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An investigation of hydrogen diffusion in nanocrystalline Pd by neutron spectroscopy

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Abstract

The diffusion of H interstitials in nanocrystalline Pd was investigated by neutron spectroscopy (temperatures of 288 and 300 K, grain diameters between 7 and 25 nm, H concentrations of 2.9 and 3.7 at.%). The experiments indicate that a high fraction of the dissolved H is located in grain boundaries (this agrees with previous studies). They show further that the H atoms in the grain boundaries perform a diffusion process which (i) is partially locally restricted and (ii) exhibits jump rates that are up to a factor ~100 higher than those of diffusion within the grains.

Keywords: Diffusion; Nanocrystalline Pd; H metal systems; H in metals

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1. Introduction

Nanocrystalline materials are polycrystals with grain sizes in the range of a few (~2–50) nanometers [1–3]. Therefore, the number of atoms in the grains, which have a regular crystalline surrounding, is comparable with the number of atoms in grain boundaries with a disordered structure. Two prominent methods for the production of nanocrystalline materials, particularly suitable for materials of high purity, are inert gas condensation (IGC) [1,2,4] and pulsed electrodeposition (PED) [5,6].

The properties of H interstitials in conventional coarse-grained (or single-crystalline) Pd were probably more intensively studied than in any other metal [7–10]. In contrast to this, H behavior in nanocrystalline Pd was only rarely investigated [11–14]. What was studied so far is (i) the solubility of the H [11–14], (ii) its vibrational properties [14] and (iii) its chemical diffusion [11]. Compared with conventional Pd, the studies revealed an increase of the solubility of the H, a shift of its solubility limit (or of the miscibility gap of the Pd–H phase diagram) to higher H concentrations and an increase of its chemical diffusion coefficient (up to a factor of ~4) for H concentrations above ~0.4 at.% (for lower concentrations, the diffusion coefficient was smaller than that in conventional Pd). The results indicate that a large fraction of the dissolved H is located in grain boundaries where it can diffuse faster than in the grains, provided that low-energy traps are sufficiently saturated (e.g., for H concentration above ~0.4 at.% [11,12]). This fact makes H in nanocrystalline Pd an ideal model system for a study of grain boundary diffusion processes.

The present paper reports experiments in which we studied H diffusion in nanocrystalline Pd by quasi-elastic neutron scattering [15]. Our data show that the H interstitials in the grains of the nanocrystalline sample have a diffusivity similar to that in the grains of conventional coarse-grained Pd, whereas the H atoms in the grain boundaries —i.e. a large fraction of the total number of H atoms— perform a fast diffusive motion with jump rates that are up to ~100 times higher than those in the grains.

2. Experimental

Two nanocrystalline Pd samples were investigated, one prepared by IGC (5.4 g, grain diameters between 10 and 25 nm) and the second one by PED (26.2 g, grain diameters between 7 and 18 nm). The samples were enclosed in Al containers and doped with 2.9 at.% H (IGC-sample) and 3.7 at.% (PED-sample), respectively. The H concentrations were sufficiently low to ensure that

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the samples were well within the pure α-phase (at room temperature) [11–14].

Nanocrystalline materials prepared by different techniques tend to differ in their properties (grain diameter, porosity and impurity content) [1–3]. For this reason, we investigated two differently prepared samples in order to establish a possible influence of the preparation technique on the H diffusion behavior.

The quasi-elastic neutron scattering experiments were carried out at 288 and 300 K with the backscattering spectrometer IN 16 and the time-of-flight spectrometer IN 5 at the ILL in Grenoble. The energy resolutions (FWHM) were ~0.6 μeV (IN 16) and ~60 μeV (IN 5). The investigated Q values ranged from 0.24 to 1.81 $\mathring{A}^{-1}$ for IN 16 and from 0.47 to 1.80 $\mathring{A}^{-1}$ for IN 5 ($\hbar Q$ is the momentum transfer in the scattering process). The resolution functions were determined either from a vanadium standard (IGC sample) or from a low temperature (~7 K) spectrum of the PED sample where H diffusion is expected to be frozen in.

3. Experimental results and discussion

A detailed description of the technique of quasi-elastic neutron scattering is found in [15]. For the present situation and because of the large incoherent scattering cross-section of the H, the measured neutron spectra represent nearly exclusively the incoherent scattering from the H, plus an elastic contribution from the Pd atoms and the sample container. The incoherent scattering from the H is described by the incoherent scattering law $S(Q,\omega)$ which is the two-fold Fourier transform of the self correlation function of the H in space and time. Accordingly, the scattering law $S(Q,\omega)$ contains the information on the self diffusion of the H interstitials.

Fig. 1 and Fig. 2 show neutron spectra taken from the IGC sample with instrument IN 16 (288 K, $Q=1.01$ $\mathring{A}^{-1}$) and IN 5 (300 K, $Q=1.24$ $\mathring{A}^{-1}$), respectively. Both spectra exhibit, besides an elastic intensity, a quasielastically broadened component due to H diffusion [7,15]. The solid lines in the figures show the results of a fit to the data. The IN 16 data (Fig. 1) were fitted with an elastic line and a single quasi-elastically broadened Lorentzian line 1 with a linewidth Γ_1 (FWHM). The IN 5 data (Fig. 2) could not satisfactorily be fitted with a single quasi-elastically broadened Lorentzian line. Therefore, these data were analyzed with an elastic line and two separate Lorentzian lines 2 and 3 with the linewidths Γ_2 and Γ_3, respectively. For all fits, the lines above were convoluted with the measured resolution curves and a constant background was assumed. It is seen that the fits describe the experimental data well.

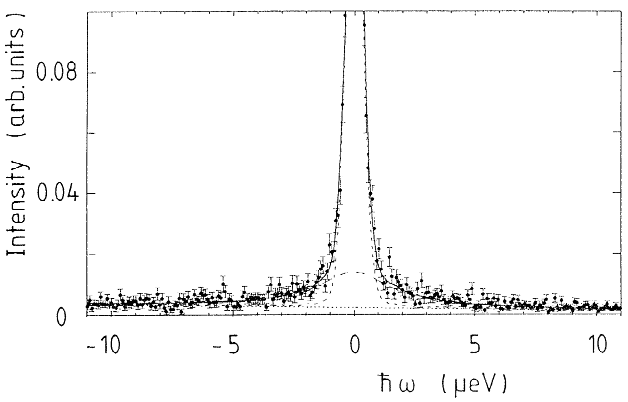

Fig. 1. Neutron spectrum of the IGC sample (IN 16, 288 K, $Q=1.01$ $\mathring{A}^{-1}$). The solid line is the fit result for the total scattering intensity, whereas the broken lines stand for the elastic intensity, the quasi-elastic intensity contribution from the Lorentzian line and the background, respectively.

The measurements on the PED sample yielded results that were essentially identical to those of the IGC sample. Therefore, we shall concentrate our subsequent discussion on the data of the IGC sample.

For such a discussion, we consider the quasi-elastic broadening due to H diffusion in conventional coarse-grained Pd first. In this case, the quasi-elastic linewidth for the temperature and the Q value of the IN 16 spectrum in Fig. 1 is ~2.6 μeV (FWHM) [7,8,10,15]. Within experimental accuracy, this value is identical to our result $\Gamma_1=(3.3\pm0.6)$ μeV for the quasi-elastic component (Lorentzian line 1) in this spectrum. Further, the Q dependence both of the linewidth Γ_1 (Γ_1 has a maximum around 1.3 $\mathring{A}^{-1}$) and the quasielastic intensity (~20% of the total intensity, Q independent) of the IN 16 spectra agree with

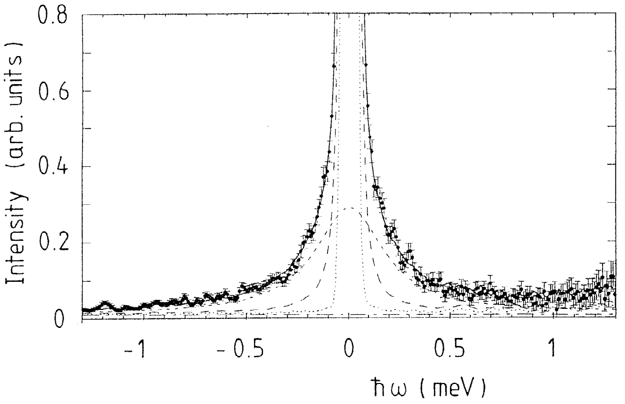

Fig. 2. Neutron spectrum of the IGC sample (IN 5, 300 K, $Q=1.24$ $\mathring{A}^{-1}$). The solid line is the fit result for the total scattering intensity, whereas the broken lines stand for the elastic intensity, the quasi-elastic intensity contributions from the two Lorentzian lines and the background, respectively.

what is expected for an ordinary long-range diffusion process [7,15]. Accordingly, we conclude that the quasi-elastic component of the IN 16 spectra results from the long-range self diffusion of H interstitials in the grains of our nanocrystalline sample.

We discuss the IN 5 data in Fig. 2 now. In our fits to these data, the quasi-elastic component obtained from the IN 16 spectra (Lorentzian line 1) cannot be found since the energy resolution of instrument IN 5 (~60 μeV) is much larger than Γ_1. Therefore, our fits attribute in fact line 1 to the elastic intensity of the IN 5 spectra. The fit results for the linewidths of the two Lorentzian lines 2 and 3 in the IN 5 spectrum of Fig. 2 are $\Gamma_2=(22\pm8)$ μeV and $\Gamma_3=(400\pm40)$ μeV, respectively ($Q=1.24$ Å^{-1}). These linewidths are larger than the total energy range of the spectrometer IN 16 (and much larger than its energy resolution), so that the quasi-elastic intensity described by the lines 2 and 3 could not be obtained in our fits to the IN 16 data since they were attributed to the background there. The linewidth Γ_3 is a factor ~100 larger than the (maximum) linewidth expected for ordinary long-range H diffusion within the grains (at 300 K) [7,8,10,15]. We conclude, therefore, that the broad quasi-elastic components (line 2 and 3) of the IN 5 spectrum reflect the diffusion of the H interstitials in the grain boundaries, and that the highest jump rates of this diffusion process are about 100 times larger than the jump rates for ordinary long-range H diffusion in the grains (~$3\cdot10^{-9}$ s^{-1} at 300 K [8,10]). Further, the intensity fraction of the quasi-elastic components (line 2 and 3) of our IN 5 spectra becomes larger with increasing Q (from ~20% for $Q=0.47$ Å^{-1} to almost 40% for $Q=1.8$ Å^{-1}), such as expected for a diffusion process that is restricted to a number of interstitial sites [15]. The IN 5 data show, therefore, that the H in the grain boundaries performs diffusion processes that are, at least partially, locally restricted (low-temperature H diffusion in $Nb(OH)_x$ exemplifies such a local diffusion between only two sites [16]).

Finally, the intensities of the quasi-elastic components of our neutron spectra provide information on the ratio between the diffusing H interstitials in the grain boundaries and in the grains. For the highest Q, the quasi-elastic component (line 1) of the IN 16 spectra was about 20% of the total scattering intensity, whereas the quasi-elastic components of the IN 5 spectra (line 2 and 3) were almost 40% of the total intensity. Accounting for the fact that our fits attributed (i) the lines 2 and 3 to the background of the IN 16 data and (ii) the line 1 to the elastic intensity of the IN 5 data, we find a ratio of ~2.4 between the sum of the intensities of line 2 and 3 and the intensity of line 1. Considering further that only a fraction of the incoherent scattering intensity is quasi-elastically broadened in the case of a diffusion process that is locally restricted (such as H diffusion in the grain boundaries at least partially is) [15], we can conclude that the concentration of the diffusing H interstitials in the grain boundaries (causing line 2 and 3) is more than 2.4 times larger than the H concentration in the grains (leading to line 1). This demonstrates again that H in nanocrystalline Pd is an ideal model system for the study of grain boundary diffusion.

The high H concentration (~2 at.%) that is responsible for the broad quasi-elastic lines 2 and 3 shows that these lines cannot result from fast H diffusion in dislocation cores (pipe diffusion). Studies on heavily deformed Pd report, for instance, that the concentration of H found in dislocation cores amounts only up to ~200 at.ppm [17]. Although dislocation densities can in fact be high in nanocrystalline Pd [18], the concentration of the H in the dislocation cores is certainly expected to be far below the at.% level in such a material. This means that the broad quasi-elastic lines must (nearly exclusively) be attributed to H interstitials in grain boundaries, in agreement with previous studies which report similar high concentrations for the H in the grain boundaries as we conclude from our present investigation.

4. Conclusions

We investigated H diffusion in nanocrystalline Pd by quasi-elastic neutron scattering. We find that H diffusion in the grains of the nanocrystalline Pd is similar to its diffusion in the grains of conventional coarse-grained Pd. The H atoms in the grain boundaries perform a diffusion process that is partially locally restricted and exhibits jump rates that are up to a factor ~100 higher than those of diffusion in the grains.

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