laplacians in Equations (17) and (21). We found the divergence $\nabla \cdot M(\phi) \nabla \mu$ on grid points by calculating $M(\phi) \nabla \mu$ on half-points and taking the centered difference. To avoid singularities when calculating $1/g(\phi)$ in Equation (21), we add a small constant to the denominator, $\sigma = 10^{-12}$, such that $1/g(\phi) \approx 1/[g(\phi) + \sigma]$.

We parametrize the simulations with dimensionless parameters in the code implementation. The connection to the experimental system is then made by rescaling length and time,

$$x_{\text{exp}} = \ell x_{\text{sim}} \quad (25)$$

and

$$t_{\text{exp}} = \tau t_{\text{sim}} + t_{\text{init}}, \quad (26)$$

where the scaling length ℓ is set to a convenient value (e.g., the experimental resolution), the scaling time τ can be determined theoretically if material parameters are known or empirically by comparing the results of the simulation to experimental data during the coarsening stage, and the time offset t_{init} is the experimental time corresponding to the simulation initial condition. To obtain the theoretical scaling time τ , we first consider how the sharp-interface equations can be made dimensionless by scaling them with ℓ and τ . It can be shown [43] that $B_{\text{bulk}} = B_{\text{bulk}}^{\text{dl}} \frac{\ell^3}{\tau}$ and $B_{\text{surf}} = B_{\text{surf}}^{\text{dl}} \frac{\ell^4}{\tau}$ for the bulk and surface diffusion cases, respectively, where the superscript “dl” indicates a dimensionless quantity. Then, if we assume that the phase-field models accurately represent the corresponding sharp interface coarsening dynamics [45, 46], we have

$$B_{\text{bulk}} = B_{\text{bulk}}^{\text{PF}} \frac{\ell^3}{\tau} \text{ or } \tau = \frac{B_{\text{bulk}}^{\text{PF}}}{B_{\text{bulk}}} \ell^3 \quad (27)$$

and

$$B_{\text{surf}} = B_{\text{surf}}^{\text{PF}} \frac{\ell^4}{\tau} \text{ or } \tau = \frac{B_{\text{surf}}^{\text{PF}}}{B_{\text{surf}}} \ell^4. \quad (28)$$

However, the expressions for the dimensional Mullins coefficients in Equations (3) and (10) have materials parameters that are not precisely known, such as the metal/molten salt interfacial energy and the surface and bulk diffusion coefficients, motivating our approach of combining the simulation and experiment to obtain the estimated value of τ .

The dimensionless time step size of all simulations was $\Delta t = 0.04$ and the dimensionless spacing between grid points was $\Delta x = 1.0$. The energy barrier for the double-well potential was $W = 0.4$ and the gradient energy coefficient was $\epsilon^2 = 0.2$. These parameters result in an interfacial width of $\delta = 4$ and an interfacial energy of $\gamma_{\text{PF}} = 1/30$. For solid bulk diffusion, the mobilities were $M^+ = 1$ and $M^- = 10^{-3}$, and the reverse, $M^+ = 10^{-3}$ and $M^- = 1$, were used for liquid bulk diffusion. These result in phase-field Mullins coefficients of $B_{\text{bulk}}^{\text{PF}} = 1/30$ for bulk diffusion according to Equation (20) and $B_{\text{surf}}^{\text{PF}} = 1/6$ for surface diffusion according to Equation (24).

The simulations are initialized from data obtained in the X-ray nanotomography experiment described in Ref. [9]. We used the scan at $t_{\text{init}} = 65$ min, which was estimated to be the end of the dealloying-dominated stage of evolution based on analysis of the evolution of the wire radius shown in Section S2 of the Supplementary Materials. This scan measured a 3-D volume, and a sub-volume was cropped to remove the empty region, with resulting dimensions $34.8 \mu\text{m}$ by $34.1 \mu\text{m}$ by $21.5 \mu\text{m}$ discretized into cubic voxels with a voxel side length of 43.3 nm. Within this volume is the Ni-20Cr wire, oriented along the z direction. We adopt the experimental dataset as our computational domain, resulting in 810, 793, and 500 grid points in the x , y , and z directions, respectively, and setting the scaling length for nondimensionalization to be $\ell = 43.3$ nm. The initial condition consisted of segmented data (i.e., with binary values of 0 or 1, representing liquid or solid phases, respectively) that was smoothed to create the diffuse interface between $\phi = 0$ and $\phi = 1$. The methods used for segmentation and smoothing are described in Section S3 of the Supplementary Materials. This smoothing was necessary to ensure numerical stability at the beginning of the surface diffusion simulation. Furthermore, we applied the same smoothing process to each of the subsequent tomography scans prior to characterization to remove noise in the data and to ensure a valid basis for comparison to the simulations.

For both the smoothing step and the simulations, periodic boundary conditions were employed in the x and y directions, perpendicular to the wire axis, where the domain boundaries are entirely or almost entirely in the liquid phase. Homogeneous Neumann boundary conditions, in which gradients in the normal direction are set to zero, were employed in the z direction, perpendicular to the faces of the wire. The Neumann boundary condition in the chemical potential μ enforces a no-flux

condition for transport, while the Neumann condition for ϕ enforces a 90° contact angle between diffuse interfaces and the computational domain boundary. Together, these boundary conditions can be interpreted as mirroring the structure at the boundaries in the z -direction.

3.2. Microstructural characterization

To compare the simulated microstructures to the 4-D X-ray nanotomography dataset, we focus on statistical and morphological characteristics rather than direct point-to-point comparisons. The evolution of characteristics also provides insight into the coarsening process. The characteristics that we use to match to the experimental time scale are the radius of the wire r_{cyl} and the radial distribution function (RDF) of the solid phase as a function of the distance from the wire axis. To gain insight into the driving forces for the evolution that we observe, we calculate mean curvature H on the microstructure surface. To obtain the RDF, we fit a central axis to the microwire, then calculate the normalized density of the solid phase within a shell some distance from the center. This is shown on a cutout of the smoothed initial condition in Figure 2 (a), where the approximate location of the central axis is indicated as a solid red line. The boundaries of a cylindrical shell are shown as dotted red lines. The shell depicted in Figure 2(a) is enlarged as compared to the actual step size used in the RDF calculation for the purpose of visualization. The RDF for the initial condition is found in Figure 2(b), with a vertical line at r_{cyl} . We obtain r_{cyl} by linear interpolation of the RDF at a threshold value of 0.3. The methods for calculating r_{cyl} , the RDF, and H are described in detail in Appendix A.

3.3. Relating simulation and experimental time scales

To calculate the scaling time τ for a given simulation and microstructural characteristic, we define E as the relative error between experimental and simulated data points. E can be computed for all available pairs of simulation outputs and experimental scans, which can be thought of as a discretization of the two-dimensional space defined by the entire time ranges of the simulation and the experiment (excluding experimental times before t_{init}). For measures such as τ and E that can be calculated for any characteristic or simulation, we specify the microstructural characteristic by a superscript (rad for r_{cyl} and RDF for the RDF) and the coarsening mechanism of the simulation by a subscript (surf for surface diffusion, liq for liquid bulk diffusion, and sol for solid bulk diffusion). Figure 3 depicts the important steps in the calculation of $\tau_{\text{liq}}^{\text{rad}}$, the scaling time for the liquid bulk diffusion case calculated based on r_{cyl} .

Figure 3a plots in pseudocolor $E^{\text{rad}} = |r_{\text{cyl,exp}} - r_{\text{cyl,sim}}|/r_{\text{cyl,exp}}$ for the liquid diffusion case, i.e., $E_{\text{liq}}^{\text{rad}}$. We use this case to illustrate this method for calculating errors because it is easier to visualize than other cases. The yellow regions in Figure 3a correspond to high E (poor agreement) and the blue region corresponds to low E (good agreement). The region of good agreement extends upward and rightward from the lower left corner, where the initial point $(t_{\text{init}}, 0)$ has $E = 0$. The solid black line extending from $(t_{\text{init}}, 0)$ in Figure 3a depicts the relationship between t_{exp} and t_{sim} defined by a possible value τ_{trial} for the scaling time. To assess the agreement between simulation and experiment for a given value of τ_{trial} , we define the objective function $\bar{E}(\tau_{\text{trial}})$ as the average value of $E(t_{\text{exp}}, t_{\text{sim}})$ along the line defined by τ_{trial} (i.e., the line described by Equation (26)). We then find τ for each simulation and characteristic as the optimal value of τ_{trial} that minimizes the objective function. The minimized value of the objective function, $\bar{E}(\tau)$, is used to characterize the degree of agreement between simulation and experiment for a given microstructural characteristic and coarsening mechanism.

To calculate $\bar{E}(\tau_{\text{trial}})$ from experimental and simulation datasets at discrete times, we iterate over the available experimental times $t_{\text{exp},i}$ in the index i . For each experimental time, we compute the corresponding

simulation time according to Equation (26), i.e., $t_{\text{sim},i} = (t_{\text{exp},i} - t_{\text{init}}) / \tau_{\text{trial}}$. This time does not necessarily correspond to a simulation output; therefore, we find $E(t_{\text{exp},i}, t_{\text{sim},i})$ by linearly interpolating between E values for discrete simulation outputs $t_{\text{sim},i}$, as shown in Figure 3b. We then compute $\bar{E}$ as an average of the values $E(t_{\text{exp},i}, t_{\text{sim},i})$ weighted by the length l_i of the line segment associated with each point $t_{\text{exp},i}$. One such line segment is illustrated by a red segment overlaid on the solid black line with slope τ_{trial} in Figure 3a. This calculation of $\bar{E}$ can be expressed as

$$\bar{E} = \sum_i E(t_{\text{exp},i}, t_{\text{sim},i}) \frac{l_i}{L_T}, \quad (29)$$

where L_T is the total length of the line and the length l_i of each line segment is the sum of half of the distances to the points on either side of point i . At each of the two end points, l_i is taken to be a half of the distance between the end point i and its (single) neighbor. Figure 3c plots $\bar{E}$ versus τ_{trial} for the difference $E_{\text{liq}}^{\text{rad}}(t_{\text{exp}}, t_{\text{sim}})$ depicted in Figure 3a. To determine the optimal τ , the values of τ_{trial} are selected by sampling the $(t_{\text{exp}}, t_{\text{sim}})$ -space uniformly in the angle made by the slope and the t_{sim} axis. We then determine the value of τ to be the τ_{trial} from this sweep with the lowest $\bar{E}$.

We generalize the above approach for calculating E between points to calculate E between curves, in particular the RDFs $\hat{P}_{\text{exp}}$ and $\hat{P}_{\text{sim}}$, by taking the absolute value of the error between $\hat{P}_{\text{exp}}$ and $\hat{P}_{\text{sim}}$ normalized by the norm of $\hat{P}_{\text{exp}}$,

$$E^{\text{RDF}} = \frac{\sum_{k=1}^N W_k |\hat{P}_{\text{exp},k} - \hat{P}_{\text{sim},k}|}{\sum_{k=1}^N W_k |\hat{P}_{\text{exp},k}|}, \quad (30)$$

where $W_k = \pi r_k^2 - \pi r_{k-1}^2$ is the area of a shell of width $r_k - r_{k-1}$ at a distance r_k from the center for N shells. We set $W_k = 0$ for the central region of the wire with $r < 3.5 \mu\text{m}$ because $\hat{P}_{\text{exp}}$ and $\hat{P}_{\text{sim}}$ differed systematically in that region in all cases (see Figure 7 in Section 4), likely due to incomplete/ongoing dealloying.

4. Results

Figures 4a and b provide the experimental microstructure used as the initial condition ($t = 65 \text{ min}$) and at a late time ($t = 128 \text{ min}$). Figure 4a and Figure 4b both exhibit a bicontinuous solid/liquid structure within the approximately cylindrical domain corresponding to the dealloyed wire. Compared to Figure 4a, the structure in Figure 4b has larger and fewer ligaments and pores, and its exterior surface appears less rough and contains fewer pores that lead to the interior of the wire. Figures 4c-d provide the simulated microstructures corresponding to Figure 4b based on the agreement of the RDF assuming surface diffusion, solid bulk diffusion, and liquid bulk diffusion, respectively. Each panel includes a cross-sectional view of ϕ and a side view of $\phi = 0.5$ isosurfaces. Experimental images (Figures 4a and b) are shown after segmentation and smoothing. For the simulation images and initial condition (Figures 4a, 4c, 4d, and 4e), the cross section that best matches the experiment at 128 min near the center are shown here since the field of view had slightly shifted during the experiment. Figures 4c, 4d, and 4e depict the late-time microstructures of the surface diffusion, solid bulk diffusion, and liquid bulk diffusion simulations, respectively. Thus, there are regions that are visibly similar with the experimental structure, especially for the solid bulk diffusion case in Figure 4d, as well as regions that differ, either because the coarsening mechanism is not active or because there are other physics that our model does not consider.

The growth in the sizes of the ligaments and pores in the simulation (from Figure 4a to Figures 4c-e) is consistent with the experimentally observed evolution (from Figure 4a to Figure 4b). However, there is an apparent difference in surface morphology between experiment and

simulation: even after smoothing, the experimental structure in Figure 4b has a rougher surface and some corners or ridges, whereas the surfaces in the simulated morphologies in Figures 4c-e are uniformly smooth and rounded. This may occur due to the crystalline anisotropy of grains within the wire, which is polycrystalline, or the effects of grain boundaries, neither of which are considered in the simulations.

The radius r_{cyl} of the wire quantifies evolution during coarsening in a way that is insensitive to small-scale features, such as voids and surface roughness. Figure 5 shows the time evolution of r_{cyl} for the simulation cases, dimensionalized by their respective scaling times τ^{rad} , against the evolution of r_{cyl} in the experiment. The values for τ^{rad} and $\bar{E}^{\text{rad}}$ are provided on the plots in Figure 5. In all cases, the radius of the wire decreases by approximately $0.4 \mu\text{m}$ over the course of the simulation or experiment. This change is small in relative terms, $\sim 3\%$ of the initial wire radius. The experimental data is characterized by a nearly linear decrease in r_{cyl} vs. time, with relatively little scatter or noise after $\sim 70 \text{ min}$. This nearly linear trend is matched well by the solid bulk diffusion case in Figure 5b, but the rate of change in r_{cyl} decreases over time for the surface diffusion case in Figure 5a and the liquid bulk diffusion case in Figure 5c. For the surface diffusion case in Figure 5a, significantly longer runtime is required to match the total change in wire radius observed in the experiment; however, since a good fit is not expected based on the shape of the simulated curve and the cost of simulation was significant, we opted not to simulate further.

As a higher-dimensional description of the microstructure compared to r_{cyl} , we consider the RDFs within the wire. Since the RDF is a function, it is not possible to simply calculate the error by taking a difference between two values in the way we can with r_{cyl} . We thus calculate the error by using Equation (30). We then generate contour plots of the average relative error $E^{\text{RDF}}(t_{\text{exp}}, t_{\text{sim}})$ for each of the simulations in order to evaluate agreement between simulation and experiment across times. Figure 6 shows the resulting plots. Similarly, color levels represent E^{RDF} from Equation (30) with blue corresponding to a good agreement (small E) and yellow to a poor agreement (large E). The red lines indicate the relationship between t_{exp} and t_{sim} in Equation (26) for the optimal scaling time τ^{RDF} . Small white dots indicate the best simulation match (i.e., with the lowest error) for a given experimental data. The black plusses indicate experimental/simulation pairs for which RDF comparisons are made, specifically at $t_{\text{exp}} = 128 \text{ min}$ and 211 min and corresponding simulations that lie on the lines defined by τ^{RDF} . These RDFs are shown in Figure 7.

For all three plots in Figure 6, the lower left corner has small E^{RDF} since the simulations have not yet evolved far from the experimental initial condition. Even along the lines indicated by τ^{RDF} , E^{RDF} increases over the course of the evolution. This has the effect of increasing the weight of the later-time/upper-rightmost region of the contour plots in the determination of τ^{RDF} and $\bar{E}^{\text{RDF}}$. The region of low error follows the line defined by $\tau_{\text{surf}}^{\text{RDF}}$ well for the surface diffusion case in Figure 6a. Furthermore, the white dots indicating the local minimum of $\bar{E}^{\text{RDF}}$ at each experimental time follow most closely with the line defined by τ^{RDF} for the surface diffusion case, which may be an indication of the agreement. However, the region of low error extends the furthest along the line defined by $\tau_{\text{sol}}^{\text{RDF}}$ for the solid bulk diffusion case in Figure 6b; as a result, this case has a lower $\bar{E}^{\text{RDF}}$ than the surface diffusion or liquid bulk diffusion cases. Nevertheless, the values of $\bar{E}^{\text{RDF}}$ are similar between all cases. In particular, if we only consider experimental RDFs until approximately 120 min, $\bar{E}^{\text{RDF}} \approx 2 \times 10^{-2}$ for all cases, indicating that the poorer agreement of the late-time surface diffusion and liquid bulk diffusion RDFs is what causes those values of $\bar{E}^{\text{RDF}}$ to be higher than that of the solid bulk diffusion case. Therefore, $\bar{E}^{\text{RDF}}$ can be considered as a measure of long-time prediction accuracy; the lower the value is, the more accurate and robust the predictions are on the longer time scale.

Figure 7 shows a comparison of the RDFs between the experimental data and the simulated structures evolving under different diffusion mechanisms at selected time points. The RDF of the initial structure is indicated by a solid red curve in Figure 7. The later experimental RDFs are shown in yellow and blue dashed curves, and the simulated structures by yellow and blue solid curves. The microstructures corresponding to the experimental RDF at 128 min and those of the associated simulations (blue curves) are shown in Figure 4. The morphology information embedded in the RDFs can be examined in three distinct regions: an inner region, a plateau region, and an outer edge region. Within the inner region ($r < 4 \mu\text{m}$), the simulations have a higher solid volume fraction than the experiment. Within the plateau region (initially $4 \mu\text{m} < r < 9 \mu\text{m}$), the solid volume fraction is approximately 0.65 and decreases slightly with increasing radius. This plateau region sees minimal evolution in the experiment and simulations. We thus focus our analysis on the outer edge region, which undergoes significant evolution and contains a relatively large volume, since the volume of cylindrical shells scales with r .

In the experiments and all simulation cases, the outer edge of the RDFs in Figure 7 is characterized by a peak in solid volume fraction that evolves over time, increasing in magnitude (densifying) and moving inward. As indicated by the plots of E^{RDF} in Figure 6, all cases provide good agreement at the earlier time, with greater differences apparent at the later time. Note that our definition of r_{cyl} (the radius where the RDF intersects 0.3 as indicated in Figure 2) corresponds to the right side of this peak. The solid bulk diffusion case in Figure 7b is the only case for which the right side of the peak is in good agreement with the experimental RDF at later time. This is consistent with the evolution of r_{cyl} shown in Figure 5, where the solid bulk diffusion case yields the best agreement with the experiment. Considering the rest of the RDF, however, the solid bulk diffusion case is not significantly closer to the experiment than the other simulations, consistent with their similar values of E^{RDF} in Figure 6. In all simulation cases, the density of the edge peak increases to a greater extent than in the experiment, particularly between the intermediate- and late-time RDFs (blue and yellow curves, respectively).

We investigate the evolution observed in the RDFs by visualizing the mean curvatures H as a function of the distance from the wire axis. Figure 8a shows the $\phi = 0.5$ isosurface of this microstructure with the surface colored according to H . It illustrates how mean curvature varies locally at the solid/liquid interfaces. We show an early-time simulated result rather than the initial condition because the surface is smoother, which reduces the noise in the data. The distribution of curvatures within the wire is similar between coarsening mechanisms, so we opt to show the microstructure from the surface diffusion simulation. We note that the outer surface (associated with the original wire surface) has relatively large positive H ; the characteristic value of $H \approx 1 \mu\text{m}^{-1}$ (red

coloring) corresponds to a spherical cap of radius $\approx 1 \mu\text{m}$, which is consistent with the features observed on the surface. The most negative mean curvatures seen are $H \approx -2 \mu\text{m}^{-1}$ (dark purple coloring), which are found near the center of the wire. This is likely a remnant of corrosion progressing deeper into the wire later in the dealloying regime, resulting in less time than the outer regions for coarsening to occur. However, in both regions, there are surfaces with opposite curvatures, which reduces the average curvature over the regions.

Figure 8b shows the corresponding radial function (RF) of the area-weighted mean curvature $\bar{H}$ (blue circles) and the RDF (red curve) for the surface diffusion simulation at a relatively early time, $t_{\text{sim}} = 3700$. We describe how $\bar{H}$ is calculated in Appendix A. The inner, plateau, and outer edge regions identified for the RDFs in Figure 7 are clearly identifiable in the RF of mean curvature in Figure 8a. The inner region has the most negative $\bar{H}$, the plateau region has nearly constant $\bar{H}$ between $0.4 \mu\text{m}^{-1}$ and $0.5 \mu\text{m}^{-1}$, and the outer edge contains a rapid transition to positive $\bar{H}$. These trends in curvature are consistent with the observations from Figure 8a above. Specifically, the wire interior has more features with highly negative H (blue coloring), the plateau region contains ligaments with slightly negative mean curvature (green coloring), and the exterior of the wire has solid ‘caps’ with positive mean curvature (red coloring).

Recalling Figure 1 and the sharp-interface models, Ni atoms are expected to flow from regions of more positive H to less positive H . Following this principle, the distribution of mean curvature in Figure 8 offers an explanation for why the radius of the wire decreases: Ni atoms flow from the ‘caps’ with positive mean curvature at the outer edge of the wire inward to regions with negative mean curvature. This flow increases the fraction of solid phase immediately inward of the caps, forming the outer edge peak in the RDFs in Figure 7. Interestingly, this increase in solid phase fraction could restrict flow of Ni atoms from the caps in the surface and liquid bulk diffusion cases (by reducing interfacial area and liquid volume, respectively), resulting in a decreasing rate of change of r_{cyl} that was not observed for the solid bulk diffusion case. From a practical standpoint, a densified surface observed experimentally and in all simulations regardless of diffusion mechanism may obscure an underlying porous structure, which could compromise mechanical integrity despite the surface appearing intact.

Elsewhere in the structure, Ni atoms should flow inward from the plateau region to the inner region of the wire, which has more negative mean curvature. This is what occurs in the coarsening simulations, but not in the experiment, suggesting that another physical process is taking place, most likely additional dissolution of Cr. The plateau region itself has little variation in $\bar{H}$ in Figure 8, which may explain why there is so little evolution in this region in the RDFs in Figure 7.

Table 1 lists the scaling times τ computed for each coarsening mechanism and microstructural characteristic. For morphological

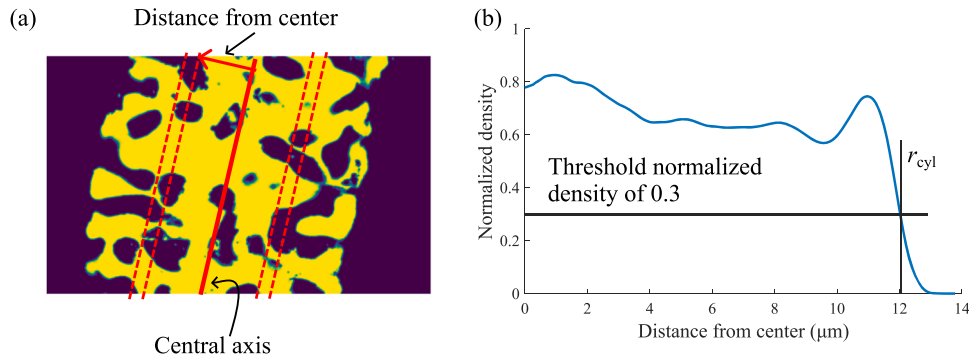


Figure 2. (a) A vertical cross section near the center of the wire for the smoothed initial condition with an approximation of the central axis of the wire shown in a solid red line. A region used to calculate the normalized density a certain radial distance away from the wire is indicated between the dotted lines. The area of this shell is enlarged as compared to the actual step size used for the RDF calculation for the purpose of visualization. (b) RDF of the initial condition with a vertical line indicating where r_{cyl} lies on the RDF. The value for r_{cyl} is obtained by linear interpolation of the RDF at a threshold normalized density of 0.3.

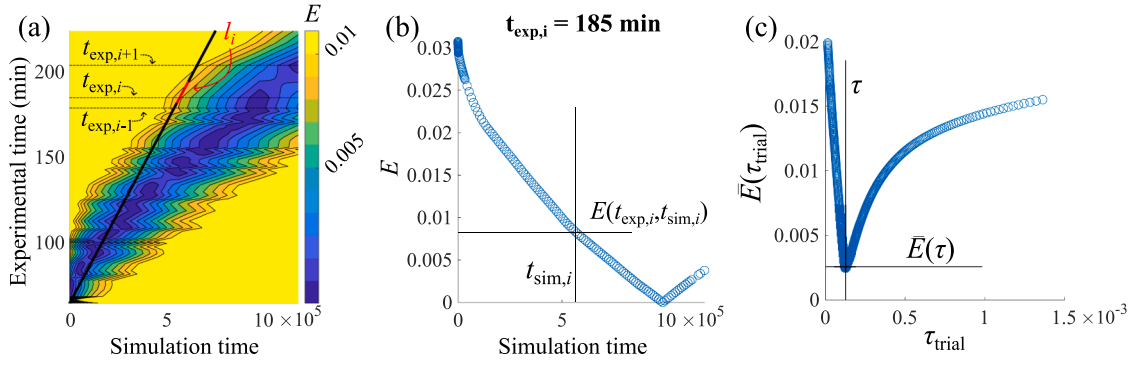


Figure 3. Our method for matching simulation and experimental timescales, illustrated for the liquid bulk diffusion case with r_{cyl} as the characteristic used for matching. (a) Filled contour plot of the relative error $E(t_{\text{exp}}, t_{\text{sim}})$, with the color ranging from low (blue) to high (yellow) and the contour levels capped at 0.01 to highlight regions where $E_{\text{liq}}^{\text{rad}}$ is small. The black line has a slope τ_{trial} and a length of l_r , and the red line segment indicates the length l_i that weights the E value at the point $(t_{\text{exp},i}, t_{\text{sim},i})$ in Equation (29). (b) An example calculation of $E(t_{\text{exp},i}, t_{\text{sim},i})$ by interpolation to $t_{\text{sim},i}$, the point on the line defined by τ_{trial} , from neighboring points representing simulation outputs. (c) Plot of the objective function $\bar{E}_{\text{liq}}^{\text{rad}}(\tau_{\text{trial}})$ vs. τ_{trial} , illustrating how τ is taken to be the τ_{trial} value with the lowest value of $\bar{E}$.

Table 1

Scaling times τ (min) determined by matching to the experiment for all simulation cases and microstructural characteristics and the relative standard deviation in τ for each simulation case.

	τ^{rad}	τ^{RDF}
Surface diffusion	5.44×10^{-5}	6.48×10^{-5}
Solid bulk diffusion	5.84×10^{-4}	6.02×10^{-4}
Liquid bulk diffusion	1.24×10^{-4}	1.99×10^{-4}

similarity between a simulation and the experiment, the scaling times for each characteristic should be approximately equal. The solid bulk diffusion case has the best match between scaling times for r_{cyl} and the RDF (~3% difference); however, the two values are not too far from each other for the surface diffusion case also (~16% difference).

5. Discussion

Our simulations and analysis offer the opportunity to evaluate the likelihood of each mechanism's involvement in the experimentally observed evolution based on how closely their morphological evolution resembles that of the experiment even when the material properties associated with the mechanism are not known. As discussed above, the solid bulk diffusion simulation results in the best agreement between the matched time scales in Table 1 and the lowest value of $\bar{E}^{\text{RDF}}$. The comparison of RDFs is most informative in this study because it retains more details than r_{cyl} , which is single-valued. However, the differences in $\bar{E}^{\text{RDF}}$ are marginal between mechanisms, suggesting that morphological evolution alone may not be sufficient to determine the primary coarsening mechanism.

Another approach to evaluating the coarsening mechanisms is to focus on how the extracted scaling times relate to literature values for the physical properties of the system. Recalling Equations (27) and (28), the values of τ in Table 1 can be used to calculate sharp-interface Mullins coefficients for bulk and surface diffusion. Physical constants that can be used to estimate the Mullins coefficients via Equations (3) and (10) are given in Table 2. These physical constants were collected to model as closely as possible Ni metal in contact with equimolar KCl-MgCl₂ at 800°C for which the X-ray tomography data was obtained. For surface diffusion, Haremski et al. [34,69] has recently provided a meta-analysis of literature and new data regarding the surface diffusivity and surface energy of a Ni metal/vacuum interface at 750°C. While there are uncertainties in experimental measurements for both quantities (as well as anisotropy, which we do not include in our simulations), we adopt $\gamma =$

Table 2

Physical constants for the calculation of Mullins coefficient from the literature.

Parameter	Value
D_s of Ni at Ni/vacuum interface	$1 \times 10^{-20} \text{ m}^2/\text{s}$ [34]
γ of Ni at Ni/vacuum interface at 750 °C	2.29 J/m^2 [69]
V_M of Ni	$6.59 \times 10^{-6} \text{ m}^3/\text{mol}$ [34]
D^* for Ni at 800 °C	$2.78 \times 10^{-18} \text{ m}^2/\text{s}$ [72]
ΔH_V^f in Ni	$2.77 \times 10^{-19} \text{ J}$ [70]
$D_{\text{Ni}^{2+}}$ in KCl-NaCl-MgCl ₂ at 800 °C	$2.27 \times 10^{-9} \text{ m}^2/\text{s}$ [22]
$X_L(\text{NiCl}_2)$ in KCl-NaCl-MgCl ₂ at 800 °C	1.85×10^{-17} [21]

2.29 J/m^2 for the interfacial energy from Ref. [69] and $D_s = 1 \times 10^{-20} \text{ m}^2/\text{s}$ for the surface diffusivity, which corresponds to the largest diffusivity measured by Ref. [34] for 750°C and reasonable agreement with Blakely and Myakura [33] at 800°C. For solid bulk diffusion, we calculate X_V^∞ from ΔH_V^f , the vacancy formation enthalpy for Ni [70], using the regular solution model and the assumption that there are sufficient vacancy sources and sinks within the solid such that $\mu_V = \Delta H_V^f + k_B T \ln(X_V^\infty) = 0$ [71], which yields $X_{V,\text{eq}}^\infty = 7.5 \times 10^{-9}$. For liquid bulk diffusion, we use the solubility limit of NiCl₂, $X_L(\text{NiCl}_2)$, in a Mg-Na-K chloride salt at 800°C [21] as an order of magnitude estimate for $X_{\text{Ni}^{2+}}^\infty$, and $D_{\text{Ni}^{2+}}$ is also available for this salt composition and temperature [22].

Table 3 summarizes the calculated Mullins coefficients from the time scaling constants obtained in Section 4 and physical constants from literature. It is evident that only the surface diffusion case has a literature-based Mullins coefficient at a similar order of magnitude to those obtained from our simulations, and the disagreements are large for solid bulk diffusion and even larger for liquid bulk diffusion. These disagreements imply that either the bulk diffusion mechanisms are inactive or certain physical parameters used in Equation (10) differ significantly from those of the experimental system. Most of the parameters are known to an order of magnitude except for the diffusivities, and, for the bulk diffusion cases, the equilibrium concentrations of the

Table 3

Sharp interface Mullins coefficients B for all simulation cases and microstructural characteristics based on the scaling times in Table 1 and computed from the physical constants in Table 2.

	B^{rad}	B^{RDF}	B^{lit}
Surface diffusion (m^4/s)	1.80×10^{-28}	1.51×10^{-28}	1.69×10^{-29}
Solid bulk diffusion (m^3/s)	7.72×10^{-23}	7.50×10^{-23}	9.40×10^{-27}
Liquid bulk diffusion (m^3/s)	3.63×10^{-22}	2.26×10^{-22}	1.38×10^{-34}

dilute components, $X_{\text{Ni}^{2+}}^{\infty}$ and $X_{\text{V,eq}}^{\infty}$.

If we were to reconcile the Mullins coefficients for the liquid bulk diffusion case, the product $D_{\text{Ni}^{2+}} X_{\text{Ni}^{2+}}^{\infty}$ would have to change by a factor of approximately 10^{12} . We note that the actual $X_{\text{Ni}^{2+}}^{\infty}$ may differ significantly from its value in Table 3 due to the presence of oxides, water, or other contaminants that modify the redox potential of the salt [9], and the properties of the Mg-Na-K chloride may differ from those of KCl-MgCl₂. However, we conclude that these effects will fall short of the necessary factor of 10^{12} , and thus we rule out liquid bulk diffusion as the primary mechanism for coarsening.

In our calculation of $D_{\text{sol}}^{\text{lit}}$, we assume that X_{V}^{∞} is close to the vacancy fraction at thermal equilibrium. However, vacancy fractions in nanoporous structures formed via dealloying have been recorded as high as on the orders of 10^{-5} to 10^{-3} [71,73]. We use the Mullins coefficients in Table 3 obtained from the scaling times in Table 1 to extract a vacancy diffusivity from the Ni self-diffusivity in Table 2 using the linear approximation $D^* \approx f D_{\text{V}} X_{\text{V,eq}}^{\infty}$ [54] (where the correlation factor f is 0.85 for FCC metals like Ni), $D_{\text{V}} = D^* / (X_{\text{V,eq}}^{\infty} f) = 4.4 \times 10^{-10} \text{ m}^2/\text{s}$. We find that these Mullins coefficients correspond to a narrow range of values for X_{V}^{∞} around 6×10^{-5} . For solid bulk diffusion to be the dominant coarsening mechanism, vacancy concentration would have to remain above the equilibrium vacancy concentration by approximately a factor of 10^4 over the course of the entire experiment. A recent study by Yang et al. [74] on dealloying of Cu-Au suggests that vacancy injection due to the inverse Kirkendall effect facilitates solid bulk diffusion during dealloying when the dissolving alloy component is the faster diffuser, which is also the case with the Ni-Cr alloy we examined. If the wire continues to undergo dealloying due to residual Cr, a vacancy concentration well above the equilibrium value could be maintained. However, this mechanism competes with vacancy diffusion and annihilation at surfaces and grain boundaries. Further investigation, such as simulations that explicitly track the vacancy concentration during corrosion and coarsening, must be conducted to evaluate when and where vacancy concentration remains sufficiently high to support the coarsening of the porous structure observed in this work.

We can use the Mullins coefficients calculated from surface diffusion simulations to extract a value for surface diffusivity of Ni along a Ni/molten salt interface. It is challenging to directly measure the surface diffusivity at a metal/molten salt interface. If we assume an interfacial energy of 2.29 J/m^2 , we obtain a surface diffusivity $D_{\text{S}} = 8.9 \times 10^{-20} \text{ m}^3/\text{s}$ at 800°C from the Mullins coefficient calculated from the RDF. This Ni surface diffusivity is outside the range of values measured by Haremski et al. [34] at 750°C ($0.3 \times 10^{-21} \text{ m}^3/\text{s}$ to $12.0 \times 10^{-21} \text{ m}^3/\text{s}$), but it is within the range of literature values at 800°C for (111) surfaces ($3.0 \times 10^{-19} \text{ m}^3/\text{s}$ reported by Wolfe [75] and $1.8 \times 10^{-20} \text{ m}^3/\text{s}$ reported by Blakely and Mykura [33]), which are known to have high diffusivity relative to other orientations [33] and it is close to the diffusivity of $3.0 \times 10^{-19} \text{ m}^3/\text{s}$ for a high-diffusivity direction, $[1\bar{1}0]$, on (110) surfaces [76]. (We are following Ref. [34] in converting values from m^2/s to m^3/s by multiplying by a length scale of 0.5 nm .) Thus, the effective surface diffusivity that we calculate for coarsening is in reasonable overall agreement with literature values for Ni/vacuum interfaces, suggesting that the presence of the molten salt may not have a strong effect on the surface diffusivity of Ni. Since our simulations do not consider anisotropic surface diffusivities, we cannot assess the role of different surface orientations in the coarsening process.

To summarize, even though morphological comparisons alone may not be sufficient to distinguish the dominant coarsening mechanisms, calculations of coarsening kinetics based on physical properties found in literature suggest that surface diffusion is most plausible under equilibrium conditions. The primary issue with surface diffusion as the dominant mechanism is the disagreement between simulated and experimental microstructures at later times, particularly in Figures 5 and

6. One possibility is that the metal has a non-uniform distribution of Cr, and dissolution of Cr has reached steady state rather than the near-equilibrium condition assumed in our coarsening simulations. While local composition of the metal ligaments was not analyzed by Liu et al. [9], ex situ characterization of structures resulting from driven corrosion of Ni-Cr by Ghaznavi et al. [7] found composition gradients in metal ligaments, with Cr-enriched cores and Cr depletion near the surface. Additional dissolution of Cr could explain why the RDF of the experiment is consistently lower than those of the simulations in the outer edge peak and why the wire radius of the experiment decreases more quickly than the surface diffusion simulation. More complex effects of Cr dissolution on interfacial motion could contribute to the qualitative differences between the simulated and experimental structures in Figure 4. On the other hand, if the surfaces of the ligaments are depleted of Cr, that would support our assumption in Section 2.1 of neglecting the effects of residual Cr on coarsening via surface diffusion and bulk diffusion through the liquid.

Effects of crystallinity are not considered in our simulations and provide another possible source of differences between simulation and experiment. These effects include interfacial energy anisotropy, anisotropic surface and/or bulk diffusion, and the presence of grain boundaries. Interfacial energy anisotropy of Ni is relatively small [77], but it could help explain differences in surface condition between the simulations and experiment. Surface diffusivity is known to depend strongly on surface orientation [34,76], although it is unclear how this would affect our results. Grain boundaries would affect the thermodynamics of coarsening, leading to grain boundary grooving [34,51], which may also explain differences in surface morphology between the simulations and experiment.

Even with advances in computing power that have facilitated large-scale multi-physics simulations, it is challenging to simulate complex phenomena such as corrosion and subsequent morphological evolution of an alloy in molten salt. Many important parameters, such as vacancy concentration and diffusivity, are not known precisely. Furthermore, it is difficult to obtain and post-process experimental data such that noises are removed but microstructural features are captured. Segmentation of tomography data is difficult and laborious even with the assistance of AI. This limits our analysis to methods that are not sensitive to noise, since characteristics like genus, mean curvature, and the inverse of the specific surface area S_{V}^{-1} are strongly affected by noise that manifests as interfacial roughness. In this work, we identified the RDF as an information-rich characteristic that both undergoes significant evolution during coarsening and is insensitive to surface roughness/noise. The density function expressed for general geometries is simply the solid phase fraction as a function of distance from the original metal surface. It has already been used to compare to more coarse-grained simulations [26], and we find it to be a promising microstructural characteristic for quantifying and comparing microstructures from phase-field simulations and corrosion experiments.

6. Conclusion

In this work, we demonstrate a novel technique for understanding microstructural evolution during coarsening that combines 4-D in situ X-ray nanotomography with phase-field simulations. By comparing morphological characteristics between the simulation and experiment, we identified temporal scaling factors (i.e., scaling times) that optimally matches their evolution. For coarsening via a single mechanism, the scaling time can be related to material properties through a single quantity, the Mullins coefficient [44], that contains all of the relevant thermodynamic and kinetic parameters. The Mullins coefficient obtained by matching a simulation and experiment can be compared to an estimate based on literature values of the relevant property to provide information about the plausibility of the mechanism. Assuming one mechanism is dominant, its Mullins coefficient can be used to estimate

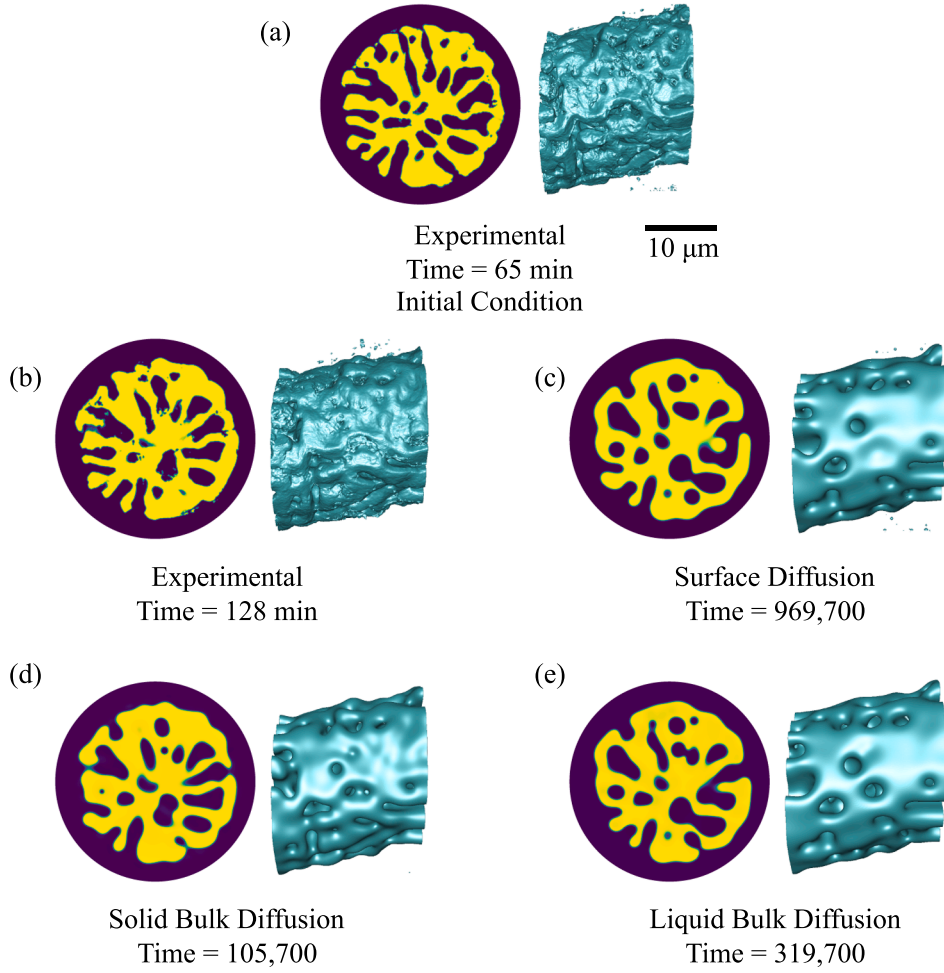


Figure 4. Cross-sectional views of ϕ (yellow indicates $\phi = 1$, purple indicates $\phi = 0$) and side views of $\phi = 0.5$ isosurfaces. The cross-sectional views were taken across the center, rather than the edge, of the domain to avoid artifacts from the Neumann boundary condition imposed on the domain boundaries. (a) & (b): The X-ray nanotomography snapshot, after segmentation and smoothing, at (a) 65 min and (b) 128 min. The structure in (a) was used as the initial condition for the simulations. (c) The surface diffusion simulation at $t_{\text{sim}} = 969,700$. (d) The solid bulk diffusion simulation at $t_{\text{sim}} = 105,700$. (e) The liquid bulk diffusion simulation at $t_{\text{sim}} = 319,700$. The simulation times were selected such that the RDFs are in good agreement with that of the experimental microstructure in (b), i.e., at 128 min.

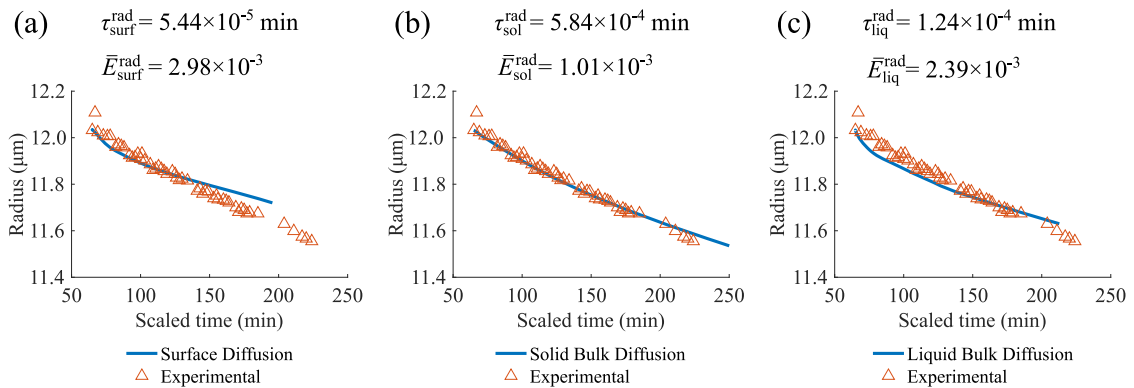


Figure 5. Plots comparing cylinder radius r_{cyl} vs. time between the experimental data (orange triangles) and simulations (blue circles) for (a) the surface diffusion case, (b) the solid bulk diffusion case, and (c) the liquid bulk diffusion case. The simulated data are plotted with respect to time dimensionalized by the scaling time τ^{rad} calculated for each case, which is indicated on its respective plot along with the corresponding value of $\bar{E}^{\text{rad}}$.

an unknown thermodynamic or kinetic parameter if the other parameters are known (or a combination of parameters if multiple parameters are unknown).

We applied this technique to elucidate the dominant transport mechanisms for coarsening in the bicontinuous microstructure resulting

from dealloying of a Ni-20Cr microwire in an equimolar KCl-MgCl₂ molten salt at 800°C. In situ X-ray nanotomography measurements of the dealloying and coarsening of the Ni-20Cr wire were previously reported by Liu et al. [9], and for the present work we have conducted phase-field simulations to model the evolution in the coarsening regime.

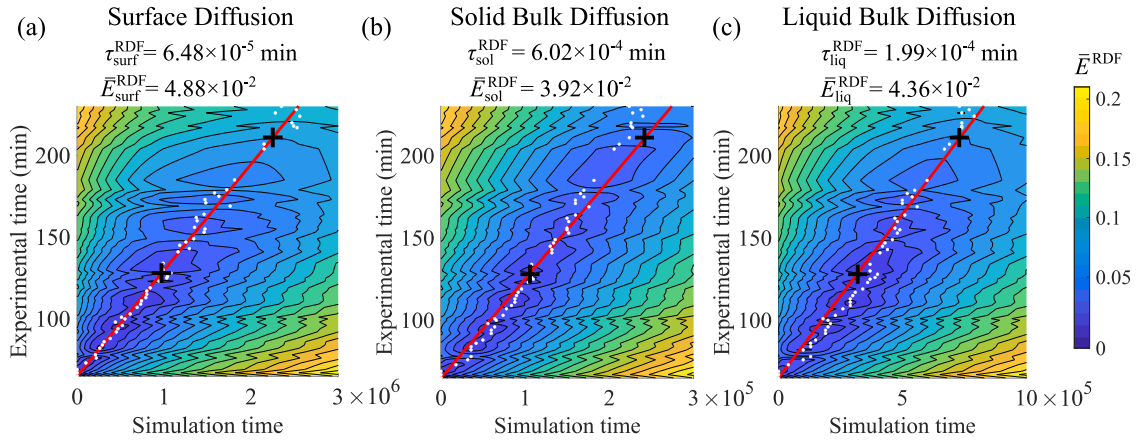


Figure 6. Average relative error E^{RDF} between RDFs for experimental data and simulated data for (a) the surface diffusion case, (b) the solid bulk diffusion case, and (c) the liquid bulk diffusion case. The blue regions correspond to smaller E^{RDF} , i.e., a closer match between experimental and simulated microstructures. The yellow regions correspond to larger E^{RDF} . For each panel, the line that yields the minimum cumulative difference is shown as a red line, which has a slope τ^{RDF} . The values of τ^{RDF} and the respective $\bar{E}^{\text{RDF}}$ are provided above the plots. The black pluses represent the time coordinates of the RDFs plotted in the same color in Figure 7.

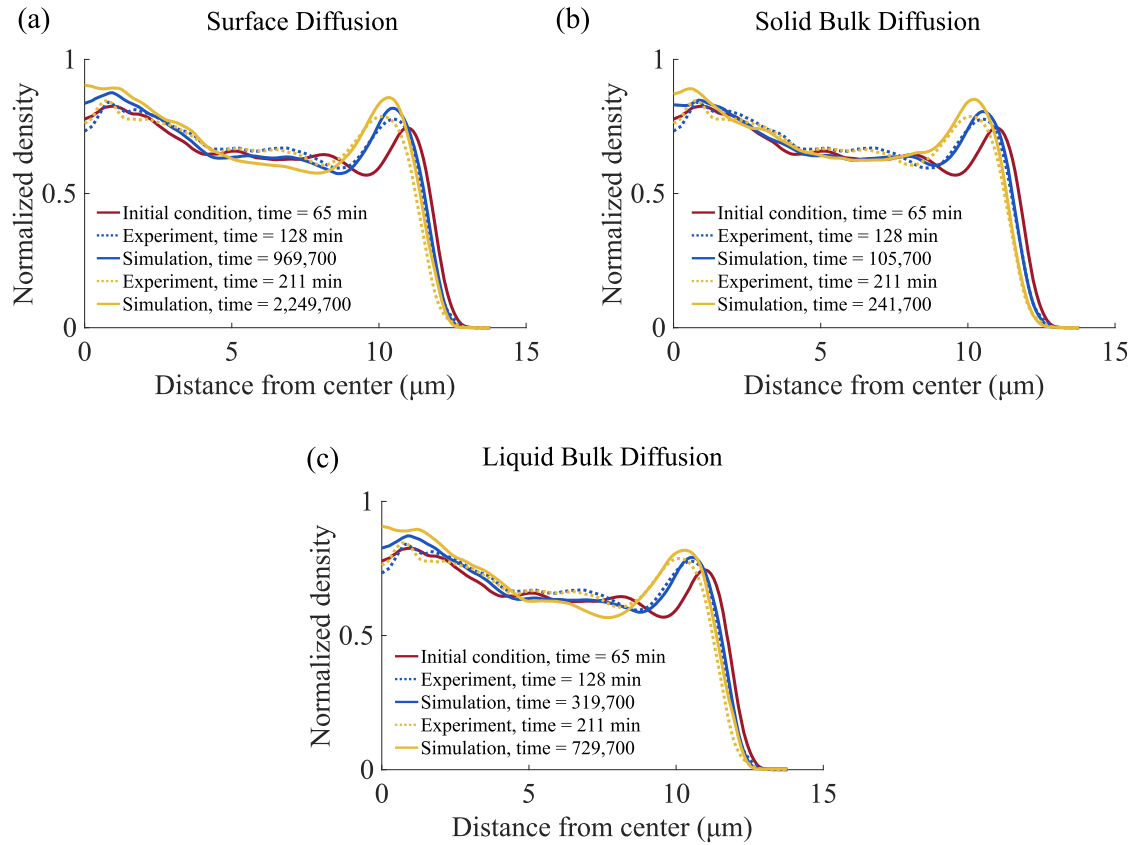


Figure 7. Radial distribution functions (RDFs) for (a) surface diffusion, (b) liquid bulk diffusion, and (c) solid bulk diffusion simulations compared to selected experimental structures. The solid red curve is the initial condition, taken at 65 min in the experiment. The dotted blue and yellow curves correspond to the experimental structures at 128 min and 211 min, respectively. The simulation times for the solid blue and yellow curves correspond to the respective experimental times based on the scaling time τ^{RDF} .

We performed three simulations initialized based on the same nanotomography scan, each modeling a different transport mechanism for coarsening: surface diffusion, liquid bulk diffusion (of Ni^{2+} ions through the molten salt), and solid bulk diffusion (vacancy-mediated self-diffusion of the Ni metal).

We characterized the evolution of the wire structure during coarsening by computing the wire radius and radial distribution function (RDF) of the solid phase, and we calculated scaling times by matching

the evolution of these characteristics between the simulations and the experiment. The wire was found to decrease in radius and undergo densification at its outer edge. This process of surface densification may be of practical significance since it can obscure the porous dealloyed structure beneath the dense outer layer, which may hinder the detection of the loss of mechanical integrity. We find that both densification and the decrease in radius result from the large difference in (radially averaged) mean curvature between the exterior surface and interior of

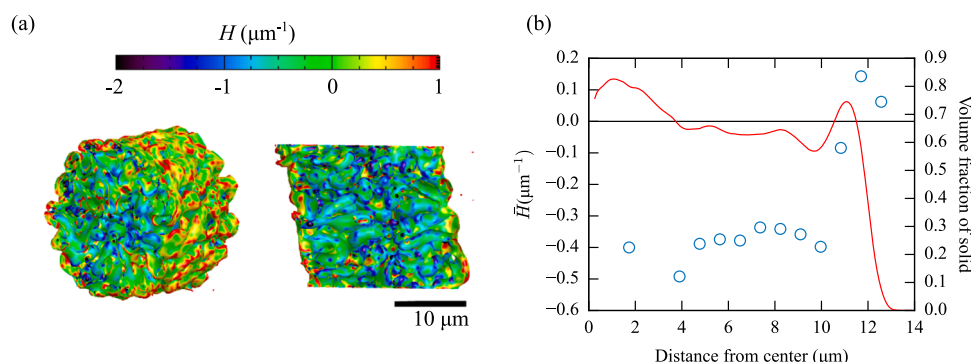


Figure 8. Distribution of mean curvature in a wire microstructure, specifically the surface diffusion simulation at $t_{\text{sim}} = 3700$. (a) $\phi = 0.5$ isosurfaces colored by mean curvature for the entire wire structure (left) and a cutout showing the interior of the wire (right). (b) RF of mean curvature $\bar{H}$ (blue circles, left y-axis) and RDF (red curve, right y-axis). The outer edge of the wire contains more areas with positive mean curvature, colored red in (a), while the center of the wire contains more features with highly negative mean curvature, colored dark purple in (a). The structure on the left is not to scale due to its perspective.

the dealloyed structure, which drives rapid evolution at the outer edge compared to the interior.

For this particular application, the differences in morphological evolution between coarsening mechanisms were not sufficient on their own to determine which coarsening mechanism dominates the evolution in the experiment since the results yielded similar differences with respect to the experimental data. We therefore compared the Mullins coefficients extracted from the scaling times to those estimated from material parameters in literature. Based on these estimates, surface diffusion was found to be the most likely dominant mechanism. However, solid bulk diffusion may also be active if the concentration of vacancies is significantly enhanced relative to equilibrium (e.g., due to the inverse Kirkendall effect). Additional investigation of the evolution of vacancy concentrations during corrosion and coarsening would be necessary to determine the role of solid bulk diffusion.

For the evolution of the RDF, which takes into account most of the sample volume and is unlikely to be influenced by differences in surface condition between the simulation and experiment, the Mullins coefficient we extracted corresponds to a surface diffusivity of $D_s = 8.9 \times 10^{-20} \text{ m}^3/\text{s}$ if the surface energy of 2.29 J/m^2 (assessed for a Ni-vacuum interface [69]) is assumed. This surface diffusivity value is in reasonable agreement with literature values for Ni-vacuum interfaces at 800°C [33, 34,75,76]. This estimate could be improved by increasing the complexity of the phase-field model and by integration of additional experimental characterization. Other factors not considered here, including the effects of crystallinity (e.g., anisotropic surface diffusion) and continued dissolution of residual Cr, can be included in the model to close the gap between the experimental observation and simulated microstructures. This requires additional model size development and collection of experimental data such as the grain size and grain orientations in the microstructure and/or Cr distribution.

7. Data availability statement

The digital data for all figures, tables, charts, and any other media contained in this publication and its associated ESI files will be made accessible in the MSEE Community of the Zenodo repository, under Digital Object Identifier (DOI): <https://doi.org/10.5281/zenodo.15748059>. The data presented in this work is published at Materials Commons [78] (materialscommons.org) under DOI: <https://doi.org/10.13011/m3-chve-g816>.

CRedit authorship contribution statement

Ellery J Hendrix: Writing – review & editing, Writing – original

draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation. **W. Beck Andrews:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Xiaoyang Liu:** Writing – review & editing, Validation, Software, Resources, Methodology, Investigation, Data curation. **Yu-chen Karen Chen-Wiegart:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Katsuyo Thornton:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.actamat.2025.121299](https://doi.org/10.1016/j.actamat.2025.121299).

Appendix A Radial distribution function (RDF), cylinder radius, and the radial function of mean curvature

In this section, the indices i , j , and k refer to the indices of a point in the x , y , and z direction, respectively.

To analyze the microstructure of the wire sample statistically, we employ two quantities, the solid fraction and the mean curvature, averaged over a cylindrical shell as a function of the distance from the wire axis. We will refer to the first quantity as the radial distribution function (RDF) of the solid phase. The wire is assumed to be a cylinder with an axis that is slightly skewed from the z -axis of the simulation/nanotomography scan, and we compute the RDFs of the solid phase and the radial function of interfacial mean curvature H as functions of distance from the cylinder axis. The symbol ϕ represents the phase field or the smoothed segmented experimental data, which in both cases approximates an indicator function for the solid phase: apart from the interfacial region, $\phi = 1$ in the solid and $\phi = 0$ outside of the solid. To find the cylinder axis, we calculate the centroid $\mathbf{M}(z) = (\bar{x}, \bar{y})$ of the wire at each slice in the xy -plane,

$$\mathbf{M}(z) = \frac{1}{N_x N_y} \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \mathbf{x}_{ij} \phi(\mathbf{x}_{ij}). \quad (\text{A.1})$$

Then, we use linear regression to fit the centroids of the x - y slices as a function of z , $\mathbf{M}_{\text{fit}}(z) = \mathbf{x}_0 + (\mathbf{x}_1 - \mathbf{x}_0)z/L_z$, where $\mathbf{x}_0$ and $\mathbf{x}_1$, the top and bottom points of $\mathbf{M}_{\text{fit}}$, define the cylinder axis. We now define the radial coordinate r as the distance of a point $\mathbf{x}$ from the cylinder axis,

$$r = |(\mathbf{x} - \mathbf{x}_0) - (\mathbf{x} - \mathbf{x}_0) \cdot \hat{\mathbf{v}} \hat{\mathbf{v}}|, \quad (\text{A.2})$$

where $\hat{\mathbf{v}} = (\mathbf{x}_1 - \mathbf{x}_0)/|\mathbf{x}_1 - \mathbf{x}_0|$. We calculate r for every point in the domain and construct a discrete RDF for the solid phase as a histogram of ϕ binned according to r ,

$$P_n = \sum_{i,j,k=1}^{N_x N_y N_z} \phi_{ijk} I(R_n \leq r_{ijk} < R_{n+1}), \quad (\text{A.3})$$

where $I(R_n \leq r_{ijk} < R_{n+1})$ is an indicator function for the cylindrical shell defined by the condition $R_n \leq r_{ijk} < R_{n+1}$. That is, $I(R_n \leq r_{ijk} < R_{n+1})$ returns one when the point is within that cylindrical shell and zero otherwise. The sum $S_n = \sum_{i,j,k=1}^{N_x N_y N_z} I(R_n \leq r_{ijk} < R_{n+1})$ gives the volume of the shell in voxels and can be used to normalize the RDF: $\hat{P}_n = P_n/S_n$. We map from P_n and $\hat{P}_n$ to approximate continuous RDFs $P(r)$ and $\hat{P}(r)$ by representing the first bin at $r = 0$, $P(0) = P_1$, and subsequent bins at the bin midpoint, $P((R_{n+1} + R_n)/2) = P_n$ for $n = 2, 3, 4, \dots$

We determine the cylinder radius r_{cyl} by finding the radius at which $\hat{P}(r)$ crosses a threshold value $\hat{P}(r_{\text{cyl}}) = 0.3$. The value 0.3 is roughly half of the plateau value for $\hat{P}(r)$ in the corroded region of the wire. It occurs where $\hat{P}(r)$ is monotonically decreasing, which allows r_{cyl} to be specified uniquely. The radius r_{cyl} and the points $\mathbf{x}_0$ and $\mathbf{x}_1$ fully describe the geometry of the cylinder encapsulating the wire sample.

To calculate the mean curvature H at the interface, we pre-process the structure using the level-set method and calculate H at each grid point following the methodology in Ref. [80]. The $\phi = 0.5$ isosurface is then approximated by a triangular mesh, and the values of H at grid points are interpolated to the center of each triangle. As illustrated in Figure 1, the sign convention for mean curvature H is such that $H > 0$ for convex bodies with $\phi = 1$; that is, the surface of a solid sphere has a positive mean curvature.

The radial function of mean curvature is calculated analogously to Equation (A.4), but now we are summing over triangles in the mesh rather than points in the computational/experimental domain. The area-weighted average of mean curvature is calculated within each cylindrical shell according to

$$\bar{H}(r_n) = \sum_{i=1}^{N_{\text{tri}}} \frac{A_i}{A_n} H_i I(R_n \leq r_i < R_{n+1}), \quad (\text{A.5})$$

where A_i is the area of a single triangle in the mesh, N_{tri} is the number of triangles in the mesh of the $\phi = 0.5$ isosurface, $A_n = \sum_i A_i I(R_n \leq r_i < R_{n+1})$, and the radius r_i used in the indicator function is calculated based on the center of the triangle.

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