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Hydrogen-diffusion in $Pd_{1-x}Ag_x$ ($0 \leqslant x \leqslant 1$)

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Abstract

By further improvement of the electrochemical pulse time-lag technique it has now become possible to measure the hydrogen diffusion coefficient on the silver rich side of the series of PdAg-alloys, despite the extremely low hydrogen solubility in pure silver and the silver rich alloys. The measured macroscopic diffusion coefficient of hydrogen in Ag reaches values comparable to the diffusion in pure Pd, but is, by orders of magnitude, higher than in the $Pd_{0.5}Ag_{0.5}$ alloy. In order to describe this the diffusion process has been regarded theoretically from a microscopical point of view. This process has been simulated by computer calculations assuming hydrogen as a random walker in a Pd matrix (with high hydrogen solubility) where silver is distributed statistically, blocking the hydrogen diffusion paths to a great extent due to the extremely small hydrogen solubility. The calculated mean square distance shows an analogous behavior with increasing silver content as the measured macroscopic diffusion coefficient. This means that hydrogen diffusion through PdAg alloys takes place preferably by a roundabout way via ‘‘Pd-rich diffusion paths’’ avoiding Ag-rich regions.

Keywords: Hydrogen diffusion; Palladium–silver–hydrogen; Mean square distance

1. Introduction

The palladium–hydrogen system is a suitable model system to study diverse influences on the diffusion of hydrogen in metals. Several measurements applying quite different methods have already been carried out on this system, so the thermodynamics of hydrogen solubility, but also the diffusion behavior as a function of temperature and concentration are well known [1]. Besides pure palladium several palladium alloys have been investigated with regard to hydrogen solubility and diffusion, including the homogeneous alloy series Pd–Ag, especially in the Pd rich region. The solubility behavior in this system could be described theoretically to a good approximation [1], however, the diffusion behavior has not been explained theoretically. Additionally, reliable measurements for high silver content ($x \geqslant 0.7$) have not been carried out so far.

Therefore, in this paper the hydrogen diffusion behavior has been investigated in the $Pd_{1-x}Ag_xH_n$ system ($0 \leqslant x \leqslant 1$) using the electrochemical current pulse time-lag technique [2,3]. The measured dependence of the hydrogen diffusion coefficient on the silver concentration will be described microscopically by computer simulations applying a simple diffusion model.

2. Experimental

Hydrogen diffusion measurements were carried out using the electrochemical double cell technique, first described by Frumkin [4] and Devanathan et al. [5]. The metal foil to be investigated, separates two electrochemical half cells from each other. Applying the current pulse method [3], the charging side is exposed to a short cathodic current pulse producing a small hydrogen concentration peak which enters the sample and then equalizes by diffusion throughout the whole sample thickness. At the other side (detection side) of the sample the hydrogen concentration change is followed by recording the electrical potential as measured against a reference electrode. To obtain the exact diffusion coefficient the measured potential–time curve has been fitted by the corresponding solution of the diffusion equation, taking the diffusion coefficient as fit parameter [3,6].

Hydrogen diffusion coefficients have been measured on a series of commercially available $Pd_{1-x}Ag_x$-alloys with $0 \leqslant x \leqslant 1$ (purity $\geqslant$99.99% (Degussa)) at low hydrogen concentrations. Before measurement the samples were annealed several hours at 500 °C under high vacuum conditions ($P < 10^{-4}$ Pa). The electrochemical measurements were carried out at 296 K in 1 N H_2SO_4-solutions which were deaerated for 24 h with high purity N_2-gas

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before starting the diffusion experiments (for details see [3,6]).

3. Results and discussion

Fig. 1 shows the measured (macroscopic) hydrogen diffusion coefficients D as a function of the silver content x_{Ag} for low hydrogen concentrations (α-phase). Up to silver contents of about 20% the diffusion coefficient remains nearly constant, with increasing silver content it decreases drastically by three orders of magnitude. For $0.6<x<0.8$ no potential–time curves could be obtained, however, on the silver rich side the time-lag curves again became measurable: the diffusion coefficient reached values of about 8×10^{-8} cm^2 s^{-1} for $Pd_{0.2}Ag_{0.8}$ to 6×10^{-8} cm^2 s^{-1} for pure silver.

The diffusion coefficient as obtained by electrochemical measurements is a macroscopic quantity. It describes long range diffusion. It is controlled by microscopic individual jumps from one octahedral site to the next. For pure palladium which has identical octahedral sites a simple correlation between jump frequency or mobility and the macroscopic diffusion coefficient exists [7,8]. However, in PdAg alloys, different octahedral sites will be found, so one has to assume there will be other favourable paths for hydrogen in the alloy. This means that it becomes impossible to determine the microscopic diffusion steps or the mobility from the measured macroscopic overall diffusion coefficient.

Therefore, we tried to simulate the diffusion process by computer calculations using a simple model in order to calculate the dependence of the mean square distance on the silver content in PdAg alloys. This quantity can be taken as a measure of the macroscopic experimentally determined diffusion coefficient.

Hydrogen is taken as a random walker in an infinite face centered cubic (fcc) palladium matrix where palladium atoms are substituted statistically by silver atoms, corresponding to the silver content of the PdAg alloy. The hydrogen jumps from one octahedral site into one of the neighboring ones choosing the starting point and the jump direction arbitrarily. The square distance is determined for a fixed number of jumps of a hydrogen atom. Then the hydrogen atoms start again from an arbitrary point. This process is repeated more than 50 000 times and the mean square distance is calculated. Due to the extremely high solubility of hydrogen in Pd compared to Ag it was assumed that hydrogen diffusion paths in Pd rich alloys are blocked by Ag. In the first step of calculations of the mean square distance it is assumed that the arbitrary distribution of Ag is equivalent to a corresponding distribution of blocked sites. Thus, whether a site is blocked or not, hydrogen diffusion takes place by a roundabout way via unblocked diffusion paths. With increasing blocking (increasing Ag content) the favourable diffusion paths and the mean square distance decreases (Fig. 2, curve a). To describe the hydrogen diffusion behavior in Ag rich alloys, in a second step it is presumed that hydrogen atoms are also allowed to jump with a certain probability into blocked sites. The ratio of jump probabilities into an unblocked or a blocked site (L) is the result of different hydrogen solubilities in Pd and in Ag. The comparison of the simulations (Fig. 2) and the measured values show at least a sufficient qualitative agreement. A problematic point is to assign the number of blocked sites to the silver content.

To improve the calculation the structural arrangement of the sites has been included in the calculation in such a way that the number of silver atoms forming the octahedral sites together with the palladium atoms were considered. It is assumed that a diffusion path through an octahedral site is blocked totally when a certain number (1–6) of silver atoms are constituents of the octahedron. The calculated

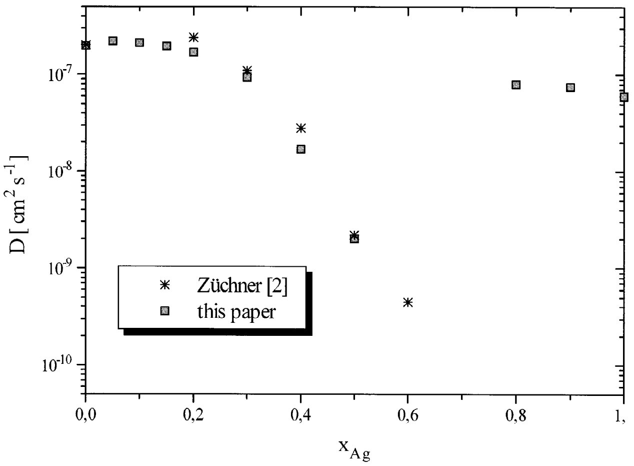

Fig. 1. Hydrogen diffusion coefficients in $Pd_{1-x}Ag_x$ as a function of the silver content; results from electrochemical current pulse measurements at small hydrogen concentrations and $T=296$ K.

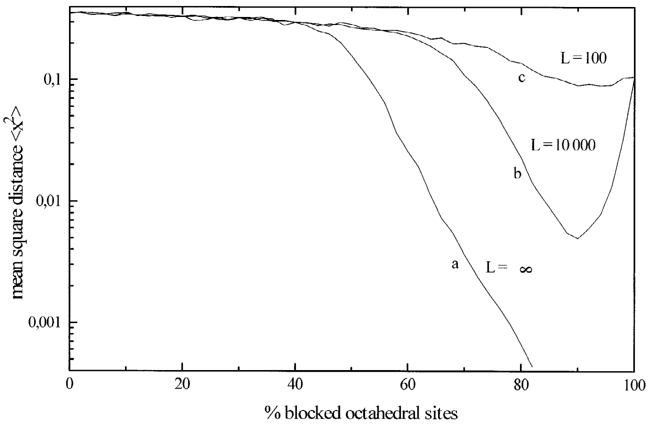

Fig. 2. Calculated mean square distance (arb. units) as a function of the percentage of totally ($L=\infty$) and partly blocked sites ($L=10\,000$ and $L=100$). The mean square distance in pure Pd and pure Ag are standardized to the diffusion coefficients in Pd and Ag, respectively.

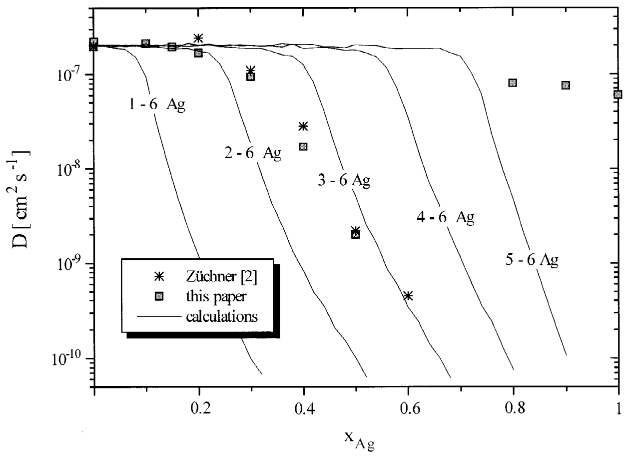

Fig. 3. Calculated and measured hydrogen diffusion coefficients in $Pd_{1-x}Ag_x$ as a function of the silver content; the diffusion via blocked sites is totally ignored.

curves (Fig. 3) standardized to the hydrogen diffusion coefficient in pure Pd show that octahedral sites formed by about 40% (2.5 Ag atoms per octahedron) and more silver are blocked completely for hydrogen.

In order to describe the diffusion behavior in silver rich PdAg alloys one could assume a certain, but small, probability for hydrogen jumping into blocked sites. The results of such a calculation for different ratios L of jump probabilities is presented in Fig. 4 assuming that 2 or more silver atoms in the octahedron block the hydrogen diffusion partly.

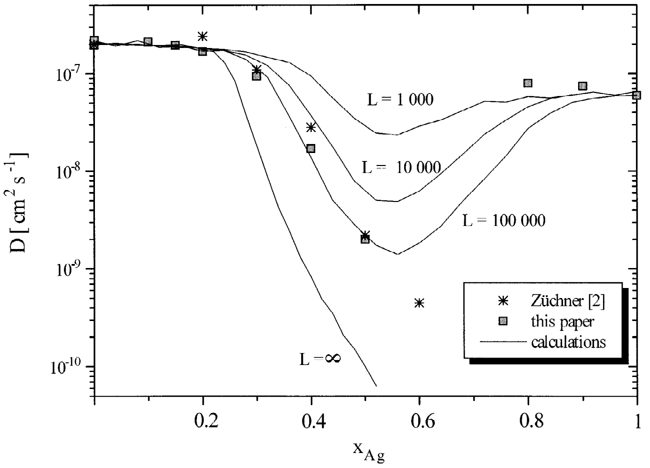

Fig. 4. Comparison of the measured diffusion coefficients and the standardized mean square distances calculated for different jump probabilities into partly blocked ($L=1000$, 10 000 and 100 000) and totally blocked ($L=\infty$) sites, assuming that a site is blocked or partly blocked if 2 or more Pd atoms are substituted by Ag.

The agreement between the measured D values and the calculated and standardized mean square distances is excellent if one considers the simple microscopic diffusion model.

4. Conclusions

Good agreement between the measured macroscopic diffusion coefficient and the calculated (standardized) mean square distance, based on a simple microscopic diffusion model, can be obtained if one assumes that octahedral sites are mostly blocked if two or more of the Pd atoms per octahedron are substituted by Ag atoms. The ratio of probabilities for jumping into unblocked and partly blocked sites is larger than 10^5.

Another way to include the diffusion in Ag-rich alloys would be to calculate the diffusion in silver-rich regions as a diffusion in silver with an extremely small solubility. Pd acts as a hydrogen trapping element, not contributing to the diffusion process. Corresponding calculations are in progress.

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