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Hydrogen diffusion in palladium based f.c.c. alloys

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Abstract

The macroscopic hydrogen diffusion coefficient D in homogeneous $Pd_{1-x}Ag_x$ alloys obtained by electrochemical current pulse time-lag measurements shows for small hydrogen concentrations a strong dependence on the alloy composition. For small silver concentrations up to 25% the diffusion coefficient remains nearly constant. Then it falls off drastically by about three orders of magnitude reaching a minimum value at 60% silver content before increasing again with rising silver content directly towards the value for pure silver, which is nearly the same as for Pd. The results could be fitted satisfactorily for the complete range of alloy composition by Monte Carlo simulations on the basis of a simplified model. In this model two different octahedral sites are assumed to exist showing different hydrogen occupation probabilities (i.e. different hydrogen solubilities). At smaller silver contents the silver atoms partly block the energetically favored diffusion paths in the Pd matrix leading to a round-about way diffusion. At high silver concentrations, Pd atoms act as traps for hydrogen in a silver matrix. The interplay of the hydrogen transport via two kinds of occupation sites with different hydrogen solubilities determines the shape of the curve for the macroscopic diffusion coefficient as a function of the alloy composition. If Ag is substituted by Ni or Cu an analogous behavior is observed for the f.c.c. phase region. When alloying V or Nb to Pd — both metals have a higher hydrogen solubility compared to Pd — these metals act as traps for hydrogen in the Pd matrix similar to Pd in a silver matrix.

Keywords: Hydrogen in alloys; Diffusion; Time-lag measurements; Microscopic jump process

1. Introduction

An objective of scientists working in the field of metal–hydrogen systems is to develop metal hydrogen storage materials with optimal properties regarding hydrogen uptake and release kinetics, solution capacity, cycle stability and simplicity of servicing, with good availability and reasonable production costs. Favorites with promising properties are TiFe [1] and nowadays, especially, $LaNi_5$ base alloys [2]. Alloying small amounts of different components can change hydrogen storage properties, although the kind and quality of influences on the essential properties are a priori not predictable.

The aim of basic research is to develop universally applicable models for appropriate systems which then are transferable to technically usable systems. Palladium based alloys are ideal model systems for such investigations because of their easy servicing and high availability [3], even though these alloys themselves are not suited for hydrogen storage because of unsuited equilibrium pressures and high costs for palladium.

We have studied the macroscopic hydrogen diffusion behavior in the palladium–silver alloy series at small hydrogen concentrations and we have used the results to explain more generally the influence of alloying components other than silver (for instance Ni, Cu, Nb, V) on the diffusion behavior [4].

2. Experimental

The macroscopic or effective hydrogen diffusion coefficient in the alloy series palladium–silver has been determined applying the cp-np-method (concentration-pulse-non-permeation), the so-called pulse method [5–7].

In an electrochemical double cell, hydrogen is liberated at one side of the metal diffusion foil by a short cathodic current pulse at time $t=0$. For $t>0$ the hydrogen penetrates through the surface into the foil and diffuses from the entrance side to the opposite (measuring) side. This side is part of an electrochemical cell and works itself as a hydrogen electrode. Its potential can be measured and followed against a standard reference electrode as a function of time. It is determined by the hydrogen activity at the surface and therefore by the hydrogen concentration

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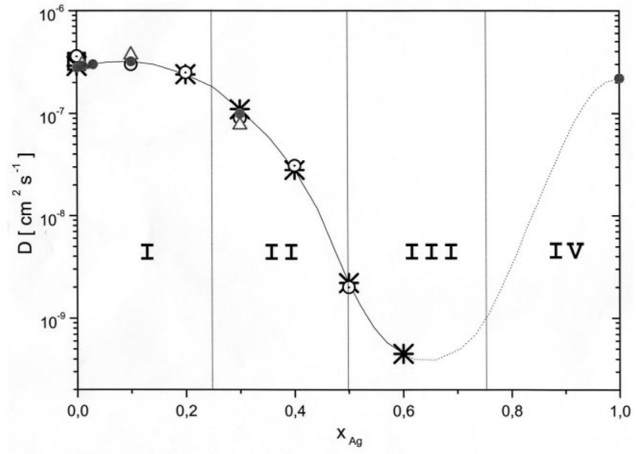

Fig. 1. Hydrogen diffusion coefficients $D(x_{Ag})$ in $Pd_{1-x}Ag_x$ for small hydrogen concentrations; ● from time-lag measurements [4], Δ NMR-PFG [4], * [5,6], ⊙ [9], □ [7,8].

arriving from the entrance side. Fitting the potential–time curve with the theoretical solution for this diffusion problem, considering the corresponding boundary conditions and the foil thickness, yields the effective diffusion coefficient [7,8].

Diffusion coefficients obtained in this way are plotted on a logarithmic scale as a function of the silver content for $T=294$ K for well annealed palladium–silver alloys in Fig. 1. For comparison, Fig. 1 also contains results from previous investigations [7,9], also applying time-lag techniques.

3. Results and discussions

Attempts to describe the diffusion behavior and its dependence on the alloy composition thermodynamically were less successful. Calculations applying the method of Monte Carlo simulation showed that the dependence of the macroscopically measured diffusion coefficients on the silver content can be well described and explained by a model based on a microscopic picture.

3.1. The two-state model

The simple model of a round-about way diffusion is based on the assumption of at least two different jump frequencies of the hydrogen atoms when moving from one interstitial site to a neighboring one[1]. The different frequencies are caused by the two types of octahedrals differing from each other by their direct environment, according to the kind of the surrounding metal atoms. Interstitial lattice sites of type (1) are formed predominantly by Pd atoms. The fit of the experimentally obtained values for the diffusion coefficients $D(x_{Ag})$ by Monte Carlo simulation shows that the minimum number of Pd atoms forming the octahedrals is four [11,12]. Sites of type (2) are those octahedrals where more than two surrounding particles in the octahedral shell are silver atoms.

Despite the fact that palladium and silver are homogeneously miscible over the complete concentration range, it is assumed — in this microscopic model for the binary alloys with a statistical distribution of the alloying component (silver) in the matrix of the host lattice (palladium) — that two discrete solution energies (enthalpies) exist in the two different types of interstices. Since the solution enthalpy of hydrogen in pure silver is much higher (smaller solubility) than that in palladium, the substitution of palladium by silver atoms should cause at least a local increase of the solution enthalpy. In the simple two-state model the octahedrals with predominant Pd environment are energetically favored for hydrogen occupation. Accordingly different activation energies exist for jumps from one site into a neighbored one in the binary alloy. The activation energy for jumps from sites (1) to sites (1) is E_{a1} and from sites (2) to sites (2) is E_{a2}. Since the hydrogen diffusion coefficients in the pure metals do not differ essentially from each other, it is assumed that the difference between E_{a1} and E_{a2} is relatively small. In contrast, the activation energy for jumps from site (1) into site (2) should be quite different, due to the difference in the solution enthalpies of hydrogen in the different sites. Therefore hydrogen movement from site (1) into site (2) is generally less probable than that from site (1) into site (1) or from site (2) into site (2).

3.2. The microscopic picture of hydrogen diffusion in $Pd_{1-x}Ag_x$

This microscopic picture can explain the curve of the macroscopic (effective) diffusion coefficient as a function of the silver content. For section I in Fig. 1 sites of type (1) dominate up to ~25% silver admixture. Jumps between neighbored sites happen via the energetically preferred interstices bypassing sites of type (2). This leads to the round-about way diffusion and a gradually decreasing diffusion coefficient. Octahedrals with palladium poor and silver rich environment block — at least partly — diffusion paths. The slow increase of the diffusion coefficient up to ~10% silver addition is caused by the lattice expansion due to the higher lattice parameter of silver ($a=407.8$ pm) compared to palladium ($a=388.4$ pm).

With increasing silver content (section II in Fig. 1) the portion of interstices of type (2) grows and the blocking affects the diffusion more and more adversely. Energetical-

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[1] An exact model should consider seven different octahedrals in an A_xB_{1-x} alloy, however, such a model is not easily or even not at all possible to calculate. The fit of the experimentally obtained results for the diffusion coefficients as a function of the silver content by Monte Carlo simulation shows that the strongly simplifying assumption of a two interstice model allows description and explanation of the experimental curve with sufficient accuracy. Additionally the microscopic diffusion measurements applying the NMR spin-lattice relaxation method [10] support the results obtained by the simplified model.

ly favored diffusion paths become much longer and the macroscopically measurable diffusion coefficient drastically falls off, but in section III the fall-off is decelerated and the diffusion coefficient runs through a minimum as a function of the silver content at ~60% silver content. In this section diffusion via sites of type (2) contribute noticeably to the total transport. The transport via sites of type (1) nearly disappears since directly connected diffusion paths of type (1) sites from one side of the measuring foil to the other side no longer exist. In section IV the diffusion coefficient steeply increases on a quite low permeation level and runs directly towards the value for pure silver. The course of the curve at the silver rich side clearly differs from that on the palladium rich side. It can be explained — when starting from pure silver — by the formation of octahedrals of type (1) when alloying palladium to silver. These octahedrals in the silver matrix act as traps for hydrogen due to the higher hydrogen solubility of palladium. The traps impede the hydrogen diffusion via sites of type (2) as long as sites of type (1) do not form a connected region throughout the complete measuring foil.

The behavior of the diffusion coefficient in the PdAg alloy as a function of the silver content, therefore, can be understood as an interplay of the phenomenon of roundabout way diffusion on one side and hydrogen trapping on the other side, which is principally only due to the difference in the enthalpies of hydrogen solution of the pure metals. The influence of alloying on the general diffusion behavior seems to be a more universal effect. If this is true, an analogous hydrogen diffusion behavior as a function of the concentration of the alloyed partner should be expected also for other palladium base alloys crystallizing in an f.c.c. lattice.

3.3. Analogies in the hydrogen diffusion behavior in Pd based alloys other than PdAg

In Fig. 2 values for the hydrogen diffusion coefficients in PdNi [13] and PdCu [14] alloys obtained by macroscopic measurements are plotted together with the curve for the palladium–silver alloy (solid line). Ni as well as Cu take up only small contents of hydrogen, analogously to silver, but in contrast to palladium. The diffusion coefficients in these alloys indeed show a nearly analogous behavior (on the Pd rich side) as the PdAg alloy series. However, the diffusion coefficient promptly decreases with increasing Ni or Cu content without running through a flat maximum. In contrast to silver the addition of Ni ($a=352.4$ pm) or Cu ($a=361.5$ pm) causes a 'diffusion impeding' lattice contraction.

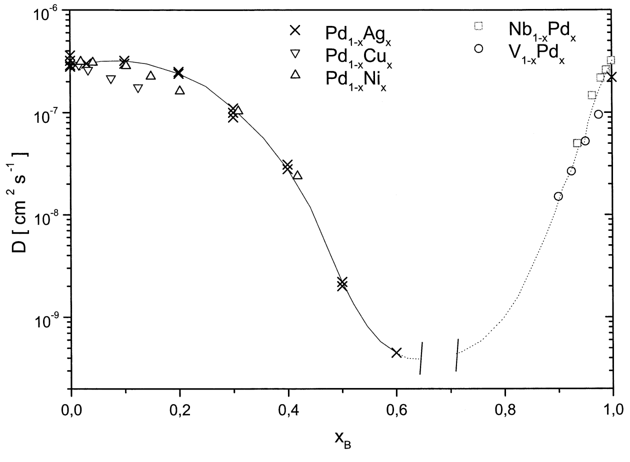

Fig. 2. Hydrogen diffusion coefficients $D(x_B)$ in $A_{1-x}B_x$ alloys for small hydrogen concentrations; hydrogen solubility in A is higher than in B; x [4–9], Δ [13], ∇ [14], □ [14], ○ [15].

Admixture of relatively small amounts of vanadium or niobium to palladium (for small contents of the alloying components the lattice structure remains f.c.c.) leads to alloys with quite different behavior from the alloys containing Ag, Ni or Cu. Both metals possess a clearly higher hydrogen solubility than palladium at normal pressures and temperatures. Assuming the validity of a more universal model the results obtained for the hydrogen diffusion behavior in PdV or PdNb alloys at small V or Nb concentrations, respectively, should be comparable with that in the PdAg system at the silver rich side. Vanadium and niobium take the place of palladium, while palladium takes the place of silver. By admixture of vanadium or niobium to palladium, hydrogen traps are inserted causing a prompt and clear decrease of the diffusion coefficient with increasing V [15] or Nb [14] addition (Fig. 2). To demonstrate this behavior in Fig. 2 the diffusion coefficients are plotted against the content x of the component B with the smaller hydrogen solubility in the alloy $A_{1-x}B_x$ (B=Ag in $Pd_{1-x}Ag_x$; B=Pd in $V_{1-x}Pd_x$ or $Nb_{1-x}Pd_x$). The course of the diffusion coefficient with increasing V or Nb content corresponds quite well with the curve (dotted line) for the PdAg alloy at the silver rich side. Since palladium forms a homogeneous f.c.c. alloy only for small V or Nb contents, such behavior is only observable in a restricted range.

The successful transferability of results obtained from measurements on the model system PdAg to other palladium based alloys is on one hand a good proof for the existence of an interplay of round-about way diffusion and trapping, and on the other hand, can be taken as an indication that the universal model should be transferable also to other alloy systems.

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