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Thermodynamics of open two-phase systems with coherent interfaces: Application to metal–hydrogen systems

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Abstract

We develop a thermodynamic theory for the absorption/desorption of interstitial atoms by a solid crystalline host forming a coherent mixture of two phases with different compositions of interstitial solutes. It is shown that the misfit-generated strain produces a macroscopic energy barrier between the transforming phases. The energy barrier is proportional to the macroscopic volume and thus cannot be surmounted by the thermally assisted nucleation of the new phase. The barrier splits the phase-transition pressure (temperature) into two pressures (temperatures): one during increase of pressure (cooling) and another during decrease of pressure (heating). The difference between these pressures (temperatures) determines the system hysteresis. It is also shown that the chemical potential of interstitials within the two-phase region of the coherent phase diagram is a linear function of composition rather than a constant, as is the case in the absence of coherency strains. We apply the theory to the absorption/desorption of H atoms by a metal that is free to exchange hydrogen atoms with an external source (reservoir). The theory explains the ubiquitous hysteresis in the 'plateaus' of the pressure–composition isotherms and the critical pressure–composition point for the disappearance of the hysteresis. The proposed theory is generic in the sense that it is applicable to any open interstitial systems forming coherent hydrides or other interstitial phases in the host lattice of the same symmetry.

Keywords: Hydrides; Hysteresis; Coherency strain; Decomposition

1. Introduction

Hydrogen can be reversibly stored in many crystalline solids. At a low hydrogen concentration, the hydrogen atoms usually form a dilute interstitial solid-solution, α. Increasing the hydrogen concentration causes part of the solid solution to precipitate into a β phase of larger interstitial concentration and lower density. Whereas the metal atoms form spatial lattice frames in both phases, the interstitials in the α and β phases may be disordered or may form an ordered sublattice. According to classical thermodynamics, equilibrium between the α and β phases requires the equality of the respective chemical potentials for interstitials, $\mu_\alpha(c_\alpha) = \mu_\beta(c_\beta)$. Here, c_α and c_β are concentrations of interstitial atoms in the α and β phases. If the solid can exchange interstitials with an external gas source (open system), equilibrium further requires the equality between the internal and external chemical potentials, i.e., $\mu_\alpha(c_\alpha) = \mu_\beta(c_\beta) = \mu_g(p_g,T)$, where $\mu_g\ (p_g,T)$ is the chemical potential of single atomic interstitials in the gas phase formed by a dissociation of the diatomic gas at the partial pressure of the diatomic gas, p_g, and temperature T. The equality of chemical potentials means that the $\alpha \rightarrow \beta$ transformation takes place at a constant gas pressure, resulting in a 'plateau' on the pressure–composition isotherm within the $(\alpha + \beta)$ two-phase composition range. Such plateaus are ubiquitous to crystalline–metal/hydrogen systems, and measuring plateau pressures as a function of temperature is the main method for the experimental determination

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of the metal/hydrogen phase diagram and the enthalpy and entropy of hydride decomposition [1].

Often the plateau pressure for hydride formation exceeds that for hydride decomposition, in what is termed hysteresis. This hysteresis is reproducible upon cycling the transformation over thousands of hydriding–dehydriding cycles. Since the presence of reproducible hysteresis in a reversible transformation cannot be explained by conventional thermodynamics, the phenomenon has been attributed to dissipative phenomena such as the generation of a large density of misfit dislocations [2]. Although localized plastic deformation is often observed during hydride formation and decomposition, a dislocation mechanism cannot explain the repetitious nature of the hysteresis in the plateau pressures. Dislocations and other lattice defects are indeed generated when a crystalline host is first loaded with hydrogen, and this generation dissipates energy, contributing to the hysteresis. However, after several cycles, work hardening and fracture blocks the motion of the dislocations and thus the dislocations can no longer contribute to the hysteresis observed in subsequent cycles. To explain the reproducible nature of the hysteresis, one would have to make the unrealistic assumption that the dislocation distribution generated during one half of the cycle is reversibly annihilated during the following half cycle. Such a plasticity mechanism is contrary to the theories of work hardening and so far has not been observed in any system.

The coherency strain generated by the crystal lattice misfit between the phases plays an important role in the thermodynamics of the phase diagram by shifting the solubility lines [3–5]. The resultant coherent diagram may be appreciably different from the stress-free one. However, the most interesting effect is that the strain-induced interaction between the coexisting coherent phases results in a violation of the basic assumptions in the Gibbsian thermodynamics of phase transformations, namely the additivity of the free energy of a two phase mixture: the strain energy of the coherent system depends non-linearly on the volume fractions of the coexisting phases [6,7]. Another effect is that, in the most general case, the strain energy depends also on the spatial pattern (microstructure) of the coexisting coherent phases and, therefore, the microstructure also becomes a self-adjusting internal thermodynamic parameter [7].

Some of these implications were considered by Roytburd [8,9] and Cahn and Larché [10]. These authors studied the thermodynamics of a closed two-phase system (conserved number of atoms). They considered an elastically isotropic cubic system that decomposes isostructurally into a coherent mixture of two cubic phases of the same symmetry that are distinguished only by their compositions. These models assume that the lattice parameters of the two coexisting phases are different but do not depend on composition. These theories show that the equilibrium between the coherent phases cannot be described by a common-tangent construction, and that sometimes the two-phase system fails to obey the Gibbs phase rule. According to [8,10] the compositions of the two coherent phases within the two-phase region of the phase diagram depend on the average alloy composition. A dependence of the solubility of the coexisting phases on the average alloy composition was reported by Huh et al. [3] for the $\alpha + \alpha_2$ decomposition in Ti–Al alloys.

As shown by Lee [11], the unusual effects in [8,10] vanish if the crystal lattice parameters follow the Vegard law – or are close to it. However, it is possible to observe these effects when the crystal lattice reconstruction for the coherent decomposition meets a special condition, viz., that the crystallography of the transformation only allows the formation of one type of orientation domains. In the case of multiple orientation domains, their patterning can eliminate the coherency strain responsible for the modification of the two-phase equilibrium. The theory in [8,10] is conceptually very important because it provides a clear demonstration that there is a specific case of coherent decomposition in a closed system where the thermodynamics of the transformation is qualitatively different from the predictions of the conventional Gibbs thermodynamics.

In a previous letter [12] we examined the thermodynamics of the isotropic coherent decomposition in an open system that is in thermodynamic equilibrium with a source of interstitials H atoms. The source of H atoms was assumed to be a gas maintained at a constant pressure (constant chemical potential). The crystal was assumed to be elastically isotropic and its lattice parameters to depend linearly on concentration. We demonstrated in [12] that the coherency strain contribution to the free energy of the open system results in a new effect: the appearance of a macroscopic energy barrier for the isostructural phase transformation. Although free energy barriers are common features of conventional first-order phase transformations, these barriers are microscopic, i.e., commensurate with kT. Thus, temperature may retard the transformation but cannot eliminate it. The strain-induced macroscopic barrier found in [12] is different. To overcome this barrier, the system must increase its free energy by a value proportional to the volume of the entire system. Since thermal activation cannot provide this energy, the macroscopic barrier fully suppresses the nucleation of the α and β phases in isostructural transformations within the stability range of the $(\alpha + \beta)$ phase mixture. This also makes it impossible for the α and β phases to coexist in the open system. The model yielded a closed equation for the hysteresis between the chemical potential needed to drive the forward and reverse transformations. In the present paper we expand this model, deriving expressions for the chemical potential. We demonstrate that for a coherent isostructural decomposition in a closed system with a linear concentration dependence of the crystal lattice parameters the chemical potential within the two-phase range is a linear function of the average composition. This is contrary to the results for a conventional stress-free system, where the chemical potentials of the components within the two-phase range are independent of the average composition. The linear dependence of the chemical potential has been also established for the case where the crystal lattice parameters of the phases do not depend on the composition [10]. Our paper, however,