

SEGREGATION OF HYDROGEN AT DISLOCATIONS

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ABSTRACT

The interaction of hydrogen with dislocations affects the strength of a material in three ways. It may

1. Enhance or retard dislocation mobility (HELP mechanism or solute drag)
2. Enhance the transport of hydrogen towards a crack tip (pipe diffusion and H-transport by gliding dislocations)
3. Lower the energy of formation of a dislocation (by a generalized Gibbs' adsorption isotherm)

The last aspect has not been discussed so far and will be shortly introduced. Experimental results for the segregation of H atoms at dislocations in Pd will be presented which were obtained by measuring H-solubility, H-diffusivity, partial molar volume of H and small angle neutron scattering. The results clearly show that a strong segregation is caused by both elastic interaction and solute-solute interaction. Thus segregation is described better by a hydride formation at the dislocation and not by a less dense Cottrell cloud. Measured radii of hydrides within the expanded region of the glide plane of an edge dislocation are compared with results of a simple thermodynamic model.

1 INTRODUCTION

Theoretical models describing the interaction of solute atoms with dislocations (Hirth and Lothe [1]) are based on an elastic interaction between the stress field around dislocations and the strain caused by a solute atom. The interaction is strongest for edge dislocations because of their hydrostatic stress field. Thus solute atoms changing the volume during dissolution, i.e. containing a non-vanishing trace in their strain tensor experience a strong elastic interaction with edge dislocations. Hydrogen in metals causes volume expansion and, therefore, interacts strongly with the stress field of edge type dislocations. As stresses of dislocations are calculated by applying continuum theory they are less reliable within the dislocation core and, therefore, trapping of hydrogen in dislocation cores has to be treated separately. In the following section the density of site energies $n(E)$ is calculated based on these considerations for edge dislocations. The interstitial sites with varying energy are filled according to Fermi-Dirac Statistics (Kirchheim [2]) yielding the total concentration of hydrogen c , i.e. the ratio of the number of H-atoms N and the number of interstitial sites N_0

$$c = \frac{N}{N_0} = \int_{-\infty}^{\infty} \frac{n(E)dE}{1 + \exp[(E - \mu)/kT]}, \quad (1)$$

where μ is the Fermi energy or the chemical potential, respectively. Thus the dislocations give rise to an energy landscape for the migrating H-atoms and the H-diffusivity will be decreased because H-atoms are trapped within the low energy sites of the distribution.

2 DENSITY OF SITE ENERGIES

The hydrostatic part of the stress field of an edge dislocation is given by [72]

$$p = \frac{\sigma_{ii}}{3} = \frac{Gb(1+\nu)}{3\pi(1-\nu)} \frac{\sin \theta}{r}, \quad (2)$$

where G is the shear modulus, ν Poisson's ratio, b the magnitude of the Burger's vector, θ and r are cylindrical coordinates as defined in Fig. 4 with the z -axis along the dislocation line. Then the interaction energy with H-atoms on a circle of constant pressure is obtained from

$$pV_H = \frac{Gb(1+\nu)}{6\pi(1-\nu)R} V_H \equiv \frac{AV_H}{R}, \quad (3)$$

where R is the radius of the cylinder and A is defined by the last equation.

For H in Pd the number of octahedral sites which are chosen by hydrogen is the same as the number of Pd-atoms. We assume that like in the β -phase of Pd only the fraction α (being ca. 0.6 at room temperature) is occupied. Then in a material containing ρ dislocations per unit area the number of sites, n, in a cylinder of radius R and unit length is $\rho\pi R^2$ and the DOSE becomes

$$n(E) = \alpha\rho \frac{dn}{dE} = \alpha\rho \frac{dn}{dR} \frac{dR}{dE} = \alpha\rho\pi R \frac{AV_H}{E^2} = \frac{\alpha\rho\pi AV_H}{E^3}. \quad (4)$$

Inserting this in Eq. (1) and solving for μ by using the step approximation for the Fermi-Dirac distribution (Kirchheim [2]) gives

$$\mu = \sqrt{\frac{\alpha\rho\pi AV_H}{c}}. \quad (5)$$

3 COMPARISON WITH EXPERIMENTAL RESULTS

The last equation is checked by plotting in Fig. 1 measured values of μ for H in cold rolled Pd [73] versus the reciprocal square root of concentration.

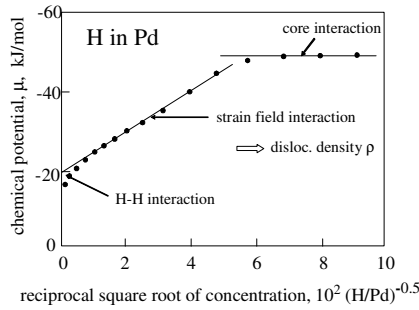


Figure 1: Electrochemically measured chemical potentials of hydrogen in heavily deformed palladium plotted according to Eq. 5 versus $1/\sqrt{c}$. The various regions of the data points represent regions of a predominant interaction mechanism.

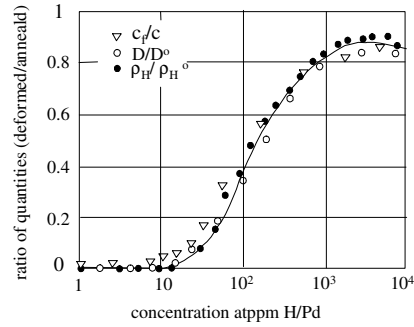


Figure 2: Hydrogen resistivity increment, hydrogen diffusivity and the concentration of free hydrogen in heavily deformed palladium divided by the corresponding values in single crystalline Pd. These ratios are plotted versus H-concentration and in agreement with Eq. (7) they are about the same over the whole range of concentrations within the α -phase of Pd.

Different to the theoretical prediction the interaction energy (difference of chemical potentials between deformed and annealed sample) becomes constant at very low concentrations which is explained in terms of a direct interaction with the dislocation core which was not included in Eq. (1). The value of about -50 kJ/Mol-H has been also determined for H in Fe (Kumnick and Johnson [3]). The linear dependence on $1/\sqrt{c}$ in Fig. 1 yields a slope which corresponds to reasonable dislocation densities for heavily deformed metals ($\rho=2 \cdot 10^{11} \text{ cm}^{-2}$). Contrary to Eq. (5), the straight line corresponding to the interaction with the long range stress field of the dislocation does not

intercept the ordinate at 0 but at a value of about -20 kJ/Mol-H. This is attributed to a direct H-H interaction. It can be calculated from the values obtained for this interaction in well annealed Pd at high H-concentrations where W is defined as $\mu = \mu(\text{ideal-dilute}) + Wc(\text{local})$ and it was measured to be $W = -30$ kJ/mol-H (Wicke and Blaurock [4]). With a maximum local concentration $c = \alpha = 0.6$ the contribution to μ from H-H interaction becomes -18 kJ/mol-H in good agreement with the intercept in Fig. 5.

During the electrochemical measurements of μ the standard value was defined such that

$$\mu = k_B T \ln c_f \quad (6)$$

This is also the chemical potential for the single crystalline metal, where the concentration of free hydrogen c_f is equal to the total concentration. Besides measuring μ for a metal with a high dislocation density in comparison with a single crystal, the concentration of free hydrogen can be determined also from measurement of the electrical resistance. It has been shown for Pd (Rodrigues and Kirchheim [6]) that hydrogen trapped as a hydride at the dislocation lines contributes to the resistivity to a negligible part only when compared to the same number of H-atoms distributed homogeneously. Thus the resistivity increment ρ_H caused per unit of H-concentration divided by the same increment in a single crystal ρ_H^0 yields the fraction of H-atom being free. The same is true for a dislocated metal and its tracer diffusion coefficient $D^* = D^0 \gamma$ (Kirchheim [2]) where $\gamma = \exp(\mu/kT)/c$ is the activity coefficient and D^0 has a well defined operational meaning being the tracer diffusion coefficient in the single crystal. Therefore, we have

$$\gamma = \exp\left(\frac{\mu}{k_B T}\right) = \frac{c_f}{c} = \frac{\rho_H}{\rho_H^0} = \frac{D^*}{D^0} \quad (7)$$

It is shown in Fig. 2 that this simple relation holds for hydrogen in strongly deformed palladium. At very low H-concentrations the fraction of free hydrogen is negligible and, therefore, all the hydrogen is trapped at dislocations. At intermediate concentrations hydrogen atoms are partitioned between sites far away from dislocations and those close to them. But sites at dislocations never become saturated because of both the long range elastic interaction and an attractive H-H interaction. Thus the corresponding cylinder being enriched in hydrogen is steadily growing.

The concentration dependence of the chemical diffusion coefficient of H in deformed crystalline Pd is shown in more detail for very low concentrations in Fig. 3. Using measured values of the chemical potential for the same deformed Pd and a diffusion coefficient obtained for a single crystalline Pd the lines in Fig. 3 were calculated without a fitting parameter (Kirchheim [2]). Deviations occurring at very low concentrations are either due to an enhancement of diffusion along the dislocation core or they arise because of difficulties measuring chemical potentials at very low H-concentrations.

By measuring volume changes caused by dissolved hydrogen in severely deformed crystalline palladium (99% reduction in cross section by cold rolling) it was shown (Kirchheim [7]) that samples contracted for the first 50 to 100 atppm of H. This was attributed to trapping in vacancies which supposedly form during cold-rolling. After saturating the vacancies hydrogen was trapped by dislocation. In this concentration range the molar volume of hydrogen was slightly smaller than in single crystalline Pd. This behavior is in accordance with the assumption of hydrogen being dissolved in the expanded region below the glide plane of edge dislocations. With increasing concentration the dislocations became saturated and additional hydrogen was predominantly dissolved in normal octahedral sites far away from dislocations. As a consequence the hydrogen partial molar volume approached that of the single crystal.

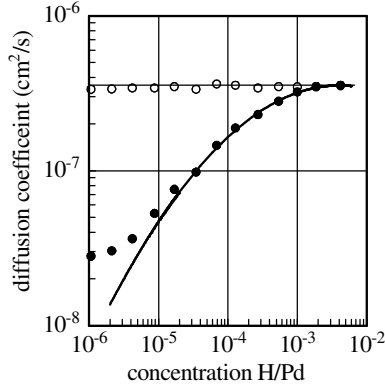


Figure 3: Diffusion coefficient of hydrogen in heavily deformed Pd (closed circles) and well annealed Pd (open circles). The line following the values of deformed Pd was calculated from measured chemical potentials without a fitting parameter (Kirchheim [2]).

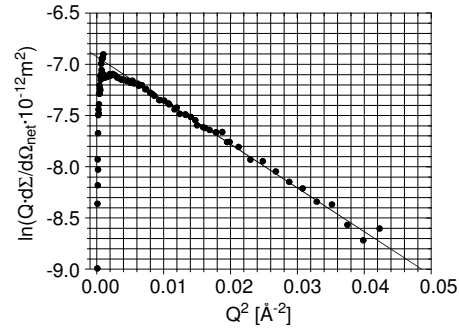


Figure 4: A modified Guinier Plot of the macroscopic scattering cross section $d\Sigma/d\Omega$ (cf. Eq. 8) measured by small angle neutron scattering for deformed Pd with 1 at.-% H. The slope of the linear part yields the radius of hydrogen enriched cylinders formed by segregation at the dislocation line.

So far the segregation of hydrogen at edge dislocation and the concomitant formation of hydride cylinders below the glide plane have been proven in an indirect way only. Direct evidence can be provided by small angle neutron scattering (SANS). Scattering by randomly oriented cylinders has to be described by the following macroscopic cross section (Maxelon et al. [8])

$$\frac{d\Sigma}{d\Omega} = \frac{2\pi^3 \rho R_0^4 \Delta g^2}{Q} \exp\left[-\frac{1}{4} Q^2 R_0^2\right], \quad (8)$$

where ρ is the dislocation density, R_0 the radius of the cylinders, Δg is the difference of scattering length densities and Q is the magnitude of the scattering vector. By plotting the logarithm of the product of Q and measured values of the macroscopic cross section (after appropriate subtraction of background and incoherent scattering) versus Q^2 straight lines are expected according to Eq. (8). This is in agreement with experimental findings as shown in Fig. 4. The slope of the straight lines yields the radius of the cylinders and the intercept with the ordinate yields the dislocation density. Similar plots have been evaluated for different H-concentrations and the results are presented in Fig. 5.

However, the natural choice for SANS is deuterium instead of hydrogen because the former has a larger cross section for coherent scattering. In addition, hydrogen gives rise to pronounced incoherent scattering, i.e. raises the background. In agreement with the larger coherent scattering measurements with deuterium lead to larger macroscopic cross section as shown in Fig. 6. However, they are larger by a factor of 1.5 only, whereas Eq. (8) predicts a factor of 3.2 corresponding to the squared ratio of scattering length densities. This discrepancy is overcome by taking into account that there are two contributions to the scattering contrast. The first one is due to the H- or D-atoms having a higher concentration at the dislocation lines. The second one is a consequence of this segregation, because both isotopes expand the Pd-lattice and, therefore, reduce the scattering contrast of Pd with respect to the matrix far away from dislocations. H-atoms have a negative scattering length for neutrons and the corresponding negative contrast (difference

of scattering length density) is exaggerated by the lattice expansion. For deuterium with a positive scattering length the opposite is true. Thus the peculiar scattering behavior of the hydrogen isotopes yields additional insight into the segregation at dislocations.

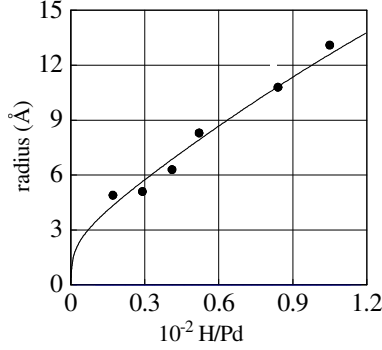


Figure 5: Radii obtained from small angle neutron scattering for a deformed Pd-sample at various H-concentrations. The line is calculated by assuming the formation of a hydride of cylindrical shape in the strain field of dislocations. The dislocation density ($\rho=2 \cdot 10^{11} \text{ cm}^{-2}$) was used as a fitting parameter to obtain agreement with experimental data.

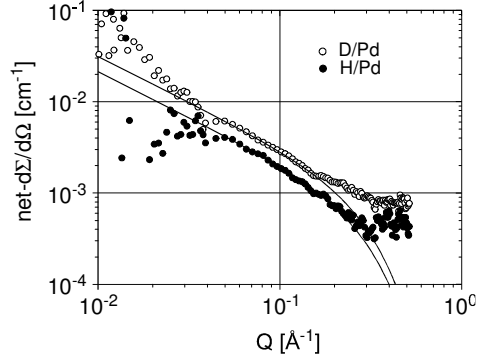


Figure 6: Macroscopic cross section for a deformed Pd sample containing 0.8 at.-% hydrogen (closed circles) or deuterium (open circles). The lines are calculated by using Eq. (8). The difference of $d\Sigma/d\Omega$ between the two isotopes is less than expected from their scattering length which is evidence for a volume expansion during the “hydride” formation at the dislocation lines (cf. text).

A thermodynamic model is presented in the following that treats the pronounced segregation as a hydride formation in a hydrostatic stress field. Without stresses ($p=0$) and for equilibrium between the hydride and saturated solid solution, the chemical potentials in the two phases have to be the same, i.e.

$$\mu_{(\text{hydride}, p=0)} = \mu^0 + kT \ln c_{ts} \quad (9)$$

where c_{ts} is the terminal solubility of hydrogen in Pd in equilibrium with the β -phase (of composition PdH_α). As the terminal solubility of H is 0.01 H/Pd at room temperature, the ideal solution approach for the configurational entropy (logarithmic term in Eq. (9)) is justified. At the border between the cylindrical hydride and the solid solution a constant hydrostatic pressure p is present, and the chemical potential is changed to

$$\mu = \mu^0 + kT \ln c_{ts} + pV_H, \quad (10)$$

where V_H is the partial molar volume of hydrogen. Far away from the dislocation where hydrogen is free and where it has a local concentration of c_f , the chemical potential is given by $\mu = \mu^0 + kT \ln c_f$ (here with the standard value μ^0). Then the last equations yield

$$c_f = c_{ts} \exp\left(\frac{Gb(1+\nu)V_H}{6\pi(1-\nu)kTR}\right) = c_{ts} \exp\left(\frac{C}{R}\right) \quad (11)$$

where C is 1.0 nm for edge dislocations of $b=0.275$ nm in Pd. Besides c_f the hydrogen trapped as a cylindrical hydride of composition $\alpha=0.6$, radius R and length ρ contributes to the total concentration c_{tot} . Thus we have in terms of H/Pd

$$c_{tot} = \alpha \rho \pi R^2 + c_f = \alpha \rho \pi R^2 + c_{is} \exp\left(-\frac{C}{R}\right). \quad (12)$$

If we use this implicit function of $R(c_{tot})$ and compare it in Fig. 5 with measured values, a good agreement is obtained by using a dislocation density of $2.2 \cdot 10^{11} \text{ cm}^{-2}$. This is considered to be additional evidence for an extended segregation of hydrogen, which requires taking into account both elastic and solute/solute interaction.

The experimental results presented in this section are in qualitative agreement with a variety of studies by other groups (Flanagan and Lynch [9], Züchner [10], Heuser et al. [11] and Ross and Stefanopoulos [12]).

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