



# Effect of different solute diffusivities on precipitate coarsening in ternary alloys

M.S. Bhaskar<sup>a,\*</sup>, T.A. Abinandanan<sup>b</sup>

<sup>a</sup> Research and Development Department, Mishra Dhatu Nigam Ltd., Hyderabad 500058, India

<sup>b</sup> Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India

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## ABSTRACT

According to Gibbs phase rule, ternary two phase alloys have a single degree of freedom at equilibrium at a given temperature. Thus, multiple precipitate-matrix equilibrium compositions are possible at the interface. From Philippe-Voorhees' (PV) theory (Philippe and Voorhees, 2013), it is known that during coarsening in multicomponent alloys, precipitate-matrix compositions at the interface during coarsening are not just dependent on the Gibbs-Thomson effect but also on the relative mobilities of the solute elements. Our computer simulations, based on a phase field model, show that this effect of different solute diffusivities on size-dependent particle composition is more pronounced in alloys richer in the slower diffusing solute.

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## 1. Introduction

Coarsening, or Ostwald ripening, is observed during late stages of phase transformations; in the case of coarsening of precipitates embedded in a matrix phase, there is an increase in average particle size, accompanied by a corresponding decrease in particle number density (the number of particles per unit volume). According to the classical LSW theory, due to Lifshitz and Slyozov [2] and Wagner [3], coarsening is characterized by a scaling regime in which (a) the number density is inversely proportional to time, (b) the cube of the average particle size increases linearly with time, and (c) the scaled size distribution of particles is time invariant.

The LSW theory has been extended in two key directions to deal with (a) coarsening in systems with a finite volume fraction of the particle phase, and (b) coarsening in ternary and higher order systems.

Due to its mean field nature, and the way it solves the underlying diffusion problem, LSW theory is applicable for coarsening in systems with a vanishingly small volume fraction of particles. There have been several approaches, both theoretical [4–6] and computational [7–9], which have examined coarsening in systems with finite precipitate volume fractions ( $f_v$ ) (see Ratke and Voorhees [10] for a book-length review). Their predictions are identical

to those of LSW theory, but the quantitative details are different; specifically, the scaled size distribution is broader, and the coarsening rate is higher in systems with larger  $f_v$ .

Precipitate coarsening in ternary and higher order systems is more complex to study due to at least two reasons: thermodynamically, there is an extra degree of freedom for (local) chemical equilibrium across the particle-matrix interface, and kinetically, the diffusivity of the solute species could be different. Morral and Purdy [11,12] have argued that in the multicomponent systems, coarsening is independent of the solution thermodynamics of the system because the thermodynamic term,  $\left(\frac{\partial^2 G}{\partial c_i \partial c_j}\right)$ , appearing in both diffusivity and Gibbs-Thomson coefficient cancels itself; However coarsening in multicomponent systems would still depend on the mobility matrix. Kuehmann and Voorhees (kV) [13], have extended the LSW formalism to ternary alloys by invoking the ternary version of the Gibbs-Thomson effect, and by making precipitate and matrix interfacial compositions depend on the rate of solute arrival at the interface. Once again, while the quantitative details differ, the predictions of kV theory are the same as those of LSW theory. In particular, it is notable that the shape of the size distribution curve is the same in LSW theory (for binary alloys) and kV theory (for ternary alloys). A more recent extension of this work by Philippe and Voorhees (PV) [1] has reiterated these conclusions for coarsening in general multicomponent systems.

Since their treatment of the diffusion problem is similar to that in LSW theory, the kV and PV theories are also applicable only to systems with vanishingly small volume fractions. For multicomponent

\* Corresponding author.

E-mail addresses: [ms.bhaskar@midhani.com](mailto:ms.bhaskar@midhani.com) (M.S. Bhaskar), [abinand@materials.iisc.ernet.in](mailto:abinand@materials.iisc.ernet.in) (T.A. Abinandanan).

systems with finite  $f_v$ , a general theory is not available, and computer simulations will continue to play an important role in developing our understanding further.

In this paper, we have used a ternary Cahn-Hilliard model to study coarsening in a ternary ( $ABC$ ) alloy system in which the  $BC$  binary is isomorphous, and the  $AB$  and  $AC$  binaries exhibit a miscibility gap in the phase diagram. Our model is a ternary extension of the classical Cahn-Hilliard model for a binary alloy, and allows for different solute mobilities and is similar to other studies (see Refs. [14–18] and references therein).

The paper is organized as follows: In Section 2 we describe the formulation of the Cahn-Hilliard model used in this study. Section 3 presents our results in terms of microstructure, various tests to establish that the simulations enter the scaling regime, and the effect of differential mobility on the coarsening rates and precipitate composition. In Section 4 we discuss these results vis-a-vis other experimental and computational studies regarding coarsening in multicomponent systems. Finally we present the conclusions of this study in Section 5.

## 2. Model formulation

We consider a ternary alloy system in which the local composition is given by  $(c_A, c_B, c_C)$  where  $c_i$  is the mole fraction of component  $i$ . These variables obey  $c_A + c_B + c_C = 1$  everywhere. We follow Huang et al. [19] (who studied the spinodal decomposition in ternary polymer blends) in developing the formulation given below. We begin by writing the free energy of a ternary alloy with non-uniform composition fields  $c_i(\vec{r})$  by generalizing the Cahn-Hilliard formulation [20].

$$F = N_v \int_V [f(c_A, c_B, c_C) + \sum_{i=A,B,C} \kappa_i (\nabla c_i)^2] dV. \quad (1)$$

where  $N_v$  is the No. of moles per unit volume. Eq. (1) consists of two parts:

1. The bulk free energy (per atom) ( $f$ ) which depends on local composition given by  $(c_A, c_B, c_C)$ .
2. The gradient energy terms  $\kappa_i (\nabla c_i)^2$ , which accounts for the energy due to non-uniformity in composition fields.

For the bulk chemical free energy per atom  $f(c_A, c_B, c_C)$ , we have used a regular solution model:

$$f(c_A, c_B, c_C) = \frac{1}{2} \sum_{i \neq j} \chi_{ij} c_i c_j + \sum_i c_i \ln c_i, \quad (2)$$

where  $i, j = A, B, C$  and  $\chi_{ij} = \chi_{ji}$  is the effective interaction energy between components  $i$  and  $j$ . From the nearest neighbour bond model,  $\chi_{AB}$  (for example) may be obtained as:

$$\chi_{AB} = \frac{Z[2E_{AB} - E_{AA} - E_{BB}]}{2k_B T}, \quad (3)$$

where  $E_{AB}, E_{AA}, E_{BB}$  are the bond energies between A/B, A/A and B/B bonds, respectively,  $Z$  is coordination number,  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature. In our study we have used  $\chi_{AB} = 3.2$ ,  $\chi_{AC} = 3.2$ , and  $\chi_{BC} = 0$ ; the last condition ( $\chi_{BC} = 0$ ; i.e.,  $B$  and  $C$  form an ideal solution) ensures that there is complete solubility along B-C edge of the ternary phase diagram.

The evolution equations are given by:

$$\frac{\partial c_B}{\partial t} = M_{BB} \left[ \nabla^2 \left( \frac{\partial f}{\partial c_B} \right) - 2(\kappa_B + \kappa_A) \nabla^4 c_B - 2\kappa_A \nabla^4 c_C \right] - M_{BC} \left[ \nabla^2 \left( \frac{\partial f}{\partial c_C} \right) - 2(\kappa_C + \kappa_A) \nabla^4 c_C - 2\kappa_A \nabla^4 c_B \right] \quad (4)$$

and

$$\frac{\partial c_C}{\partial t} = M_{CC} \left[ \nabla^2 \left( \frac{\partial f}{\partial c_C} \right) - 2(\kappa_C + \kappa_A) \nabla^4 c_C - 2\kappa_A \nabla^4 c_B \right] - M_{BC} \left[ \nabla^2 \left( \frac{\partial f}{\partial c_B} \right) - 2(\kappa_B + \kappa_A) \nabla^4 c_B - 2\kappa_A \nabla^4 c_C \right] \quad (5)$$

We solve Eqs. (4) and (5) using a ternary extension [21] of semi-implicit Fourier spectral method [22].

### 2.1. Interfacial energy and interfacial width

In Cahn-Hilliard type formulations the interfacial energy and width are interconnected, and depend on the gradient energy coefficients,  $\kappa_i$ , and the height of the barrier between the free energies of the two phases in equilibrium across this interface. The interfacial energy of a ternary two phase system is given by Eq. (6).

$$\sigma_{\alpha\beta} = N_v \int_{-\infty}^{\infty} \left[ \Delta f + \sum_{i=A,B,C} \kappa_i (\nabla c_i)^2 \right] dx \quad (6)$$

where  $\Delta f$  is given by Eq. (7) in which  $f(c_i)$  is the bulk free energy given by Eq. (2) and  $\mu_i^{\alpha/\beta}$  is the chemical potential of species  $i$  when  $\alpha$  and  $\beta$  phases are in equilibrium with each other.

$$\Delta f = f(c_i) - \sum_i c_i \mu_i^{\alpha/\beta} \quad (7)$$

We have measured the interfacial energy given by Eq. (6), using 1D simulation in which the two phases are equilibrated.

In our simulations  $\kappa_A = \kappa_B = \kappa_C = 15$ . The value of  $\kappa_i$  should be such that the gradients at the interface are sufficiently gentle so that the interface is sufficiently resolved. In our calculations we have used  $\Delta x = 1$ , the interfacial energy is  $\gamma = 2.32$ , and interface width is  $w = 10.82$ .

## 3. Results

We have used a model alloy system in which the  $AB$  and  $AC$  binary alloys have a miscibility gap, and the  $BC$  binary is an ideal solution. Specifically, we have used  $\chi_{AB} = \chi_{AC} = 3.2$ , and  $\chi_{BC} = 0$ ; the isothermal section of the ternary phase diagram for this system is shown in Fig. 1, which also marks the compositions of six alloys (three alloys each on two different tie-lines) we have studied. We will refer to the tie-lines with the smaller and larger slopes as, respectively, the low-C and high-C tie lines. On each tie line, we have chosen alloys with three different equilibrium volume fractions of precipitate phase i.e. 10.9%, 16.7% and 20.4%. For easy identification, these alloys are referred to as 10%, 15% and 20% alloys. The alloy compositions studied in our simulations along with their corresponding tie line end compositions are given in Table 1.

Fig. 1 also shows the region of phase diagram which undergoes spinodal decomposition. In this region, the Jacobian of free energy with respect to composition is not positive definite i.e.  $\left| \frac{\partial^2 f}{\partial c_i \partial c_j} \right| < 0$ .

Our primary focus is on studying the effect of difference in solute diffusivities on coarsening. Since diffusivity does not appear directly in the model, the difference in solute diffusivity is implemented through differential mobilities. Specifically, our simulations use either  $M_C = 1$  or  $M_C = 0.1$ , while  $M_A = M_B = 1$  always.

For each alloy, we performed four independent simulations; each simulation starts with a number of precipitates of radius  $r_0$  which is just above the critical radius. They are placed at random locations in a 2D simulation cell (with  $1024 \times 1024$  grid points, and  $\Delta x = \Delta y = 1$ ) in such a way that each precipitate is separated by at least  $4r_0$  from its neighboring precipitates.

Since our primary focus in this part of the study is on coarsening, the initial number of precipitates is such that the matrix has

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