Alloy destabilization by dislocations

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Thermodynamic phase diagrams of alloys are usually computed or experimentally determined under the assumption of perfect crystallinity of the material. Here, we show that dislocations can change the phase stability of alloys and increase the size of the miscibility gap. This dislocation-induced destabilization of the alloy originates from an interaction between the elastic fields of the dislocations and those due to composition variations. We predict that the characteristic time scale for the growth of compositional fluctuations depends inversely on the dislocation mobility. © 2005 American Institute of Physics. [DOI: 10.1063/1.1922578]

Determining the equilibrium phase diagrams of materials and the mechanisms by which equilibrium is achieved is a fundamental area of research, with an impact on materials technology. Most theoretical calculations of phase diagrams assume perfect crystallinity of the material; however, such perfect crystals are difficult to obtain and study experimentally, and most materials contain various defects. Of these, dislocations are ubiquitous, and because of the long-range elastic fields that they create, they can strongly affect phase stability.

This is the case in alloys which undergo spinodal decomposition with unequal lattice spacings within the compositional domains ("misfitting alloys"). In these alloys, there generally exist two spinodals, namely the so-called "coherent" and "chemical" spinodals, respectively.[1] The coherent spinodal describes the phase stability of domains which are coherent (and hence strained) across the compositional interfaces, while the chemical (or thermodynamic) spinodal dictates the thermodynamics of the alloy where interfacial misfit dislocations have relaxed these coherency strains. Although the presence of these spinodals in misfitting alloys is well known, the effect of dislocation mobility on phase stability within the chemical spinodal has not been investigated. To this end, here we present a stability analysis of the early time evolution of a binary alloy in the presence of mobile dislocations due to, e.g., prior cold work. We show that a binary alloy outside of the dislocation-free miscibility gap can be destabilized by dislocations, and quantify how the presence of mobile dislocations modifies the dispersion relation.

We now introduce our theoretical approach. The binary alloy is described by a continuous composition $c(\mathbf{r})$ and a continuous Burger's vector density $\mathbf{b}(\mathbf{r})$,[2] and the misfit between the two alloy elements is modeled as a linear dependence of the lattice constant on the composition. Thus, both the dislocation and composition fields lead to elastic displacements in the system. The free energy consists of three terms, $\mathcal{F} = \mathcal{F}_c^0\{c\} + \mathcal{F}_{\mathbf{b}}^0\{\mathbf{b}\} + \mathcal{F}_{\mathrm{el}}\{\mathbf{u}\}$, representing the free energy due to composition variations in the absence of misfit, the dislocation core energy, and the elastic free energy due to elastic displacements $\mathbf{u}$. By assuming that elastic relaxations are much faster than composition or dislocation diffusion, we eliminate $\mathbf{u}$ by solving the mechanical equilibrium equations with instantaneous composition and dislocation density profiles.[3] Substituting the obtained $\mathbf{u}(c, \mathbf{b})$ in $\mathcal{F}_{\mathrm{el}}\{\mathbf{u}\}$ gives $\mathcal{F}_{\mathrm{el}} = \mathcal{F}_{\mathrm{el}}^c\{c\} + \mathcal{F}_{\mathrm{el}}^{\mathbf{b}}\{\mathbf{b}\} + \mathcal{F}_{\mathrm{coupl}}\{c, \mathbf{b}\}$. We adopt a standard Ginzburg–Landau model for $\mathcal{F}_c^0$, giving

$$\mathcal{F}_c = \mathcal{F}_c^0 + \mathcal{F}_{\mathrm{el}}^c = \int d\mathbf{r}\left[-\frac{a}{2}c^2 + \frac{u}{4}c^4 + \frac{\xi^2}{2}|\nabla c|^2 \right], \quad (1)$$

where $a = a_0(T_c^0 - T)$ with T the temperature and T_c^0 the critical temperature in the absense of dislocations but renormalized due to composition strain fields (i.e., T_c^0 is the coherent critical point), and a_0, u, and ξ are positive constants.[4] This expression for $\mathcal{F}_c$ provides a simplified but generic description of the alloy phase diagram. $\mathcal{F}_{\mathbf{b}}$ is given by

$$\mathcal{F}_{\mathbf{b}} = \mathcal{F}_{\mathbf{b}}^0 + \mathcal{F}_{\mathrm{el}}^{\mathbf{b}} = \int d\mathbf{r}\left[\frac{\alpha}{2}|\mathbf{b}|^2 + \frac{1}{2Y}(\nabla^2 \chi_d)^2 \right]. \quad (2)$$

The first term in Eq. (2) describes the local dislocation core energy (α is a positive constant) and corresponds to $\mathcal{F}_{\mathbf{b}}^0$, while the second term accounts for the nonlocal elastic interactions between dislocations, and corresponds to $\mathcal{F}_{\mathrm{el}}^{\mathbf{b}}$. Y and χ_d denote Young modulus and Airy stress function due to dislocation strain fields, respectively. Under mechanical equilibrium conditions, the Airy stress function satisfies (Ref. 5) $\nabla^4 \chi_d = Y(\nabla_x b_y - \nabla_y b_x)$. Finally, the interaction between the composition and the dislocations arises from the linear dependence of the lattice constant on the composition and its coupling to the local compression $\nabla^2 \chi_d$,[3]

$$\mathcal{F}_{\mathrm{coupl}} = \eta \int d\mathbf{r}\, c\nabla^2 \chi_d, \quad (3)$$

where η is proportional to the misfit between the alloy elements. The dynamics of the composition and dislocation density satisfy conservation laws and are given by

$$\frac{\partial c}{\partial t} = \Gamma\nabla^2 \frac{\delta\mathcal{F}}{\delta c}, \quad (4)$$

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$$\frac{\partial b_x}{\partial t} = (\Gamma_g \nabla_x^2 + \Gamma_c \nabla_y^2) \frac{\delta \mathcal{F}}{\delta b_x}, \qquad (5)$$

and

$$\frac{\partial b_y}{\partial t} = (\Gamma_c \nabla_x^2 + \Gamma_g \nabla_y^2) \frac{\delta \mathcal{F}}{\delta b_y}. \qquad (6)$$

In Eqs. (4)–(6), Γ is the composition mobility while Γ_c and Γ_g are the dislocation mobilities in the climb and glide directions, respectively.

To simplify the analysis of the above equations and to illustrate the basic effects, we consider the case where $\Gamma_c = \Gamma_g$. Using the transformations $c \to (|a|/u)^{1/2}c$, $\mathbf{r} \to (\xi^2/|a|)^{1/2}\mathbf{r}$, $t \to (\xi^2/\Gamma|a|^2)t$, and $\mathbf{b} \to (|a|^3/Y\xi^2 u)^{1/2}\mathbf{b}$, $\chi_d \to (Y\xi^4/u)^{1/2}\chi_d$, and taking ∇_y of Eq. (5) minus ∇_x of Eq. (6), we obtain the two dimensionless *linearized* equations

$$\partial_t \delta c = \nabla^2[(\pm 1 + 3\bar{c}^2)\delta c - \nabla^2 \delta c + \gamma \Theta] \qquad (7)$$

and

$$\partial_t \Theta = -m(\Theta - \epsilon \nabla^2 \Theta + \gamma \delta c), \qquad (8)$$

where $\delta c = c - \bar{c}$, $\Theta = \nabla^2 \chi_d$, and where we have set $m_c = m_g = m$. The new dimensionless parameters are $\gamma = \eta Y^{1/2}/|a|^{1/2}$, $\epsilon = \alpha|a|/\xi^2 Y$, and $m = \Gamma_c \xi^2 Y/\Gamma|a|^2$. The top (bottom) sign in Eq. (7) represents temperatures above (below) T_c^0. Equations (7) and (8) thus contain three dimensionless parameters: γ represents the lattice misfit between the two elements of the alloy, m represents the ratio of the dislocation mobility to the composition mobility, and ϵ is the dislocation core energy.

The stability analysis is performed by letting $\delta c = \int \hat{c}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}+\sigma(\mathbf{q})t}d\mathbf{q}$ and $\Theta = \int \hat{\Theta}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}+\sigma(\mathbf{q})t}d\mathbf{q}$ and solving for $\sigma(\mathbf{q})$. Note that because the two variables are coupled, they evolve with the same dispersion relation σ and that positive (negative) values of σ lead to exponential growth (decay) of the fluctuations and thus to instability (stability). The two solutions for σ are

$$\sigma(q) = \frac{1}{2}[(\mp 1 - 3\bar{c}^2)q^2 - q^4 - m(1 + \epsilon q^2)]$$

$$\pm \frac{1}{2}\sqrt{[m(1 + \epsilon q^2) + (\mp 1 - 3\bar{c}^2)q^2 - q^4]^2 + 4m\gamma^2 q^2}. \qquad (9)$$

In the absence of coupling between the dislocations and composition, $\gamma = 0$, the solutions are $\sigma(q) = (\mp 1 - 3\bar{c}^2)q^2 - q^4$ and $\sigma(q) = -m(1 + \epsilon q^2)$. The first of these is the dispersion for the alloy without dislocations, which is positive in a range of q when the alloy is inside the dislocation-free (coherent) spinodal. The second relation is the dispersion for the dislocations in a homogenous system, which is always negative.

In the presence of the coupling γ, the behavior can be understood by performing an expansion of σ in the long-wavelength limit $q \to 0$. For a nonzero dislocation mobility $m > 0$, a straightforward calculation yields

$$\sigma(q) = (\pm 1 - 3\bar{c}^2 + \gamma^2)q^2 + O(q^4). \qquad (10)$$

Because the $O(q^4)$ terms are always negative, a necessary condition for an instability is for the coefficient of q^2 to be positive. Setting this coefficient to zero leads to the new spinodal line
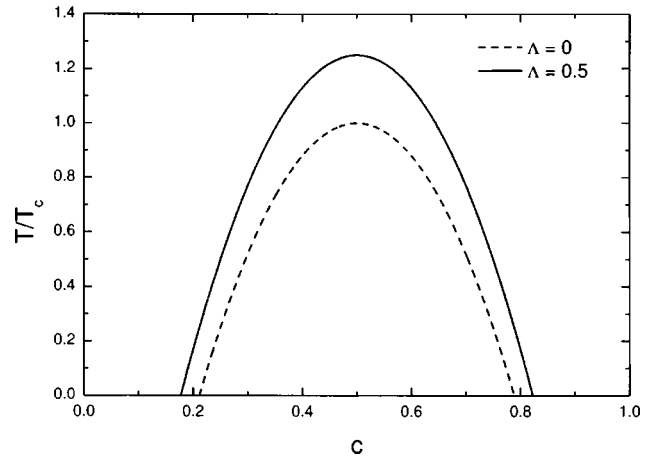

FIG. 1. Spinodal line for the binary alloy in the presence of dislocations (solid line) and without dislocations (dashed line).

$$\frac{T}{T_c^0} = 1 + \Lambda^2 - 3\left(\bar{c} - \frac{1}{2}\right)^2, \qquad (11)$$

where $\Lambda = \sqrt{\eta^2 Y / a_0 T_c^0}$. The presence of the Λ^2 term increases the size of the spinodal region, as shown in Fig. 1. In particular, the critical temperature is increased to $T_c = T_c^0(1 + \Lambda^2)$. Note that the new spinodal line is independent of the dislocation mobility, as long as it is nonzero. Physically, this is due to the fact that dislocations with nonzero mobility adiabatically follow and amplify compositional fluctuations by relaxing coherency strains in the long wavelength limit $q \to 0$.

For *immobile* dislocations ($m = 0$), the dispersion relation in Eq. (9) reduces to the dislocation-free dispersion. Hence, while immobile dislocations may locally affect the distribution of the alloy constituents around them,[3,6,7] they do not shift the location of the critical point. The increase in T_c is ultimately related to the migration of dislocations to compositional interfaces, which increases the surface tension.[8]

While the above discussion indicates that any nonzero dislocation mobility will lead to a mobility-independent shift of the spinodal line, the dislocation mobility can affect the rate at which spinodal decomposition proceeds inside of the new spinodal. This can be higlighted by looking at the dispersion relation as a function of m. Figure 2(a) shows the dispersion for an alloy above the dislocation-free critical temperature, with $\gamma = 2$ and $\epsilon = 0$. Clearly, for any nonzero mobility m, there is a region of wavevectors q where the dispersion is positive; while the size of this region is independent of m, the maximum value of the dispersion σ_{max} depends on m. Figure 2(b) indicates that the characteristic time scale $\tau = 1/\sigma_{max}$ for the growth of compositional fluctuations depends strongly on the dislocation mobility. For small dislocation mobilities, τ diverges as $1/m$. For large m, τ saturates to a value independent of m. Indeed, in the fast dislocation limit Eq. (8) gives a solution for Θ that is independent of m, and $\tau_{m\to\infty} = 4/(\gamma^2 - 1)^2$. The value of q that gives the maximum in the dispersion relation, q^*, determines the most unstable wavelength of the instability, $\lambda = 2\pi/q^*$, i.e., the composition pattern wavelength at early times. Figure 2(b) shows λ as a function of the dislocation mobility, indicating that it is much less sensitive to the dislocation mobility than τ, the dependence being close to $\lambda \sim m^{-1/4}$.
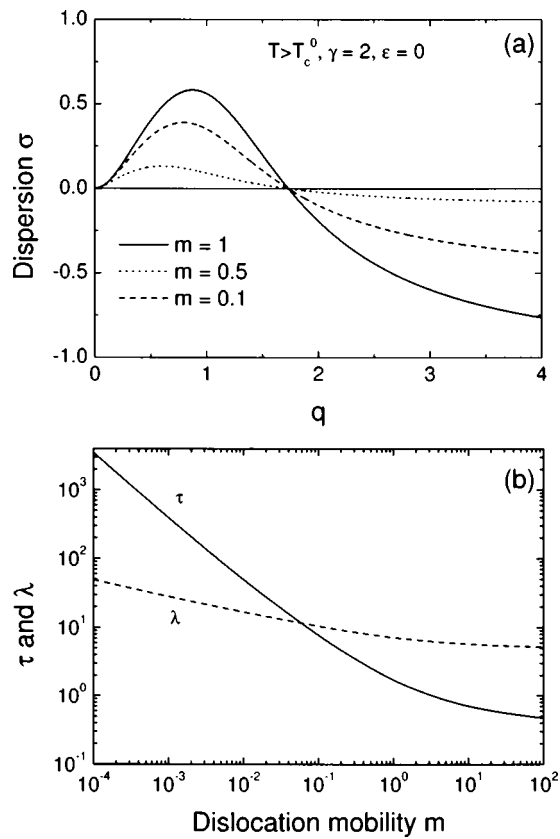
FIG. 2. Panel (a) shows the dispersion relation for different values of the dislocation mobility. Panel (b) shows the time scale for spinodal decomposition and the most unstable wavelength as a function of the dislocation mobility.
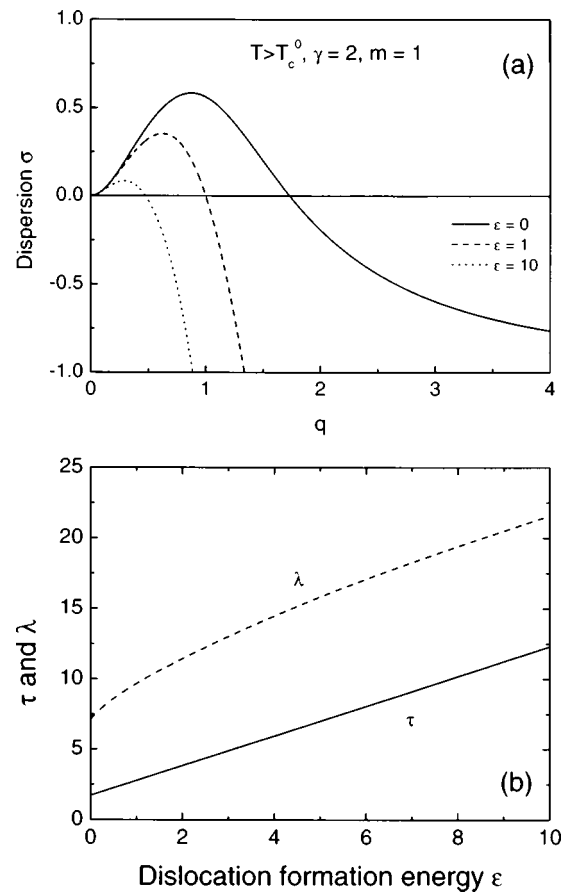

FIG. 3. Panel (a) shows the dispersion relation for different values of the dislocation formation energy. Panel (b) shows the time scale for spinodal decomposition and the most unstable wavelength as a function of the dislocation formation energy.

A parameter of importance in the current model is the core energy (i.e., the energy cost of forming dislocations) ϵ. To illustrate the role of this parameter, Fig. 3(a) shows the dispersion relation for $\gamma=2$ and $m=1$ for different values of ϵ. It is clear from the figure that the maximum of σ, the most unstable wavevector and the range of unstable modes decrease with increasing ϵ. Thus, the energy cost of forming dislocations impedes the spinodal decomposition. This is a consequence of the competition between a decrease in total energy due to the coherency strain relaxation and an increase in the total energy due to dislocation cores. The dependence of τ and λ on ϵ is shown in Fig. 3(b) which shows that the time scale for phase separation increases linearly with the dislocation formation energy, with a similar behavior for λ.

The effects described here should be most clearly observable in alloys with a large misfit, such as Al–Zn, for which $(T_c-T_c^0)/T_c^0 \approx 0.07$ and $\Lambda \approx 0.27$.[9] By subjecting the alloy to prior cold work and annealing at a temperature between the chemical and coherent critical temperatures, our predictions for the dispersion σ can be directly tested by scattering experiments (see, e.g., Refs. 9 and 10).

In summary, we have demonstrated that mobile dislocations modify the phase stability of binary alloys, leading to an increase in the size of the miscibility gap. We hope that this work will stimulate experiments and further theoretical considerations to correlate phase transformation behavior and dislocations.

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