

Spinodal decomposition in fine grained materials

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Abstract. We have used a phase field model to study spinodal decomposition in polycrystalline materials in which the grain size is of the same order of magnitude as the characteristic decomposition wavelength (λ_{SD}). In the spirit of phase field models, each grain (i) in our model has an order parameter (\mathbf{h}_i) associated with it; \mathbf{h}_i has a value of unity inside the i th grain, decreases smoothly through the grain boundary region to zero outside the grain. For a symmetric alloy of composition, $c = 0.5$, our results show that microstructural evolution depends largely on the difference in the grain boundary energies, g_{gb} , of A-rich (\mathbf{a}) and B-rich (\mathbf{b}) phases. If $g_{gb}^{\mathbf{a}}$ is lower, we find that the decomposition process is initiated with an \mathbf{a} layer being formed at the grain boundary. If the grain size is sufficiently small (about the same as λ_{SD}), the interior of the grain is filled with the \mathbf{b} phase. If the grain size is large (say, about $10\lambda_{SD}$ or greater), the early stage microstructure exhibits an A-rich grain boundary layer followed by a B-rich layer; the grain interior exhibits a spinodally decomposed microstructure, evolving slowly. Further, grain growth is suppressed completely during the decomposition process.

Keywords. Spinodal decomposition; grain boundary effects; phase field models.

1. Introduction

With the advent of techniques capable of producing metastable crystalline phases with a grain size in the range of 10–100 nm (examples of such processes would include rapid solidification, laser processing and mechanical milling), there is considerable interest in phase transformations in such materials. In particular, if the metastable alloy has a homogeneous composition which is unstable with respect to phase separation by spinodal decomposition (SD), the characteristic wavelength of SD process is also in the size range of 10–100 nm. Thus, one might expect interesting effects due to the fine grain size on the SD process; this study addresses these effects.

While our emphasis in this study is on fine grained polycrystalline materials, several studies have been reported recently in a related field: surface assisted SD. During the initial stages, a surface layer is formed of that phase for which the surface energy is lower. With increasing distance from the surface, one observes alternating layers of the two phases; deep in the interior, a microstructure similar to that produced by ‘normal’ (i.e. bulk) SD is observed (see Puri and Binder 1992, 1993, 1994; Fischer *et al* 1997; Puri *et al* 1997; Bastea *et al* 2001). A wide variety of models and simulation techniques have been employed in these studies. Experiments on polymers also reveal a surface wetting layer coexisting with interior, spinodally decomposed two-phase microstructure (Geoghegan *et al* 2000).

In our study of phase separation in polycrystalline alloys, we have employed a phase field model, which is a modified version of that used by Fan and Chen (1997) in their study of grain growth in two-phase materials. The essential features of this model are described briefly in the next section. The key results from our study of SD process in a fine grained alloy are presented in §3, followed by the main conclusions of this study in §4.

2. Formulation

We use a phase field model similar to the one employed by Fan and Chen (1997). In such phase field models, the variables needed are: c , the composition field, and \mathbf{h}_i ($i = 1, 2, \dots, n$) the ‘order parameter’ fields which represent the n different orientations of the grains present in the microstructure. The \mathbf{h}_i variables are continuum analogs of the orientation variables used in the Potts model (Fan and Chen 1997). \mathbf{h}_i takes an equilibrium value (taken to be unity) within the i th grain and drops to zero outside it, through a grain boundary region where it varies smoothly.

The free energy used in the model is a function of composition, c and the orientation order parameters, \mathbf{h}_i . We use the rescaled composition variable, c , defined by

$$c = \frac{c' - c_{\mathbf{a}}}{c_{\mathbf{b}} - c_{\mathbf{a}}},$$

where c' is the composition expressed in mole fraction of species B, $c_{\mathbf{a}}$ and $c_{\mathbf{b}}$ are the equilibrium compositions of the \mathbf{a} and \mathbf{b} phases, respectively.

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The equilibrium states at low temperature are defined by composition $c=0$ and $c=1$ and $\mathbf{h}_i=1$ and $\mathbf{h}_{j \neq i}=0$, ($i=1, 2, \dots, n$). We have chosen the following form for $f(c, \mathbf{h})$, the bulk free energy density, so that it exhibits these $2n$ degenerate equilibrium states

$$f(c, \mathbf{h}) = Ac^2(1-c)^2 + B(mc+1) \left\{ 1 + \sum_i (-\mathbf{h}_i^2 - 2\mathbf{h}_i^3 + 2\mathbf{h}_i^4) + \mathbf{e} \sum_i \sum_{j \neq i} \mathbf{h}_i^2 \mathbf{h}_j^2 \right\},$$

where A , B and m are phenomenological constants. The constant, m , couples the composition, c , and the orientation order parameters, \mathbf{h} , such that the energy of the grain boundary formed in the \mathbf{a} phase ($\mathbf{g}_{\mathbf{a}}$) is lower than that formed in the \mathbf{b} phase ($\mathbf{g}_{\mathbf{b}}$). This model can account for the following different types of interfaces at low temperatures: grain boundary in \mathbf{a} and \mathbf{b} phases, coherent interface (within the same grain) and incoherent interface (across two different grains) between \mathbf{a} and \mathbf{b} phases.

The total free energy, F , of an inhomogeneous system is given by

$$F = \int_V \left[f_0(c, \mathbf{h}) + \frac{\mathbf{k}_c}{2} (\nabla c)^2 + \sum_i \frac{\mathbf{k}_i}{2} (\nabla \mathbf{h}_i)^2 \right] dV,$$

where \mathbf{k}_c and \mathbf{k}_i are the gradient energy coefficients associated with inhomogeneities in composition and in \mathbf{h} , respectively.

The evolution of the composition is governed by Cahn–Hilliard equation

$$\frac{dc}{dt} = M \nabla \cdot \left(\nabla \left(\frac{\mathbf{d}F}{\mathbf{d}c} \right) \right),$$

where M is the mobility, assumed to be independent of composition. On the other hand, the evolution of the \mathbf{h} variables is governed by Cahn–Allen equation

$$\frac{d\mathbf{h}_i}{dt} = -L_i \frac{\mathbf{d}F}{d\mathbf{h}_i},$$

where L_i are the relaxation parameters.

3. Results

We have used a control volume method (see Patankar 1980) for solving the above evolution equations in two dimensions. The simulation is carried out on a 256×256 square grid with $\Delta x = \Delta y = 1.0$. For time integration, we used a time interval of $\Delta t = 0.1$. Our simulation has used the following values of the model parameters: $A = 1.0$, $B = 0.5$, $m = 1.0$, $L_i = 1.0$, $M = 1.0$. The above equations are given in their dimensionless forms; the characteristic energy, length and time used for this scaling procedure are chosen in such a way that the parameters A , M and \mathbf{k} are of order unity. The simulation starts with an alloy with a composition of $c = 0.5$, on which we superimpose

an initial (uniform) random noise of 0.01 at the grid points.

3.1 Spinodal decomposition in a single crystal

Figure 1 shows the evolution of spinodally decomposed microstructure in a single grain after 100, 500, 1000 and 2000 time steps. During early stages, it is clear that the initial fluctuations have grown in amplitude. Those fluctuations with a wavelength of

$$\mathbf{l}_{\max} = 4\mathbf{p}[-\mathbf{k}/(\partial^2 f / \partial c^2)]^{1/2},$$

grow the fastest (Cahn 1961); therefore, in the microstructure after, say, 100 time steps, the typical distance between two neighbouring white features (B-rich regions) is about $\mathbf{l}_{\max} \approx 17$. The A-rich and B-rich regions form a bicontinuous network which, beyond 1000 steps, undergo coarsening. Further, only after about 1000 steps, the composition of the A-rich and B-rich regions reach the equilibrium values of $c = 0$ and $c = 1$, respectively.

3.2 Grain boundary assisted spinodal decomposition

For this simulation, an initial polycrystalline microstructure is needed. Such a microstructure was obtained using a prior simulation, which started with an initial configuration with $\mathbf{h}_i = 0 + \mathbf{d}\mathbf{h}_i$ (where $\mathbf{d}\mathbf{h}_i$ is a small positive noise); the integration of Cahn–Allen equation was carried out up to 3000 time steps, and it produced a microstructure with grain boundaries (see figure 2(a) in which the grain boundaries are decorated by being enriched with species A). The spinodal decomposition in a polycrystalline alloy was simulated using this microstructure, by adding a homogeneous composition of $c = 0.5$ (with a noise of 0.01) to this configuration. Figure 2 shows the sequence of microstructures of a polycrystalline system after 100, 500, 1000 and 2000 time steps.

The very early stages of decomposition are characterized by enrichment of the grain boundaries by the species A; this can be seen in the figure as early as $t = 100$ time steps. As time progresses, the grain boundaries become decorated with the A-rich \mathbf{a} phase, with the B-rich \mathbf{b} phase on either side of it. This process can be thought of as one in which the A-enrichment triggers a composition wave normal to the grain boundary, which travels into the grain interior. By 500 time steps, it is clear that the composition of the A-rich phase at the grain boundary has reached its equilibrium value of $c = 0$. This may be compared with that in single crystal, wherein the A-rich phase composition is only about 0.3 after 500 steps. Thus, it is clear that the GB-initiated spinodal decomposition occurs much faster than the normal one.

While the GB-initiated composition wave propagates into the grains, normal spinodal decomposition could—

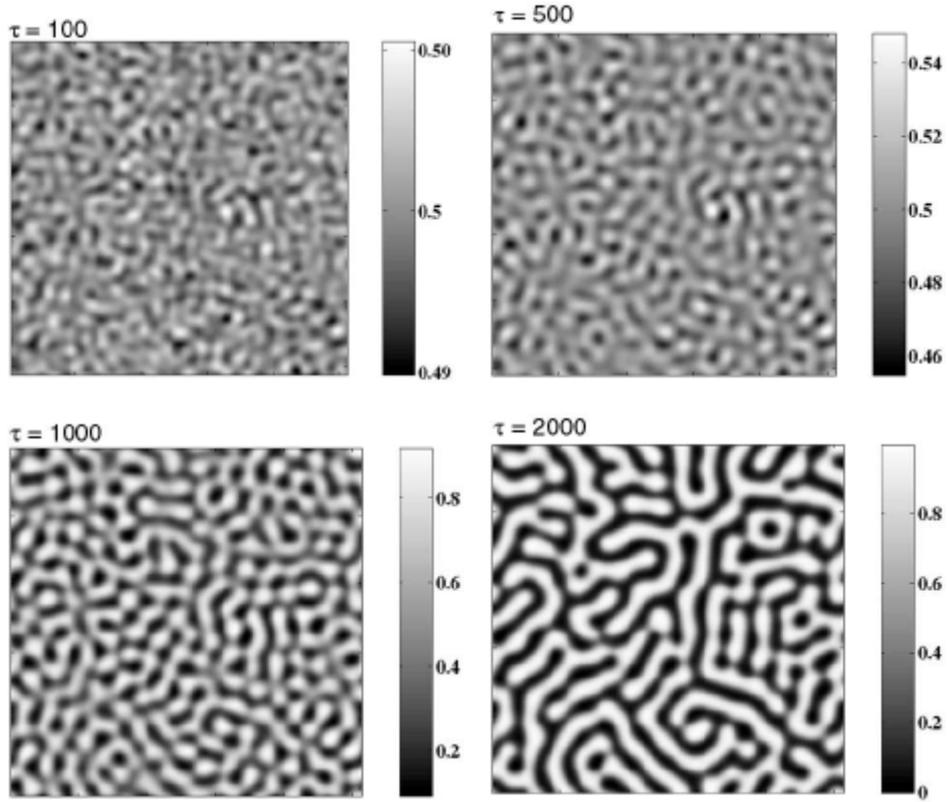


Figure 1. The evolution of SD microstructure in a single crystal after $t = 100, 500, 1000$ and 2000 time steps.

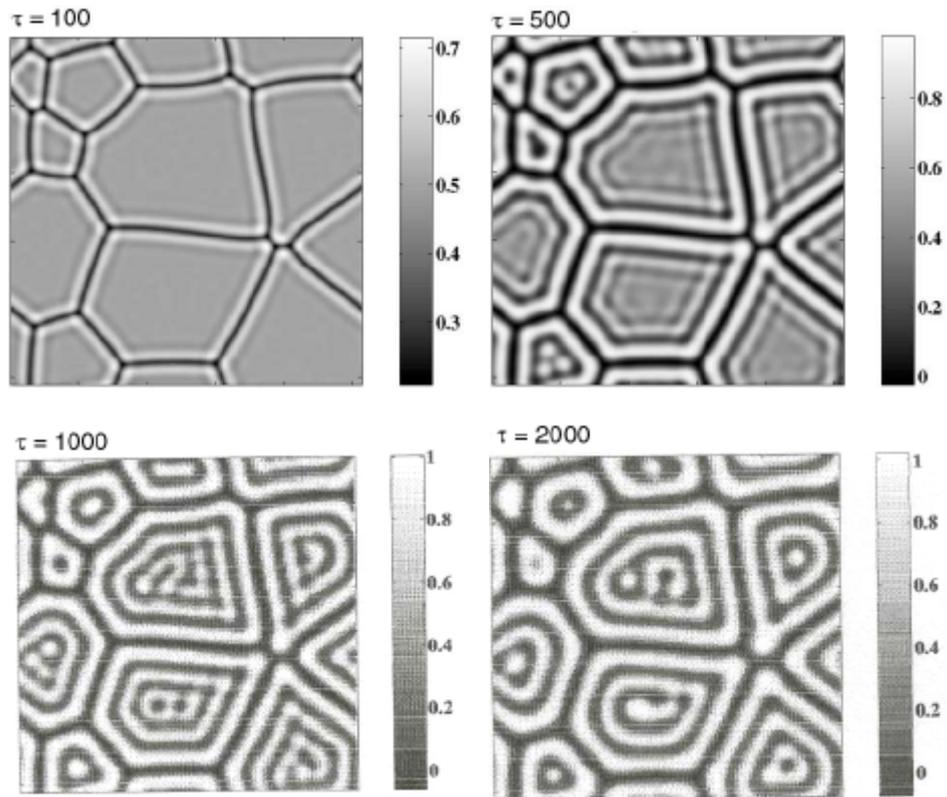


Figure 2. The evolution of SD microstructure in a polycrystalline alloy after $t = 100, 500, 1000$ and 2000 time steps.

and indeed does—take place deep in the grain interiors (see the top right regions in figure 2 after 1000 steps). Thus, the late stage microstructure (say, after 2000 time steps) shows a mixture of GB initiated composition waves co-existing with the usual spinodal waves in the grain interiors of large grains. In small grains, however, the GB-initiated waves travel fast enough to cover the entire grain, before normal spinodal decomposition occurs in the interior; in these grains, the dominant features are concentric alternating rings of A-rich and B-rich phases. During this entire course of events, the grain boundaries are virtually immobile; since the grain boundaries are covered by the A-rich phase, any movement on their part normal to themselves will take them through a configuration in which they lie between A-rich and B-rich regions; in other words, such a movement leads to converting an **a** phase grain boundary into an incoherent interface with a much higher energy, thus rendering the process of grain growth virtually impossible.

Figure 3 shows the structure factor, $S(k)$, during different times both for the single crystal as well as the polycrystalline case. The structure factor, $S(k)$ is plotted as a function of k for 100, 500 and 2000 time steps. A comparison of the plots for the same time (e.g. 500 time steps) shows that the peak in $S(k)$ in the polycrystalline

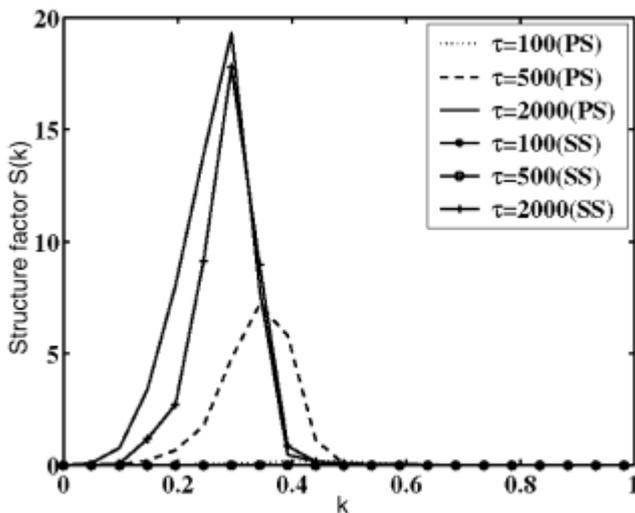


Figure 3. The evolution of the structure factor, $S(k)$ for single crystal (dotted line) and polycrystalline system (continuous line) for $t = 100, 500$ and 2000 time steps. The symbol 'ps' and 'ss' refer to polycrystalline and single crystalline alloys, respectively.

case is much higher than that in the single crystal; this indicates that spinodal decomposition has taken place to a larger extent in the former than in the latter. Further, the peak in the polycrystalline case shifts to the left from $k = 0.4418$ through 0.3436 to 0.2945 at $t = 100, 500$ and 2000 time steps, respectively. For the single crystal, on the other hand, the peak in $S(k)$ remains at $k = 0.3436$ up to $t = 500$ and shifts to a lower value of $k = 0.2945$ at $t = 2000$ time steps. This is clearly due to the influence of the grain size (which is several times larger than the characteristic spinodal wavelength).

4. Conclusions

We have studied the spinodal decomposition process in a polycrystalline alloy with a grain size, which is similar to the dominant decomposition wavelength. When the grain boundary energy, γ_{gb} , of A-rich **a** phase is lower than that of the B-rich **b** phase, the decomposition process is initiated with the formation of **a** layer at the grain boundaries. In small grains, the interior of the grain is filled with the **b** phase, while in large grains, the interior exhibits the usual spinodal microstructure. The kinetics in a polycrystalline alloy is much faster than that in a single crystal. Further, during the phase separation process, the grain growth is completely suppressed.

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