Lattice Constants of Solid Solution Microstructures: The Case of Nanocrystalline Pd-H

Jörg Weissmüller* and Christian Lemier
Fachrichtung Technische Physik, Universität des Saarlandes, Saarbrücken, Germany

(Received 15 June 1998)

We present an analysis of the effect of interface stress on strain in bulk in an open system with a large interface-to-volume ratio, at equilibrium with the solute at a controlled chemical potential. The results are relations for interface stress and for solute concentration in the bulk as a function of measurable parameters: interfacial "stretch" and changes in the lattice constant. Stretch models a change in the average normal component of the interatomic spacing at interfaces. X-ray diffraction and dilatometry provide experimental data showing a significant variation of grain boundary stress and stretch in nanocrystalline Pd-H with hydrogen chemical potential. [S0031-9007(98)08132-0]

PACS numbers: 81.05.Ys, 64.75.+g, 68.35.–p, 82.65.Dp

In studies of hydrogen solubility in nanoscale microstructures, such as clusters [1,2], thin films [3], multilayers [4], or nanocrystalline bulk samples [5,6], it is generally found that, in thermodynamic equilibrium at a given hydrogen chemical potential μ, the overall hydrogen concentration in the nanoscale microstructures differs from that in the coarse-grained material at the same μ. Interfacial segregation isotherms [7], which rationalize such composition change in terms of enrichment or depletion of hydrogen at interfaces, provide *local* equilibrium equations where free energy densities in the bulk and at the interfaces depend only on the local concentration. However, at large interface-to-volume ratio, a *nonlocal* interaction between interfaces and bulk may become significant: This interaction is due to *interface stress* [8,9], $\mathbb{S}$, that entails stress and strain in the crystal lattice, thereby affecting the bulk concentration at equilibrium [10]. When area is measured in coordinates of the undeformed material, $\mathbb{S}$ is then the derivative of an interfacial free energy with respect to bulk strain tangential to the interface plane [11,12]. Contrary to the *scalar* and positive-valued interfacial free energy, $\mathbb{S}$ is a *tensor* with entries which may be of either sign. These entries are independent material parameters that can be nonzero even when there is no strain. Because of its potential effect on hydrogen concentration in nanoscale microstructures, it is of interest to measure $\mathbb{S}$ in a metal-hydrogen system. Also of relevance is the effect of $\mathbb{S}$ on the lattice constant a, since the concentration in nanoscale solid solutions is frequently inferred from experimental data for a. When a depends simultaneously on the concentration and on $\mathbb{S}$, the effect of $\mathbb{S}$ must be taken into account in deriving the concentration. In this paper, we explore the relation between $\mathbb{S}$, a, and the concentration in an open system at equilibrium. In combination with experimental data, the results of the analysis lead to the measurement of interface stress in nanocrystalline (n-) Pd-H as a function of μ. We also show that varying μ leads to interfacial *stretch* [12], $\mathbb{V}$. In continuum mechanics, $\mathbb{V}$ is a jump in the normal component of the displacement at an interface that models a change in the average normal component of the interatomic spacing at the interface. Experimental data for stretch provide an independent estimate for interface stress.

We consider an interstitial solid solution that exchanges solute, exclusively, at equilibrium with a reservoir at chemical potential μ. As the composition variable in the bulk we take the solute fraction c, the ratio of the solute concentration (atoms per volume) over the concentration of sites (sits per volume) available to solute ρ_0. Attention is restricted to alloys where concentration changes induce isotropic strain, so that, at equilibrium, c depends only on the pressure P, not on shear stress [13]; thus, at equilibrium outside the spinodal region of the phase diagram, $c = c(\mu, P)$. The variable for elastic change in volume V is the volumetric strain ε; the trace of the strain tensor is $dV = V d\varepsilon$. Material parameters relevant in the discussion of equilibrium are a "solute susceptibility" $\chi = \rho_0^{-1} \partial c/\partial\mu|_P$, the concentration-strain coefficient $\eta = \frac{1}{3}\,\partial\varepsilon/\partial c|_P$, the bulk modulus at constant composition $K = -\partial P/\partial\varepsilon|_c$, and the open system bulk modulus $K^* = -\partial P/\partial\varepsilon|_\mu$. Considering experiments on the Pd-H α phase, we take η and K as being independent of c [14,15]. The relation between K and K^* [13],

$$K^* = K/(1 + 9K\chi\eta^2)\,, \tag{1}$$

takes account of the fact that, in the open system, stress results in a combination of elastic strain and of strain due to concentration change.

When external pressure is neglected, mechanical equilibrium then requires that the pressure in the bulk is related to the scalar interface stress $f = \mathrm{trace}(\mathbb{S})/2$ by [16]

$$3\langle P\rangle_V = 2\alpha\langle f\rangle_A\,, \tag{2}$$

where $\alpha = A/V_G$ denotes the specific interface area, A is the total area, and V_G is the total volume of the (undeformed) grains. The brackets denote the volumetric and areal mean over V_G and A, respectively [16], as indicated by the subscripts.

Consider ε measured relative to a reference state of the microstructure at $c = 0$ and $f = 0$, where the lattice constant is that of coarse-grained pure solvent. The total

0031-9007/99/82(1)/213(4)$15.00

strain in the bulk at chemical potential μ can then be described as the result of two separate processes. The first is a concentration change at $f = 0$, resulting in the strain $\varepsilon_1 = 3\eta c(\mu, 0)$. The second process is a change of interface stress, at constant μ, to the actual value of f at equilibrium; this leads to an additional strain $\varepsilon_2 = -\int_0^P (K^*)^{-1} dP$, with P related to f by Eq. (2). The total volumetric strain relative to the coarse-grained pure solvent is thus $\varepsilon = \varepsilon_1 + \varepsilon_2$. Experimentally, it is more convenient to measure the strain ε' relative to an *experimental* reference state where approximately $c = 0$ in the bulk, and where the pressure has a finite value P^0, related to the interface stress in the experimental reference state f^0 by Eq. (2). It is readily seen that $\varepsilon' = \varepsilon + P^0/K$. With Eq. (1) for K^*, and for a microstructure with uniform material constants, the total experimental strain is then

$$\langle \varepsilon' \rangle_V = 3\eta c(\mu, 0) - \frac{2}{3}\alpha\left(\langle f - f^0 \rangle_A / K + \int_0^{\langle f \rangle_A} 9\chi\eta^2 d\langle f' \rangle_A \right). \tag{3}$$

In general, the argument of the integral in Eq. (3) depends on the concentration, hence, on P and, by Eq. (2), on the integration variable $\langle f' \rangle_A$. For the discussion of our experiments on Pd-H, we used a regular solution equation of state [14] for the bulk, $\mu = m_1 + m_2 c + RT \ln[c/(1 - c)] + 3P\eta/\rho_0$ with constant m_1 and m_2 that does not lead to a closed form expression for the integral in Eq. (3). To obtain $\langle f \rangle_A$ for given experimental values of $\langle \varepsilon \rangle_V$, $\langle f^0 \rangle_A$, and μ, Eq. (3) was inverted numerically (with better than six digit accuracy), with the dependence of c on μ and P evaluated numerically from the implicit equation $c = c_R(\mu, P)$ intimated by the equation of state. With $\langle f \rangle_A$ and, hence, $\langle P \rangle_V$ known, the solute enrichment ratio r (the actual value of c in the bulk over the value of c in the coarse-grained material at same μ) was determined from $r = c_R(\mu, \langle P \rangle_V)/c_R(\mu, 0)$.

For the discussion of experimental data for strain, it is useful to derive a relation between strain in the microstructure and stretch, $\mathbb{V}$. Since $\mathbb{V}$ is equivalently identified with a change in an interfacial excess volume [11,12], changes in total volume V_M of the microstructure are related to changes in total grain volume V_G by an integral of stretch over the interfaces: $\Delta V_M = \Delta V_G + \int \mathbb{V} dA$. In terms of the corresponding volumetric strains, ε_M and ε_G, this implies

$$\varepsilon_M = \langle \varepsilon_G \rangle_V + \alpha \langle \mathbb{V} \rangle_A . \tag{4}$$

A simple qualitative model suggests that f and $\mathbb{V}$ should depend on the solute concentration at the interface and, hence, on μ. Let the interface be modeled by a planar, uniform, and isotropic layer of material with thickness t, concentration-strain coefficient η_L, site density ρ_L, Young modulus Y_L, and Poisson number ν_L. As the composition variable for the layer we take the quantity $\mathbb{N} = [N] - c\rho_0 t$, where $[N]$ is the specific layer content [11] of solute (amount of solute in the layer per area) and where c and ρ_0 refer to the bulk phase. $\mathbb{N}$ is an excess of solute, per area of layer, over a reference system with uniform solute concentration throughout the bulk and the layer. If the layer was detached from the abutting crystals at $\mathbb{N} = 0$, and $\mathbb{N}$ then changed at constant stress, the layer would undergo an isotropic expansion with a volumetric strain $3\mathbb{N}\eta_L/(\rho_L t)$. At constant $\mathbb{N}$ and constant normal load, a tangential stress S_L, isotropic in the plane, would be required to bring the layer back in registry with the abutting crystals. The product $S_L t$ is a force per unit length of the perimeter and, by the definition in Ref. [8], is identified as the interface stress of the layer. Straightforward continuum mechanics theory leads to $f = -\mathbb{N}\eta_L \rho_L^{-1} Y_L (1 - \nu_L)^{-1}$, that is, to a linear dependence of interface stress on $\mathbb{N}$.

In the layer model, the change in thickness of the layer due to elastic strain is the equivalent to interfacial stretch. Adding the thickness changes due to the change in $\mathbb{N}$ at constant stress and due to the application of the tangential stress S_L at constant normal load and constant $\mathbb{N}$, one finds

$$\mathbb{V} = \mathbb{N}\eta_L \rho_L^{-1} (1 + \nu_L)(1 - \nu_L)^{-1} \tag{5}$$

and, in combination with the result for f,

$$\mathbb{V} = -(1 + \nu_L) Y_L^{-1} f . \tag{6}$$

We shall proceed to present experiments that lead to the independent determination of f and $\mathbb{V}$.

The experiment was performed on a bulk sample of n-Pd prepared by inert gas condensation, as described in [17]. Warren-Averbach analysis (compare details in [18]) indicates a specific grain boundary area $\alpha = 0.32(5)\ \text{nm}^{-1}$, corresponding to a grain size of 10 nm. *In situ* measurements of the macroscopic length change Δl in a dilatometer and of the lattice constant change Δa in a diffractometer were performed at $T = 40\,^\circ\text{C}$ and with hydrogen charging from an Ar-H_2 flow at atmospheric pressure. Hydrogen partial pressure p_{H_2} was adjusted by flow controllers. Deformation is specified relative to a reference state with the sample in pure Ar, which was repeatedly reestablished during measurement to verify reproducibility. Subsequent to changes in p_{H_2}, signals were followed at constant p_{H_2} until a constant asymptotic strain was reached. The results were found to be reversible and reproducible during a large number of loading/unloading cycles, except for an irreversible strain when the sample was first exposed to hydrogen that indicates hydrogen uptake in deep traps at grain boundaries [19]. All experiments presented here are restricted to the Pd-rich α phase, avoiding hysteresis [20] at the phase transition. Material constants used in the analysis are [14] $\eta = 0.063$, $K = 187$ GPa, $Y = 121$ GPa, $\nu = 0.39$, $m_1 = 7.08$ kJ/mol, $m_2 = -45.62$ kJ/mol, and $\rho_0 = 67.95\ \text{nm}^{-3}$.

The interface stress in the experimental reference state, $\langle f^0 \rangle_A = +0.1(4)$ N/m, was determined by comparing lattice constants of the material under pure Ar (after several loading/unloading cycles) in the as-prepared nanocrystalline state and in the annealed coarse-grained state. As suggested in Ref. [21], the lattice constants were corrected for residual stress through a suitable choice of scattering geometry [22]. Residual stress in the nanocrystalline reference state was found to be compressive and to result in a pressure of about 10 MPa, which is negligible compared to the pressure induced by interface stress upon hydriding.

Figure 1 displays the experimental values for $\Delta l/l$ and $\Delta a/a$ in n-Pd as a function of p_{H_2}, along with reference data for $\Delta l/l$ in coarse-grained Pd. The change in lattice parameter Δa is found to be considerably higher than that in coarse-grained Pd, Δa_0; for the arbitrary example $p_{\mathrm{H}_2} = 2$ kPa, the ratio is $\Delta a/\Delta a_0 = 2.6$. The dilatometer data evidence an even higher total strain; at $p_{\mathrm{H}_2} = 2$ kPa, the ratio is $\Delta l/\Delta l_0 = 6.6$. The large difference of the respective measures for strain indicates that there are degrees of freedom for deformation that do not affect the lattice constant. In conjunction with Eq. (4), this result suggests measurement of $\mathbb{V}$: Since the material is macroscopically isotropic, we take $\varepsilon_M = 3\Delta l/l$ and $\varepsilon_G = 3\Delta a/a$. It is emphasized that Δa indeed measures ε_G, not ε_M: In polycrystals, the distribution of interatomic spacings across high-angle grain boundaries does not give rise to constructive interference in wide-angle scattering (compare [17] and references therein); therefore, stretch is of no consequence to the Bragg reflection position and, hence, to Δa. The results for $\mathbb{V}$ obtained from Eq. (4) (Fig. 2) indicate that most stretch occurs at $p_{\mathrm{H}_2} < 0.1$ kPa, but that $\mathbb{V}$ continues to increase at higher p_{H_2}.

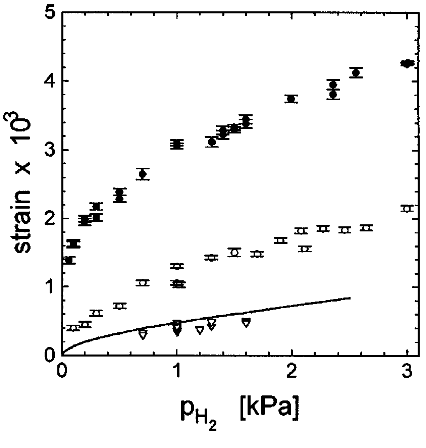

FIG. 1. Experimental strain relative to a reference state in pure Ar versus hydrogen partial pressure p_{H_2}. (●) External strain $\Delta l/l$ of n-Pd, dilatometer. (○) Crystal lattice strain $\Delta a/a$ of n-Pd; diffractometer. (∇) $\Delta l/l$ for a coarse-grained Pd foil reference sample. (Solid line) strain for coarse-grained Pd (Ref. [14]).

Figure 3(a) shows grain boundary stress f determined by analyzing the experimental ε_G in terms of the equilibrium condition [Eq. (3)]. It is seen that f is not a constant, but varies with p_{H_2}. The sign of f is found to be negative, that is, grain boundary stress in Pd-H *expands* the crystal lattice, in contrast to the effect of interface tension in fluids, which is always *compressive.* At $p_{\mathrm{H}_2} = 2$ kPa, we find $f = -1.7(4)$ N/m, corresponding by Eq. (2) to $\langle P \rangle_v = -0.36$ GPa. The enrichment ratio r, displayed in Fig. 3(b), is seen to vary with partial pressure, with a value of $r = 1.3$ at $p_{\mathrm{H}_2} = 2$ kPa. If the lattice strain $\Delta a/a$ was (incorrectly) attributed entirely to change in composition, so that $\Delta a/a = \eta c$, then the much higher value of $r = 2.6$ would be obtained. In fact, our results show that the majority of the strain is from the elastic reaction of the lattice to the change of interface stress, not from the change of composition.

We shall now assess the experimental results and will, for the sake of a simplistic estimate, assume that the elastic constants Y_L and ν_L in the interfacial layer may be approximated by the bulk values. Equation (6) with the experimental value for $\mathbb{V}$ then yields $f = -1.7(2)$ N/m at $p_{\mathrm{H}_2} = 2$ kPa, which is identical to the more rigorous results obtained, independently, by evaluation of Eq. (3). The agreement supports the validity of our treatment of equilibrium.

To assess the result for the stretch, assume further that $\eta_L = \eta$, and that the maximum excess of solute in the layer corresponds to one atomic monolayer (ML), a value that is typical for solute segregation to grain boundaries [7]. For Pd, a densely packed ML has an areal site density of $\mathbb{N}_1 = 15.3\ \mathrm{nm}^{-2}$. Equation (5) with $\mathbb{N} = \mathbb{N}_1$ yields an estimated stretch of $\mathbb{V} = 32$ pm and implies that 0.6 ML of H would be required for the measured value, $\mathbb{V} = 19(2)$ pm at $p_{\mathrm{H}_2} = 2$ kPa. Thus, the measured stretch has a realistic order of magnitude. Note also that, in addition to the enrichment in the bulk, 0.6 ML of H at grain boundaries would contribute by $0.6\mathbb{N}_1\alpha/\rho_0 = 0.04$(H/Pd) to the overall H/Pd atom ratio in the material, roughly a factor of 4 increase over the equilibrium value of 0.011 H/Pd in bulk at $P = 0$ and $p_{\mathrm{H}_2} = 2$ kPa. This is compatible with previously reported values between 0.03 H/Pd and

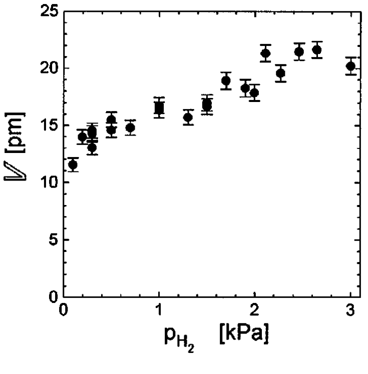

FIG. 2. Stretch $\mathbb{V}$ versus hydrogen partial pressure p_{H_2}.

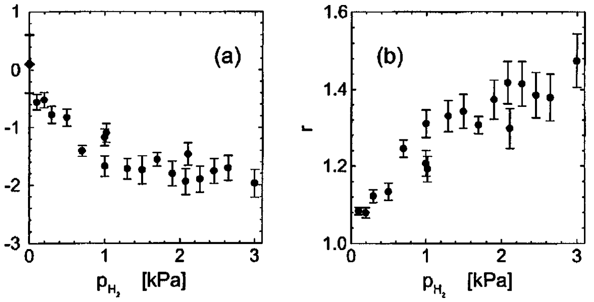

FIG. 3. Scalar interface stress f (a) and solute enrichment ratio in bulk r (b) versus hydrogen partial pressure p_{H_2}.

0.10 H/Pd for the solubility in nanocrystalline α-Pd-H [5,19].

In conclusion, our analysis of simultaneous chemical and mechanical equilibrium in an open system with large interface-to-volume ratio has led to an expression for strain at equilibrium as a function of solute chemical potential μ and of interface stress f that allows the values of f and the solute fraction c in the bulk to be determined from experimental lattice constant data. The results testify to a strong dependency of f on chemical potential and, hence, on the hydrogen concentration at the grain boundaries. We find that reliable values for the solute fraction in the bulk can only be obtained from lattice constant data when the effect of f is taken into account. A qualitative microscopic model relates f to solute segregation and to an additional, measurable, degree of freedom for interfacial deformation, the stretch $\mathbb{V}$. The experimental results for f and $\mathbb{V}$ are consistent with that model, supporting the validity of our analysis.

A previous analysis [1] of a similar problem, the surface effect on hydrogen solubility in Pd clusters, ignores both the distinction between interface stress and interface free energy and the long-range stresses originating from solute excess at interfaces that cause f to depend on μ. Measurements of a in n-Pd-H have been reported before, but interface stress was neglected in the data analysis, and the erroneously high solute fraction thus obtained was discussed with relation to hydrogen enrichment at grain boundaries [6]. While such enrichment is well supported by experiment, our analysis demonstrates that it is *not* measured by lattice constant data.

We are grateful to C. E. Krill for performing the Warren-Averbach analysis, and to R. Birringer and M. Hoffmann for helpful discussions. This work was supported by DFG (Heisenberg program and SFB 277).

*Author to whom correspondence should be addressed. FB 10 Physik, Gebäude 43B, Universität des Saarlandes, P.O. Box 151150, D-66041 Saarbrücken, Germany. Phone: +49 681 302 5199. Fax: +49 681 302 5222. Email address: weissm@rz.uni-sb.de

[1] E. Salomons, R. Griessen, D. G. De Groot, and A. Magerl, Europhys. Lett. **5**, 449 (1988).
[2] R. J. Wolf and M. W. Lee, Phys. Rev. Lett. **73**, 557 (1994).
[3] G. Song, M. Geitz, A. Abromeit, and H. Zabel, Phys. Rev. B **54**, 14 093 (1996).
[4] A. Weidinger, D. Nagengast, Ch. Rehm, F. Klose, and B. Pietzak, Thin Solid Films **275**, 48 (1996).
[5] T. Mütschele and R. Kirchheim, Scr. Metall. **21**, 1350 (1987); *ibid.* **21**, 1101 (1987).
[6] J. A. Eastman, L. J. Thompson, and B. J. Kestel, Phys. Rev. B **48**, 84 (1993).
[7] E. D. Hondros, M. P. Seah, S. Hofmann, and P. Lejček, in *Physical Metallurgy,* edited by R. W. Cahn and P. Haasen (Elsevier, Amsterdam, 1996), 4th ed.
[8] J. W. Gibbs, *The Collected Works of* J. W. Gibbs (Longmans and Green, New York, 1928), Vol. I, p. 315.
[9] R. Shuttleworth, Proc. Phys. Soc. A **63**, 444 (1950).
[10] C. W. Cahn, Acta Metall. **28**, 1333 (1980).
[11] J. W. Cahn, in *Interfacial Segregation,* edited by W. C. Johnson and J. M. Blakely (ASM, Metals Park, OH, 1978), p. 3.
[12] M. E. Gurtin, J. Weissmüller, and F. Larché, Philos. Mag. A **78**, 1093 (1998).
[13] F. Larché and J. W. Cahn, Acta Metall. **21**, 1051 (1973).
[14] E. Wicke and H. Brodowsky, in *Hydrogen in Metals II,* edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978).
[15] F. A. Lewis, *The Palladium-Hydrogen System* (Academic Press, London, 1967).
[16] J. Weissmüller and J. W. Cahn, Acta Mater. **45**, 1899 (1997).
[17] J. Löffler and J. Weissmüller, Phys. Rev. B **52**, 7076 (1995).
[18] C. E. Krill and R. Birringer, Philos. Mag. A **77**, 621 (1998).
[19] U. Stuhr, H. Wipf, T. J. Udovic, J. Weissmüller, and H. Gleiter, J. Phys. Condens. Matter **7**, 219 (1995).
[20] R. B. Schwarz and A. G. Khachaturyan, Phys. Rev. Lett. **74**, 2523 (1995).
[21] M. Hoffmann, Ph.D. thesis, Universität des Saarlandes, 1998, R. Birringer and M. Hoffmann (to be published).
[22] I. C. Noyan and J. B. Cohen, *Residual Stress: Measurement by Diffraction and Interpretation* (Springer, New York, 1987).