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Surface-controlled deuterium-palladium interactions

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Measurements were made of the uptake of deuterium (D) into traps within the bulk of palladium, and the release of D back to the gas phase. The study was done with bare metal surfaces under UHV conditions using a novel method based on ion-beam analysis. The D uptake rate was proportional to gas pressure and about a factor of 3 less than the rate of impingement onto the surface from the gas. The release of D was limited by molecular recombination at the surface. A model for surface-limited release of D is presented which shows how the difference in energy between D in traps and recombination sites is a critical parameter in determining the time dependence of the D release. The observed kinetics of the D release from Pd lead to the conclusion that D in recombination sites is less strongly bound than D in traps which in turn is less strongly bound than D in the low-coverage surface chemisorption sites. Molecular recombination must therefore occur from sites with weaker binding, while the low-coverage chemisorption sites with stronger binding are nearly fully occupied, but do not contribute significantly to the release because of the strong binding.

I. INTRODUCTION

Surface-limited release of hydrogen from bulk solution in metals is an important process in many technologies including hydrogen storage, hydrogen sensors, and materials for magnetic fusion energy. One would like to be able to predict the flux of hydrogen from a surface given the concentration of hydrogen in solution. However, the kinetics of surface-limited release of hydrogen from solution in metals has not been understood well enough to make this prediction for most metals. Models have been proposed in which hydrogen release is controlled by molecular recombination from chemisorption sites on the surface which are replenished with hydrogen from solution in the bulk.[1-3] Other models have been proposed in which hydrogen passes from solution to the gas phase without going through the chemisorbed state.[4,5] Data to test the various models have been scarce, largely due to the dominating influence of surface impurities and to inadequate control over surface composition in many of the previous experiments.

In an earlier investigation surface-limited release of D from Fe was studied using experimental methods based on ion-beam analysis.[6] The study on Fe was done in ultrahigh vacuum (UHV) allowing D release from the bare metal surface to be characterized. The observed D release from Fe was described quite well by second-order recombination from surface chemisorption sites.[1] Here we apply the same experimental method used in the Fe study to examine surface-limited release of D from Pd. Pd differs from Fe in that it dissolves D exothermically rather than endothermically. Pd therefore provides a qualitatively different system for comparison to the models for surface-limited release. Studies of D recombination kinetics on Pd surfaces are also of interest because of indications from previous studies for the existence of sites with weaker binding energy than the low-coverage chemisorption sites.[7,8] In addition to D release, this study also examines the uptake of D from the gas phase into Pd, and the trapping of D at defects created by implantation of helium.

II. EXPERIMENTAL METHOD

In these experiments we observe the uptake of D from D_2 gas into the sample and the release back to the gas. This is done by first implanting helium into the samples to produce traps for the D. The flow of D into and out of the traps is then monitored using $D(^3He,p)^4He$ nuclear-reaction analysis (NRA) to measure the areal density of D in the traps as a function of time. The traps can be reversibly filled and emptied by changing the gas pressure at the sample surface. This experimental method has been used previously to study the uptake and release of D in iron[6,9] and other metals.[10]

The samples were 99.997 wt. % pure polycrystalline Pd foils 80 and 250 μm thick. The samples were annealed in a vacuum of 10^{-8} Torr at 1000 °C for 2 h. This resulted in grain growth to hundreds of microns. The surface was smooth with slight etching at grain boundaries as observed by optical microscopy. The traps were produced by implanting helium at 15 keV to a dose of 4×10^{16} He/cm^2. This gives a mean helium depth of 56 nm and a peak helium- to metal-atom ratio of about 0.08. The energy and dose of the helium implant was chosen to be the same as in previous studies on iron[6,9] to facilitate comparison between results for Pd and Fe. The implanted helium produces small bubbles which trap D by a mechanism believed to be similar to chemisorption of D on the internal surfaces of the bubbles.[10] The number of traps was determined from the areal density of D in the traps after equilibration with D_2 gas at temperatures and pressures where the traps are nearly fully occupied. The difference in free energy between D in traps and in solution was determined from gas-phase equilibration studies at temperatures and pressures where the traps are only

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partially occupied and from the temperature dependence of the D release.

The D uptake and release measurements were done in a UHV chamber equipped with Auger-electron spectroscopy for analysis of surface composition. After overnight bakeout at 170 °C a base vacuum of 1×10^{-10} Torr was achieved. This was adequate to maintain a clean surface on the sample during the measurements. The procedures for cleaning and analysis of residual surface impurities used in this study are similar to those used in the previously reported studies of D uptake and release in iron, and are described in further detail in Refs. 6 and 9. Samples were cleaned, prior to the D uptake and release measurements, by sputtering with 1-keV argon ions with the sample near room temperature. The only significant surface impurity remaining after sputter cleaning was carbon. The amount of residual carbon was estimated to be on the order of 0.1 monolayer (ML). This estimate is based on the ratio of the amplitudes of the 272-eV carbon peak relative to the 330-eV Pd peak, which was typically about 0.05. The interfering effect from a Pd Auger peak at 279 eV was reduced by subtracting a reference spectrum for a well-cleaned Pd surface. This reference spectrum was taken to represent a surface with less than 0.1 ML of carbon for the reasons that similar cleaning treatment on Fe and Ta produced surfaces with less than 0.1 ML of carbon and that carbon is not mobile enough in Pd to segregate to the surface from the bulk at the temperatures used in our studies. Changes in the difference spectrum clearly resolved changes in the carbon coverage as small as a few percent of a monolayer. The oxygen Auger peak was barely detectable indicating an oxygen coverage less than a few percent of a monolayer. The samples were analyzed for surface impurities before and after the measurements of D uptake and release. The only detectable change in surface composition during the D uptake-release measurements was a slight increase, less than 0.1 ML, in the carbon coverage. This shows that the surfaces remained clean throughout the measurements of D uptake and release. The amounts of residual carbon on the Pd in the present study and on the Fe in the earlier study were similar, while the amount of oxygen was much lower on the Pd than on the Fe. Our previous study of D release from iron showed that oxygen and carbon coverages below 0.1 ML had a relatively small effect on the D release. We therefore believe that the D release from Pd in the present study was not significantly influenced by the residual carbon remaining on the cleaned Pd surfaces. Since the samples were not annealed at high temperature after sputtering, it is possible that surface defects produced by the sputtering remained during the D release measurements. It is possible that surface defects might influence D release, although this is not obvious and has not, to our knowledge, been systematically studied.

For a measurement of D uptake, the sample was brought to the desired temperature, and then D_2-gas was let into the chamber to the desired pressure. The D_2-gas delivery system included a Pd-alloy diffusion cell to remove impurities. Gas pressures during the uptake measurements were typically between 10^{-9} and 10^{-5} Torr, low enough to avoid contamination of the surface during the measurements. The gas pressure was measured with an ion gauge which was calibrated against a capacitance manometer.

Nuclear-reaction analysis was used to monitor the areal density of D within a few hundred nanometers of the surface, almost all of which is in the traps. A ^{3}He beam at 700 keV was used for the NRA. The limit of detection was about 10^{13} D/cm^2. Some of the measurements were repeated at high and low analysis-beam fluence to insure that the D uptake and release were not significantly affected by the analysis beam.

III. UPTAKE

Figure 1 shows typical measurements of retained D versus time during uptake. The retained D increases linearly with time initially, but the uptake slows at longer times as equilibrium with the gas is approached. First we consider the initial uptake rate. The following processes could limit the initial uptake rate: rate of impingement onto the surface from the gas, molecular dissociation on the surface, and transport by bulk diffusion from the surface to the traps. In a previous study on iron[9] it was found that the initial D uptake rate was limited by bulk transport when the surface was clean and by molecular dissociation when chemisorbed oxygen was present on the surface. In Fig. 2 the measured initial D uptake rate for Pd is plotted versus pressure. The flux of D onto the surface from the gas,

$$\phi_i = 2p(2\pi m k T_g)^{-1/2} , \tag{1}$$

and the bulk transport limited uptake rate,

$$\phi_b = Cd/x , \tag{2}$$

are also shown for comparison, where p and T_g are the pressure and temperature of the gas, respectively, m is the mass of a D_2 molecule, k is Boltzmann's constant, C is the concentration and d the diffusivity of D in Pd, and x is the distance from the surface to the traps. Values for C and d were obtained from

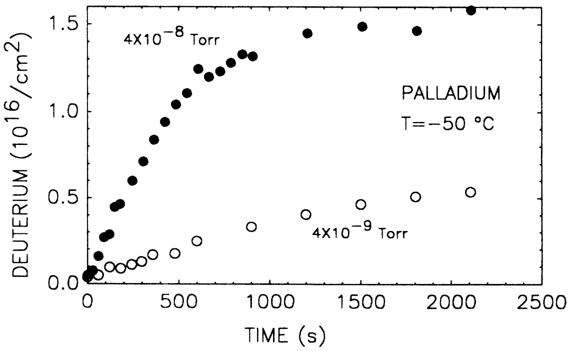

FIG. 1. Uptake of D into Pd. The time scale begins at the moment when the D_2 gas enters the chamber. The closed and open circles show measurements for D_2 gas pressures of 4×10^{-8} and 4×10^{-9} Torr, respectively.

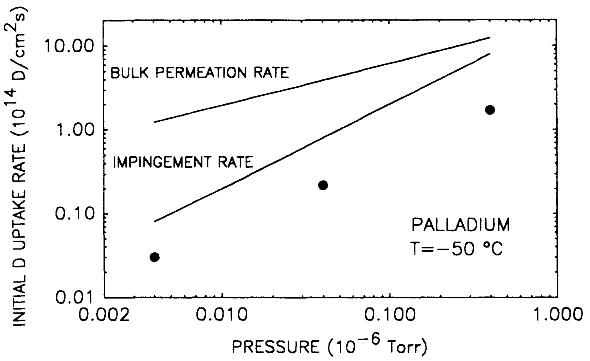

FIG. 2. Initial D-uptake rate vs gas pressure (closed circles). For comparison the rate of impingement on the surface from the gas [Eq. (1)] and the bulk transport limited-uptake rate [Eq. (2)] are shown by the two solid lines.

$$C=(p/p_0)^{1/2}\exp(-G_s/kT)\ \text{D/metal-atom} \tag{3}$$

with free energy of solution $G_s=E_s-TS_s$ (values for E_s and S_s are given in Table I) and

$$d=d_0\exp(-E_d/kT) \tag{4}$$

with $d_0=0.0017$ cm^2/s and $E_d=0.206$ eV.[11]

Bulk transport should not be rate limiting since $\phi_b \gg \phi_i$. As shown in Fig. 2 the present results are consistent with an almost-linear dependence of uptake rate on pressure compared to the $p^{1/2}$ dependence of ϕ_b. The measured initial uptake rates are slightly smaller than the impingement rate indicating a sticking probability in the range of 0.2–0.4. In a previous study[12] of the uptake of hydrogen into Pd the uptake rate was limited by bulk transport. This result does not conflict with the results of the present study since the relevant diffusion length in the present study is about 10^4 times smaller than in the previous study and the gas pressures used in the present study were many orders of magnitude lower than those used in the previous study.

The second important aspect of the D uptake is the amount of D trapped at long times when equilibrium between the traps and the gas phase is approached. Equilibration between D in traps and D_2 gas can be analyzed to determine the number of traps and the strength of the trapping. To model the trapping, we assume that each trap or solution site is either empty or occupied by a single D atom. It follows from Fermi-Dirac statistics that in equilibrium the fugacity is given by

$$\Theta_t/(1-\Theta_t)\exp(G_t/kT)=\Theta_s/(1-\Theta_s)\exp(G_s/kT)$$
$$=(p/p_0)^{1/2}, \tag{5}$$

where Θ_i is the fraction of sites of type i occupied by D and G_i is the free energy of a D in site i relative to a D atom in D_2 gas at pressure p_0 (one-half the free energy per molecule of gas), with $i=t,s$ for traps and solution sites, respectively. The areal density (n) of trapped D in equilibrium with gas can then be expressed as

$$n/(n_t-n)=(p/p_0)^{1/2}\exp(S_t/k)\exp(-E_t/kT), \tag{6}$$

where n_t is the areal density of traps and S_t and E_t are the entropy and energy of trapped D relative to gas at pressure p_0, respectively. In previous gas-phase equilibration (GPE) studies[6,13] of trapping of D in Fe and Ni, E_t and n_t were determined from measurements of n versus p and T using an expression similar to Eq. (6). However, such measurements cannot be made over a range of temperatures sufficient to allow independent determination of S_t and E_t from the GPE data alone. In the earlier GPE studies values of E_t were obtained by assuming that $S_t=S_s$ (i.e., that the entropy was the same for traps and solution sites). In the next section we will show how E_t can be determined from the temperature dependence of the D release. S_t and n_t can then be determined from the GPE data using Eq. 6 and the value of E_t obtained from the D release measurements.

IV. RELEASE

The release of D was observed by monitoring the areal density of D in the traps versus time after the gas was pumped from the chamber. Measurements were made at several temperatures in the range from −50 to +50 °C. Figure 3 shows an example of such release measurements taken at −50 °C. Also shown in Fig. 3 is the release curve calculated for diffusion-limited release. From the fact that the observed release is much slower than diffusion-limited release, we conclude that the release is limited by molecular recombination at the surface.

The following model has been developed to describe recombination limited release.[1] The model is based on the assumption of second-order kinetics for molecular recombination,

$$dn/dt=-k_r\Theta_r^2 \tag{7}$$

with

$$k_r=k_{r0}\exp(2E_r/kT), \tag{8}$$

where Θ_r is the occupied fraction of sites from which molecular recombination occurs, k_r is the second-order rate constant, and E_r is the activation energy per atom

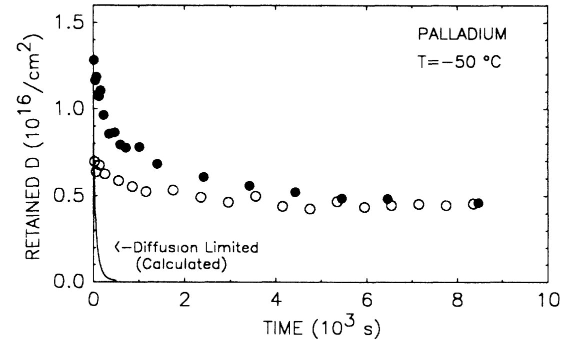

FIG. 3. Areal density of D vs time during release after equilibrating at pressures of 4×10^{-9} Torr (open circles) and 4×10^{-7} Torr (closed circles). The curve shows the calculated D release when surface processes are not rate limiting. The time scale begins when the D_2 gas was pumped from the chamber.

for molecular recombination. Since bulk transport is not limiting the release, the D in traps and in recombination sites will be in quasiequilibrium during the release,

$$[\Theta_r/(1-\Theta_r)]\exp(G_r/kT)=[\Theta_t/(1-\Theta_t)]\exp(G_t/kT)\ . \tag{9}$$

We have assumed that the site energy E_r in $G_r=E_r-TS_r$ is the same as appears in the activation energy for k_r in Eq. (8). Thus, any activation barrier for adsorption above the one-half D_2 level has been neglected here. Equations (7)–(9) can be analytically solved to give the following expression for n the areal density of trapped D as a function of time,

$$y-2\varepsilon\ln(y)+\varepsilon^2(1-1/y)=1+t/\tau\ , \tag{10}$$

where

$$y=\Theta_t(0)n_t/n\ ,$$

$$\varepsilon=\Theta_t(0)\{1-\exp[(G_t-G_r)/kT]\}\ ,$$

$$1/\tau=\Theta_t(0)(k_r/n_t)\exp[2(G_t-G_r)/kT]\ ,$$

or

$$1/\tau=\Theta_t(0)(k_{r0}/n_t)\exp[2(S_r-S_t)/k]$$
$$\times\exp(2E_t/kT)$$

and

$$\Theta_t(0)=n(0)/n_t$$

is the fraction of traps occupied at $t=0$. This expression is similar to the one obtained by Davenport *et al.*[3] for recombination-limited release of hydrogen from solution in metals. Figure 4 illustrates the time dependence of the D release for different values of ε. When $G_t=G_r$ then $\Theta_t=\Theta_r$, $\varepsilon=0$, and the solution reduces to

$$y=1+t/\tau \tag{11}$$

regardless of the level of saturation, since the traps and release sites are equally saturated. When $G_r>G_t$ then $\varepsilon>0$ and the release proceeds more quickly at short times, and when $G_r<G_t$ then $\varepsilon<0$ and the initial release is slower compared to Eq. (11). The nonlinearity of $y(t)$ results from unequal saturation of the traps and recombination sites when $G_r\neq G_t$.

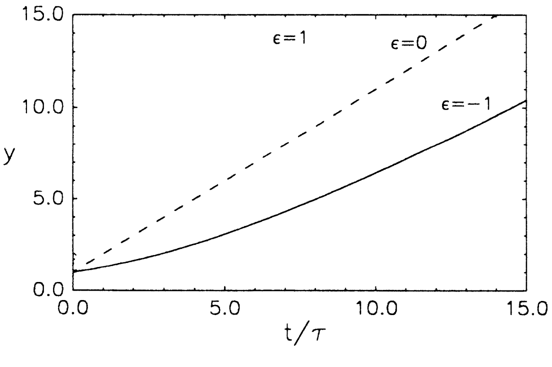

FIG. 4. D release calculated using Eq. (9).

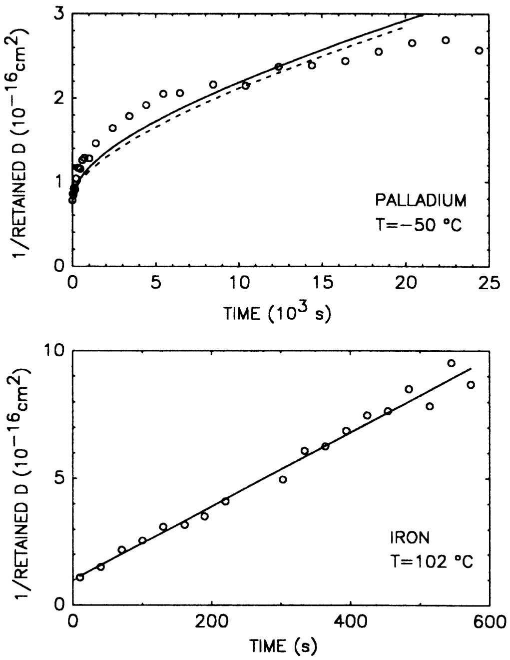

FIG. 5. Plots of the reciprocal of the areal density of retained D vs time during D release for Pd and Fe. The open circles show measured values, the solid lines were calculated from Eq. (10) with the parameters given in Table I, and the dashed line for Pd was calculated from the transport formalism described in Ref. 10.

According to the model the slope of $1/n$ versus t at long times is

$$\alpha=1/[\tau n(0)]=\alpha_0\exp(2E_t/kT)\ . \tag{12}$$

The temperature dependence of α therefore provides an experimental method to determine E_t, the binding energy of D to the traps. The data from the D release measurements at various temperatures were plotted as $1/n$ versus time as shown in Fig. 5. Values for α were obtained from the slope of these plots at long times. Figure 6 shows α

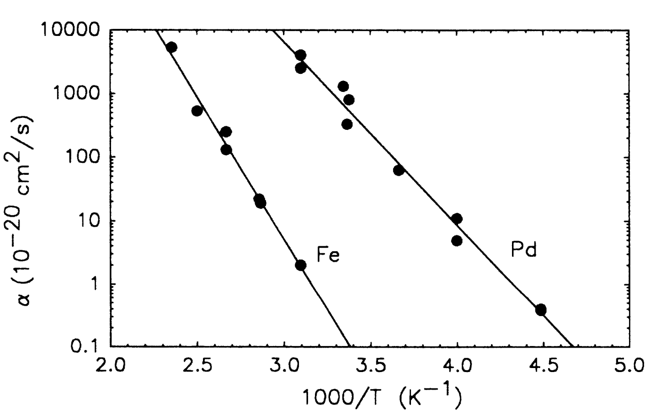

FIG. 6. The time derivative of the reciprocal of the retained D (i.e., slope of curves in Fig. 5) at long times vs reciprocal temperature. The closed circles are measurements, and the solid lines are fits using Eq. (12) to determine E_t and α_0.

TABLE I. Parameters used to describe trapping and surface-limited release of D in Pd and Fe. E_t and α_0 were determined from the *D*-release measurements, n_t and S_t were determined from the gas-phase equilibration measurements, the K_{r0} were calculated using Eq. (17), and E_s and S_s are from Refs. 18 for Pd and Ref. 19 for Fe. Energies E_i and entropies S_i are per atom and relative to D_2 gas at pressure $p_0 = 1$ Torr.

	E_t (eV)	α_0 (10^{-8} cm^2/s)	n_t (10^{16}/cm^2)	S_t/k	K_{r0} (10^{-20} cm^4/s)	E_s (eV)	S_s/k
Pd	-0.286 ± 0.01	$3\ {}^{+3}_{-1.5}$	1.5 ± 0.1	-5.6 ± 0.4	500	-0.082	-9.72
Fe	-0.430 ± 0.02	$60\ {}^{+120}_{-40}$	1.1 ± 0.1	-8.8 ± 0.5	5.4	0.297	-11.43

versus $1/T$. Table I gives values for α_0 and E_t determined from least-squares fits to the data shown in Fig. 6 using Eqs. (12). The values of E_t obtained from the D-release measurements can then be used to obtain values for n_t and S_t from a fit of Eq. (6) to the gas-phase equilibration data. The GPE data and the trapping isobars calculated from the fit are shown in Fig. 7. The values obtained for n_t and S_t from this fit are given in Table I. This procedure gives a unique set of parameters consistent with both the D-release experiments and the gas-phase equilibration experiments. The entropy of D in a trap is larger than the entropy of D in a solution site for both Pd and Fe.

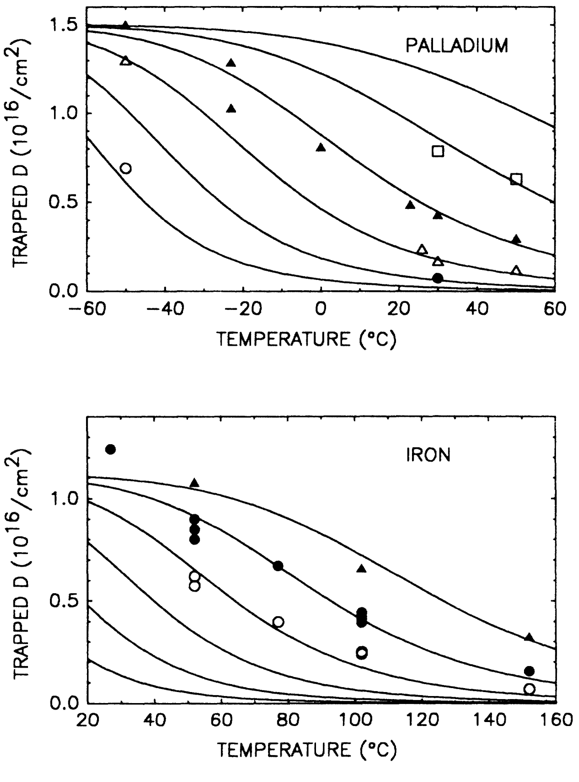

FIG. 7. Areal density of trapped D at various temperatures and gas pressures from the gas-phase equilibration measurements (symbols) and the isobars calculated from a fit of Eq. (6) to the data. The isobars are plotted for pressures from 4×10^{-9} to 4×10^{-4} Torr in decade increments. The different symbols correspond to the gas pressure of the line which fits best.

V. DISCUSSION

The studies of D trapping and release reported here are in good agreement with earlier studies of D trapping at He bubbles in Fe and Pd by observing internal redistribution of D between traps during ramp heating.[10] The temperature-ramp experiments gave values of $E_s - E_t = 0.29$ eV for Pd and 0.78 ± 0.08 eV for Fe for the energy difference between D in traps and solution. These values are somewhat higher than our values for $E_s - E_t$ due to the difference in entropy between traps and solution sites which was included in our analysis but neglected in the analysis of the temperature-ramp experiments. As with the GPE measurements, it is difficult to extract separate values for S_t and E_t from the temperature-ramp data. The differences in free energy between D in traps and solution $G_s - G_t = (E_s - E_t) - T(S_s - S_t)$ obtained in the two experiments are in excellent agreement. Using a value of T corresponding to the middle of the range over which our measurements were made we obtain $G_s - G_t = 0.31$ eV for Pd and 0.81 eV for Fe which are very close to the values quoted above from the temperature-ramp studies. The temperature-ramp method for determining E_t does not involve release from surfaces or gas-phase equilibration and therefore provides an independent test of the methods used here to determine E_t.

The curvature of the plot of $1/n$ versus time gives information on the value of G_r relative to G_t as illustrated in Fig. 4. Figure 5 shows that $1/n$ remains linear in time over the whole range of the measurements for Fe. It can be concluded from this linear time dependence that $|G_r - G_t| \ll kT$, i.e., D in the sites from which recombination occurs has the same free energy as D in the traps within a few hundredths of an electron volt.[1] In contrast, the curvature in the corresponding plot of $1/n$ versus time for Pd shows that $G_r - G_t > kT$ for Pd. A difference in energy between traps and recombination sites of a few hundredths of an electron volt or more would produce the curvature seen for Pd in Fig. 5. The solid lines in Fig. 5 were calculated by the analytic model [Eq. (10)] with the parameters given in Table I and with $G_r = G_t$ for Fe and $\exp[(G_t - G_r)/kT] \ll 1$ for Pd. As G_r becomes larger than G_t the release curve evolves from a straight line towards the limiting curve for $\exp[(G_t - G_r)/kT] \ll 1$ shown in Fig. 5. This allows a bound of $E_r > E_t + kT \simeq -0.26$ eV to be placed on the energy of the recombination site.

The dashed curve in Fig. 5 shows the release numerically calculated using the transport formalism described in Ref. 10. The difference between dashed and solid curves is due to the D in bulk solution which is included in the numerical calculation, but not in the analytical model. The numerical calculation also includes finite bulk diffusion, so the fact that the dashed and solid curves are similar also indicates that diffusion does not limit the D release. For the Pd data shown in Fig. 5 the sample was initially equilibrated with D_2 gas at 4×10^{-7} Torr. This results in 2.7×10^{-6} D/Pd in bulk solution. The total areal density of D in solution throughout the sample is therefore about one tenth of the amount in the traps, and this has a relatively small effect on the D-release measurements. In the iron experiments there was always much less D in solution than in the traps.

The fit for Pd in Fig. 5 could be considerably improved by introducing a slight distribution of trap energies with a width of 0.05 to 0.1 eV. However, this distribution must still have the trap energies well below the recombination-site energy in order to reproduce the observed curvature in the release. Inclusion of a distribution of trap energies would therefore not alter our basic conclusions. A range of trap energies is possible and has been observed in other systems such as multiple occupancy of D trapped at lattice vacancies in Ni.[10] However, in the absence of further evidence for such a distribution for trapping at He bubbles in Pd, we have chosen not to pursue this in detail here.

Chemisorption energies have been determined for Fe (Ref. 14) and Pd (Refs. 7 and 15) by means of thermal desorption, work function, and low-energy electron diffraction (LEED) measurements. Depending on the crystallographic orientation of the surface the chemisorption energies for H on Fe range from −0.46 to −0.56 eV/atom.[14] From our release measurements we know that the activation energy for recombination, $E_r = -0.42$ eV/atom, is very similar to the chemisorption energy for D on Fe, thus, it is likely that recombination occurs from the chemisorption sites for Fe. The energy of chemisorption of H on Pd at low coverage ranges from −0.45 to −0.52 eV/atom for (111), (110), and (100) surfaces.[7,15] For the Pd(100) surface the energy of chemisorption was observed to decrease and a new low-temperature stage in the thermal-desorption spectra appeared as the coverage increased beyond $\Theta_c = 1$.[7] These effects were interpreted as due to formation of a second adsorbed state at high coverages.[7] This is consistent with our conclusion that in Pd the recombination site is a higher-energy state than the traps and that recombination must therefore occur from sites which are less strongly bound than the low-coverage chemisorption sites by at least 0.15 eV. The binding energies of D to the various types of sites are illustrated in Fig. 8.

According to our picture of recombination-limited release where different types of sites are involved, the recombination rates should be similar for both types of sites at low occupancies. The smaller rate constant for recombination from the stronger site, due to the larger activation energy, will be compensated by the higher occupancy of the stronger site. At higher occupancies the stronger site saturates first and the recombination is then dominated by the weaker site due to its smaller activation energy. This is discussed in Ref. 2. In our experiments on Pd the stronger low-coverage chemisorption sites should be nearly saturated during the D release since they are lower in energy than the traps. The occupied fraction Θ_c of chemisorption sites is related to the occupied fraction Θ_t of trap sites by an expression similar to Eq. (9). Assuming trap and chemisorption-site entropies are equal, then chemisorption energies in the range −0.45– −0.52 eV gives Θ_c in the range 0.997–0.9998 at 50 °C when $\Theta_t = 0.5$. Thus, although the different chemisorption sites on the different crystallographic surfaces have slightly different energies, all would be nearly fully occupied during our D release measurements. To not be saturated, the surface sites would need a binding energy comparable to or weaker than the −0.286-eV binding energy of the traps.

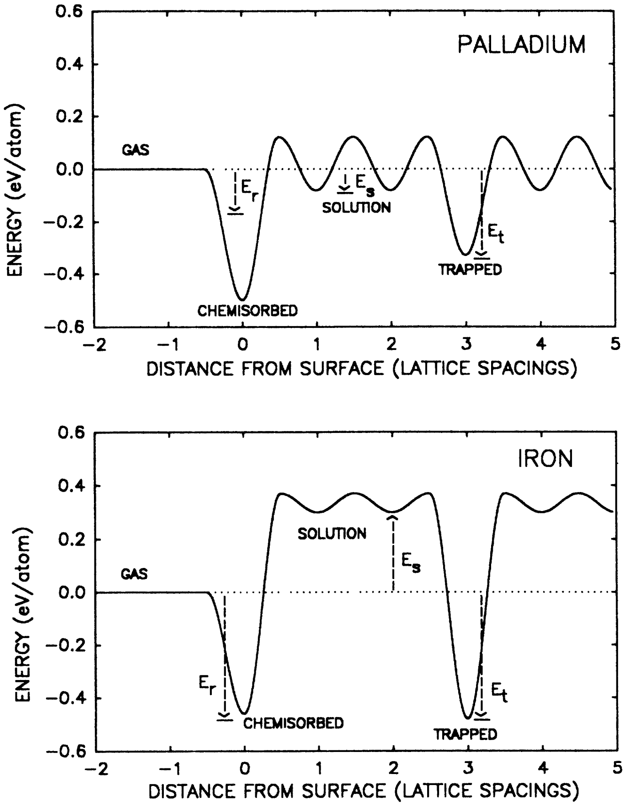

FIG. 8. Energy of D in Pd and Fe in traps, solution sites, chemisorption sites and recombination sites relative to D_2 gas. The horizontal scale is intended only for illustrative purposes.

Measurements of isothermal release of H from Pd foils have been reported by Auer and Grabke[8] and discussed in the review by Wicke and Brodowski.[16] Their release kinetics are different from ours, but are still consistent with our model for the release. Whereas we find a negative curvature in the plot of $1/n$ versus time, similar plots of their data have a positive curvature. The difference is that their H was mainly in solution sites which is a higher-energy state than the recombination sites, whereas in our experiments the D is mainly in traps which are lower in energy than the recombination sites. As noted above, the sign of the curvature in the plot of $1/n$ versus time is determined by the sign of the energy difference between the recombination sites and the sites which store the major portion of the H. Thus, our results and those of Auer and Grabke are both consistent with release from sites whose energy is between solution and helium traps, i.e., between about 0.1 and 0.3 eV/atom below the one-half H_2 level.

Recombination-limited release of D from metals is often described in terms of a recombination coefficient K_r relating the release rate to the concentration of D in solution:

$$dn/dt = -K_r(N_0C)^2 \; . \tag{13}$$

If the true release rate is given by Eqs. (7) and (8), then K_r will be independent of C only when recombination sites and solution sites are not saturated, i.e., when $\Theta_r \ll 1$ and $\Theta_s \ll 1$. Then, an expression for K_r in terms of quantities measured in this study is obtained by equating Eqs. (7) and (13) which gives

$$K_r = [k_r/(zN_0)^2](\Theta_r/\Theta_s)^2$$

or

$$K_r = [k_r/(zN_0)^2]\exp[2(G_s - G_r)/kT] \tag{14}$$

which is related to α by

$$K_r = \{[n_t/(zN_0)]\exp[(G_s - G_t)/kT]\}^2\alpha \; , \tag{15}$$

where N_0 is the metal atomic density and $z = C/\Theta_s$ is the number of solution sites per metal atom. Also,

$$K_r = K_{r0}\exp(2E_s/kT) \tag{16}$$

with

$$K_{r0} = [n_t/(zN_0)]^2\exp[2(S_t - S_s)/k]\alpha_0 \; . \tag{17}$$

The closed circles in Fig. 9 show the values of K_r obtained using the measured values of α and Eq. (15), and the solid lines show the values of K_r from Eq. (16) using the parameters listed in Table I. Also shown in Fig. 9 is a value reported for K_r for Pd measured using a permeation technique.[17] Although the permeation experiment was done at a higher temperature, the value of K_r agrees well with the extrapolation of the present measurements based on the model.

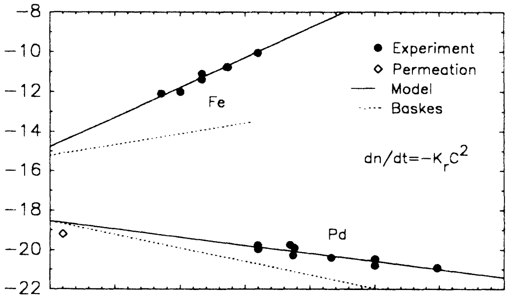

FIG. 9. Recombination coefficient vs reciprocal temperature. The closed circles are our measurements and the open diamond is from permeation studies (Ref. 17). The solid lines were calculated from Eqs. (15) and (16), and the dashed lines were calculated from the model of Baskes (Ref. 4).

In the earlier study of surface-limited release of D from iron[9] a value for K_{r0} was estimated from first principles using $k_{r0} = n_r\nu$ with the areal density of recombination sites $n_r = N_0^{2/3}$ and the attempt frequency for recombination $\nu = 10^{13}\ \text{s}^{-1}$. This gives

$$K_{r0} = n_r\nu/(zN_0)^2 \tag{18}$$

or $K_{r0} = 7.4\times10^{-20}\ \text{cm}^4/\text{s}$ for Fe and $3.6\times10^{-18}\ \text{cm}^4/\text{s}$ for Pd which are very close to the values obtained from Eq. (17) and listed in Table I. The difference in values of K_{r0} for Pd and Fe is mainly due to the different values of z which is 1 for Pd and 6 for Fe. Although the physical nature of the recombination sites cannot be deduced from the D-release kinetics, the agreement between the recombination prefactors experimentally determined and calculated from Eq. (18) shows that recombination occurs from sites which have an areal density close to 1 per surface metal atom and not from a small number of sites such as might be associated with surface defects.

A model for recombination has been proposed by Baskes[4] which is based on a different mechanism in which chemisorbed atoms recombine with atoms in solution. This mechanism gives rise to a temperature dependence for the recombination coefficient which is different from the model presented here. The recombination coefficients predicted by the Baskes model for Fe and Pd, shown by the dashed lines in Fig. 9, do not agree with our measured values of K_r.

VI. CONCLUSIONS

The D-release and gas-phase equilibration experiments described here provide an accurate characterization of trapping of D at defects associated with implanted helium in Pd and Fe. In the *D*-release experiments molecular recombination at the surface was the rate-limiting step in the release. An analytical model based on second-order recombination was developed and was found to accurately reproduce the observed D release from Pd and Fe. In Pd the traps bind D less strongly than the surface chemisorption sites. The chemisorption sites are therefore nearly fully occupied during the release. The release kinetics show however that molecular recombination occurs from sites which bind D less strongly than the traps. This leads to the conclusion that in Pd there exist sites which dominate the release when the stronger chemisorption sites are saturated. The binding energy of D to these sites is weaker than the binding to the low-coverage chemisorption sites by 0.15 eV or more. In Fe the D-release kinetics show that molecular recombination occurs from sites which have nearly the same energy as the traps. Furthermore, the binding energy of D to the traps and to surface chemisorption sites is very similar. This leads to the conclusion that in iron, recombination occurs from the usual surface chemisorption sites with no observable contribution from weaker sites. For both Pd and Fe, the recombination-rate prefactors are consistent with the number of recombination sites being about equal to the number of metal atoms on the surface and an attempt frequency per site of $\sim 10^{13}\ \mathrm{s}^{-1}$.

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