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Hydrogen in nanocrystalline palladium

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Abstract

Hydrogen solubility and diffusion experiments were performed on nanocrystalline palladium prepared by pulsed electrodeposition (PED). Compared with polycrystalline palladium we found a faster hydrogen diffusion, a narrower two phase region and a larger solubility of the α-phase.

Keywords: Nanocrystalline palladium; Hydrogen diffusion; Electrochemistry; Pulsed electrodeposition

1. Introduction

Nanocrystalline materials consists of crystallites with typical diameters in the range 5–80 nm and an increasing volume fraction of grain boundaries with decreasing crystallite size. The nanostructure (porosity, texture, grain boundary structure, impurities) of nanocrystalline samples can be influenced by the preparation technique. For this reason it is important to compare the properties of samples prepared by different methods. The hydrogen solubility and hydrogen diffusion in nanocrystalline palladium prepared by inert gas evaporation was measured by Kirchheim et al. [1].

The Pulsed Electrodeposition (PED) allows the preparation of large amounts (several g per day) of nanocrystalline metals (Pd [2], Cu [3], Ni [4,5]) and alloys (CuNi [6]). By proper choice of the plating parameters (bath composition, pulse parameters) the grain size can be varied from 8 to more than 100 nm. The samples produced by this technique are essentially free of texture and porosity (density: 99%). Their thickness can be varied from 1 μm to 0.5 mm. Nanocrystalline palladium samples prepared by this technique were used for hydrogen solubility experiments and electrochemical diffusion measurements.

2. Experimental

2.1. Sample preparation

Our nanocrystalline palladium samples were electrodeposited by PED using an electrolyte containing $(NH_4)SO_4$, $PdCl_2$ and an organic complex former [2]. A pulse generator generates rectangular current pulses (t_{on}: 1 ms, t_{off}: 80 ms) and a galvanostatic unit keeps the pulse current (I_{pulse}: 1.0 A/cm^2) constant. The samples can be mechanically removed from the titanium cathode. The grain size was determined by a modified Warren-Averbach analysis [2] and by different kinds of electron microscopy (STM, TEM, HR–SEM). The interstitial impurities (H: 200 wt.-ppm, O: 2500 wt.-ppm, N: 3500 wt.-ppm) were analysed by hot extraction. The samples exhibit a very low bulk porosity of ≈1% (helium pycnometry, Archimedes method).

2.2. Hydrogen loading

3 g of nanocrystalline palladium (grain size: 10 nm) were stepwise loaded with gaseous hydrogen (99.99%) in a high vacuum gas volumetric apparatus. The pressure–composition-isotherms were recorded at 318 and at 348 K.

2.3. Electrochemical diffusion experiments

A n-palladium foil (diameter: 1 cm, thickness: 120 μm) with a grain size of 17 nm and a polycrystalline sample (diameter: 2 cm, thickness: 120 μm) were used for electrochemical permeation experiments (time-lag) at 288 K. We use the electrochemical double cell method (electrolyte: 1 N H_2SO_4) according to Züchner [7]. Hydrogen was electrochemically deposited (current pulse: 50 mA, pulse-duration: 100 ms) on one side of the sample and the e.m.f. (vs. Ag/AgCl reference-electrode) of the opposite side was recorded as a function of time (Fig. 1).

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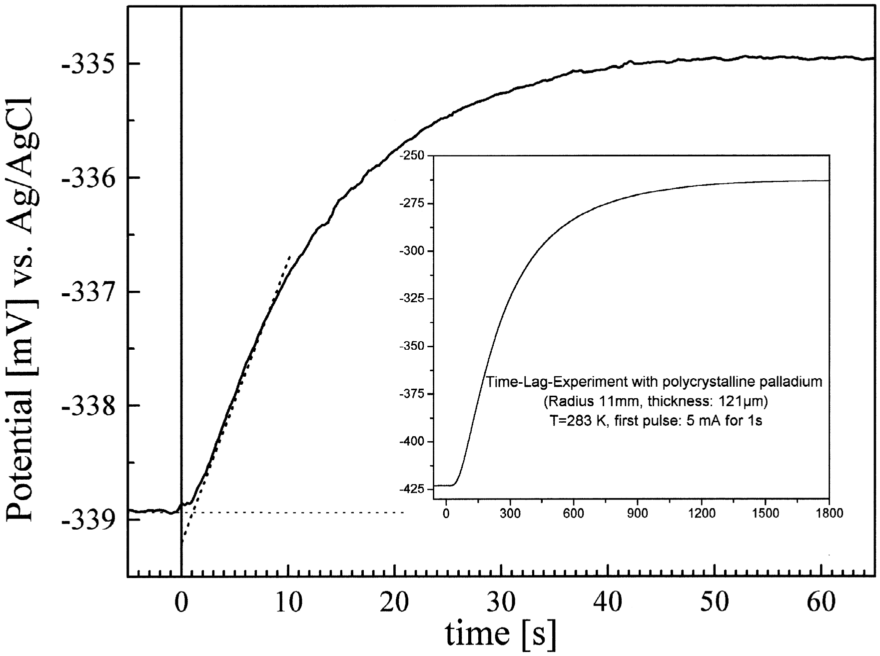

Fig. 1. Electrochemical time-lag experiment with nanocrystalline and polycrystalline (inlay) palladium at 283 K (thickness 120 µm, Ø: 10 mm).

3. Results

Compared to polycrystalline palladium the nano-Pd/H system exhibits a narrower two phase region. For 318 K we found a maximum α-phase concentration (PdH_x) of x=0.04 and for 348 K x=0.035 (poly Pd: x=0.017 [8]) as observed by Wicke and coworkers [9]. The β-phase minimum was determined at x=0.45 (318 K) and at x=0.35 (348 K). Polycrystalline palladium has a β-phase minimum at x=0.575 at room temperature [8]. From these data we calculate an absorption enthalpy of −46.3 kJ/mol (poly Pd: −19.4 kJ/mol [8]) and an absorption entropy of 171.3 J/K mol (poly Pd: 106.8 J/ K mol [8]).

From the electrochemical permeation experiment we determined for n-Pd a time lag of 0.7 s at 283 K whereas for polycrystalline palladium a time lag of 37 s (Fig. 1) was found. The diffusion coefficients were received from the time lag evaluation [6]. The hydrogen diffusion in nanocrystalline palladium is faster ($D=7\cdot10^{-6}$ cm^2 s^{-1}) than in polycrystalline palladium ($D=1.9\cdot10^{-7}$ cm^2 s^{-1}).

4. Discussion

The faster hydrogen diffusion in nanocrystalline palladium probably originates from the defect structure (grain boundaries, triple line junctions) of the nanocrystalline materials. The complete diffusion mechanisms are not known yet but these previous results are the starting point for further experiments (e.g., QENS [10], diffusion experiments in dependence on the grain size).

The hydrogen absorption experiment shows the same effect as Kirchheim et al. [1] observed for nanocrystalline palladium prepared by inert gas condensation. The decreased hydrogen concentration of the β-phase minimum was explained with a β-phase transformation only in the grains but not in the grain boundaries. The hydrogen concentration in the grain boundaries stays constant at the α-phase value whereas the phase transformation takes place in the grains. To verify these assumptions further experiments with n-Pd samples of different grain sizes are in progress.

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