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Quasi-thermodynamic model on hydride formation in palladium–hydrogen thin films: Impact of elastic and microstructural constraints

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ARTICLE INFO

Article history:

Received 4 October 2015

Accepted 9 November 2015

Available online xxx

Keywords:

Palladium

Hydrogen

Thin films

Stress

Phase transformation

Critical temperature

ABSTRACT

The impact of elastic and microstructural constraints on structural phase transitions is investigated by using (10–300) nm Pd–H films of different microstructures. Hydrogen-induced stress mainly arises from the film's adhesion to a substrate. Stress changes the hydrogens' chemical potential μ_H , modifying the hydride phase stability. Microstructural constraints channel stress release in films.

A thermodynamic model is proposed to deduce the H–H interaction energy E_{HH} and an effective critical temperature T_c^{eff} of hydride formation in films. It allows for occasionally observed sloped plateaus of μ_H below T_c^{eff} . E_{HH} (between 15 and 30 kJ/mol_H) and T_c^{eff} (340 K to 490 K) are reduced by up to 50% compared to bulk ($E_{HH} = 36.8$ kJ/mol_H, $T_c = 563$ K), for all films. Concentration-dependent contributions of substrate-induced stress (of about (2–5) kJ/mol_H) and microstructure (of about (5–8) kJ/mol_H) are separated. For all films phase separation is still found at 300 K.

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Introduction

Reducing the dimension of physical systems to the nano-scale, finite size effects and interface contributions change the systems' physical properties [1–9]. These changes are important both fundamentally and for the design of devices used e.g. in energy conversion [1,10,11].

Interface contributions generate elastic (stress) and microstructural constraints [12,13]. Considering thin metal films on rigid substrates, intrinsic stress arises both from the films' lattice mismatch to the substrate, i.e. stress at external interfaces, and at internal interfaces such as grain boundaries [12–14]. These stress contributions modify the thermodynamics of thin films when they undergo structural phase

transitions. As an archetypical example we choose the formation of a hydride phase in thin films absorbing hydrogen [15–19]. In this case additional internal stresses arise at the interfaces between hydride precipitates and metal-matrix of the film, and stresses between film and substrate are enhanced.

The variety of interfaces is classified from a structural point of view. At coherent interfaces evolving stress contributions are largest. At semi- or incoherent interfaces formed by plastic deformation stress can be partially released. In metal–hydrogen alloys on top of this microstructural defects reveal H-solubilities differing from the undisturbed metal lattice, further modifying the thermodynamics in a fundamental way [2,20].

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<http://dx.doi.org/10.1016/j.ijhydene.2015.11.063>

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Utilizing palladium hydrogen (Pd–H) thin films as a model system, it is the aim of the present paper to separate the impact of the constraints resulting from substrate-induced stress and microstructure on the driving force of the phase transition. Based on a thermodynamic model differences between thin films' and bulk thermodynamic parameters, such as the H–H interaction energy and an effective critical temperature of the phase transition, will be quantified for films with different microstructures and different adhesion conditions.

A similar approach has been proposed by Steiger, Song and Edelmann et al. [21–23] for epitaxial Nb–H thin films. These authors, however, did not quantitatively consider the impact of stress in analyzing film isotherms. Using the shape anisotropy of interstitial sites Hjörvarsson et al. [24,25] investigated the impact of elastic constraints on the site occupancy in V–H films. They focused on very thin films and multi-layers and, therefore, did not consider plastic deformation and defect generation.

The basic thermodynamic quantity describing the interaction of hydrogen with a metal is the hydrogens' chemical potential, introduced in the following section.

Chemical potential of hydrogen in palladium

The palladium hydrogen system

The Pd–H bulk system shows a simple phase diagram [26–29]. Its profound knowledge will facilitate identifying changes of thermodynamic parameters in Pd–H thin films. In Pd, H is dissolved in interstitial sites with octahedral symmetry [26]. At low H-concentration x_H hydrogen is distributed statistically on the lattice sites for entropic reasons, forming a solid solution α -phase. Below a critical temperature of 563 K [29], precipitation of an α' -hydride-phase with concentration $x_{\alpha'}^{\text{min}}$ sets in when the average hydrogen concentration exceeds the solid solution limit x_{α}^{max} . The phases are separated by a miscibility gap Δx_H , where the solid solution limit is $x_{\alpha}^{\text{max}} = 0.008 - 0.017 H/Pd$ [26,27], while $x_{\alpha'}^{\text{min}} = 0.6 H/Pd$ at 300 K [26].

In real structures, a number of microstructural defects are present, such as surface, grain boundaries and dislocations. These may offer more negative site energies E_0 than interstitial sites, resulting in a preferable H-occupation of defects. These microstructural constraints are well known to cause a narrowing of the miscibility gap [2,28]. Additionally, Weißmüller and Lemier [12,13] predict a reduction of the critical temperature T_c for Pd–H bulk samples with nano-sized grains due to interfacial stresses.

Hydrogen absorption in bulk Pd results in an isotropic lattice expansion

$$\frac{\Delta a}{a} = \varepsilon_0 = \alpha_H x_H. \quad (1)$$

The expansion factor $\alpha_H = 0.063(3)$ [30] and a is the lattice constant. This relation also holds for the two-phase region [30]. Therefore, each dissolved H-atom is surrounded by an elastic strain field of the Pd lattice [31]. The H atoms attractively interact via the strain fields, yielding an elastic contribution to the chemical potential [29], acting against the entropy contribution. It becomes visible at the solid solution

limit, when the elastic interaction initiates the phase transition. In total, with a linear approximation of the elastic interaction [25] the chemical potential μ_H of H in bulk Pd is commonly given by [26,29]

$$\mu_H = RT \ln \left(\frac{x_H}{r - x_H} \right) + E_0 - E_{HH} x_H, \quad (2)$$

with gas constant R and absolute temperature T . The H–H interaction is characterized by an interaction strength parameter E_{HH} . The first term in Equation (2) describes the configurational entropy of H dissolved on octahedral sites, with the maximum number r of sites that can be occupied by hydrogen. r is determined both by the electronic structure [32] and the microstructure [28] of the metal host. Following Song and Edelmann et al. [22,23], we will leave r as a fitting parameter. Note that the increment of fitted isotherms according to Equation (2) will be larger than that of measured isotherms in the hydride phase, as the entropy term diverges at $x_H = r$. Alternatively, the electronic interaction could be regarded as a separate fitting parameter, while the number of available interstitial sites could be chosen to match the geometrical value $r = 1$ [33].

Stress contribution to the chemical potential in thin films

In Pd films adhered to rigid substrates in-plane expansion is suppressed [34]. Therefore, large in-plane compressive stresses occur upon H-absorption. Within linear elastic theory H-induced stress changes $\Delta\sigma = M_{[hkl]} \cdot \varepsilon$ are calculated. $M_{[hkl]}$ is the direction dependent biaxial modulus, and ε is the unrestrained H-induced lattice expansion. For the example of Pd films with [111]-texture in-plane stresses $\sigma_{xx} = \sigma_{yy} = \sigma_{(111)}$ are isotropic [35], yielding [36,37]

$$\Delta\sigma_{(111)}/x_H = -\frac{6}{4S_{11} + 8S_{12} + S_{44}} \cdot \alpha_H = -18.0(9) \text{ GPa}, \quad (3)$$

with the elastic compliances $S_{11} = 13.66 \text{ TPa}^{-1}$, $S_{12} = -5.95 \text{ TPa}^{-1}$ and $S_{44} = 13.97 \text{ TPa}^{-1}$ of Pd [38].

As the Pd lattice expands linearly with H concentration in the whole concentration range, it fulfills Vegard's law [30]. Then, Equation (3) also holds in the two-phase region with nominal (average) H-concentration x_H of the film. However, if stress relaxation appears between film and substrate by the emission of dislocations or local film detachment (buckling), the H-induced stress gets smaller [34].

Additional shear stresses result at coherent interfaces between α - and α' -phase in thin films due to the concentration gap Δx_H . We will neglect this contribution in this paper, assuming that the volume density of phase-interfaces is small in the films, as observed with in-situ STM by Nörthemann and Pundt [39] for Nb–H thin films. In general, far away from phase-interfaces both within the precipitates and the matrix the film expands freely in vertical direction. Then $\sigma_{[111]} = \sigma_{zz} \equiv 0$ [35]. Considering the direct vicinity of phase-interfaces the vertical stresses counteract. The precipitates are compressed, whereas the matrix is stretched. Therefore, the total strain energy of the interface is not zero, but its contribution to the strain energy of the film is small when the volume density of interfaces is small.

Elastic constraints resulting from mechanical stress change the chemical potential μ_H . Larché and Cahn [40–42] have

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