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Thermodynamics of the solid-liquid phase equilibrium of a binary system: Effect of a chemical reaction in the liquid and epitaxial strain in the solid

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ABSTRACT

We introduce two thermodynamics models of solid-liquid phase equilibrium of a binary system in the presence of (a) a chemical reaction in the liquid involving only one of the binary components and, (b) strain-inducing epitaxial conditions on the solid in addition to the chemical reaction in the liquid. These models show the existence of the counter intuitive behavior that epitaxy may promote recrystallization of the solid in spite of the reaction driving dissolution. The conditions for this recrystallization behavior are determined by the value of the epitaxial lattice matching composition, the temperature and the overall composition of the binary solid-liquid system.

1. Introduction

Inoculation is a powerful strategy for microstructure control in traditional and emerging processing of structural alloys. Inoculation suppresses columnar grain growth during solidification resulting in a refined equiaxed microstructure with corresponding superior and uniform properties. Inoculation is introduced either through master alloys (in casting) [1] or inoculant particulate (in casting and metal additive manufacturing) [2,3]. In metal additive manufacturing, oxide, carbide or boride particles have been explored for incorporating into the metal-alloy powders [4–6]. These particles either directly promote heterogeneous nucleation of the solid from the melt or form thin layers of compounds that initiate a solidification (peritectic) reaction [1]. Both mechanisms may lead to epitaxial solidification on a solid substrate [7]. Understanding the process of solidification in casting of multicomponent alloys and especially in additive manufacturing is a major challenge as a large number of physical and chemical phenomena are at play at various length and time scales [8]. One of the major challenges is to account for the coupling between thermal, chemical, and mechanical effects acting on phases during solidification [9]. Specifically, epitaxial stresses arising from epitaxial solidification may play a significant role [10] in both casting and additive manufacturing processes. In parallel to solidification, chemical reactions such as oxidation may take place in the melt [11]. In additive manufacturing involving rapid solidification, thermal stresses may further complicate the thermodynamics (and kinetics) of the process. The seminal work of Larché and Cahn on the development of a thermodynamics of stressed solids [12–14] offers a framework for shedding light on the interplay between solid-liquid phase equilibria in the presence of mechanical stress. While solidification, especially in additive manufacturing, involves strongly nonequilibrium processes, thermodynamics may still play a crucial role in the prediction of the materials behavior during processing. In this paper, we investigate two thermodynamic model systems. The first model (model I) addresses the solid-liquid phase equilibrium of a binary system under hydrostatic pressure in the presence of a chemical reaction occurring in the liquid. The chemical process involves a third species dissolved in the liquid that reacts with only one of the components of the binary liquid. This model may therefore be used to understand the interplay between solid-liquid phase equilibrium of metallic alloys and oxygen dissolved in the melt as it combines chemically with the most reactive alloy component to form an oxide. The chemical reaction is shown to modify the composition of the solid in equilibrium with the reactive liquid. Furthermore, it is shown that a reactive species in the liquid will reduce the total amount of solid, i.e., result in dissolution. The second model (model II) extends the first one by considering the additional effect of epitaxial stress, i.e., solidification on a substrate. Here, the phenomenon of epitaxy is associated with a composition dependent elastic energy. This energy depends on the solid composition that results in lattice

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matching with the substrate. Epitaxy is shown to lead to deviations of the solid and liquid compositions from their equilibrium values under hydrostatic pressure conditions. In particular, the solid composition deviates toward the lattice matching composition to reduce the elastic energy. Furthermore, in addition to a compositional change, we show that under some circumstances, the interplay between epitaxy and the chemical reaction in the liquid, results in recrystallization, that is, an increase in the amount of solid compared to the hydrostatic value. Recrystallization occurs under specific conditions of lattice match composition, temperature and overall alloy composition. This work serves a proof of existence of solid-liquid phase equilibrium conditions such that epitaxial stress may counteract the dissolution of the solid due to chemical reactivity in the liquid by promoting recrystallization.

2. Model I: thermodynamic equilibrium between solid and liquid alloys with a chemical reaction in the liquid

Consider a composite thermodynamic system composed of a solid (S) and liquid (L). The solid is a binary solid solution (constituents 1 and 2). The liquid is composed of the species 1 and 2 but also contains a third species, 3, which can react chemically with species 1 to form a new species ($\widehat{13}$). This system is illustrated in Fig. 1. The chemical compositions of the two phases are defined by the number of moles, N_1^S and N_2^S, and N_1^L, N_2^L, N_3^L, and $N_{\widehat{13}}^L$.

The composite is in thermal and mechanical contact with a thermal reservoir and a pressure reservoir which maintain temperature (T) and pressure (P) constant. The chemical in the liquid is given by the stoichiometric reaction:

$$1_l + 3_l \rightleftharpoons \widehat{13}_l \tag{1}$$

In Eq. (1), the subscript reinforces the fact that the reaction is taking place in the liquid. We choose a 1:1:1 stoichiometry for the sake of algebraic simplicity. This choice ought not affect the conceptual conclusions of our models. The following derivations can be generalized to reactions of any stoichiometry by introducing appropriate stoichiometric coefficients.

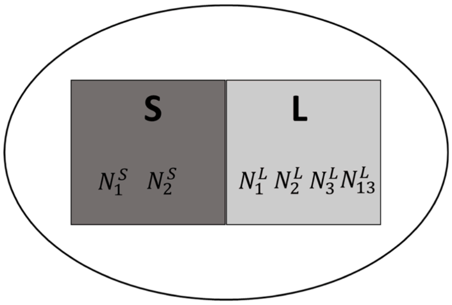

Fig. 1. Schematic representation of the two-phase solid-liquid composite system.

reaction. These two quantities can vary independently. So conservation of species 1 is written in differential form as:

$$dN_1^S = -dN_1^{L(\varphi)} \tag{5}$$

and

$$dN_1^{L(r)} = dN_3^L = -dN_{\widehat{13}}^L \tag{6}$$

Eq. (5) is a statement of the conservation of species between solid and liquid. Eq. (6) states the conservation of species 1 and 3 involved in the chemical reaction. Eq. (6) is written for the 1:1:1 stoichiometry for simplicity but can be generalized for any reaction by inserting appropriate stoichiometric coefficients without loss of linear character of the expression.

Since temperature and pressure are constant (in all equations that follow we drop any dependency on T and P), we use a Gibbs free energy representation of the composite system, G_c:

$$G_c = G^S\left(N_1^S, N_2^S\right) + G^L\left(N_1^{L(\varphi)}, N_1^{L(r)}, N_2^L, N_3^L, N_{\widehat{13}}^L\right) \tag{7}$$

The conditions for equilibrium are obtained by finding a minimum of G_c with respect to the independent variables.

The differential form of the Gibbs free energy is given by

$$\begin{aligned} dG_c = {} & \left(\frac{\partial G^S}{\partial N_1^S}\right)_{N_2^S} dN_1^S + \left(\frac{\partial G^S}{\partial N_2^S}\right)_{N_1^S} dN_2^S + \left(\frac{\partial G^L}{\partial N_1^{L(\varphi)}}\right)_{N_1^{L(r)}, N_2^L, N_3^L, N_{\widehat{13}}^L} dN_1^{L(\varphi)} + \left(\frac{\partial G^L}{\partial N_1^{L(r)}}\right)_{N_1^{L(\varphi)}, N_2^L, N_3^L, N_{\widehat{13}}^L} dN_1^{L(r)} + \\ & \left(\frac{\partial G^L}{\partial N_2^L}\right)_{N_1^{L(\varphi)}, N_1^{L(r)}, N_3^L, N_{\widehat{13}}^L} dN_2^L + \left(\frac{\partial G^L}{\partial N_3^L}\right)_{N_1^{L(\varphi)}, N_1^{L(r)}, N_2^L, N_{\widehat{13}}^L} dN_3^L + \left(\frac{\partial G^L}{\partial N_{\widehat{13}}^L}\right)_{N_1^{L(\varphi)}, N_1^{L(r)}, N_2^L, N_3^L} dN_{\widehat{13}}^L \end{aligned} \tag{8}$$

The conservation of species 2 states that:

$$N_2^S + N_2^L = N_2 \tag{2}$$

where N_2 is a constant. In differential form, conservation of two reduces to

$$dN_2^L = -dN_2^S \tag{3}$$

For species 1, we define the number of moles of 1 in the liquid as arising from two sources, namely the phase equilibrium between the solid and liquid, indicated by φ, and the chemical reaction in the liquid, indicated by r: $N_1^L = N_1^{L(\varphi)} + N_1^{L(r)}$.

Conservation of species 1 in the composite system is written as

$$N_1^S + N_1^{L(\varphi)} + N_1^{L(r)} + N_{\widehat{13}}^L = N_1 \tag{4}$$

The two quantities identified by the upper scripts φ and r refer to moles of species 1 in the liquid due to the phase equilibrium and the

Using Eqs. (3), (5) and (6) to express Eq. (8) in terms of the independent differentials dN_1^S, dN_2^S and dN_3^L and setting $dG_c = 0$, one obtains the conditions for phase and chemical equilibrium:

$$\frac{\partial G^S}{\partial N_2^S} = \frac{\partial G^L}{\partial N_2^S} \tag{9a}$$

$$\frac{\partial G^S}{\partial N_1^S} = \frac{\partial G^L}{\partial N_1^{L(\varphi)}} \tag{9b}$$

$$\frac{\partial G^L}{\partial N_1^{L(r)}} + \frac{\partial G^L}{\partial N_3^L} - \frac{\partial G^L}{\partial N_{\widehat{13}}^L} = 0 \tag{9c}$$

In Eqs. (9a)–(9c), for the sake of simplifying the notation, we have dropped the reference to the species that are kept constant. The differentials in Eqs. (9) are effectively chemical potentials. Since the chemical potential of species 1 in the liquid does not differentiate about the origin of the variation in the concentration of species 1, we can replace in Eqs.

(9b) and (9c), $\frac{\partial G^L}{\partial N_1^{L(\varphi)}}$, $\frac{\partial G^L}{\partial N_1^{L(r)}}$ by $\frac{\partial G^L}{\partial N_1^L}$. For the sake of simplicity, we choose chemical potential equations of states for ideal mixtures:

$$\frac{\partial G^I}{\partial N_i^I} = \mu_i^I = \mu_i^{0I} + RTlnX_i^I \tag{10}$$

with $I = S, L$ and $i = 1,2,3,\widehat{13}$. μ_i^{0I} are the chemical potentials of the pure species i in phase I in the standard state. X_i^I are mole fractions. This choice implies complete solubility in the solid and liquid phases.

The thermodynamic problem to solve is now the following: we start from phase equilibrium without the chemical reactions. We denote by $N_3^{L(0)}$ the initial concentration in reactive species 3. Initially, the number of moles $N_{\widehat{13}}^{L(0)} = 0$, and $N_1^{L(r)} = 0$. We define δ as a measure of the advancement of the chemical reaction. As the reaction proceeds,

$$N_3^L = N_3^{L(0)} - \delta \tag{11a}$$

$$N_{\widehat{13}}^L = 0 + \delta \tag{11b}$$

$$N_1^L = N_1^{L(\varphi)} + N_1^{L(r)} = N_1^{L(\varphi)} + 0 - \delta \tag{11c}$$

To find the equilibrium state, we have to solve for the value of the 5 quantities N_2^S, N_2^L, N_1^S, $N_1^{L(\varphi)}$ and δ. We have 3 conditions for equilibrium, Eqs. (9a)–9c) and two conditions of conservation of species, namely Eqs. (2) and (4). These five equations combined with the equations of state ((10) are sufficient to solve for the equilibrium state. To simplify the notation we redefine the variable $N_1^{L(\varphi)} = \varphi_1$ and the initial mole number $N_3^{L(0)} = n_3$. With this change in notation and Eqs. (11a)–(11c), the mole fractions for the different species in the two phases in Eq. (10) take the form:

$$X_1^S = \frac{N_1^S}{N_1^S + N_2^S} \tag{12a}$$

$$X_2^S = \frac{N_2^S}{N_1^S + N_2^S} \tag{12b}$$

$$X_1^L = \frac{\varphi_1 - \delta}{\varphi_1 - \delta + N_2^L + n_3} \tag{12c}$$

$$X_2^L = \frac{N_2^L}{\varphi_1 - \delta + N_2^L + n_3} \tag{12d}$$

$$X_3^L = \frac{n_3 - \delta}{\varphi_1 - \delta + N_2^L + n_3} \tag{12e}$$

$$X_{\widehat{13}}^L = \frac{\delta}{\varphi_1 - \delta + N_2^L + n_3} \tag{12e}$$

Using the equations of state, the conditions for equilibrium (9a) and (9b) become

$$RTln\frac{X_2^S}{X_2^L} = \mu_2^{0L} - \mu_2^{0S} \tag{13a}$$

$$RTln\frac{X_1^S}{X_1^L} = \mu_1^{0L} - \mu_1^{0S} \tag{13b}$$

Since the right-hand sides of Eqs. (13a) and (13b) represent differences in molar Gibbs free energies of the pure solid and liquids at the temperature T, they can be approximated in terms of temperature, melting point, $T_m^{(i)}$, and latent heat of fusion, L_i, of pure species, $i = 1,2$, using standard thermodynamics approaches. For instance, at the melting point of the pure substance 1, $\mu_1^{0L}(T_m^{(1)}) = \mu_1^{0S}(T_m^{(1)})$. Expressing the molar Gibbs free energies in terms of molar enthalpy and entropy, we get $h_1^{0L}(T_m^{(1)}) - T_m^{(1)} s_1^{0L}(T_m^{(1)}) = h_1^{0S}(T_m^{(1)}) - T_m^{(1)} s_1^{0S}(T_m^{(1)})$ or $h_1^{0L}(T_m^{(1)}) - h_1^{0S}(T_m^{(1)}) = T_m^{(1)}[s_1^{0L}(T_m^{(1)}) - s_1^{0S}(T_m^{(1)})]$. At the temperature, T, the right-hand side of Eq. (13b) is $\mu_1^{0L}(T) - \mu_1^{0S}(T) = (h_1^{0L}(T) - h_1^{0S}(T)) - T[s_1^{0L}(T) - s_1^{0S}(T)]$. Assuming that the difference in enthalpies and in entropy are not too sensitive to temperature, this later relation can be approximated by $\mu_1^{0L}(T) - \mu_1^{0S}(T) = (h_1^{0L}(T_m^{(1)}) - h_1^{0S}(T_m^{(1)})) - T[s_1^{0L}(T_m^{(1)}) - s_1^{0S}(T_m^{(1)})]$. Replacing the difference in entropy by the difference in enthalpy divided by the melting temperature, yields $\mu_1^{0L}(T) - \mu_1^{0S}(T) = (h_1^{0L}(T_m^{(1)}) - h_1^{0S}(T_m^{(1)}))\left[1 - \frac{T}{T_m^{(1)}}\right]$. Note that the difference in enthalpy between the pure liquid and the solid at the melting temperature is the latent heat of fusion of species 1, namely L_1. Employing a similar argument for the pure species 2, the conditions for equilibrium (Eqs. (13a) and (13b)) become:

$$X_2^S = E_2 X_2^L \tag{14a}$$

$$X_1^S = E_1 X_1^L \tag{14b}$$

where $E_i = e^{L_i\left(1 - \frac{T}{T_m^{(i)}}\right)\Big/RT}$. We note that if $T_m^{(1)} > T_m^{(2)}$, then $L_1\left(1 - \frac{T}{T_m^{(1)}}\right)\Big\rangle 0$ and $L_2\left(1 - \frac{T}{T_m^{(2)}}\right)\Big\langle 0$, leading to $E_1 > 1$ and $E_2 < 1$. Similarly, if $T_m^{(1)} < T_m^{(2)}$, $E_1 < 1$ and $E_2 > 1$.

The condition for equilibrium (9c), takes the familiar form:

$$K = e^{\left(\mu_1^{0L} + \mu_3^{0L} - \mu_{\widehat{13}}^{0L}\right)/RT} = \frac{X_{\widehat{13}}^L}{X_1^L X_3^L} \tag{14c}$$

where K is the reaction constant for the chemical reaction (1).

Inserting the conservation Eq. (2), $N_2^L = N_2 - N_2^S$ and (4) expressed in terms of φ_1 and δ namely, $\varphi_1 = N_1 - N_1^S$, into the conditions for equilibrium (14a)–(14c) yields three equations which can be used to solve for the three unknowns N_1^S, N_2^S, and δ. These three equations take the form:

$$\frac{N_2 - Y_2}{N_1 + N_2 - Y_1 - Y_2} = E_2 \frac{Y_2}{Y_1 + Y_2 + Y_3} \tag{15a}$$

$$\frac{N_1 - Y_1}{N_1 + N_2 - Y_1 - Y_2} = E_1 \frac{Y_1 + Y_3 - n_3}{Y_1 + Y_2 + Y_3} \tag{15b}$$

$$K = \frac{(n_3 - Y_3)(Y_1 + Y_2 + Y_3)}{(Y_1 + Y_3 - n_3)Y_3} \tag{15c}$$

where we have made the change in variables, $Y_1 = \varphi_1 = N_1 - N_1^S$, $Y_2 = N_2^L = N_2 - N_2^S$ and $Y_3 = n_3 - \delta$.

After a significant number of algebraic steps, we have eliminated the variable Y_3 and obtained two equations in Y_1 and Y_2:

$$-\frac{n_3 + (1 - E_2)Y_2}{1 - E_1} = \frac{E_2}{E_1} Y_2 \frac{(N_1 - Y_1)}{(N_2 - Y_2)} \tag{16a}$$

$$(1 - E_1)Y_1 + (1 - E_2)Y_2 + E_1 n_3 \left[(1 - E_1)\frac{f(Y_2)}{K + E_1 f(Y_2)} + 1\right] = 0 \tag{16b}$$

In Eq. (16b) we have defined

$$f(Y_2) = 1 - \frac{E_2(1 - E_1)}{E_1} \frac{Y_2}{n_3 + (1 - E_2)Y_2} \tag{17}$$

Finally, eliminating Y_1, we obtain a single equation in Y_2 alone:

$$-\frac{N_2 - Y_2}{1 - f(Y_2)} = N_1 + \frac{(1 - E_2)}{(1 - E_1)} Y_2 + E_1 n_3 \left[\frac{1}{(1 - E_1)} + \frac{f(Y_2)}{K + E_1 f(Y_2)}\right] \tag{18}$$

We are now seeking an approximate solution to Eq. (18) by assuming that n_3 is small. That is, the initial number of moles of reactive species 3 in the liquid is small. Using Taylor expansions, we approximate the function $f(Y_2)$ in the limit of small n_3 by:

$$f(Y_2) \sim 1 - \frac{E_2}{E_1}\frac{(1-E_1)}{(1-E_2)}\left[1 - \frac{n_3}{(1-E_2)Y_2}\right] \tag{19}$$

Inserting this approximate function into Eq. (18) and making additional use of Taylor expansions, Eq. (18) can be linearized in n_3:

$$\begin{aligned}&\frac{N_1E_2(1-E_1)+N_2E_1(1-E_2)}{E_2(1-E_1)}\\ &\quad + n_3E_1\left\{\frac{E_1(1-E_2)-E_2(1-E_1)}{E_1[(K+E_1)(1-E_2)-E_2(1-E_1)]}+\frac{1}{(1-E_1)}\left(1-\frac{1}{E_2}\right)\right\}\\ &\quad + \frac{(1-E_2)}{(1-E_1)}\frac{(E_2-E_1)}{E_2}Y_2 + n_3\frac{N_2E_1}{E_2(1-E_1)}\frac{1}{Y_2}\\ &\quad = 0\end{aligned} \tag{20}$$

We note that when $n_3 = 0$, i.e., there is no chemical reaction, Eq. (20) gives the solution

$$Y_2^{(0)} = -\frac{E_1}{(E_2-E_1)}\left[N_1\frac{E_2(1-E_1)}{E_1(1-E_2)}+N_2\right] \tag{21}$$

We can further linearize Eq. (20) by assuming that the quantity $Y_2 = Y_2^{(0)} + \Delta Y_2$. The change ΔY_2 is therefore considered to be small since n_3 is small. Making use of Taylor expansions to first order, Eq. (20) enables us to get the expression:

$$\Delta Y_2\frac{(1-E_2)}{(1-E_1)}\frac{(E_2-E_1)}{E_2} \sim -n_3\left[\frac{E_1(1-E_2)-E_2(1-E_1)}{[(K+E_1)(1-E_2)-E_2(1-E_1)]}+\frac{E_1}{E_2(1-E_1)}\left(E_2-1+\frac{N_2}{Y_2^{(0)}}\right)\right] \tag{22}$$

If we further assume that the reaction constant, K, is large the first term in the square bracket on the right-hand side of Eq. (22) can be neglected. This is the case if the chemical reaction favors the formation of species $\widehat{13}$. Eq. (22) simplifies to

$$\Delta Y_2\frac{(1-E_2)}{(1-E_1)}\frac{(E_2-E_1)}{E_2} \sim -n_3\frac{E_1}{E_2(1-E_1)}\left(E_2-1+\frac{N_2}{Y_2^{(0)}}\right) \tag{23}$$

We now consider two cases. Case I corresponds to $E_1 > 1$ and $E_2 < 1$ and Case II corresponds to $E_1 < 1$ and $E_2 > 1$. Furthermore, we note that since $Y_2^{(0)} = N_2 - N_2^{S(0)}$, the quantity $\frac{N_2}{Y_2^{(0)}}$ is greater than one.

In case I, the quantity $V = \frac{(1-E_2)}{(1-E_1)}\frac{(E_2-E_1)}{E_2} > 0$ and $W = \frac{E_1}{E_2(1-E_1)}\left(E_2 - 1 + \frac{N_2}{Y_2^{(0)}}\right)\Bigg\langle 0$, Eq. (23) results in $\Delta Y_2 > 0$. In case II, $V < 0$ and $W > 0$ so $\Delta Y_2 > 0$ as well. This result means that $Y_2 > Y_2^{(0)}$ in both cases. Since $Y_2 = N_2 - N_2^S$ and $Y_2^{(0)} = N_2 - N_2^{S(0)}$, we must have $N_2^S < N_2^{S(0)}$. The chemical reaction involving species 1, reduces the number of moles of species 2 in the solid in both cases.

The question that remains concerns the number of moles of species 1 in the solid in the presence of the chemical reaction in the liquid. Eqs. (16a) and (17) can be combined to give:

$$N_1 - Y_1 = -\frac{N_2-Y_2}{1-f(Y_2)} \tag{24}$$

To zeroth order in n_3, Eq. (24) yields:

$$N_1^S \sim -\frac{E_1(1-E_2)}{E_2(1-E_1)}N_2^S \tag{25}$$

In both cases I and II, $\frac{E_1(1-E_2)}{E_2(1-E_1)}$ is negative, leading to N_1^S to be proportional to N_2^S. A decrease in N_2^S due to the chemical reaction results also in a decrease in N_1^S. The total number of moles of solid $N^S = N_1^S + N_2^S$ is reduced due to the chemical reaction. In other words, the chemical reaction in the liquid involving species 1 promotes the dissolution of the entire solid.

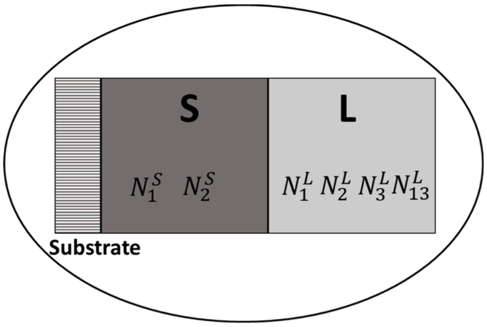

Fig. 2. Schematic representation of the two-phase solid-liquid composite system with the solid forming epitaxially on a substrate.

In summary, we can understand the behavior of model I, by considering first the solid-liquid phase equilibrium without chemical reaction. There are two contributions to the total free energy of the composite system. Both are related to the free energy of mixing of chemical species in the solid and in the liquid. Solid-liquid phase equilibrium is achieved by minimizing the sum of these two contributions. Finding the equilibrium compositions of the solid and liquid at a given temperature is equivalent to the usual common tangent construction. Turning on the chemical reaction, one effectively adds to the composite free energy a free energy of reaction. Finding the equilibrium states requires minimization of the sum of three contributions: solid and liquid free energies of mixing and the reaction free energy. This later contribution displaces the equilibrium composition of the liquid and subsequently the composition of the solid. A large reaction constant, K, dissolves the solid.

3. Model II: thermodynamic equilibrium between a solid alloy growing epitaxially on a substrate and a liquid alloy with a chemically reactive species

The system is similar to that introduced in Section 2 but now the solid is forming epitaxially on a substrate (see Fig. 2).

Since the lattice parameter of the crystalline solid depends on the solid composition, we assume that there exists a solid mole fraction, X_C, for which the lattice matches that of the substrate. For all other compositions, the epitaxial condition imposes deformation of the solid. The epitaxial lattice matching condition, therefore, introduces a source of elastic energy in the composite system. Considering a linear relation between the lattice spacing in the solid alloy as a function of mole fraction, the epitaxial strain will be proportional to the quantity, $X_2^S - X_C$. One could equivalently use compositions in terms of species 1. The elastic energy is subsequently given by a quadratic function of the strain leading to an epitaxial energy of the form:

$$E^S = AN^S\left(X_2^S - X_C\right)^2, \tag{26}$$

where $N^S = N_1^S + N_2^S$ is the total number of moles of solid (which is not constrained).

The first parenthesis in Eq. (26) indicates that the elastic energy scales as the amount of solid alloy. The positive quantity A is related to the elastic coefficient of the solid. We make the simplifying assumption that the elastic coefficients and subsequently A are independent of the solid composition. Eq. (26) is inspired by models of liquid-phase epitaxy developed to investigate the effect of epitaxial stress on solid-liquid equilibria [15,16]. Eq. (26) can be understood as follows. A solid free from any mechanical constraint which composition X_2^S differs from the epitaxial lattice matching composition X_C, would exhibit, within a linear approximation, a chemical strain described by the tensor: $\boldsymbol{\varepsilon}^c = \eta(X_2^S - X_C)\boldsymbol{I}$, where $\boldsymbol{I}$ is the identity matrix.This strain is measured with respect to the lattice spacing at the composition X_C. The linear coefficient η is the chemical expansion coefficient of the solid. Epitaxial match of the lattice parameters of the film and substrate can be achieved by applying a two-dimensional stress on to the film. This plane stress should compensate the chemical expansion and is related to $\boldsymbol{\varepsilon}^c$ by:

$$\sigma_{11} = (\lambda+2\mu)\left(-\varepsilon_{11}^c\right) + \lambda\left(-\varepsilon_{22}^c\right)$$

$$\sigma_{22} = \lambda\left(-\varepsilon_{11}^c\right) + (\lambda+2\mu)\left(-\varepsilon_{22}^c\right)$$

$$\sigma_{12} = \sigma_{21} = 0$$

where λ and μ are the Lamé coefficients of the solid assumed to be isotropic for simplicity. The strain elastic energy per unit volume of solid involves sums of the square of σ_{11}, σ_{22} and cross terms $\sigma_{11}\sigma_{22}$ which will all be proportional to $(X_2^S - X_C)^2$. Dividing by the molar volume of the solid and multiplying by the total number of moles of solid, $N_1^S + N_2^S$, gives the total elastic energy of the solid or Eq. (25). Following the original formulation by Larché and Cahn [12], we consider elastic effects to be the dominant non-chemical energy contribution controlling the amount of solid in equilibrium with the liquid. The interfacial energy may also play a role; however, the epitaxial condition implies that the interfacial energy is at its minimum. Furthermore, the interfacial energy contribution is confined to the interfacial regions, while the elastic energy acts in the bulk.

This additional energy affects the functional form of the chemical potentials of species 1 and 2 in the solid.

$$\mu_2^S = \frac{\partial(G^S + E^S)}{\partial N_2^S} = \mu_2^{0S} + RTlnX_2^S + A\left(X_2^S - X_C\right)^2 + 2A\left(X_2^S - X_C\right)X_1^S \tag{27a}$$

$$\mu_1^S = \frac{\partial(G^S + E^S)}{\partial N_1^S} = \mu_1^{0S} + RTlnX_1^S + A\left(X_2^S - X_C\right)^2 - 2A\left(X_2^S - X_C\right)X_2^S \tag{27b}$$

Here, the mole fractions are pertinent variables. For the epitaxial system, the conditions for equilibrium (9a) and (9b) become:

$$RTln\frac{X_2^S}{X_2^L} + A\left(X_2^S - X_C\right)^2 + 2A\left(X_2^S - X_C\right)X_1^S = E_2 \tag{28a}$$

$$RTln\frac{X_1^S}{X_1^L} + A\left(X_2^S - X_C\right)^2 - 2A\left(X_2^S - X_C\right)X_2^S = E_1 \tag{28b}$$

In writing Eq. (28) similarly to Section 2 we have approximated the difference in molar Gibbs free energy of the pure substances in their standard state in terms of temperature, the latent heat of fusion and the melting point.

To advance further, we are now assuming that the epitaxial elastic energy affects the mole fractions of the species 1 and 2 in the solid and the liquid only slightly. That is, we use the equilibrium state under hydrostatic pressure investigated in Section 2 as a reference. With this, we write:

$X_1^S = X_1^{oS} + \delta X_1^S$, $X_2^S = X_2^{oS} + \delta X_2^S$, $X_1^L = X_1^{oL} + \delta X_1^L$, and $X_2^L = X_2^{oL} + \delta X_2^L$. The quantities, X_i^{oI} are the equilibrium mole fraction of species i in phase I, in the presence of the chemical reaction in the liquid but in absence of epitaxial elastic energy (i.e., under hydrostatic pressure). The δX_i^I that represent the change in mole fraction of i as a result of epitaxy are hypothesized to be small. Inserting these expressions in Eqs. (28), linearizing the ln functions using Taylor expansions and realizing that the terms $RTln\frac{X_2^{0S}}{X_i^{0L}} = E_i$, the conditions for equilibrium reduce to:

$$\frac{\delta X_2^S}{X_2^{oS}} - \frac{\delta X_2^L}{X_2^{oL}} + A\left(X_2^{oS} + \delta X_2^S - X_C\right)^2 + 2A\left(X_2^{oS} + \delta X_2^S - X_C\right)\left(X_1^{oS} - \delta X_2^S\right) = 0 \tag{29a}$$

$$-\frac{\delta X_2^S}{X_1^{oS}} + \frac{\delta X_2^L}{X_1^{oL}} + A\left(X_2^{oS} + \delta X_2^S - X_C\right)^2 - 2A\left(X_2^{oS} + \delta X_2^S - X_C\right)\left(X_2^{oS} + \delta X_2^S\right) = 0 \tag{29b}$$

To write Eqs. (29) we have also used the property of mole fractions $X_1^S = 1 - X_2^S$ and $X_1^L = 1 - X_2^L$ leading to $\delta X_1^S = -\delta X_2^S$ and $\delta X_1^L = -\delta X_2^L$.

Note that we have here two equations and two unknowns δX_2^S and δX_2^L. We do not need to use the condition for equilibrium relative to the chemical reaction in the liquid at this time. Since Eq. (29) give only variations in mole fractions, we will use the third condition for equilibrium to extract values of the number of moles in the solid under epitaxial conditions.

Eliminating δX_2^L between Eq. (29) give the quadratic equation in δX_2^S:

$$\begin{aligned}&-\left(X_1^{oL} + X_2^{oL}\right)\left(\delta X_2^S\right)^2 + \left[\frac{1}{A}\left(\frac{X_2^{oL}}{X_2^{oS}} - \frac{X_1^{oL}}{X_1^{oS}}\right) - 2\left(X_1^{oL}X_2^{oS} - X_2^{oL}X_1^{oS}\right)\right]\delta X_2^S \\ &\quad + \left(X_2^{oS} - X_C\right)\left[\left(X_2^{oS} - X_C\right) - 2\left(X_1^{oL}X_2^{oS} - X_2^{oL}X_1^{oS}\right)\right] \\ &\quad = 0\end{aligned} \tag{30}$$

To first order for small δX_2^S, the quadratic term is neglected and after some algebraic manipulations we get

$$\delta X_2^S \sim -AX_2^{oS}\left(1 - X_2^{oS}\right)\left(X_2^{oS} - X_C\right)\left[\frac{X_2^{oS} - X_C}{X_2^{oS} - X_2^{oL}} - 2\right] \tag{31}$$

Establishing that $X_C = X_2^{oS} \pm \alpha$, that is, X_C is either on the left (- sign) or right (+ sign) side of X_2^{oS} with a small deviation α. The square bracket is always negative and the sign of δX_2^S is determined by the sign of $-(X_2^{oS} - X_C)$. If X_C is to the right of X_2^{oS}, then $\delta X_2^S > 0$. If X_C is to the left of X_2^{oS}, then $\delta X_2^S < 0$. In both cases, minimization of the epitaxial elastic energy pushes the equilibrium mole fraction away from the hydrostatic pressure value and toward the composition X_C. This result is consistent with other studies of the effect of epitaxy of semi-conductor alloys [15, 16].

Using Eqs. (29b) and (31), we find

$$\delta X_2^L \sim A\frac{X_2^{oL}\left(1 - X_2^{oS}\right)}{X_2^{oS} - X_2^{oL}}\left(X_2^{oS} - X_C\right)^2 \tag{32}$$

So irrespectively of the sign of $X_2^{oS} - X_C$, δX_2^L has always the same sign.

We recall that the hydrostatic pressure compositions X_2^{oS} and X_2^{oL} are those derived in the presence of chemical reaction in the liquid. So far, we have focused on the effect of epitaxy on the mole fraction in the solid. The question that arises is that of the effect of epitaxy on the number of moles of species 1 and 2 in the solid and the overall amount of solid.

Let us denote by N_1^{oS}, N_2^{oS}, N_1^{oL}, N_2^{oL}, the number of moles of species 1 and 2 in the solid and liquid in equilibrium in the presence of the chemical reaction under hydrostatic pressure. Let us also define the number of moles of species $i = 1$ or 2 in the phase $I =$ S,L (liquid with chemical reaction) when the solid is subjected to epitaxial conditions by:

$$N_i^{eI} = N_i^{oI} + \delta N_i^{eI} \tag{33}$$

δN_i^{eI} is the change in the number of moles of i in I due to epitaxy. We can write:

$$X_2^S = X_2^{oS} + \delta X_2^S = \frac{N_2^{oS} + \delta N_2^{eS}}{N_1^{oS} + \delta N_1^{eS} + N_2^{oS} + \delta N_2^{eS}}$$

Again using Taylor expansion for small variations in the number of moles due to epitaxy, leads to a relationship between δX_2^S and δN_1^{eS} and δN_2^{eS}, that is:

$$\delta X_2^S = \frac{N_1^{oS} N_2^{oS}}{\left(N_1^{oS} + N_2^{oS}\right)^2}\left(\frac{\delta N_2^{eS}}{N_2^{oS}} - \frac{\delta N_1^{eS}}{N_1^{oS}}\right) \tag{34a}$$

Similarly, we find for the liquid

$$\delta X_2^L = \frac{N_1^{oL} N_2^{oL}}{\left(N_1^{oL} + N_2^{oL}\right)^2}\left(\frac{\delta N_2^{eL}}{N_2^{oL}} - \frac{\delta N_1^{eL}}{N_1^{oL}}\right) \tag{34b}$$

We now have four unknowns δN_1^{eS}, δN_2^{eS}, δN_1^{eL}, δN_2^{eL}. Conservation of the number of species 2 implies $\delta N_2^{eS} = -\delta N_2^{eL}$ which reduces the number of unknowns to three: δN_1^{eS}, δN_2^{eS}, and δN_1^{eL}.

We also express the advancement of the chemical reaction when the solid is under epitaxial conditions in terms of the advancement of the reaction under hydrostatic pressure as follows:

$\delta^e = \delta^o + d\delta$ where $d\delta$ is the variation in the reaction advancement δ. Extension of Eq. (11c) to the case of an epitaxial solid yield $N_1^{eL} = \varphi_1^e - \delta^e$ with $\varphi_1^e = N_1 - N_1^{eS}$. Similarly to the definition of epitaxial quantities in terms of hydrostatic quantities, we write $\varphi_1^e = \varphi_1^o + d\varphi_1$. These relations can be used to show that $d\delta = -\left(\delta N_1^{eL} + \delta N_1^{eS}\right)$.

In addition to Eqs. (31) and (32), we can use the condition for chemical equilibrium given by Eq. (15c) but expressing in the case of an epitaxial solid:

$$K = \frac{(n_3 - Y_3)(Y_1 + Y_2 + Y_3)}{(Y_1 + Y_3 - n_3)Y_3} = \frac{\delta^e\left(N_1 - N_1^{eS} + N_2 - N_2^{eS} + n_3 - \delta^e\right)}{\left(N_1 - N_1^{eS} - \delta^e\right)(n_3 - \delta^e)} \tag{35}$$

Expressing all epitaxial quantities in Eq. (35) in terms of hydrostatic quantities and their corresponding variations and using again Taylor expansions to first order, Eq. (35) becomes:

$$K = \frac{\delta^o\left(N_1 - N_1^{oS} + N_2 - N_2^{oS} + n_3 - \delta^o\right)}{\left(N_1 - N_1^{oS} - \delta^o\right)(n_3 - \delta^o)}(1 - B + C) \tag{36}$$

where

$$B \sim \frac{\delta^o\left(\delta N_2^{eS} - \delta N_1^{eL}\right) + \left(\delta N_1^{eL} + \delta N_1^{eS}\right)\left[N_1 - N_1^{oS} + N_2 - N_2^{oS} + n_3 - \delta^o\right]}{\delta^o\left[N_1 - N_1^{oS} + N_2 - N_2^{oS} + n_3 - \delta^o\right]} \tag{37}$$

$$C \sim \frac{\delta N_1^{eS}(n_3 - \delta^o) - \left(\delta N_1^{eL} + \delta N_1^{eS}\right)\left(N_1 - N_1^{oS}\right)}{\left(N_1 - N_1^{oS}\right)(n_3 - \delta^o)} \tag{38}$$

Since under hydrostatic pressure, we have $K = \frac{\delta^o\left(N_1 - N_1^{oS} + N_2 - N_2^{oS} + n_3 - \delta^o\right)}{\left(N_1 - N_1^{oS} - \delta^o\right)(n_3 - \delta^o)}$, Eq. (36) reduces to the condition $C = B$. This condition involves δN_1^{eS}, δN_2^{eS}, and δN_1^{eL} and serves as our third equation.

This condition is reformulated as

$$\begin{aligned}\delta N_1^{eS}&\left[\frac{1}{N_1 - N_1^{oS}} - \frac{n_3}{\delta^o(n_3 - \delta^o)}\right] \\ &+ \delta N_1^{eL}\left[\frac{1}{N_1 - N_1^{oS} + N_2 - N_2^{oS} + n_3 - \delta^o} - \frac{n_3}{\delta^o(n_3 - \delta^o)}\right] \\ &= \delta N_2^{eS}\frac{1}{N_1 - N_1^{oS} + N_2 - N_2^{oS} + n_3 - \delta^o}\end{aligned} \tag{39}$$

In the limit of small concentration of species 3, n_3, and subsequently small advancement of the reaction under hydrostatic conditions, δ^o, Eq. (39) is approximated by retaining only the large term $\frac{n_3}{\delta^o(n_3 - \delta^o)}$ in the square brackets. Eq. (39) simplifies to

$$\delta N_1^{eS} + \delta N_1^{eL} = \delta N_2^{eS}\frac{-\delta^o(n_3 - \delta^o)}{n_3\left(N_1 - N_1^{oS} + N_2 - N_2^{oS}\right)} \tag{40}$$

Combining Eqs. (31), (32), (34) and (40) yields:

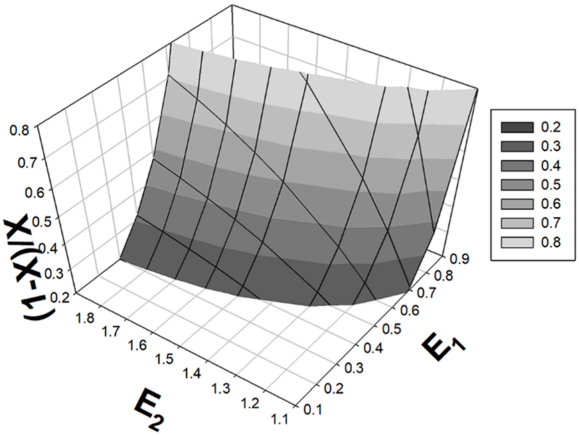

Fig. 3. Physically realistic conditions that satisfy the relation $-\frac{E_1(1-E_2)}{E_2(1-E_1)} = \frac{1-X}{X}$. Here we have chosen $E_1 < 1$ and $E_2 > 1$ corresponding to pure substances with melting points $T_m^{(1)} < T_m^{(2)}$.

$$\begin{aligned}&\delta N_2^{eS}\left[\frac{N_1^{oS}}{N_2^{oS}} - \frac{N_1^{oL}}{N_2^{oL}} + \frac{\delta^o(n_3 - \delta^o)}{n_3\left(N_1 - N_1^{oS} + N_2 - N_2^{oS} + n_3 - \delta^o\right)}\right] \\ &= \frac{\left(N_1^{oS} + N_2^{oS}\right)^2}{N_2^{oS}}\delta X_2^S + \frac{\left(N_1^{oL} + N_2^{oL}\right)^2}{N_2^{oL}}\delta X_2^L\end{aligned} \tag{41}$$

The second term on the right-hand side of this equation is always positive since $\delta X_2^L > 0$ (see Eq. (34b). The first term can be either positive or negative depending on the sign of δX_2^S (see Eq. (34a). It is definitively positive when $X_C > X_2^{oS}$. In that case the right hand-side of Eq. (41) is positive. We therefore need to address the sign of the square bracket on the left-hand side of (41). The third term in the bracket is positive since δ^o cannot exceed n_3. We rewrite the first two terms $\frac{N_1^{oS}}{N_2^{oS}} - \frac{N_1^{oL}}{N_2^{oL}} = \frac{N_1^{oS}N_2 - N_2^{oS}N_1 + \delta^o N_2^{oS}}{N_2^{oS}(N_2 - N_2^{oS})}$ using conservation of species relations. This quantity is positive if $N_1^{oS}N_2 - N_2^{oS}N_1 > 0$, or $\frac{N_1^{oS}}{N_2^{oS}} > \frac{N_1}{N_2}$. Using Eq. (25) for the hydrostatic case, the inequality becomes $-\frac{E_1(1-E_2)}{E_2(1-E_1)} > \frac{N_1}{N_2}$. Introducing the overall composition of the composite system in terms of a mole fraction $X = \frac{N_2}{N_1 + N_2}$, the inequality becomes $-\frac{E_1(1-E_2)}{E_2(1-E_1)} > \frac{1-X}{X}$. Note that the left term in that inequality is always positive. The adjustable parameters to achieve physically realistic conditions that satisfy this inequality are X and temperature T which determines the values of E_1 and E_2 (see Fig. 3). Figure 3 indicate that there is a wide range of values for these parameters that leads to an increase in δN_2^{eS}.

The inequalities $X_C > X_2^{oS}$ and $-\frac{E_1(1-E_2)}{E_2(1-E_1)} > \frac{1-X}{X}$ enable us to make a statement about the existence of conditions for $\delta N_2^{eS} > 0$. $\delta N_2^{eS} > 0$ means that the solid forming epitaxially leads to an increase in the number of moles of species 2 in the solid compared to the hydrostatic pressure case.

We finally consider the effect of epitaxy on δN_1^{eS}. Combining Eqs. (34b) and (40) gives

$$\delta N_1^{eS} = \frac{\left(N_1^{oL} + N_2^{oL}\right)^2}{N_2^{oL}}\delta X_2^L + \delta N_2^{eS}\left[\frac{N_1^{oL}}{N_2^{oL}} - \frac{\delta^o(n_3 - \delta^o)}{n_3\left(N_1 - N_1^{oS} + N_2 - N_2^{oS}\right)}\right] \tag{42}$$

In the limit of small n_3 and δ^o, the term inside the square bracket is positive. Since δX_2^L is always positive, when the inequalities $X_C > X_2^{oS}$ and $-\frac{E_1(1-E_2)}{E_2(1-E_1)} > \frac{1-X}{X}$ are satisfied, then $\delta N_2^{eS} > 0$ and subsequently $\delta N_1^{eS} > 0$.

The epitaxial condition leads to an increase in the number of moles of species 1 and 2 in the solid and therefore an increase in the amount of solid compared to the hydrostatic case. While the chemical reaction in the liquid state decreases the amount of solid that can form at equilibrium, i.e., lead to dissolution of the solid, epitaxy can counteract this effect and lead to recrystallization.

This observation can be rationalized as follows. The equilibrium state of the composite system with chemical reaction in the liquid and with epitaxial strain energy is found by minimizing the total free energy. This free energy is now the sum of solid and liquid free energies of mixing, free energy of reaction and elastic energy. By changing its molar fraction composition, X_2^S toward X_C, the solid reduces the quadratic term in the elastic energy Eq. (26), namely, $(X_2^S - X_C)^2$. However, by increasing the amount of solid, the composite system may attempt to approach the low free energy associated with the equilibrium of the composite system without chemical reaction. More solid increases the elastic energy by increasing the term $(N_1^S + N_2^S)$ in Eq. (26). However, the increase in this linear term is more easily compensated by the faster decreasing quadratic term $(X_2^S - X_C)^2$.

4. Summary and conclusion

The thermodynamic analysis of models of solid-liquid phase equilibrium of a binary system in the presence of (a) a chemical reaction in the liquid involving only one of the binary components and, (b) epitaxial conditions on the solid in addition to the chemical reaction in the liquid, leads to the counter intuitive observation that epitaxy may promote recrystallization of the solid in spite of the reaction driving dissolution. As expected, the composition of the epitaxial solid deviates, from its hydrostatic pressure counterpart, toward the lattice matching composition. However, the models demonstrate the existence of solid-liquid phase equilibrium conditions such that epitaxial stress may counter act the dissolution of the solid due to chemical reactivity. These conditions are determined by the value of the lattice matching composition, the temperature and the overall composition of the binary solid-liquid system. These models were presented in the context of powder bed fusion additive manufacturing of metallic alloys, however, they are readily applicable to other multicomponent materials systems involving equilibrium between a solid phase and a liquid phase with chemical reactivity in the liquid. The effect of internal epitaxial strain/stress (i.e., composition dependent elastic energy) on dissolution/recrystallization reported here may also be extended to externally applied strain/stress provided the elastic constants of the solid are composition dependent. This may be the case in the dissolution and recrystallization of minerals in biological tissues such as bone in the presence of stress and chemical reaction in physiological fluids [17]. Further, the developed models are equally applicable to understanding the melt-recrystallization process of multicomponent geo-materials [18] and aqueous altering of planetary minerals [19], where the role of non-hydrostatic stresses when coupled with chemical reactivity can significantly affect the equilibrium composition and phase stability of the minerals. To the best of our knowledge, thermodynamic models that are used to interpret the processing conditions that underlie the formation of these minerals, do not account for the interplay of epitaxial stresses and chemical reactivity, and the ready extension of the developed models can enable new insights as well as better constraints on processing of geo and planetary materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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