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Hydrogen migration in Pd–H alloys around 50 K anomaly at various hydrogen concentrations

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Abstract. The migration of hydrogen atoms in quenched Pd–H alloys is investigated around 50 K for specimens of various hydrogen concentrations by electrical resistivity measurement. The disordered hydrogen atoms are introduced by quenching from 100 K into liquid helium. The disordered hydrogen atoms order by migration of the atoms during the annealing of the specimens around 50 K. The resistivity increase due to hydrogen ordering largely depends on the hydrogen concentration but the amount is not proportional to the concentration. The activation energy of hydrogen migration is obtained by the cross cut method on the kinetic analysis of the resistivity increase due to the ordering. The obtained value is nearly the same for the hydrogen concentration from PdH_{0.06} to PdH_{0.66} though the value increases with the concentration within the experimental error. The energy value is smaller than the high temperature value and this is caused by a tunnelling effect on diffusion.

1. Introduction

Mazolai *et al* [1, 2] investigated hydrogen diffusion at low temperature ranges by measurement of the Gorsky effect between 130 and 270 K in the PdH_{0.71} alloy and between 90 and 380 K in PdD_{0.65}–PdD_{0.72} alloys. Arons *et al* [3] investigated the hydrogen migration by the elastic after-effect between 50 and 125 K in PdH_{0.60}–PdH_{0.77} and PdD_{0.61}–PdD_{0.73} alloys. Kronmüller *et al* [4] obtained the migration energies by the magnetic after-effect between 40 and 150 K for hydrogen isotopes of a few atomic per cent in Pd₉₅Fe₅ alloy. The migration energies of hydrogen isotopes have been also obtained by NMR for specimens of high hydrogen concentrations in wide ranges of temperature [5–8].

On the other hand, using the ordering of hydrogen around 50 K, Vajda *et al* [9] have investigated the migration of hydrogen isotopes in PdH_{0.62} and PdD_{0.63} alloys by electrical resistivity measurements for both fast cooled and electron irradiated specimens. Vajda *et al* obtained small activation energies (about half of our values) for hydrogen isotopes compared with the results of our quenched cases.

Similar investigations for Pd–H(D) alloys were done by us by measurements of the electrical resistivity [10–12] and the diffusivities of hydrogen isotopes in pure Pd have been obtained by the cross cut method. In those experiments the disordered hydrogen atoms were produced by quenching into liquid helium from a temperature at which the hydrogen atoms are structurally in the disordered state and the resistivities were measured at liquid helium temperature.

The concentration dependence of migration energy of hydrogen atoms in Pd–H alloys has not been investigated elaborately until now especially in the low temperature range.

Even in the investigation by electrical resistivity measurements the data for the dependence are fragmentary. In the present experiment the migration energy of hydrogen has been determined systematically for a wide range of hydrogen concentration. The resistivity change, which is measured in liquid helium, has been analysed by the cross cut method differing from the method used by Vajda *et al* [9]. The present results are discussed compared with the results obtained by other methods.

2. Experimental procedures

The Pd–H alloy specimens used in the present experiment were prepared from the pure material supplied by Tanaka Kikinzoku Kogyo Corporation. Before hydrogen charging the specimen wires of 0.15 mm in diameter were annealed in vacuum for longer than 3 h at 870–970 K. The hydrogen atoms were charged by the electrolysis and the charged amount of hydrogen was determined by the resistivity ratio at 273 K to pure Pd [13]. The hydrogen/metal ratios, H/M, were from 0.06 to 0.66 which corresponded to the phase from the ($\alpha + \beta$) mix phase to the β phase [14] in Pd–H alloys. After the hydrogen charging, the specimens were mounted on a base block in a temperature-variable chamber.

For isochronal annealing, the specimens were heated up to various annealing temperatures to obtain an isochronal cooling-down curve. Before each isothermal annealing, the specimens were held for 10 min at 100 K to obtain disordered hydrogen atoms and then were quenched into liquid helium. After the quenching, the specimens were heated up to various annealing temperatures around 50 K in isothermals. After successive annealing, isochronal and isothermal, the specimens were quenched into liquid helium to measure the electrical resistivities. The resistivities of the specimens during the annealing were measured always in liquid helium by the standard four probe method. The specimens for the isothermal annealing were the same as the specimens used for the isochronal annealing experiments.

3. Experimental results and discussion

In figure 1 some examples of the isochronal annealing curves for cooling down are shown for various hydrogen concentrations of Pd–H alloy specimens. The annealing time at each temperature was 10 min. The electrical resistivities measured at 4.2 K increased steeply from around 70 K with decrease of the temperature and then held to be constant below around 45 K. The resistivity increase was especially apparent for the specimens of high hydrogen concentration. The total amount of the resistivity increase, which was obtained as the difference of the resistivity between 100 and 4.2 K annealing, on each cooling-down curve was dependent on the hydrogen concentration. The amount is shown in figure 2 against the hydrogen/metal ratio (H/M) for Pd–H alloys and corresponds to 5%–6% and 0.04% of total resistivity at 4.2 K of the PdH_{0.66} and PdH_{0.06} alloy, respectively. The figure shows that the amount of resistivity increase is not proportional to hydrogen concentration and increases abruptly from around H/M = 0.55 with concentration increase of hydrogen.

It has been already clarified by the previous investigations [9, 12, 15–17] with electrical resistivity and/or neutron scattering that the electrical resistivity of Pd–H(D) alloys increases with hydrogen ordering and decreases with hydrogen disordering at the early stage of the transition. By neutron diffraction studies, Blaschko *et al* [16] and Kennedy *et al* [17] showed that the interstitial hydrogen atoms on octahedral sites in fcc Pd lattice order at the 50 K anomaly though the structures in detail are still under discussion. Therefore if the hydrogen atoms in the specimen are disordered by holding the specimen at high temperatures or by

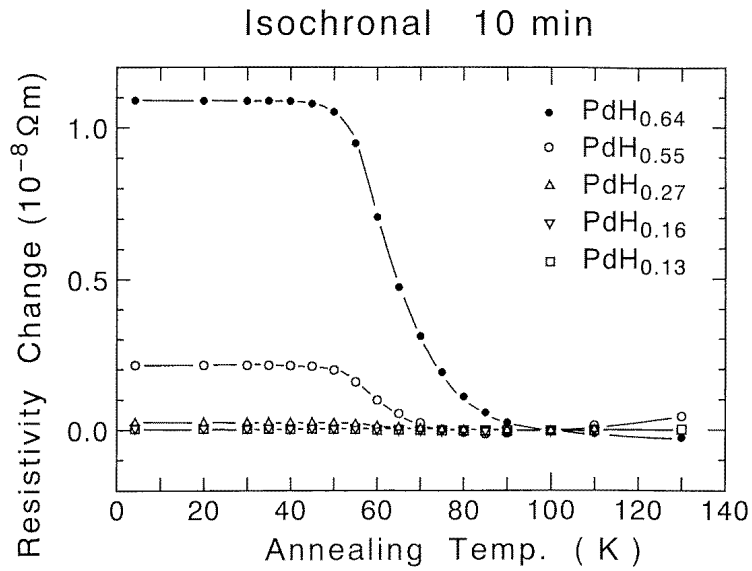


Figure 1. Isochronal cooling-down curves for various hydrogen concentrations in Pd-H alloys. The amount of resistivity change increases with the hydrogen concentration. The specimens were annealed for 10 min at each annealing temperature.

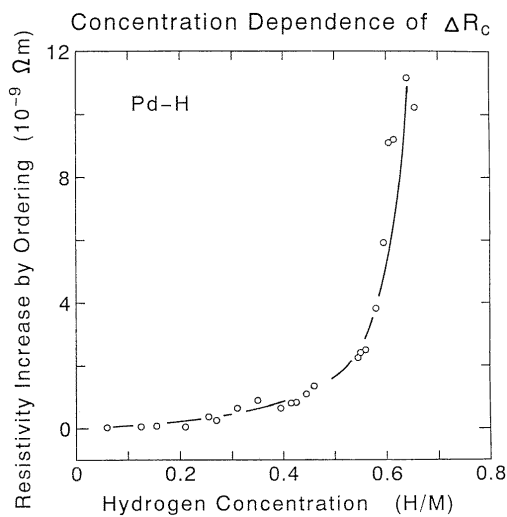


Figure 2. Amount of total resistivity increase on isochronal cooling curves for various hydrogen concentrations. The amount was obtained as resistivity difference between 100 and 4.2 K in the isochronal curves. The amount increased abruptly above around $H/M = 0.55$.

electron irradiation, the resistivity of the specimen decreases corresponding to the degree of disordering. In contrast, the resistivity increases together with the ordering in the early stage of the transition during the annealings.

The behaviour of the isochronal cooling curves was interpreted as follows. The hydrogen atoms at higher temperatures are in the disordered state and the disordered atoms migrate to order from below around 70 K because the hydrogen atoms in the Pd lattice must be in the ordered state in equilibrium at low temperatures though the amount of ordering in equilibrium depends on each temperature. As result, the resistivity increases with decreasing temperature

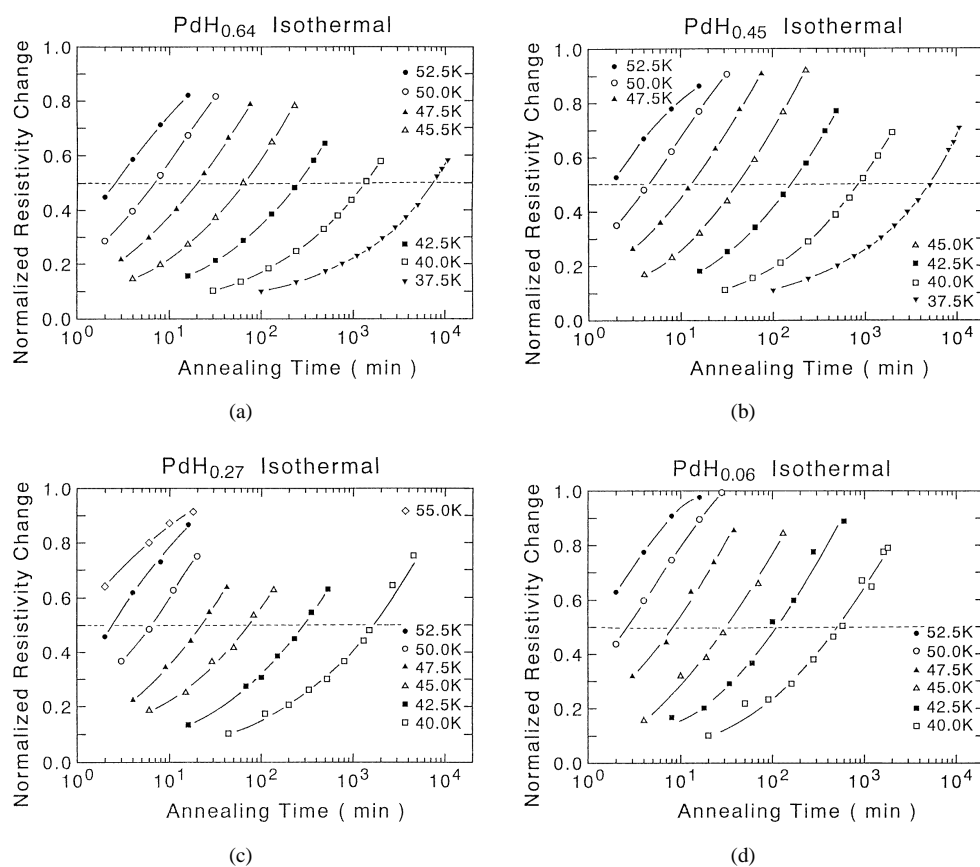


Figure 3. Isothermal resistivity curves at various annealing temperatures. Resistivity change is normalized by the total resistivity increase of the isochronal curve for the same specimen. The specimen was quenched into liquid helium from 100 K before each isothermal annealing. (a) PdH_{0.64}; (b) PdH_{0.45}; (c) PdH_{0.27}; (d) PdH_{0.06}.

as seen in figure 1 because the resistivity of the Pd-H alloys increases with ordering of hydrogen and decreases with disordering at the early stage of the transition as mentioned before. The hydrogen atoms can sufficiently migrate to order around the temperature 70 K within the isochronal annealing time (10 min). On further temperature decrease the hydrogen atoms cannot migrate during the annealing and the resistivity stops increasing around 45 K. As shown in isothermal annealing curves, below 45 K we need a longer annealing time to obtain an appreciable resistivity increase.

The sets of isothermal annealing curves are shown in figure 3 for various annealing temperatures. The amount of resistivity increase was normalized by the total resistivity increase on the isochronal curve for the same specimen. The specimen was quenched to obtain a set of isothermal curves before each isothermal annealing for the same specimen. The amount of the normalized resistivity increase depended on the annealing temperature and the curve shifted to shorter time with increasing annealing temperature for each specimen with different hydrogen concentration. This fact shows that a process in the curve is thermally activated. Similarly, the behaviour of the isothermal curves was interpreted as follows. The hydrogen atoms disordered by the quenching migrate to order at the annealing temperatures. Therefore

the resistivity increases with a rate dependent on the annealing temperature. The rate was sensitive to the annealing temperature and the range corresponds to four orders of time-change for only 15 K difference. Data points of the isothermal annealing at low hydrogen concentration scattered more than those at high hydrogen concentration because the amount of resistivity change decreased with decreasing hydrogen concentration as mentioned before.

With the same quenching procedure from 100 to 4.2 K nearly the same value of quench-in resistivities were obtained always for the same specimen in a series of isothermal annealing experiments and meaningful data for the isothermal annealing time were obtained. This fact shows that the hydrogen concentration in the specimen did not change during the set of isothermal annealings.

In the present investigation the analysis is based upon the following consideration. If it is assumed that the electrical resistivity change, $\Delta R(n)$, due to hydrogen disordering is any function of the amount n of hydrogen disordering, a rate equation for the thermally activated process is shown in general form as follows [18]:

$$-dn/dt = K_0 F(n) \exp(-E/kT)$$

where K_0 , $F(n)$, E and k are the reaction constant, a continuous function of n , the migration energy of hydrogen and Boltzmann's constant, respectively. By integration on the condition of isothermal annealing $T = \text{const}$, the following relation is obtained [18]:

$$\ln(\tau_1/\tau_2) = E/k(1/T_1 - 1/T_2)$$

where τ_1 and τ_2 are the annealing times at which an identical amount n is achieved at the different annealing temperatures T_1 and T_2 , respectively. It is assumed that the identical amount n corresponds to the identical value of $\Delta R(n)$. Then the annealing time, τ to attain the same resistivity change is easily estimated from figure 3 as the crossing point with the broken line and the normalized resistivity change curve. In figure 3 the value selected from the normalized one is 0.5 but from the above consideration for our analysis, other values can also be used. However, the value has to be selected on the abrupt slope of the curve in figure 3 to determine precisely the annealing time.

The value, $\ln(\tau)$, is plotted in figure 4 against the reciprocal of the annealing temperature and the data points are well on a line for each set. The migration energy of hydrogen is obtained for various hydrogen concentrations as shown in figure 5 from the slope of each line, respectively. The probable error estimated, for example, from figure 4 is about 1 meV ($0.096 \text{ kJ mol}^{-1}$) for each data point though the error increases, of course, with decreasing hydrogen concentration from about 0.5 meV ($0.048 \text{ kJ mol}^{-1}$) at high hydrogen concentration to about 1.5 meV ($0.145 \text{ kJ mol}^{-1}$) at low hydrogen concentration. As can be seen above, the analysis to obtain the migration energy of hydrogen in the present investigation does not need the order of reaction, simple form of rate equation of the process and so on which were needed by the analysis of Vajda *et al* [9].

The obtained migration energy in the present investigation is nearly constant for a wide range of hydrogen concentration and clearly larger than the value determined in the similar temperature range by Vajda *et al* [9] even at nearly the same concentration to their specimen. Therefore, the difference from the value of Vajda *et al* is not due to the difference of hydrogen concentration.

To clarify the cause of the difference between our values and the values of Vajda *et al*, almost the same experiments as those of Vajda *et al* have been also done with fast cooling of the specimens and after this with the measurements of resistivity at the annealing temperature during constant heating [19]. We have obtained a larger value, about 90 meV, as the migration energy of hydrogen from our cross cut method and a smaller value, about half of our value, from their method using the same resistivity data as ours. It must be noted that the disagreement

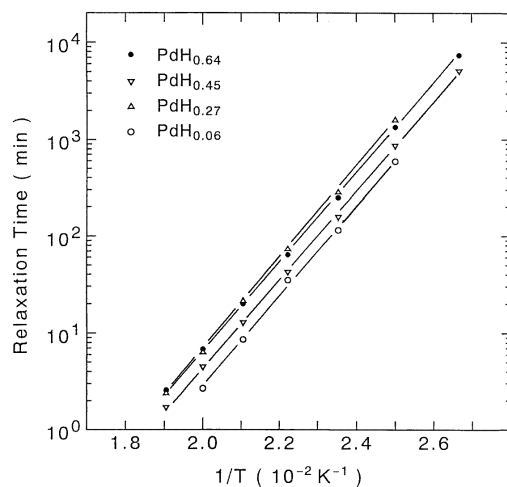


Figure 4. Logarithm of the relaxation time for various hydrogen concentrations against reciprocal annealing temperature. All of the data points are nicely on each line for each hydrogen concentration.

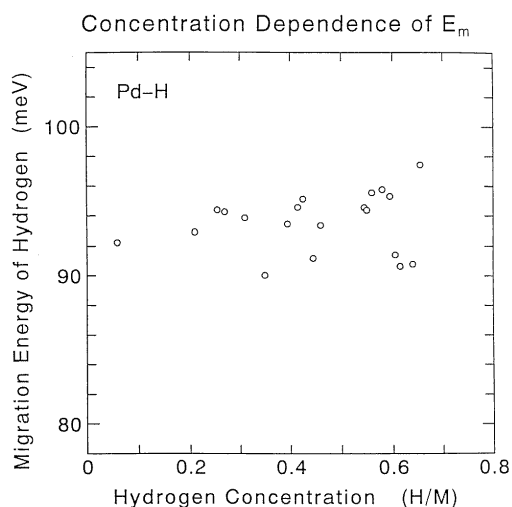


Figure 5. Concentration dependence of the activation energy of hydrogen migration.

between our value for quenched specimens and their value for the fast cooled specimen is caused by the difference of the analytical methods as mentioned in the previous paper [20]. We have claimed [20] that in their analysis, the order of reaction, γ , was mis-estimated and therefore an erroneous migration energy was obtained. The order of reaction is not needed in the present analysis as in previous papers [10–12].

Other previous values obtained are larger than our value but these differences are caused by differences in temperature range investigated. The temperature dependent migration energies of hydrogen isotopes have been shown for Pd–H(D) alloys and PdFe–H(D) alloys. By the Gorsky effect, Mazzolai and Züchner [1] obtained the migration energy of hydrogen, 0.21 eV (20.3 kJ mol⁻¹) for 250 K < T < 270 K and 0.13 eV (12.8 kJ mol⁻¹) for 130 K < T < 200 K in PdH_{0.71} and interpreted the decrease of the value at lower temperatures as tunnelling effects on diffusion.

Kronmüller *et al* [4] obtained by the magnetic after effect the value of hydrogen, 0.23 eV (22.2 kJ mol⁻¹) for 100 K < T and 0.13 eV (12.8 kJ mol⁻¹) for 60 K < T < 100 K in

Pd₉₅Fe₅-few atomic % H alloys and also interpreted the decrease as a tunnelling effect on diffusion. Arons *et al* [3] obtained by the elastic after effect 0.216 eV (20.8 kJ mol⁻¹) for 90 K < T < 125 K and 0.152 eV (14.7 kJ mol⁻¹) for 50 K < T < 70 K as the migration energy in PdH_{0.60}–PdH_{0.77}.

Two values for hydrogen migration, a high temperature value and a low temperature value, were obtained by NMR. Cornell and Seymour [7] obtained 0.228 eV (22.0 kJ mol⁻¹) (195–330 K) and 0.10 eV (9.6 kJ mol⁻¹) (100–195 K) for PdH_{0.70}. Torrey [5] obtained 0.24 eV (23.2 kJ mol⁻¹) (>220 K) and 0.08 eV (7.7 kJ mol⁻¹) (<220 K) for PdH_{0.64}. Burger *et al* [6] obtained 0.21 eV (20.3 kJ mol⁻¹) (230–320 K) and 0.06 eV (5.8 kJ mol⁻¹) (180–230 K) for PdH_{0.68}–PdH_{0.73}. These values for high temperatures agree well with the values obtained by other methods. The values for low temperatures may agree with our value and/or may be smaller than our value considering the temperature dependence of the values and rather nearer to the value of Vajda *et al* though the amount of temperature dependence of the value was not estimated. Their values determined by NMR measurements at low temperatures are uncertain due to larger data scattering [7].

At high temperature ranges the migration energy of hydrogen obtained with various methods agrees well as shown by Alefeld and Völkl [21]. The value is 0.230 eV (22.2 kJ mol⁻¹) in the temperature range above 220 K in the α phase. Even in high hydrogen concentrations (β phase) the value is about 0.23 eV (22.2 kJ mol⁻¹) as shown by previous data. The values at low temperatures are smaller than the values at high temperatures for a wide range of hydrogen concentration as shown by measurements of various methods. This fact shows that the tunnelling transitions become more important at lower temperatures.

In conclusion the migration energy of hydrogen around the 50 K range is nearly constant in a wide range of hydrogen concentration as it is at high temperatures and the value is smaller than at high temperatures, suggesting tunnelling effects for diffusion.

Acknowledgments

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