An Analysis of Trapping Effect on Hydrogen Diffusion in Cold Rolled Palladium

By

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The applicability of the "two-energy-level" trap model for hydrogen diffusion proposed by one of the present authors to the experimental diffusivity data for cold rolled palladium was examined, together with the both models of Oriani and McLellan. The present model provided a better description of the experimental results. The trap interaction energy and trap density in cold rolled palladium was determined to be $\Delta\bar{G}_{\mathrm{H}}^{t,l}=-8.4$ kJ mol^{-1} and $f_t=2.9\times10^{-2}$ respectively.

I. Introduction

It is well known that[1] the enhanced solubility and reduced diffusivity of hydrogen in plastically deformed metals, especially in cold worked iron and steels, is most likely to be attributed to the attractive interactions between the dissolved hydrogen atoms and lattice imperfections such as dislocations and their stress fields etc., produced during plastic deformation.

Flanagan and his co-workers[2],[3] observed for heavily cold worked palladium, the solubility enhancement of $n'/n=1.65$ (298 K) by the gas phase method and concluded that the stress field around the edge dislocation array is the principal cause of the solubility enhancement, where n′ and n are the H-to-Pd atom ratio for cold worked and well annealed samples respectively. Hasegawa-Nakajima[4] studied the effect of lattice strain on hydrogen permeation in palladium by an electrochemical method and observed that the solubility of hydrogen also increases and the apparent diffusivity decreases as the deformation is increased. Kirchheim[5],[6] showed that the diffusivity in deformed palladium decreases with decreasing hydrogen concentration but at very low concentrations of some at.ppm an enhancement of the diffusion is observed. He discussed that the results at high hydrogen concentration can be calculated from the activity measurements assuming that the activity gradient is the driving force for diffusion, but the increase of diffusivity at low concentration disagrees with those calculations and is explained by dislocation pipe diffusion.

One of the present authors and his co-workers[7],[8] have obtained similar results on the hydrogen concentration dependence of diffusivity in cold rolled palladium except for the results of an enhancement of diffusivity at very low concentration reported by Kirchheim[5],[6]. From the results[7],[8] on the temperature dependences of diffusivity and solubility of hydrogen in cold rolled and well annealed palladium, it was found that the cold rolling also reduces the diffusivity and that leads to a slight increase in the activation energy for diffusion, while it increases the solubility of hydrogen and decreases slightly the heat of solution in an exothermic sence. Therefore, it was discussed that[9] the major source of the more reduced diffusivity and the more enhanced solubility of hydrogen in cold rolled palladium than in annealed one is also the "hydrogen trapping" at dislocations and the surrounding stress fields.

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Recently, with the intention of obtaining more knowledge on the trap characters, such as the trap width, the jump rate, the occupation probability, as well as the trap density and trap interaction energy in the trap sites, one of the present authors[10)] has given a generalized analysis of hydrogen diffusivity in the mixed trap and multiple physical trap models. However, the resulting equations contain too many unknown factors to enable a comparison to be made of the experimental data with the models. Thus, the models have been recast in terms of a "two-energy-level" problem, in order to facilitate comparison with experimental data.

The present study was carried out in order to examine the applicability of the diffusivity equation for the "two-energy-level" trap model to the experimental data for cold rolled palladium, together with both models proposed, in the past, by Oriani[11)] and McLellan[12),13)].

II. The "two-energy-level" trap model

The generalized expression of the diffusivity for "two-energy-level" trap model can be written as[10),14)]

$$D=\frac{D_l^o\exp\left(-\frac{E_l}{RT}\right)}{1-f_t\left\{1-\exp\left(-\frac{\Delta\bar{G}_{\mathrm{H}}^{t,l}}{RT}\right)\right\}}\left[1-f_t-f_t(1-f_{tx})\left\{1-\frac{D_k^o}{D_l^o}\exp\left(-\frac{E_k-E_l}{RT}\right)\right\}\right.$$
$$\left.+f_t\exp\left(-\frac{\Delta\bar{G}_{\mathrm{H}}^{t,l}}{RT}\right)\left\{(1-f_{tx})\frac{D_p^o}{D_l^o}\exp\left(-\frac{E_p-E_l}{RT}\right)+f_{tx}\frac{D_d^o}{D_l^o}\exp\left(-\frac{E_d-E_l}{RT}\right)\right\}\right] \qquad (1)$$

where the relations of $f_l+f_t=1$ and $f_l(1-f_{lx})=f_t(1-f_{tx})$ hold. f_l, f_t: fraction (density) of normal lattice sites and trap sites respectively. f_{lx}: fraction of sites in normal lattice from which hydrogen can jump with jump rate l within the normal lattice sites. f_{tx}: fraction of sites in traps from which hydrogen can jump with jump rate d in the trap sites. This fraction implies the trap dimension, i.e., the "width" of trap. E_l and $D_l{}^o$ are the activation energy and the frequency factor for diffusion through normal lattice sites respectively. E_k and $D_k{}^o$ are also the activation energy and the frequency factor for diffusion in the jumping process with "trapping" rate k. E_p and $D_p{}^o$ are the activation energy and the frequency factor for the jumping process with "release (untrapping)" rate p. E_d and $D_d{}^o$ are also the activation energy and the frequency factor for diffusion within the trap sites respectively. $\Delta\bar{G}_{\mathrm{H}}^{t,l}$ is the difference of the free energy of a hydrogen in a normal lattice site and a trap site, and is equivalent to the difference in partial molar enthalpies of hydrogen in two sites by assuming that the difference of the corresponding excess entropies is zero. The trapping interaction energy has the following relation,

$$E_k-E_p=\Delta\bar{G}_{\mathrm{H}}^{t,l}=\bar{G}_{\mathrm{H}}^{t}-\bar{G}_{\mathrm{H}}^{l} \qquad (2)$$

The trap density f_t and trap interaction energy $\Delta\bar{G}_{\mathrm{H}}^{t,l}$ can be estimated by the relation of equation (3), if the temperature dependence of hydrogen concentration in the normal lattice, $[C_l]$ which is fully annealed sample and that of the total hydrogen concentration, $[C_T]$ in deformed sample are experimentally determined in the form of $[C_l]=[C_l{}^o]\exp(-\Delta H_c{}^l/RT)$ and $[C_T]=[C_T{}^o]\exp(-\Delta H_c{}^T/RT)$ respectively,

$$\frac{f_t}{1-f_t}\exp\left(-\frac{\Delta\bar{G}_{\mathrm{H}}^{t,l}}{RT}\right)=\frac{[C_T^o]}{[C_l^o]}\exp\left(-\frac{\Delta H_c^{T,l}}{RT}\right)-1, \qquad (3)$$

where $\Delta H_c^{T,l}=\Delta H_c^{T}-\Delta H_c^{l}$.

The more simplified models for the effect of trapping on the diffusivity have been proposed by a number of investigators[11)-13),15)-19)]. The diffusivity equation for the trap model proposed by Oriani[11)] can be written as

$$D = D_l^0 \exp\left(-\frac{E_l}{RT}\right)\left[1 - f_t\left\{1 - \exp\left(-\frac{\Delta\overline{G}_{\mathrm{H}}^{t,l}}{RT}\right)\right\}\right]^{-1} . \qquad (4)$$

The expression given by McLellan[12),13)] has the form,

$$D = D_l^0 \exp\left(-\frac{E_l}{RT}\right)\left[1 - f_t\left\{1 - \exp\left(-\frac{\Delta\overline{G}_{\mathrm{H}}^{t,l}}{RT}\right)\right\}\right]^{-2} . \qquad (5)$$

Both expressions (4) and (5) refer to the case, where the trapping site density is small, i. e., $f_t \ll 1$. However, the simplified models can sometimes provides a consistent description of experimental data in spite of their limited validity[20)-22)].

The section IV. of this paper will evolve around the comparison of the experimental data with the models given by equations (1), (4) and (5).

III. Data of hydrogen diffusivity and solubility for cold rolled palladium

The data of diffusivity and solubility of hydrogen for cold rolled and annealed palladium used in the present analysis of hydrogen trapping effect are as follows[7)]:

For fully annealed Pd specimen,

$$D_l = 1.05\times10^{-7}\exp[-21420\pm1210\,(\mathrm{Jmol^{-1}})/RT] \quad (\mathrm{m^2\,s^{-1}}) \qquad (6)$$

$$[C_l] = 4.53\times10^{-1}\exp[17070\pm1170\,(\mathrm{Jmol^{-1}})/RT] \quad (\mathrm{mol\,m^{-3}}) \qquad (7)$$

and for cold rolled Pd specimen,

$$D_a = 8.07\times10^{-8}\exp[-22180\pm960\,(\mathrm{Jmol^{-1}})/RT] \quad (\mathrm{m^2\,s^{-1}}) \qquad (8)$$

$$[C_T] = 1.85\times10^{-1}\exp[20880\pm920\,(\mathrm{Jmol^{-1}})/RT] \quad (\mathrm{mol\,m^{-3}}) \qquad (9)$$

These values were measured at cathodic current density of $i_c = 10\ A\ m^{-2}$ in the temperature range 279 to 335 K by the electrochemical permeation method. The value of $D_l = 1.85 \times 10^{-11}\ \mathrm{m^2\,s^{-1}}$ at 298 K in annealed palladium of this work is in good agreement with the values determined by Hasegawa-Nakajima[4)], Devanathan-Stachurski[23)] and Stackelberg-Ludwig[24)] using the similar electrochemical technique, although the diffusivity values that have been measured by the other measuring methods, such as the gas volumetric, Gorsky effect, nuclear magnetic resonance etc.[25)] are higher about two times than the present value.

The hydrogen concentrations in both annealed and cold rolled specimens are in relatively good agreement with those of Hasagawa-Nakajima[4)] and the solubility enhancement of 1.2 to 2.7 in cold rolled sample was obtained, these are reasonable values compared with the results of Flanagan et al[2),3)]. The cold rolled palladium used in this study had the dislocation density of $\rho_{ws} = (6.9\pm1.4)\times10^{14}\ \mathrm{m^{-2}}$ which[9)] was evaluated from the formula by Williamson-Smallman[26)], based on the lattice microstrains determined by X-ray line broadening.

IV. Comparison of the model with experimental data

It will be discussed to compare the present model of equation (1), together with both models of Oriani[11)] and McLellan[12),13)] given by equations of (4) and (5) respectively, with the experimental data of apparent diffusivity in cold rolled palladium.

In order to examine the best fit between the experimental data and equation (1), the following procedures have been used. Initially, equation (3) was used to estimate the trap density f_t and the trap interaction energy $\Delta\overline{G}_{\mathrm{H}}^{t,l}$ from the experimentally determined data of temperature dependence of hydrogen concentration in fully annealed and cold rolled samples. The calculated trap density and trapping interaction energy were $f_t = 2.9\times10^{-2}$ and $\Delta\overline{G}_{\mathrm{H}}^{t,l} = -8.4\,\mathrm{kJ\ mol^{-1}}$ respectively. In contrast to the behavior in cold worked iron[27),28)] the trapping sites in cold rolled palladium are relatively shallow to hydrogen, although the density of traps is comparatively high.

In view of the lack of the experimental data of f_{tx}, D_k, D_p and D_d, it appears that further refinements in an attempt to obtain a fit between the measured diffusivity and equation (1) is difficult. However, as the term $(E_p - E_l)$ in equation (1) can be expressed as $E_p - E_l = E_k - E_l - \Delta\bar{G}_H^{t,l}$, according to the relation of equation (2), the numerical calculations will be given to examine the applicability of the present model, according to some assumptions. Then, we assumed that for simplicity, $E_k = E_l$ and $E_d = 1/2\,E_l$, thus the difference between E_p and E_l in equation (1) is written as $E_l - E_p = \Delta\bar{G}_H^{t,l}$. These assumptions, together with f_t value calculated by equation (3) can be seen considerably to restrict the values of $(D_k^0 + D_p^0)/D_l^0$ and D_d^0/D_l^0. Thus, we will deal with the f_{tx} as an unknown variable. Under these assumptions, a computer fitting technique was used to fit equation (1) to the variation of measured apparent diffusivity as a function of the reciprocal temperature. The result is shown in Fig. 1, together with both models of Oriani [11] and McLellan[12],[13].

The good fit of the present model to the experimental data is obtained with $(D_k^0+D_p^0)/D_l^0 = 1\times10^{-3}$ and $D_d^0/D_l^0 = 1\times10^{-2}$. It can be seen that Oriani's model[11] also provides a comparatively better description of the experimental result than McLellan's model[12],[13]. Here, as far as the value

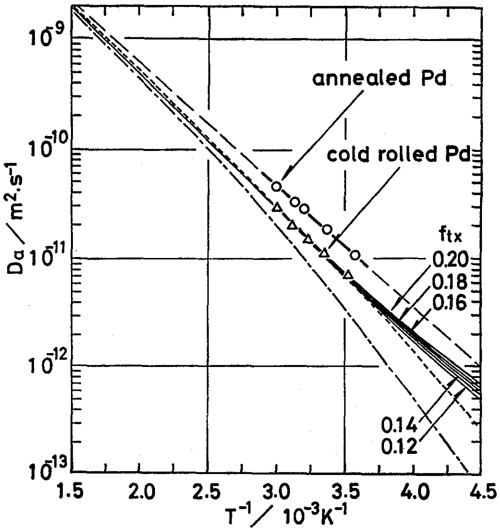

Fig. 1 Temperature dependence of apparent diffusivity as a function of f_{tx} values. $E_k = E_l$, $E_d = 1/2E_l$, $(D_k^0+D_p^0)/D_l^0 = 1\times10^{-3}$, $D_d^0/D_l^0 = 1\times10^{-2}$.
----: Oriani's model,
——-——: McLellan's model.

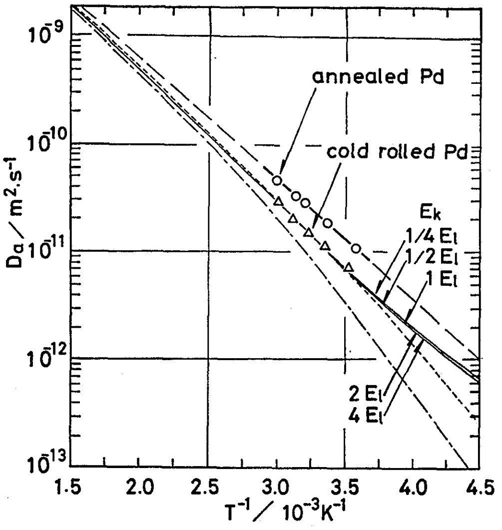

Fig. 2 Temperature dependence of apparent diffusivity as a function of $E_k = nE_l$ (n $=4,2,1,1/2,1/4$) values. $E_d = 1/2E_l$, $f_{tx} = 1.6\times10^{-1}$, $(D_k^0+D_p^0)/D_l^0 = 1\times10^{-3}$, $D_d^0/D_l^0 = 1\times10^{-2}$.
----: Oriani's model,
——-——: McLellan's model.

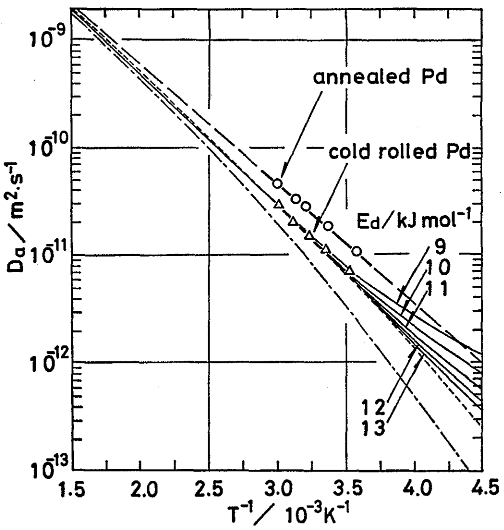

Fig. 3 Temperature dependence of apparent diffusivity as a function of E_d values. $E_k = E_l$, $f_{tx} = 1.6\times10^{-1}$, $(D_k^0+D_p^0)/D_l^0 = 1\times10^{-3}$, $D_d^0/D_l^0 = 1\times10^{-2}$.
----: Oriani's model,
——-——: McLellan's model.

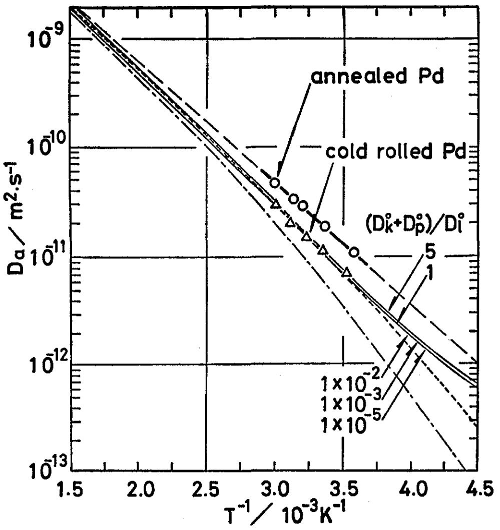

Fig. 4 Temperature dependence of apparent diffusivity as a function of $(D_k{}^0+D_p{}^0)/D_l{}^0$ values. $E_k=E_l$, $f_{tx}=1.6\times10^{-1}$, $E_d=1/2E_l$, $D_d{}^0/D_l{}^0=1\times10^{-2}$.
- - - -: Oriani's model,
——-——: McLellan's model.

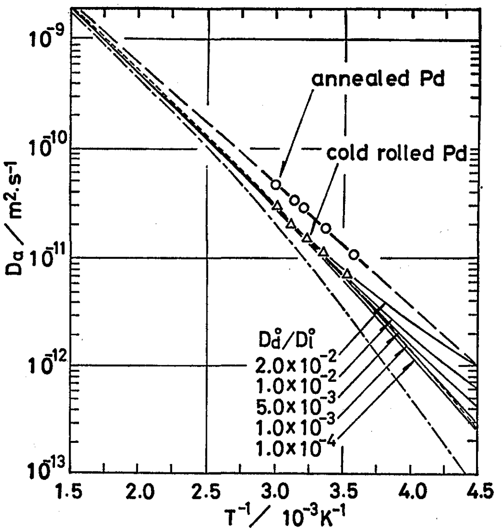

Fig. 5 Temperature dependence of apparent diffusivity as a function of $D_d{}^0/D_l{}^0$ values. $E_k=E_l$, $f_{tx}=1.6\times10^{-1}$, $E_d=1/2E_l$, $(D_k{}^0+D_p{}^0)/D_l{}^0=1\times10^{-3}$.
- - - -: Oriani's model,
——-——: McLellan's model.

of $(D_k{}^0+D_p{}^0)/D_l{}^0$ is less than about 5 and the value of $D_d{}^0/D_l{}^0$ is less than about 2×10^{-2}, their variables are nearly insensitive to the good fittness. Therefore, in the subsequent calculations we fixed $(D_k{}^0+D_p{}^0)/D_l{}^0=1\times10^{-3}$ and $D_d{}^0/D_l{}^0=1\times10^{-2}$ except for the examination of the effect of these values themselves.

The effect of variation in activation energy E_k is shown in Fig. 2, where $E_k = nE_l$ (where n = 4, 2, 1, 1/2, 1/4) and $E_d = 1/2\ E_l$, $f_{tx} = 1.6\times10^{-1}$. Figure 3 shows the apparent diffusivity with different activation energies E_d for diffusion within the trap sites, where $E_k = E_l$, $f_{tx} = 1.6\times10^{-1}$. Figure 4 and 5 show the effects of different frequency factor values of $(D_k{}^0 + D_p{}^0)/D_l{}^0$ and $D_d{}^0/D_l{}^0$ respectively, where $E_k = E_l$, $E_d = 1/2\ E_l$, $f_{tx} = 1.6\times10^{-1}$.

As one can be seen from these results, the present model provides a better description of the experimental data than both Oriani's[11] and McLellan's[12],[13] models. A marked difference can be observed in the diffusivity behavior of the present model when compared both models of Oriani[11] and McLellan[12],[13]. The diffusivity decrease in the present model decreases more slowly as the temperature is lowered than that in the previous models[11]-[13]. The difference between the apparent diffusivity D and lattice diffusivity D_l becomes smaller, as the temperature decreases and finally D value becomes equal to D_l value at the transition temperature at which the influence of lattice imperfections change from hydrogen trapping to hydrogen enhancing. The situation implies that hydrogen can diffuse easily through dislocation pipe or grain boundaries at very low temperature.

V. Conclusions

The validity of a generalized "two-energy-level" trap model for hydrogen diffusion proposed by one of the preset authors was examined with the experimental diffusivity data for cold rolled palladium, together with both models of Oriani and McLellan.

By using the trap density f_t and trap interaction energy $\Delta G_H^{t,l}$ which could be calculated by equation (3) from the experimental data, and by assuming the reasonable values of E_k and E_d in equation (1), the present model provided a better description of the experimental result than both models of Oriani and McLellan. The trap interaction energy and the trap density in cold rolled palladium was determined to be $\Delta\bar{G}_{\mathrm{H}}^{t,l}=-8.4$ kJ mol^{-1} and $f_t=2.9\times10^{-2}$ respectively.

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