Acta Materialia 132 (2017) 13–24

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Coarsening of complex microstructures following spinodal decomposition

C.-L. Park [a], J.W. Gibbs [b], P.W. Voorhees [b], K. Thornton [a, *]

[a] *Department of Materials Science and Engineering, University of Michigan, 2300 Hayward, Ann Arbor, MI 48109, USA*
[b] *Department of Materials Science and Engineering, Northwestern University, 2220 Campus Drive, Evanston, IL 60201, USA*

ARTICLE INFO

Article history:
Received 31 October 2016
Received in revised form
8 March 2017
Accepted 10 March 2017
Available online 16 March 2017

Keywords:
Coarsening
Spinodal decomposition
Interfacial velocity
Curvature evolution
Phase-field model

ABSTRACT

Coarsening plays a pivotal role in materials engineering, but our understanding of the dynamics of coarsening in morphologically complex systems is still limited. In this paper, we examine the correlations between the interfacial velocity and interfacial morphologies, and then predict the evolution of mean curvature based on the correlations. Three simulated structures with varying volume fractions, two bicontinuous and one nonbicontinuous, are generated using the Cahn-Hilliard equation. We find general correlations between interfacial velocity and mean curvature, as well as between interfacial velocity and the surface Laplacian of the mean curvature. Furthermore, we find that the probability of finding a patch of interface with a given normal velocity and the same local principal curvatures is described well by a Gaussian distribution, independent of the principal curvature values and the volume fractions of the structures. We also find that average interfacial velocity is described by a polynomial of the mean curvature and the net curvature. Based on this finding, we develop a semi-analytical approach to predicting the rate of change of the mean curvature, which determines the morphological evolution of complex microstructures.

1. Introduction

Coarsening is a phenomenon that is widely observed during thermal processing of many materials. It occurs during material processing of metallic alloys [1–4], polymers [5–8], bicontinuous nanoporous gold [9,10] and semiconductors [11–13]. Following either spinodal decomposition or nucleation and growth, a two-phase system undergoes coarsening after the concentration of each phase approaches its equilibrium value. During this capillarity-driven phenomenon, solute diffuses from regions with high chemical potential to regions with low chemical potential as a result of the Gibbs-Thomson effect, which relates the chemical potentials to interfacial curvature. This diffusion process, in response to a thermodynamic driving force, reduces the total interfacial area within the microstructure to minimize the excess energy associated with interfaces.

Understanding the mechanisms of coarsening is important since the microstructure can undergo substantial changes in morphology and topology during coarsening. These changes in microstructure, in turn, directly influence the properties of the material after processing and during its utilization. For example, in the case of precipitation hardening of metallic alloys, the precipitates that nucleate in the solid solution undergo coarsening during the aging process. While the average size of the precipitates increases during coarsening, the number density of precipitates decreases, which enables dislocations to migrate more freely in the solid. As coarsening continues, the yield strength of the alloy decreases, resulting from the microstructural evolution [14]. In the case of nickel/yttria-stabilized zirconia (Ni/YSZ) cermet, which is a commonly used anode material in solid oxide fuel cells (SOFCs), the coarsening of Ni particles in the anode reduces the density of triple-phase boundaries, thus significantly diminishing the electrochemically active regions and degrading the electrochemical performance of SOFCs over time [15–17]. The mechanical properties of nanoporous gold structures can be linked to the topology of the bicontinuous structure that can evolve during coarsening [18,19].

Coarsening of polydispersed spherical precipitates has been studied extensively in the past [20–22]. In 1960s, Lifshitz and Slyozov [23], and Wagner [24] (LSW) determined analytically the growth rate of a particle, dR/dt, as a function of radius, R. Using the growth rate, they also determined the time-independent particle

---

[*] Corresponding author.
E-mail address: kthorn@umich.edu (K. Thornton).

http://dx.doi.org/10.1016/j.actamat.2017.03.020
1359-6454/

size distribution that is scaled by a time-dependent characteristic length scale of the system. The resulting LSW theory predicts $\langle R\rangle \sim t^{1/3}$. Even though the LSW theory is derived in the limit of zero volume fraction of the particle phase, in which the diffusion fields between particles do not overlap, it provides valuable insights into the self-similar evolution of a system of particles undergoing coarsening. Furthermore, this classical theory has served as a foundation for the subsequent development of more general theories that advanced the understanding of the dynamics of coarsening in materials with polydispersed precipitates (see comprehensive reviews [25,26] and a book [27] for more information).

In contrast, the understanding of the dynamics of coarsening in materials with complex microstructures is still at an early stage. Deriving a theory of coarsening based solely on an analytical approach in these materials is extremely challenging because, unlike the simple spherical geometry that can be assumed in many theories of precipitate coarsening, the complex morphology and topology of the microstructure poses difficulties in solving the free-boundary problem describing the interfacial motion resulting from diffusion. For example, the coarsening of dendrites [28–30] has been studied by approximating the dendrite arms as a collection of cylinders [30] or cylinders with spherical caps at the end [29,31]. However, such simple geometries do not fully capture the complex structures of dendrites, and therefore experimental and computational approaches are needed in elucidating the kinetics of interfacial motion during coarsening.

The ultimate goal of this work is to develop the theory of coarsening of complex microstructures. This requires a simplification of the dynamics because the complex morphology and topology of the structure introduces significant complications. Therefore, we begin with a simplified mathematical description of the process, based solely on the thermodynamic driving force from interfacial free energy and excluding other effects such as elastic stress and unequal mobilities in different phases. Such an approach gives important insights into the dynamics of coarsening processes in these morphologically complex systems.

In our previous effort, we examined the morphological evolution of a bicontinuous structure undergoing coarsening via nonconserved dynamics [32]. We observed that, while the majority of interfaces undergo flattening, some regions of interfaces become more highly curved as they approach pinching (a topological singularity). Furthermore, while the interfacial velocity is determined by the local mean curvature in nonconserved dynamics, the evolution of mean curvature is dependent on both the local curvature and the curvatures of the nearby interfaces since they can interact diffusionally.

Building upon this previous work, we here examine the coarsening of three complex structures following spinodal decomposition, in which the evolution of interfaces is due to the interfacial-energy-driven bulk diffusion. We first elucidate the dynamics of coarsening by examining the correlation between interfacial velocity and static interfacial properties, namely the mean curvature and the surface Laplacian of the mean curvature. In situations where the interfacial motion is dictated solely by the local geometry of the surface, such as grain growth [33,34] and antiphase domain boundary motion [35], the exact relationship between the interfacial velocity and local curvatures can be determined. However, such a relationship cannot be established in a material system undergoing coarsening via bulk diffusion due to the long-range diffusional interactions. Therefore, we examine the statistical correlation (not a functional relationship) between the interfacial velocity and the mean curvature, as well as the correlation between the interfacial velocity and the surface Laplacian of the mean curvature. In addition, we explore the distribution of velocities of interfaces with given principal curvatures. Based on the information gathered from analysis of the interfacial velocity during coarsening, we develop a semi-analytical approach to predicting the rate of change of the mean curvature, which is then verified against the simulation results.

2. Computational methods

2.1. Preparation of microstructural data

The phase-field method is a computational technique for simulating phase transformations [36–38]. The phase-field method is based on the diffuse-interface theory, where the value of an order parameter, ϕ, smoothly varies across an interfacial region with a finite thickness from a value representing one phase to another value representing a different phase. The diffuse-interface approach eliminates the need to explicitly track the location of interfaces since this information is embedded in ϕ, which is evolved based on the governing phase-field equation.

The governing equation employed in our simulation is the Cahn-Hilliard equation [39,40].

$$\frac{\partial\phi}{\partial t} = \nabla\cdot L_\phi \nabla\left(\frac{\partial f}{\partial\phi} - \varepsilon^2\nabla^2\phi\right) \tag{1}$$

where L_ϕ and ε are the mobility and the gradient energy coefficients, respectively. While L_ϕ can, in general, have dependence on ϕ and may vary spatially, we take it to be constant in this work for simplicity. The bulk free energy, $f(\phi)$, is assumed to be a double-well potential,

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

with two minima at $\phi = 0$ and $\phi = 1$ (the equilibrium values of the two phases), and the height of the double-well potential is controlled by a well-height parameter, W. Note that the term $\partial f/\partial\phi - \varepsilon^2\nabla^2\phi$ is the chemical potential. The simulations are performed with a dimensionless form of the Cahn-Hilliard equation, where we define the dimensionless variables such that $x = \tilde{x}/l$, where l is the scaling length, and $t = \tilde{t}/\tau$, where τ is the associated time scale and the tilde indicates the dimensional variables. We select l such that the grid spacings are $\Delta x = \Delta y = \Delta z = 1.0$ and τ such that $L_\phi = \tilde{L}_\phi\tau/l^2\tilde{W} = 1.0$, where $\tilde{L}_\phi$ is the dimensional mobility coefficient and $\tilde{W}$ is the dimensional well-height parameter. A time step of $\Delta t = 0.05$ is employed. A computational domain size of $1024 \times 1024 \times 1024$ is chosen to generate sufficient statistics for accurate analyses of interfacial morphologies. In the phase-field method, values of ε^2 and W determine the interfacial thickness, δ. In order to ensure sufficient interfacial resolution, we use $\varepsilon^2 = 0.2$ and $W = 0.4$ to obtain $\delta = 4.0$, which results in the interfacial region (defined by ϕ in the range 0.1–0.9) being approximately four-grid-point wide.

In order to examine the influence of overall morphologies on the dynamics of coarsening, we performed three separate simulations with different initial conditions that result in different volume fractions of the phases. The three initial conditions consist of order parameters with average values $\phi_1 = 0.5$, $\phi_2 = 0.4$, and $\phi_3 = 0.3$, each with a random noise of amplitude 0.1. These initial conditions result in bicontinuous structures with 50:50 and 40:60 volume fractions of the phases, and a nonbicontinuous structure with 30:70 volume fractions of the phases. Since the Cahn-Hilliard equation is conserved, the volume fractions of the phases remain constant throughout their evolution.

The three structures were evolved for a dimensionless