Ostwald ripening in multicomponent alloys

T. Philippe *, P.W. Voorhees

Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

Abstract

A general theory of coarsening in a multicomponent alloy is developed, accounting for off-diagonal terms in the diffusion tensor. The analysis is valid for a non-ideal and non-dilute solution. The asymptotic analysis reveals that the temporal exponents for the average particle radius, number of particles per volume and both the precipitate and matrix compositions are identical to the binary limit. However, the amplitudes are different. It is found that the vector representing the matrix supersaturations coincides with the equilibrium tie-line, but in most alloys this is not the case with the precipitate compositions. It is also shown that considering only a low mobility species does not yield a description of the temporal evolution of the matrix and precipitate compositions, even though this can be the case for the average particle size and the number density of precipitates.

© 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Coarsening; Ostwald ripening; Multicomponent; Flux couplings

1. Introduction

Morphological changes due to reduction of the interfacial energy typically occurring at the end of a first-order transformation are known as Ostwald ripening [1,2] or coarsening [3,4]. Decreasing the total interfacial energy of the system leads to an increase in the size scale of the coarsening phase. Dissolution of small precipitates concomitantly entails growth of large ones through a diffusive mass flow from shrinking to growing precipitates. Lifshitz and Slyozov [3] (LS) and Wagner [4] (LSW) were the first to describe in a comprehensive manner the coarsening process in a dilute binary alloy where the interface compositions are set by the Gibbs–Thompson equation relating these compositions to the interfacial curvature of the coarsening precipitate. In multicomponent alloys, local equilibrium at the interface matrix/precipitate alone is no longer sufficient to determine the interface compositions, and thus interfacial mass balance conditions must be employed to describe the growth kinetics of the precipitate. This has

been used by Kuehmann and Voorhees [5] (KV) to describe Ostwald ripening in a ternary alloy. The present paper extends their work to higher-order alloy systems, and the theory includes the off-diagonal diffusion coefficients.

In the past few years, atom probe tomography experiments [6–10] have shown that the mean-field phenomenological models may not be able to describe the ripening behavior, particularly for the compositional trajectory of the coarsening phase, as in the Ni–Cr–Al system, for which the compositional trajectory of the precipitates was found not to follow the predictions of the KV theory [7]. The main limitation is that existing mean-field coarsening models do not incorporate the complete couplings among the diffusional fluxes. It is therefore required to develop a general theory that takes complete account of the diffusional flux couplings in concentrated multicomponent alloys.

Bjorklund et al. [10] and Slyozov and Sagalovich [11–13] extended the LSW theory to incorporate multicomponent effects, but limited themselves to dilute solutions and did not allow the precipitate composition to deviate from equilibrium. The restriction of dilute solution was removed by Umantsev and Olson [14], but they neglected off-diagonal diffusivities. Morral and Purdy [15] extended the results

---

* Corresponding author. Tel.: +1 7738225135.
   E-mail address: thomas.philippe@northwestern.edu (T. Philippe).

of Umantsev and Olson to include off-diagonal diffusion coefficients and predicted the temporal evolution of the average particle radius. In an elegant treatment, Hoyt [16] confirmed the result of Morral and Purdy and determined the temporal evolution of the matrix supersaturations. In each approach, the long-term behavior is found using either the LS or Marquee and Ross [17] approach, which allows the power law time dependence and the distribution function for the particle size of the coarsening phase to be determined. In contrast, in the KV theory [5], local equilibrium is employed so that both matrix and precipitate compositions are allowed to depart from their equilibrium values as given by the phase diagram.

With the widespread availability of both thermodynamic and atomic mobility databases, it is now possible to evaluate all the parameters that control the coarsening processes in multicomponent technical alloys. The purpose of this paper is thus to develop a general theory of coarsening in a multicomponent alloy, removing the restrictions of these past works and including the effect of the off-diagonal diffusivities on the overall ripening behavior, with a focus on the particle composition.

2. Development

A description of the Oswald ripening process is based upon a continuity equation governing the dynamics of the precipitate size distribution, a kinetic equation describing the growth rate of a particle, and a mass conservation equation. The present authors derive the growth rate of a particle of a given radius, the mass conservation equations and the particle composition in a multicomponent alloy. Following this, a long-term limit analysis is performed.

2.1. The kinetic equation

The growth rate is determined by the diffusion field surrounding the particle within the approximation of local equilibrium at the particle–matrix interface. Neglecting the composition dependence of the diffusion coefficient, solving Laplace's equation for each component in spherical coordinates gives

$$C_i = C_i^\infty + \frac{(C_i^\alpha - C_i^\infty)R}{r} \quad \text{for } i = 2 \ldots N \quad (1)$$

where r is the distance from the center of the sphere, N is the number of components in the alloy, C_i is the mole fraction of component i at r, C_i^∞ is the composition at infinity, and C_i^α is the composition of the α phase at the interface $r = R$. The composition at the interface must still be specified. Assuming that the molar volumes of both phases are the same, the mass balance at the interface is

$$\left(C_j^\beta - C_j^\alpha\right)\frac{dR}{dt} = \sum_{k=2}^N D_{jk} \frac{\partial C_k}{\partial r}\bigg|_{r=R} \quad \text{for } j = 2 \ldots N \quad (2)$$

where D_{jk} is the diffusion matrix. Eq. (2) is valid for no flux into the particle, which is the case for zero diffusivity in the

coarsening phase or if its composition is uniform (infinite diffusivity). Since the sum of the fluxes is zero, the flux of component 1 is not independent, and there are only $N-1$ mass balance equations. Since this is a multicomponent alloy, the interfacial compositions appearing on the left-hand side of Eq. (2) are not given by the phase diagram, but are determined by the diffusion process. Thus, they are not known at this point, because the shift from their equilibrium values is not only due to capillarity. Using Eq. (1) in Eq. (2) gives

$$\left(C_j^\beta - C_j^\alpha\right)\frac{dR}{dt} = \sum_{k=2}^N \frac{D_{jk}}{R}\left(C_k^\infty - C_k^\alpha\right) \quad \text{for } j = 2 \ldots N \quad (3)$$

During Ostwald ripening, the supersaturation is on the scale of the shift in local equilibrium concentrations due to interfacial curvature. Thus, assuming that this shift is small compared with the equilibrium compositions at a planar interface, it is possible to replace the difference in interfacial compositions given on the left-hand side of Eq. (3) with the differences in the equilibrium concentrations, specifically $C_j^\beta - C_j^\alpha = \overline{C}_j^\beta - \overline{C}_j^\alpha$, where $\overline{C}_j$ is the equilibrium mole fraction of component j in the noted phase at a planar interface. To determine the conditions under which this approximation is valid, write $C_j^\beta - C_j^\alpha = \left(\overline{C}_j^\beta - \overline{C}_j^\alpha\right)(1 + \varepsilon)$, where $\varepsilon = \left(\widetilde{C}_j^\beta - \widetilde{C}_j^\alpha\right)/\left(\overline{C}_j^\beta - \overline{C}_j^\alpha\right)$ for $\overline{C}_j^\beta \neq \overline{C}_j^\alpha$. $\widetilde{C}_j$ is thus the shift in composition from the equilibrium value of component j in the noted phase due to both capillarity and diffusion. Consider the limit where $\varepsilon \ll 1$ to approximate the difference in compositions as the difference between the equilibrium compositions of the phases. As a consequence, the present approximation requires that the difference in the shift in compositions is much smaller than the equilibrium difference. In a binary, for example, when the free energies have same curvature (i.e., same Hessian), $\varepsilon = 0$, so in many cases it can be very small. Eq. (3) can be therefore be rewritten as

$$\left(\overline{C}_j^\beta - \overline{C}_j^\alpha\right)\frac{dR}{dt}$$
$$= \sum_{k=2}^N \frac{D_{jk}}{R}\left(C_k^\infty - \overline{C}_k^\alpha - \left(C_k^\alpha - \overline{C}_k^\alpha\right)\right) \quad \text{for } j = 2 \ldots N \quad (4)$$

Since this is a multicomponent alloy, the compositions of the α phase at the interface are functions of the diffusion process and are not given by the usual local equilibrium condition as in a binary alloy.

To determine the interfacial compositions, local equilibrium is assumed at the precipitate interface:

$$\mu_i^\alpha\left(C_2^\alpha, C_3^\alpha, \ldots, C_N^\alpha, P^\alpha\right)$$
$$= \mu_i^\beta\left(C_2^\beta, C_3^\beta, \ldots, C_N^\beta, P^\beta\right) \quad \text{for } i = 1 \ldots N \quad (5)$$

where μ_i is the chemical potential of component i in the noted phase. The pressure in the precipitate is not equal to that in the matrix because of the presence of a non-zero interfacial energy. Assuming that the interfacial stress and