Morphological instabilities in thin films: Evolution maps

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\textbf{Abstract}

We consider morphological instabilities in binary multilayers and the post-instability evolution of the system. The alloys with and without intermediate phase are considered, as well as the cases with stable and meta-stable intermediate phase.

Using the Galerkin finite element formulation for coupled Cahn–Hilliard – elasticity problem, maps of different evolution paths are developed in the parameter space of relative thicknesses of initial phases. We consider the relative importance of elastic and chemical energy of the system and develop maps for different cases.

The systems exhibit rich evolution behavior. Depending on the initial configuration (which determines the mass conservation condition), the final equilibrium varies, but even greater variety is observed in evolution paths. The paths may consist of multiple evolution steps, which may proceed at different rates.

Except for few special circumstances, the instabilities are to perturbations non-homogeneous in the film plane. Post-instability evolution is essentially two-dimensional, and cannot be reduced to the one-dimensional model.

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1. Introduction

Multilayer thin films have been a very active research area in the past decade. When the thickness of an individual layer is reduced to micro- or nano-scale, novel mechanical [1–5], optical [6], electronic [7,8], and magnetic [6–8] properties emerge, which make such materials attractive for a number of potential applications. However, to maintain the desirable properties, the stability of phases is required, and this is affected by temperature and stress. In addition to externally applied load, internal stresses appear as a result of enforced lattice continuity and compositional strain [9–14]. For example – a significant drop of hardness occurs after annealing of Ni/Ru multilayers at 600 °C [15], Ni layers breakdown in NiAg multilayer is annealed at 600 °C [16], and pinch-off of Co layers in Co/Cu multilayers is observed after creep test at 830 °C [17].

Greer [18,19] classified the changes that can occur in thin film multilayers as their microstructures evolve. He divided these processes to the following categories: inter-diffusion (same phases coexist with changed compositions) \((Ag/Au)\ [20],\ Ni/Al, Ag/Zn [21], Al/Ni [22]), interfacial reaction (nucleation and growth of a new phase) \((Si/NI)\ [23],\ Ni/Zr [24], Al/Mn [25], Ni/Al [26]), transformation in one phase of the multilayer without any changes in other phase(s) \((Si/Al)\ [27]), and, coarsening or spinodal decomposition of the layers \((Ni/Ag)\ [15], Ni/C [28]). All of these can be modeled using the diffuse interface (phase-field) model.

Following the initial Cahn–Hilliard [29] formulation of the diffuse interface model, many numerical phase-field studies [30–43] have been reported. Very few considered thin films, and these are either based one-dimensional models [39,40] with severe restrictions on possible instabilities, or, are focused on film-fluid interactions [41–43]. The exception is the recent work by Chiranjeevi et al. [14]. They consider a special two-phase multilayer with one phase much stiffer than the other.

Here, we present a comprehensive study of binary multilayer thin films, including two-phase systems and systems with an intermediate phase (meta-stable or stable). Following the dimensional analysis, we develop the maps of the evolution behavior of multilayers, in the parameter space describing the initial geometry, and considering the cases of different relative importance of elastic and chemical energy density. In addition to having different (final) stable configurations, multilayered thin films may reach those stable configurations following different paths in configurational space. We classify the paths and map the initial configuration space corresponding to each path.

We use the recently developed Galerkin finite element formulation [44,45] for the Cahn–Hilliard diffuse interface (phase-field) model [29], coupled with elasticity [40].

The paper is organized as follows. In Section 2, formulation, dimensional analysis, and numerical solver for the coupled phase filed-elasticiy equations are presented. In Section 3, the maps of
transformations for two-phase systems are developed. In Sections 4 and 5, similar maps are developed for systems with stable and meta-stable intermediate phase. Discussion and conclusions are given in Section 6.

2. Formulation and numerical method

Concentration of a component in a binary system is subjected to a conservation law. When used a phase-field variable, it results in a nonlinear 4th order diffusion partial differential equation (PDE), which is then coupled to the 2nd order elasticity PDEs. Consider a binary system, with components A and B, which forms up to three phases (α, β, and γ), and characterized by the molar fraction of the component B, c. The total free energy, F, of a non-homogeneous system with volume V, bounded by surface S, is constructed as:

\[ F(c, u_i) = \int_V \left[ f(c) + U(\epsilon_{ij}, c) + \frac{1}{2} \kappa (\nabla c)^2 \right] \, dV - \int_S t_i u_i \, dS, \]  

(1)

where \( f(c) \) is the Helmholtz free energy density of a uniform, stress-free system, \( \kappa \) is the isotropic gradient energy coefficient, \( t_i \) and \( u_i \) are the components of surface traction displacement. The last term is the loading potential. The surface energy of the outer boundary \( S \) is neglected. \( U(\epsilon_{ij}, c) \) is the strain energy density and \( \epsilon_{ij} \) are the components of the total strain tensor, consisting of elastic (stress-induced), and compositional (stress-free) strain [46]. The latter is modeled as purely volumetric and linear in composition (Vegard’s law) [47]:

\[ \epsilon_{ij} = \frac{1}{2} (\epsilon_{ij} + \epsilon_{ji}) = \epsilon_{ij}^c + \epsilon_{ij}^p; \quad \epsilon = \eta(c - c_0). \]  

(2)

The reference composition \( c_0 \) is taken to be the average of composition over the domain, and \( \eta \) is the compositional strain parameter. \( \eta \) varies widely in binary metallic alloys, e.g., \( \eta = 0.094 \) for Al-2 at.% Cu and \( \eta = 0.264 \) for Fe-5 at.% C [48].

The 2nd order PDE governing mechanical equilibrium, which can be obtained by \( \delta F/\delta u_i = 0 \), has this form:

\[ (C_{ijkl} u_{ij})_j = \tilde{C} u_{ij}; \quad \tilde{C} = C_{ijkl} \delta \omega_i \delta \omega_j. \]  

(3)

The conserved phase field formulations results in a 4th order evolution PDE [44]:

\[ \dot{\epsilon} = B \nabla^2 M; \quad M(c, \nabla^2 c) = \frac{\partial (f - U)}{\partial c} - \kappa \nabla^2 c. \]  

(4)

The chemical potential, \( M \), is a variational derivative of the free energy (1), and \( B \) is the isotropic mobility coefficient.

The Helmholtz free energy density of a uniform unstressed system, is assumed to be a triple well potential that can produce two-phase and three-phase binary systems:

\[ f(c) = W_1(c - c^a)^2(c - c^b)^2(c - c^c)^2 + W_2(c - c^a)^2(c - c^c)^2, \]  

(5)

\( W_1 \) and \( W_2 \) are the energy coefficients, \( c^a, c^b \) and \( c^c \) are the mole fractions at which \( f(c) \) has its extremum. The non-dimensional free energy density is shown in Fig. 1, as function of the scaled composition.

In this research, we use particular non-dimensional parameters such that the results can be used to predict the transformation and evolution of different binary multilayer thin films. To analyze the space of non-dimensional parameters of the problem, we use the following dimensional reduction [40,44]. The scaled composition \( \tilde{c} \) varies between \( c^a = -1 \) and \( c^c = 1 \), with intermediate phase at \( \tilde{c}^a = 0 \). With \( \Delta c = (c^a - c^c)/2 \):

\[ \tilde{c} = (2c - c^a - c^c)/2 \Delta c. \]  

(6)

Let \( \rho_0 \) be the density of lattice sites, \( k \) – the Boltzmann constant and \( T \) – the temperature. Denote \( \alpha = \rho_0 k T \). The characteristic length \( X \), the characteristic time \( \Omega \), and the characteristic energy \( W \), are:

\[ X = \sqrt{\kappa / \alpha \Delta c^2}; \quad \Omega = \kappa / (2 B \alpha^2 \Delta c^2); \quad W = \alpha \Delta c^2. \]  

(7)

We note that \( \kappa \) affects only the length and time scale, and \( B \) affects only the time scale. Non-dimensional gradient energy coefficient and mobility are \( \kappa = B = 1 \). The isotropic elastic moduli are scaled by \( E^* = E/(1 - \nu) \), where \( E \) is the Young’s modulus and \( \nu \) is the Poisson ratio, so that their non-dimensional versions depend on the Poisson ratio only: \( C_{11} = C_{44}(1 - \nu)/(1 - 2 \nu) \), \( C_{12} = C_{44}(1 - \nu)/(2 - 2 \nu) \), and \( C_{44} = (1 - \nu)/(1 + \nu) \). The scaled compositional strain parameter is:

\[ \tilde{\eta} = \eta \sqrt{E^*/\alpha \Delta c^2}. \]  

(8)

Assuming a fixed Poisson ratio (\( \nu = 0.3 \) in this study), the system is governed by only three independent non-dimensional parameters, \( \eta, W_1 = W_1/W \) and \( W_2 = W_2/W \). We will consider three combinations of \( W_1 \) and \( W_2 \), as shown in Fig. 1:

- \( W_1 = 0, W_2 = 0.02 \) (no intermediate phase),
- \( W_1 = 0.4, W_2 = -0.04 \) (stable intermediate phase), and,
- \( W_1 = 0.4, W_2 = 0.02 \) (meta-stable intermediate phase).

The details of coupled phase-field – elasticity formulation and the corresponding Galerkin finite element implementation can be found in [44]. The optimal element size was determined to be about 1/5 of the interface width, which guarantees the uniform quadratic convergence, expected for conforming elements. The nominal (equilibrium) interface thickness is [29]:

\[ \Delta c = \frac{\kappa}{2 \Delta c_{\text{max}}}. \]  

(9)

where \( \Delta c_{\text{max}} \) is the difference between the neighboring maximum and minimum of the free energy density, as illustrated in Fig. 1.

In the following three sections, we summarize the results of a comprehensive set of computations in form of evolution behavior maps, for the three cases of multilayers (two phases, stable and meta-stable intermediate phase). Total of 580 finite element runs were performed, with 21,000–360,000 degrees of freedom, and 10^6–10^8 time steps. The cpu time per run varied between 9 and 35 h. Both, home-grown code and the commercial COMSOL Multiphysics [49] software were used. The boundary conditions for the thin film multilayers are illustrated in Fig. 2: the left and right

![Fig. 1. The non-dimensional triple-well free energy density, \( f \), as function of scaled composition, \( c \).](image-url)
boundaries are subjected to periodic boundary conditions, while the top and bottom boundaries are traction-free and flux-free. By applying these boundary conditions and imposing plane strain conditions, the results of two-dimensional simulations can be used to predict the behaviors of three-dimensional multilayer thin films.

3. Two-phase systems

We first consider binary multilayers without an intermediate phase. Denote the initial thicknesses of $a$ and $\gamma$ layers by $d_a$ and $d_\gamma$ (Fig. 2). In the 3-layers configuration shown in Fig. 2, the central layer breaks up into particles for $\eta > 0.07$. For the purpose of mapping, we will denote this type of behavior as type I. For $\eta \geq 0.15$ the breakup is followed by full homogenization at concentration equal to the average composition of the system. This is of course possible only if the $\gamma$-layer is thin enough.

In Figs. 3 and 4, the cases where the average compositions are not close to the $a$-composition are shown. The final equilibrium is (qualitatively) the same in both cases – a thicker $\gamma$-layer, but the evolution paths are different. In Fig. 3 (type II behavior), slow fragmentation of both $\gamma$-layers is followed by fast joining of the resulting patches to form a single, thicker $\gamma$-layer. In Fig. 4 (type III), slow necking of the central $a$-layer is followed by fast fragmentation and disappearance of this layer.

The maps of transformations for the 5-layers initial configuration are shown in Figs. 5 and 6, for $\eta = 0$ and $\eta = 0.1$. There are five different regions in this parameter space. In addition to the above described types I, II, and III, homogenization occurs for initially very thin $\gamma$-layers, while for very thick layers, the initial configuration is stable.

Each map is constructed from about 150 computer runs. To illustrate the accuracy, we show some computational points in Fig. 5, namely those that determine the geometry of the triple junction between regions I, II and III.

4. Systems with stable intermediate phase

We now consider binary multilayer systems with the stable intermediate phase, $\beta$. An example is shown in Fig. 7 (type IV). First, a fast growth of the intermediate phase takes place: the whole

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**Fig. 2.** Evolution of a 3-layers configuration (type I). Initially $d_c = 15$, $d_a = 30$, and $\eta = 0.07$. Color bar shows the composition. The FE mesh consists of 29,243 triangular elements. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 3.** Evolution of a 5-layers system (type II). Initially $d_c = 10$, $d_a = 15$ and $\eta = 0$. The FE mesh consists of 16,158 triangular elements.

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γ-phase and a part of α-phase are consumed. Then, slow thinning and fragmentation the central α-layer follows until it disappears. A thick β-layer remains in the final equilibrium configuration.

The maps of transformations for 5-layers system (such as the one shown in Fig. 7) with stable intermediate phase, are shown in Figs. 8 and 9, for \( \eta = 0 \) and \( \eta = 0.2 \). Since the intermediate β-phase has a lower energy level than both α-phase and γ-phase, growth of the intermediate phase occurs until all the smaller-volume (in our case γ-phase) is consumed. We define four different types of evolution.

**Type I**: Slow fragmentation of initially thin γ-layers is overtaken by fast γ-to-β transformation of the resulting particles. β-particles in α-matrix remain as the final equilibrium configuration.

**Type II**: Fast β-growth overtakes slow fragmentation and disappearance of γ-layers. This is followed by fast coalescence of β-particles into a new, thick β-layer.

**Type III**: Fast uniform growth of β-phase consumes γ-layers and two thick β-layers will remain in the final configuration of the system.

**Type IV**: Shown in Fig. 7 and discussed above.

For larger values of \( \eta \) and very thin γ-layers, there is a small homogenization region (the lower left corner of Fig. 9). The homogeneous phase is α (not exactly at the minimum). The system is constrained by mass conservation. A homogeneous β-phase would be the minimum energy configuration for an unconstrained systems. In the constrained system, β-phase first consumes γ-layers, then disappears into α, so that the final uniform phase has the average composition of the system.

The initial configuration, consisting of α and γ layers is never stable.

### 5. Systems with meta-stable intermediate phase

A meta-stable intermediate phase produces a more complex behavior than the stable one. The evolution is often characterized by partial growth of the intermediate phase, which is arrested before the other phase is consumed. Moreover, the intermediate phase itself can subsequently be consumed by another phase. Consequently, the final configurations and paths are more complex than in the case of a stable intermediate phase.
An example of evolution of systems with meta-stable intermediate phase is shown in Fig. 10 (type IV). Initially, β-phase grows fast to produce very thin β-films between α- and γ-layers. Since β-phase is meta-stable, the growth will stop. This appears to be either a meta-stable or neutrally stable equilibrium. Perturbed by numerical errors, the system slowly evolves; first by necking, then pinching of the central α-layer. β-phase then quickly consumes the α-layer, only to be (as quickly) consumed by the growing γ-phase.

The evolution maps for 5-layer systems with meta-stable intermediate phase are shown in Figs. 11 and 12, for $\eta = 0$ and $\eta = 0.2$. Owing to its high energy, β-phase growth is limited and typically consumes the thinner layer (in our case, γ-phase). In addition to

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**Fig. 7.** Evolution (type IV) of a system with stable intermediate phase. Initially $d_\alpha = 15$, $d_\beta = 20$ and $\eta = 0.2$. Color bar shows the composition. The FE mesh consists of 30,744 triangular elements. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 8.** Evolution map for the system with stable intermediate phase; $\eta = 0$. The non-dimensional interface thickness between β and γ (10) is $l_0 \approx 3.2$.

**Fig. 9.** Evolution map for the system with stable intermediate phase; $\eta = 0.2$. The non-dimensional interface thickness between β and γ (10) is $l_0 \approx 3.2$. 
homogenization to the composition (close to) \( \alpha \)-phase (Fig. 12, lower left corner), explained in the previous section, we observe five different types of evolution.

Type I: Slow fragmentation of initially thin \( \gamma \)-layers is overtaken by fast \( \beta \)-growth resulting in \( \beta \)-particles in \( \alpha \)-matrix.

Type II: Starts as type I but this is followed by fast coalescence of \( \beta \)-particles to form new, thick \( \beta \)-layer.

Type III: Starts as type I but \( \beta \)-growth is limited, so that the intermediate results are \( \gamma \)-particles surrounded by a thin \( \beta \)-films in \( \alpha \)-matrix. This is followed by fast coalescence of particles to make a thick \( \gamma \)-layer surrounded by thin \( \beta \)-films.

Type IV: Shown in Fig. 10 and discussed above.

Type V: Fast partial uniform \( \beta \)-growth, with final configuration similar to picture in the top right corner of Fig. 10.

As in the case of stable intermediate phase, the initial configuration, consisting of \( \alpha \) and \( \gamma \) layers is never stable. However, the type V behavior may include very little uniform \( \beta \)-growth, so that the equilibrium configuration may be acceptable in practical applications.
6. Conclusions and discussion

The morphological instabilities and post-instability evolution of binary multilayers, with and without intermediate phase (stable and meta-stable), is considered. Using the Galerkin finite element formulation [44,45] for coupled Cahn–Hilliard – elasticity problem, maps of different evolution paths are developed in the parameter space of relative thicknesses of initial phases.

Dimensional analysis reveals that, for isotropic materials, governing equations depend on four non-dimensional parameters: Poisson ratio, scaled compositional strain parameter (8), and two scaled energy density coefficients (5). The scaled compositional strain parameter determines the relative importance of elastic and chemical energy densities. We consider two values of this parameter. The two energy density coefficients determine the nature of the system, i.e., whether it has an intermediate phase or not, and the stability of the intermediate phase. We consider three characteristic combinations of these parameters, corresponding to: two-phase system, stable and meta-stable intermediate phase.

The systems exhibit rich evolution behavior. Depending on the initial configuration (which determines the mass conservation condition), the final equilibria vary, but even greater variety is observed in evolution paths. The paths may consist of multiple evolution steps, which may proceed at different rates. In this report, we have characterized the rates only qualitatively, as fast or slow, relative to the other steps in the evolution. The rates vary in each region of the evolution map.

Except for few special circumstances, the instabilities are to perturbations non-homogeneous in the film plane. Post-instability evolution is essentially two-dimensional and cannot be reduced to the one-dimensional model such as the one considered in [40,45,50].

References