



Hydrogen diffusivities as a measure of relative dislocation densities in palladium and increase of the density by plastic deformation in the presence of dissolved hydrogen

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Abstract—The effect of dissolved hydrogen on the dislocation density in cold-rolled palladium was investigated in order to provide evidence of a line energy reduction caused by hydrogen–dislocation interaction as proposed by the defactant concept. For this issue, palladium samples were electrochemically charged with hydrogen and subsequently cold rolled. Using conventional methods (X-ray diffraction, transmission electron microscopy) and a newly developed diffusion method, it was shown that the dislocation density after deformation increases with increasing hydrogen concentration.

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1. Introduction

A wide range of effects can be attributed to the presence of hydrogen in metals. For instance, dissolved hydrogen can enhance crack propagation [1] or lead to the formation of blisters on surfaces [2]. In the microscopic range, hydrogen can interact with all types of defects. In many metals hydrogen has a large influence on the formation and stabilization of vacancies, e.g. in Al [3], Nb [4] and Pd [5]. This is explained by a decrease in the formation energy of vacancies due to the segregation of hydrogen atoms to these vacancies [6,7].

Another effect is a transition from ductile to brittle behavior by the introduction of hydrogen into e.g. Al [8] or austenitic stainless steels [9,10]. One explanation for this effect is the enhanced mobility of dislocations due to the segregation of hydrogen to these dislocations [1,11].

The influence of hydrogen on dislocations is discussed in both an earlier report by Chen et al. [12] and this report. It will be shown that the line energy of dislocations is decreased by charging palladium with hydrogen, which in turn leads to an increase in dislocation density during cold deformation.

These effects can be explained by the defactant concept [6,7,13], the basis of which is that a decrease in the overall free energy caused by a segregation of solute atoms to the neighborhood of defects can be ascribed to a decrease in the defect formation energy. This is an alternative point of view compared to textbook concepts, according to which solute atoms migrate to defects because their energy of solution is decreased.

In this study the effect of hydrogen on the density and arrangement of dislocations in cold-rolled palladium–hydrogen alloys was investigated. Due to the high solubility of hydrogen (up to $1.0 \times 10^{-2} \frac{\text{H}}{\text{Pd}}$ at 298 K [14]) in the α -phase of the palladium–hydrogen system, this system was chosen as a model system.

For this purpose, well-annealed polycrystalline palladium samples were electrochemically alloyed with hydrogen and subsequently cold rolled. The dislocation densities of the cold-rolled samples were estimated via two different methods: a conventional Williamson and Hall method [15] and a newly developed pulse diffusion method.

2. Theory

2.1. The interaction between solute atoms and crystal defects – the defactant concept

Solute atoms in solid material segregate to defects like vacancies [16], dislocations [17] or grain boundaries [18].

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This phenomenon can be described in analogy to the segregation of surfactants to surfaces described by the well-known theory of Gibbs [19]. The defectant concept regards the surface as a crystal defect like any other internal defect. Therefore the relation of the reduction of the surface energy γ with the chemical potential of the solute μ provided by Gibbs can also be used to describe internal crystal defects [6,7]:

$$d\gamma = -\Gamma d\mu \quad (1)$$

Of key interest is the excess Γ , which represents the excess amount of segregated solute atoms to the defect surface in relation to the concentration of the solute atoms in a defect-free part of the material.

In the case of dislocations, solute atoms will enrich around the core of dislocations, thus dislocations have a positive excess Γ . Due to the stress field of a dislocation, interstitial lattice sites beneath the glide plane of an edge dislocation are expanded. This causes solute atoms to segregate to dislocations if they expand the lattice, otherwise they segregate to sites above the glide plane.

The positive excess of solute at dislocations then reduces the formation energy of dislocations when the chemical potential of the solute is increased, as described quantitatively by Eq. (1). The dependency of the formation energy of a defect with increasing chemical potential is shown schematically in Fig. 1. At low chemical potentials, only few solute atoms interact with the defect, leading to $\Gamma = 0$. With increasing chemical potential, the excess Γ increases. When the excess saturates, a constant slope can be expected (line 1), whereas line 2 shows the behavior when the excess does not saturate but increases with increasing μ . When a new phase nucleates (line 3), the defect energy does not decrease with increasing solute concentration any more because of the constant chemical potential during the phase transition.

2.2. Dislocation dynamics in the context of the defectant concept

Direct observations of the motion of dislocations in an environmental transmission electron microscopy (TEM) during straining experiments in a hydrogen atmosphere

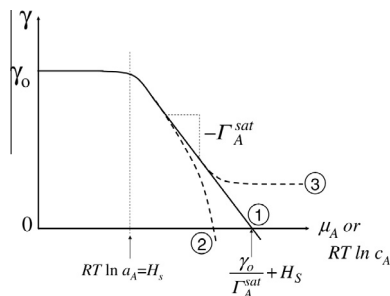


Fig. 1. Schematic representation of the course of the formation energy γ with increasing chemical potential μ . At low chemical potentials, the effect of solute atoms to the defect can be ignored. With increasing chemical potential, the excess Γ increases. When the excess saturates, a constant slope can be expected (line 1), whereas line 2 shows the behavior when the excess does not saturate but increases with increasing μ . When a new phase nucleates (line 3), the defect energy does not decrease with increasing solute concentration any more because of the constant chemical potential during the phase transition. Adopted from Refs. [6,7].

[20,21] show that the dislocation mobility is enhanced when hydrogen is present. Furthermore, it is shown that the interaction between dislocations as well as between dislocations and other obstacles [17] is diminished. This is explained by a hydrogen shielding model [22].

The defectant concept provides a different explanation of the enhanced dislocation velocity in the presence of hydrogen. Because dislocations move by the formation of kink pairs, the required defect formation energy is reduced by the presence of the defectant hydrogen. When kink pair nucleation is the rate-controlling step for dislocation motion, such a reduction in kink formation energy will lead to softening [7].

Two other defect–solute interactions can contribute to the increase in dislocation mobility: due to solute atoms, the formation energy of vacancies is changed, and for positive excess solute the formation energy is reduced [6,7]. Thus climbing of edge dislocations over obstacles can be eased. Another effect is that the interaction of dislocations on different glide planes is affected. When one dislocation cuts another dislocation on a different glide plane, kinks or jogs are introduced into the dislocations [23, chap. 22]. The ease of the formation of kinks leads to a reduction in the interaction energy between dislocations, which allows dislocations to rearrange more easily. This leads to higher local dislocation densities. Fluctuations in the density allow the formation of dislocation cells, as described by Holt et al. [24,25] in a model where the cell formation is handled like spinodal decomposition. Furthermore, the number of dislocations affected by a moving dislocation is increased. This means that the correlation length of the dislocations is increased, which, according to Hähner [26], leads to larger dislocation cells with more densely populated cell walls.

3. Experimental details

A 500 μm thick palladium sheet of 99.95% purity supplied by Wieland Edelmetalle GmbH was used for the investigation. Pieces of $6 \times 20 \text{ mm}^2$ were cut by spark erosion. The palladium pieces were annealed at 1172 K in a vacuum furnace at 10^{-6} mbar for 48 h and subsequently furnace cooled for 24 h to prevent residual stress in the samples.

The samples were charged electrochemically with hydrogen using an electrolyte composed of H_3PO_4 and glycerine (1:2 by volume). By using a maximum current density of 0.3 mA cm^{-2} , the entire hydrogen created by the electrolysis process is dissolved in the palladium, i.e. no hydrogen bubbles are observed. The hydrogen concentration c_{H} , which is the molar fraction of the number of hydrogen atoms to palladium atoms, can be determined via Faraday's law:

$$\Delta c_{\text{H}} = \frac{It}{n_{\text{Pd}}F}, \quad (2)$$

where t is the time of the loading process, F is Faraday's constant, I is the total current and n_{Pd} is the amount of palladium.

Immediately after loading with hydrogen, the samples were cold rolled to a thickness reduction of $(50 \pm 3)\%$.

TEM specimens were prepared by electropolishing using a Tenupol-2 electropolisher with an electrolyte composed of 70 vol.% acetic acid (96%) and 30 vol.% perchloric acid (60%) at 287 K and a voltage of 10 V against a Pt counter electrode.

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