Thermodynamics of Open Two-Phase Systems with Coherent Interfaces

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(Received 15 July 1994)

We develop the thermodynamic theory for the decomposition of a "coherent" two-phase open system consisting of an interstitial solid solution in equilibrium with a gas reservoir of solute atoms. It is shown that, contrary to what is expected for incoherent systems, the phase rule is inapplicable and the "plateau" on the pressure-composition isotherm does not correspond to two coexisting phases. The coherency strain introduces an unsurmountable macroscopic energy barrier between the transforming phases, which prevents the coexistence of the phases and results in a reversible hysteresis in the pressure-composition isotherm. The proposed theory is applicable to metal-hydrogen systems.

PACS numbers: 64.70.kb, 64.60.–z, 81.30.–t

It is well known that in two-phase systems with coherent interfaces the transformation-induced strain has a profound effect on the phase transformation thermodynamics, sometimes qualitatively changing its character [1,2]. The elastic strain generated by the interfaces is infinitely long ranged and thus the strain-induced interaction between the coexisting coherent phases is infinite ranged as well. This has two nontrivial implications. The first is that the elastic energy contribution to the total free energy of the coherent system is nonadditive, i.e., it does not meet the major requirement of the Gibbs thermodynamics. Instead, the total free energy of the coherent system depends nonlinearly on the volume fractions of the coexisting phases [3]. As a result, the volume fractions of the coexisting coherent phases become internal thermodynamic parameters which are determined from a minimum free energy condition. The second implication is that, in the most general case, the strain energy depends also on the spatial pattern (microstructure) formed by the coherent domains of the coexisting phases and, therefore, the microstructure also becomes a self-adjusting internal thermodynamic parameter [3]. For such a system, the conventional common tangent construction of the additive Gibbs thermodynamics used to find the equilibrium compositions of the coexisting phases ceases to be valid.

The effect of the coherency strain on the thermodynamics of a closed two-phase system with a conserved number of atoms has been investigated by Roytburd [1] and Cahn and Larche [2]. These works considered the replacive transformation (decomposition) in an elastically isotropic system producing a two-phase coherent mixture. It was assumed that the crystal lattice parameters of the two phases are different but do not depend on the compositions of these phases. However, the model assumed in [1,2] seems to have a limited application. It is inapplicable to most systems decomposing by replacive transformations where the crystal lattice parameters of the coexisting phases are mainly determined by the composition (for example, the γ-γ' transformation in Ni-Al). Furthermore, it has been shown by Lee and Tao [4] that, in the case where the crystal lattice parameters follow the Vegard law, all the unusual effects expected in coherent thermodynamics [2,3] vanish. These effects can be expected, however, in systems where the misfitting crystal lattice parameters either do not depend on the phase compositions at all, as in the Roytburd and the Cahn and Larche models, or show a very strong deviation from the Vegard law. The lack of such systems seems to be the reason why there is still no reliable experimental confirmation of the strain effects predicted in [1,2].

It will be shown in this Letter that the situation is different for open systems where the solid solution is in a dynamic equilibrium with a reservoir of solute atoms. We demonstrate that, unlike the case of replacive transformations in coherent solid solutions with a conserved number of atoms, the strain energy always has a drastic effect on the thermodynamic behavior of an open coherent system. These effects should be expected even for an infinitesimal strain energy contribution to the system's free energy. Technologically important examples of such open systems are hydrides in equilibrium with a hydrogen gas reservoir at fixed pressure p and temperature T. Particularly, we demonstrate that for these systems the coherency strain completely eliminates the two phase equilibrium and produces a large thermodynamically reversible hysteresis effect.

Typically, the decomposition of an interstitial solid solution based on a metal or intermetallic matrix results in a formation of two phases characterized by different concentrations of interstitial solute atoms. One phase may be disordered and the other ordered, or both may be ordered. According to classical thermodynamics, such a two-phase system is in thermodynamic equilibrium with the gas of interstitial atoms, if the chemical potentials μ_α and μ_β of an interstitial atom in the α and β solid phases, are equal to the chemical potential $\mu_g(p,T)$ of an atom in the gas phase $\mu_\alpha(c_\alpha) = \mu_\beta(c_\beta) = \mu_g(p,T)$, where c_α and c_β are concentrations of interstitial atoms in the α

0031-9007/95/74(13)/2523(4)$06.00

and β phases. As long as the concentration of interstitial atoms in the solid is within the two-phase field of the phase diagram, the pressure required to transform the α phase to the β phase is constant. This, in turn, results in a plateau on the pressure-composition isotherm within the two-phase composition range. It will be shown below that even a small strain introduced by the interstitial atoms drastically changes this picture.

It was shown by Eshelby [5] that the configurationally dependent strain-induced interaction between dilatation point defects in an elastically isotropic solid solution is zero (Crum's theorem). The Eshelby model, assuming solute atoms to be misfitting elastic spheres coherently imbedded into the parent phase matrix of volume V, results in the following equation for the strain energy:

$$E_{\rm el} = N v_0 G_s \frac{1+\sigma}{1-\sigma} \varepsilon_0^2 \overline{c}(1-\overline{c}), \tag{1}$$

where N is the total number of equivalent lattice sites (in the case of an interstitial solution, N is the total number of interstitial sites) $v_0 = V/N$, G_s is the shear modulus, σ is the Poisson ratio, $\varepsilon_0 = da/ad\overline{c}$ is the concentration dependence of the crystal lattice parameter a, $\overline{c} = N_1/N$, and N_1 is the total number of interstitial solutes in the system. In Eq. (1), the term proportional to $\overline{c}^2$ characterizes the configurationally independent strain-induced interaction which arises through the image forces associated with the free surface of the system. It should be noted that the energy (1) depends on the total number of atoms (through $\overline{c}$) rather than on the local concentrations. Therefore, any regrouping of these atoms over the crystal lattice, particularly the one that transforms the homogeneous solid solution of the composition $\overline{c}$ into a two-phase *coherent* mixture of α and β phases, does not change the total strain energy. It is the same for the homogeneous solid solution as for the two-phase coherent mixture formed by the decomposition of this solution.

Let the α phase be the parent phase which in the absence of disorder has no interstitials, i.e., $c_\alpha = 0$. Let β be an ordered alloy phase which in the fully ordered state has an interstitial concentration $c_\beta = 1$. With Eq. (1), the free energies (per a lattice site) of the α and β phases in their single-phase states at pressure p, temperature T, and composition c can be presented as [1,2,4,5]

$$F_\alpha(p,T,c) = f_\alpha(p,T,c) + Ac(1-c), \tag{2a}$$

and

$$F_\beta(p,T,c) = f_\beta(p,T,c) + Ac(1-c), \tag{2b}$$

where

$$A = v_0 G_s \frac{1+\sigma}{1-\sigma} \varepsilon_0^2. \tag{3}$$

In Eq. (2), $f_\alpha(p,T,c)$ and $f_\beta(p,T,c)$ are the chemical contributions to the free energies of the α and β phases. We assume that the elastic properties of the α and β phases are similar and thus A has the same value in both phases. The values c_α and c_β are related to the total interstitial concentration by the atom conservation equation

$$\omega c_\beta + (1-\omega) c_\alpha = \overline{c}, \tag{4}$$

where ω is the volume fraction of the β phase (more precisely, ω is the relative fraction of the interstitial sites occupied by the β phase).

The strain energy (per lattice site) of the coherent two-phase mixture can be presented as

$$\varepsilon_{\rm el} = A\tilde{c}(c_\alpha, c_\beta, \omega)[1 - \tilde{c}(c_\alpha, c_\beta, \omega)], \tag{5}$$

where

$$\tilde{c}(c_\alpha, c_\beta, \omega) = \omega c_\beta + (1-\omega) c_\alpha. \tag{6}$$

The total free energy (per lattice site) of a two-phase closed system at fixed p, T, and $\overline{c}$ is thus:

$$F(p,T,\overline{c}; c_\alpha, c_\beta, \omega) = \omega f_\beta(p,T,c_\beta) + (1-\omega) f_\alpha(p,T,c_\alpha) + A\overline{c}(1-\overline{c}). \tag{7}$$

Below, without a loss of generality, it is assumed that $c_\beta > c_\alpha$. The equilibrium state at fixed p, T, and $\overline{c}$ is determined by the minimization of the free energy, Eq. (7), with respect to the internal thermodynamic parameters c_α and c_β under the additional condition of Eq. (4) relating $\overline{c}$, c_α, c_β, and ω.

In the open system, however, the concentration $\overline{c}$ is not fixed but becomes an internal thermodynamic parameter. It varies until the chemical potential μ of interstitial atoms in the solid equilibrates with that in the gas reservoir. Then the equilibrium value of $\overline{c}$ (as well as c_α and c_β) at fixed p, T, and μ is determined by the minimization of the thermodynamic potential

$$G(p,T,\mu; c_\alpha, c_\beta, \overline{c}, \omega) = \omega f_\beta(c_\beta) + (1-\omega) f_\alpha(c_\alpha) + A\overline{c}(1-\overline{c}) - \mu\overline{c}, \tag{8}$$

which is obtained from Eq. (7) by a Legendre transformation [6]. The minimum condition with respect to $\overline{c}$, $(\partial G/\partial \overline{c})_{T,p} = 0$, gives $(\partial F/\partial \overline{c})_{T,p} = \mu$, relating the composition $\overline{c}$ to the chemical potential μ of the interstitial atoms in the solid. In equilibrium with the gas phase, μ equals the chemical potential of interstitial atoms in the gas phase, $\mu_g(p,T)$.

Because the parameters ω and $\overline{c}$ are related by Eq. (4), it is convenient to eliminate the variable $\overline{c}$ and use as independent internal thermodynamic parameters the set c_α, c_β, and ω. Then, Eq. (8) can be rewritten as

$$G(p,T,\mu; c_\alpha, c_\beta, \omega) = \omega f_\beta(c_\beta) + (1-\omega) f_\alpha(c_\alpha) + A\tilde{c}(c_\alpha, c_\beta, \omega)[1 - \tilde{c}(c_\alpha, c_\beta, \omega)] - \mu\tilde{c}(c_\alpha, c_\beta, \omega), \tag{9}$$

where $\tilde{c}(c_\alpha, c_\beta, \omega)$ is given by Eq. (6).

The equilibrium values of c_α, c_β, and ω (at constant p, T, and μ) can be found by minimizing G with respect to these three parameters. To minimize G with respect to

ω, it is convenient to rewrite Eq. (9) as a quadratic form of ω:

$$G(p,T,\mu;c_\alpha,c_\beta,\omega) = \phi_0(c_\alpha) + \phi_1(c_\alpha,c_\beta)\omega - \phi_2(c_\alpha,c_\beta)\omega^2, \tag{10}$$

where

$$\phi_0(c_\alpha) = f_\alpha(c_\alpha) + Ac_\alpha(1 - c_\alpha) - \mu c_\alpha\,, \tag{11a}$$

$$\phi_1(c_\alpha,c_\beta) = (c_\beta - c_\alpha)\left[\frac{f_\beta(c_\beta) - f_\alpha(c_\alpha)}{c_\beta - c_\alpha} + A(1 - 2c_\alpha) - \mu\right], \tag{11b}$$

and

$$\phi_2(c_\alpha,c_\beta) = A(c_\beta - c_\alpha)^2 > 0\,. \tag{11c}$$

Equation (10) describes three possible dependences of G on ω, shown schematically in Fig. 1 by curves a,b, and c. The curves a and c have only one minimum which means that only one stable phase can exist: the α phase for curve a and the β phase for curve c. Curve b has two minima, at $\omega = 0$ and at $\omega = 1$, separated by the maximum at $\omega = \omega^*$. For the particular curve b shown, the β phase is stable, whereas the α phase is metastable. The situation depicted by curve b is the most interesting, because the phase transition from the metastable α to the stable β phase turns out to be impossible. Indeed, the $\alpha \rightarrow \beta$ transformation requires the formation of the two-phase state with the volume fraction ω^* of the β phase. This, in turn, requires the spontaneous increase in the volume-dependent free energy by a magnitude $(V/a^3)G(c_\alpha,c_\beta,\omega^*)$, where V is the volume of the particle, and a is the lattice parameter. Such an increase is forbidden by the second principle of the thermodynamics. The present situation is quite different from that of the phase transformations in the absence of coherent interfaces and macroscopic strains, where the transformation barriers are microscopic (the formation of critical nuclei) and, as such, can be overcome by thermal fluctuations. Therefore, it follows from the ω dependence of $G(c_\alpha,c_\beta,\omega)$ in Eq. (10), as illustrated by Fig. 1, that *two-phase equilibrium in a coherent open system is impossible.* This also means that the phase rule becomes inapplicable to coherent open systems.

Since the free energy barrier between the α and β phase is not surmountable by thermal fluctuations, the $\alpha \rightarrow \beta$ transformation does not start as long as $\phi_1(c_\alpha,c_\beta) > 0$. If μ is increased, $\phi_1(c_\alpha,c_\beta)$ decreases and the α phase loses its stability when $\phi_1(c_\alpha,c_\beta)$ vanishes [$\omega = 0$ ceases to be a minimum of $G(c_\alpha,c_\beta,\omega)$]. Then, it follows from the definition (11b) and the condition $\phi_1(c_\alpha,c_\beta) = 0$ that

$$\left[\frac{f_\beta(c_\beta) - f_\alpha(c_\alpha)}{c_\beta - c_\alpha} + A(1 - 2c_\alpha) - \mu_\alpha(c_\alpha)\right] = 0\,. \tag{12}$$

It is taken into consideration in Eq. (12) that $\mu = \mu_\alpha(c_\alpha)$ for the single-phase state of the initial α phase. The chemical potential of the α phase follows from Eq. (2a),

$$\mu_\alpha(c_\alpha) = \left.\frac{\partial F_\alpha}{\partial c}\right|_{c=c_\alpha} = \left.\frac{\partial f_\alpha}{\partial c}\right|_{c=c_\alpha} + A(1 - 2c_\alpha)\,. \tag{13}$$

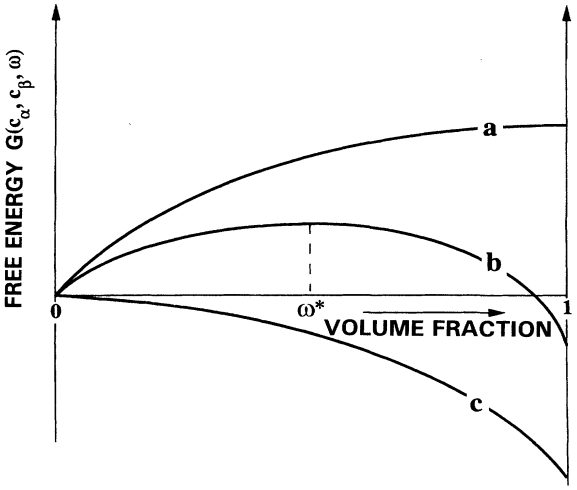

FIG. 1. Schematic plot of the dependence of the free energy of the two-phase system on the volume fraction ω of the solute-rich phase.

Using Eq. (13) to eliminate $\mu_\alpha(c_\alpha)$ from Eq. (12) we obtain the α-phase instability condition in terms of the concentrations only (no strain effects are involved). It reads

$$\frac{f_\beta(c_\beta) - f_\alpha(c_\alpha)}{c_\beta - c_\alpha} - \frac{\partial f_\alpha(c_\alpha)}{\partial c_\alpha} = 0\,. \tag{14}$$

Equations (12)–(14) can be resolved graphically in the general case without referring to specific analytical dependences of $f_\alpha(c)$ and $f_\beta(c)$ on composition, as long as these dependences provide the decomposition (i.e., have a common tangent). This graphic solution is illustrated by Fig. 2(a). The thin traces in this figure show typical *chemical* free energy vs composition curves, $f_\alpha(c)$ and $f_\beta(c)$, for the α and β phases (i.e., without the strain contributions). The heavy traces represent the corresponding total free energies F_α and F_β which include the strain contributions $Ac(1 - c)$. From this figure it is clear that Eq. (14) cannot be satisfied if $c_\alpha < c_\alpha^{\mathrm{st}}$, because then the left side of Eq. (14) is positive. With increasing c_α (i.e., increasing μ), Eq. (14) becomes satisfied when c_α in Fig. 2(a) reaches the starting composition c_α^{st}, where the tangent to the curve $f_\alpha(c)$ touches the curve $f_\beta(c)$ for the first time. Therefore, the stability limit of the α phase $c_\alpha = c_\alpha^{\mathrm{st}}$ is actually determined by the conventional common tangent construction applied to the (chemical) free energy curves $f_\alpha(c)$ and $f_\beta(c)$ in Fig. 2(a). In addition to c_α^{st}, this graphical construction also determines the other critical parameters of the transformation: the concentration c_β^{st} of the β phase formed at the beginning of

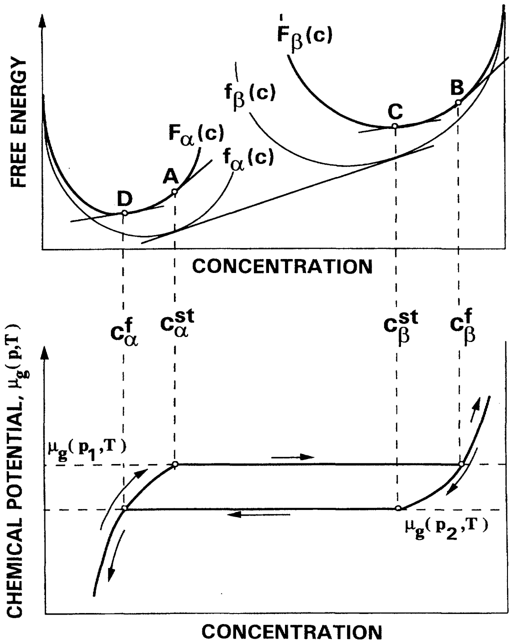

FIG. 2. Top: schematic free energy curves as a function of composition of interstitial atoms for the homogeneous α and β phases of a two-phase system with coherent interfaces. The thin curves $f_\alpha(c)$ and $f_\beta(c)$ represent the chemical contribution to the free energies. Bottom: chemical potential of the interstitial hydrogen atoms in the gas phase (proportional to the gas pressure) as a function of the composition of interstitials in the solid.

the $\alpha \rightarrow \beta$ transformation and the critical chemical potential $\mu_\alpha(c_\alpha^{st})$, which equals the slope of the tangent line to the curve $F_\alpha(c)$ at the concentration $c = c_\alpha^{st}$ (slope at point A).

The gas pressure p_1 needed to trigger the $\alpha \rightarrow \beta$ transition is determined by

$$\mu_g(p_1,T) = \mu_\alpha(c_\alpha^{st}) = \frac{\partial f_\alpha}{\partial c}\bigg|_{c=c_\alpha^{st}} + A(1 - 2c_\alpha^{st}), \quad (15)$$

which follows from Eq. (13). The composition c_β^{st} of the β phase, formed at the beginning of the $\alpha \rightarrow \beta$ transformation, is not in equilibrium with the external gas reservoir at the pressure p_1, since $\mu_\beta(c_\beta^{st}) < \mu_g(p_1,T) = \mu_\alpha(c_\alpha^{st})$. Indeed, Fig. 2(a) shows that the slopes of the tangent lines at points A and C, giving the values of $\mu_\alpha(c_\alpha^{st}) = \mu_g(p_1,T)$ and $\mu_\beta(c_\beta^{st})$, are different. Because $\mu_\beta(c_\beta^{st}) < \mu_\alpha(c_\alpha^{st})$, to establish equilibrium the β phase has to absorb interstitial atoms from the gas phase until its composition reaches the final composition c_β^f, where $\mu_\beta(c_\beta^f) = \mu_g(p_1,T) = \mu_\alpha(c_\alpha^{st})$. The composition c_β^f is defined by the condition that the slope of the $F_\beta(c)$ curve at c_β^f equals the slope of the $F_\alpha(c)$ curve at the composition c_α^{st} (i.e., slope at point B equals that at point A). Therefore, the absorption isotherm should have a plateau at the pressure p_1 within the composition range $c_\alpha^{st} < c < c_\beta^f$ [Fig. 2(b)].

The same line of reasoning gives the graphic algorithm for the desorption isotherm, also illustrated by Fig. 2. With decreasing c_β, the $\beta \rightarrow \alpha$ transformation starts at $c = c_\beta^{st}$. The desorption plateau pressure p_2 is determined from the equation

$$\mu_g(p_2,T) = \mu_\beta(c_\beta^{st}) = \frac{\partial F_\beta}{\partial c}\bigg|_{c=c_\beta^{st}} = \frac{\partial f_\beta}{\partial c}\bigg|_{c=c_\beta^{st}} + A(1 - 2c_\beta^{st}), \quad (16)$$

where $F_\beta(c)$ is given by Eq. (2b). Equation (16) determines the pressure p_2 for the reverse $\beta \rightarrow \alpha$ transformation. However, the α phase formed as a result of this transformation has the composition c_α^{st} and thus is not in equilibrium with the gas phase, since at this composition $\mu_\alpha(c_\alpha^{st}) > \mu_g(p_2,T) = \mu_\beta(c_\beta^{st})$. The α phase has to desorb interstitial atoms, reducing its composition from c_α^{st} to c_α^f, until $\mu_\alpha(c_\alpha)$ reaches the equilibrium value $\mu_\alpha(c_\alpha^f) = \mu_\beta(c_\beta^{st}) = \mu_g(p_2,T)$, where the slope at point D equals the slope at point C. Therefore, the desorption isotherm has a plateau at the pressure p_2 within the concentration range $c_\alpha^f < c < c_\beta^{st}$, as shown in Fig. 2(b).

As follows from the above graphic consideration, the absorption-desorption curves have considerable hysteresis, $\mu_g(p_1,T) - \mu_g(p_2,T) = \mu_\alpha(c_\alpha^{st}) - \mu_\beta(c_\beta^{st})$. The origin of this hysteresis is the coherent strain. From Eqs. (15) and (16), using the equality $\partial f_\alpha/\partial c|_{c=c_\alpha^{st}} = \partial f_\beta/\partial c|_{c=c_\beta^{st}}$, which follows from Fig. 2(a), we obtain the simple expression

$$\mu_g(p_1,T) - \mu_g(p_2,T) = 2A(c_\beta^{st} - c_\alpha^{st}). \quad (17)$$

The chemical potential of interstitial atoms in a diatomic gas is

$$\mu_g(p,T) = \mu(T)_g^0 + \frac{1}{2}kT \ln\frac{p}{p_0(T)},$$

where $p_0(T)$ and $\mu(T)_g^0$ are the pressure and chemical potential in the standard state. With it and Eq. (3) we obtain a simple equation for the p_1/p_2 ratio characterizing the thermodynamic hysteresis

$$\ln\frac{p_1}{p_2} = \frac{4v_0 G_s \frac{1+\sigma}{1-\sigma}\varepsilon_0^2(c_\beta^{st} - c_\alpha^{st})}{kT}. \quad (18)$$

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

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