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ESTIMATES OF TRAPPING OF HYDROGEN AT DISLOCATIONS IN Pd: SUGGESTIONS FOR FUTURE SANS EXPERIMENTS

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Introduction

Hydrogen-metal systems have been widely studied and investigated by scientists and engineers. This has been motivated by the technological importance for the future of hydrogen storage as fuel as well as the effects of absorbed hydrogen on material properties.

Hydrogen embrittlement is one of the main forms of hydrogen damage. The penetration of atomic hydrogen into the metal results in the degradation of its mechanical properties. The deterioration process is not yet well understood. One explanation is the interaction and enrichment of hydrogen at defects such as dislocations and crack tips in metals. In other words, it influences the response of the material to mechanical stress. For useful information on the mechanism of hydrogen embrittlement, quantitative determination of the local hydrogen concentration at defects is required. There have been some approaches in this area [2] [3], but critical information is still lacking. Currently, the binding energy of hydrogen to defects, the number of available sites for hydrogen in the center of dislocations, and the inner cutoff radius are estimated for calculation purposes. Even with the advanced microscopic probes now available, information on the hydrogen environment near sites of embrittlement is never obtained in transmission electron microscope studies. In this paper, an approach to the study of hydrogen effects on metals is presented.

Calculations have been performed to estimate the number of hydrogen atoms trapped at dislocations as a function of the bulk concentration of hydrogen in palladium. The calculations performed included both hydrogen trapping at the dislocation core and the strain field surrounding the defect [1]. The results of these calculations agree with the small angle neutron scattering SANS measurements previously carried out by Heuser et. al. at a deuterium bulk concentration of 5500 appm. Numerical calculations are performed at various hydrogen bulk concentrations ranging from a few hundred to a few thousand atomic parts per million. The ability of small angle neutron scattering (SANS) to directly measure the spatial distribution of deuterium at defects has previously been obtained. Heuser et. al. [2] and Kirchheim et. al. [3] have measured the total number of deuterium atoms trapped per unit length of dislocation line. This includes both the elastic field and core regions. In this research, the binding energy is calculated and uncertainties in the binding energy values are eliminated. As a result, the number of sites in the core occupied by hydrogen is estimated. As the two variables are determined, the core trapping contribution is calculated by using the modified Fermi-Dirac equation. By subtracting the core contribution from the measured value at 5500 ppm, the elastic field contribution is determined. This leads to the determination of the inner cutoff radius which is used as one of the integration limits in the strain field equation.

Apparent hydrogen trapping at dislocation cores in palladium has been observed by Rodrigues and Kirchheim [4]. The calculations presented here indicate that the increasing core size has an inversely proportional effect on the hydrogen trapping in the elastic field region as a larger core would lower the stress field. For the purpose of this research, an assumption is made that the defects are edge dislocations. Elastic strain field around screw dislocation is, to first order, zero.

Theory

Hydrogen occupies octahedral sites and this is what is included here. The stress field around an edge dislocation has a non-vanishing hydrostatic component σ_h. Point defects distributed in this stress field can be modeled for simplicity with the hydrostatic stress field. According to the linear isotropic elasticity theory for an

edge dislocation, the hydrostatic stress given in Hirth and Lothe [5] is:

$$\sigma_h = -\frac{1}{3}\left(\sigma_{rr} + \sigma_{\theta\theta} + \sigma_{zz}\right) = \frac{\mu b_e}{3\pi}\left(\frac{1+\nu}{1-\nu}\right)\frac{\sin\theta}{r} \qquad (1)$$

where σ_{ii} are the normal components of the edge dislocation stress field, μ is shear modulus, b_e is the edge component of the Burgers vector, ν is poisson's ratio, θ the angle between glide plane and point of interest, r the distance of the interstitial site from the dislocation. The hydrogen concentration near a dislocation is $C(r,\theta)$ and is represented by the Fermi-Dirac equation [5] which properly accounts for the fact that two atoms cannot occupy the same site:

$$\frac{C(r,\theta)}{1-C(r,\theta)} = \frac{C_o}{1-C_o}\exp(-\sigma_h(r,\theta)\,\vartheta / k_B T) \qquad (2)$$

where C_0 is bulk concentration far from any defect, σ_h is the hydrostatic stress, ϑ is volume expansion of hydrogen, k_b is Boltzmann's constant, T is the temperature in K. In a constant temperature and pressure equilibrated hydrogen-metal system, the total volume of the metal with dissolved hydrogen is:

$$V = \left(m_M \bar{V}_M + n_H \bar{V}_H\right) \qquad (3)$$

where $\bar{V}_M$ and $\bar{V}_H$ are the partial molar volume of metal and dissolved hydrogen, m_M and n_H are the g.atoms of metal and dissolved hydrogen respectively. Hydrogen acts as a center of isotropic expansion, an assumption that is valid in face centered cubic metals [5[. The volume expansion ϑ is related to the partial molar volume of hydrogen $\bar{V}_H$ by [6]:

$$\vartheta = \bar{V}_H\left(\frac{1+\nu}{1-\nu}\right)\frac{1}{3N_A} \qquad (4)$$

where N_A is Avogadro's number. The quantity $\bar{V}_H$ is 1.65cm^3/mol [7]. It is often determined from experimental measurements of the change in chemical potential with pressure [7]. To determine the excess amount of hydrogen atoms per unit length of dislocation for the strain field, the integral number of hydrogen atoms adsorbed in the elastic field of the dislocation per unit length $(N/L)_{\text{strain field}}$ is given by the following expression [5]:

$$\left(\frac{N}{L}\right)_{\text{strain field}} = N_O \int_{R_{min}}^{R_{max}} r\,dr \int_0^{2\pi} d\theta \left[C(r,\theta) - C_O\right] \qquad (5)$$

where R_{max} is the outer cutoff radius R_{min} is the inner cutoff radius and N_o is the atomic site density. With the Fermi-Dirac approximation of equation (2), the integrand of equation (5) becomes:

$$\left(\frac{N}{L}\right)_{\text{strain field}} = N_O\, C_O \int_{R_{min}}^{R_{max}} r\,dr \int_0^{2\pi} d\theta \left[\frac{\zeta+1}{\zeta + e^{\sigma_h \vartheta / kT}} - 1\right] \qquad (6)$$

where $\zeta = C_O/(1-C_O)$. The core contribution of hydrogen atoms needs to be considered, and is not included in equation (6). In the core, hydrogen atoms are assumed to be non interacting and to have a binding energy E_B to the core. Interstitial sites exist at intervals of one Burgers vector along the dislocation core. The derivation of the hydrogen concentration at the core follows from equation (2) through mathematical steps to be:

$$C_{core} = n\left(\frac{1}{1+\xi^{-1}\exp(-E_B/k_BT)}\right) \quad (7)$$

where n is the interstitial sites in the core. Applying equation (7) to estimate the number of hydrogen atoms per unit length of dislocation core assuming the site density is independent of the occupancy by hydrogen and the core binding energy value is constant throughout the core gives [8]:

$$\left(\frac{N}{L}\right)_{core} = \frac{\gamma}{b} \times \frac{1.0}{1.0+\xi^{-1}\times\exp\left(\frac{-E_B}{k_BT}\right)} \quad (8)$$

where $(N/L)_{core}$ is the number of hydrogen atoms per length at the core site, γ is the number of sites per repeat distance along a dislocation and E_B is the core binding energy of the dislocation in eV. Equations (6) and (8) can be used to calculate trapped hydrogen densities at edge dislocation in the elastic field and core regions respectively.

Results and Discussions

In table 1, the calculated value of the total number of hydrogen atoms, N/L, which is the core and elastic field regions contribution is compared with the measured value obtained in [2]. The calculations and the measurements are at room temperature and bulk concentration of 5500 ppm.

The calculated value of the excess hydrogen in the elastic field region $(N/L)_{strain\ field}$ is 1.21 hydrogen atoms per Angstrom of dislocation line. This is roughly half of the experimental value listed in the table for the measured sample. The difference in this result could be accounted for by either the hydrogen trapped in the core region, the hydrogen-hydrogen interactions, or both. Presently, the hydrogen-hydrogen interactions are ignored. Figure 1 shows the number of hydrogen atoms trapped in the elastic field region as a function of hydrogen bulk concentration. The curves represent the net amount of hydrogen for two core radii. As mentioned above, the core radius is one of the integration limits of the strain field equation. There is a 30% enhancement of hydrogen trapping in the elastic field region at a core radius of 1 Burgers vector compared with the 1.7 Burgers radius. This is because the strain field contribution decreases as the lower integration limit, which is the core radius in equation (6), increases. Figure 2 displays the number of hydrogen atoms trapped at the core for different core binding energies and site values, all as a function of bulk concentration. For a binding energy of 0.1eV all curves have linear shape which concludes unsaturation of the core. This indicates a weak attraction at this value for hydrogen-dislocation interactions. It is unlikely that 0.1eV is the binding energy for hydrogen to the dislocation. For binding energies of 0.2 and 0.3 eV, hydrogen trapping at the core shows saturation at bulk concentrations of 2000 ppm and above. At lower concentrations in the range of a few hundred appm, for a range of number of sites, the number of hydrogen atoms trapped varies between the two binding energies dramatically as shown in Figure 2. If SANS experiments are done at these low concentrations, 100, 500 and 1000 appm then it is possible to extract important information such as the number of sites, core radius and accurately determine these variables. Based on these results, it is suggested that SANS experiments should be carried out on samples with hydrogen concentrations of 100, 500 and 1000 atomic parts per million. Another strong indication of the importance of the core contribution, which opens the door for research to determine hydrogen trapped at the core alone, is that most of the excess hydrogen atoms are concentrated within a couple Burgers from the dislocation core. This is shown in Figure 3. The graph displays the effect of outer cutoff radius on the number of hydrogen atoms in the elastic field region. The three curves are for three inner cutoff radii. As the core radius increases the hydrogen trapping in the strain field decreases. The region under high elastic strain field decreases because it has been modeled by the core field.

Previous SANS measurements at 5500 ppm done by Heuser et. al. [2] have shown that on average, 2.6 hydrogen atoms are trapped per Angstrom of dislocation line. This measured cross section at Q=0.02 $Å^{-1}$ is $(d\Sigma/d\Omega) = 0.02$ 1/cm/steradian. The results obtained in this research are consistent with SANS measurements at a binding energy of 0.3 eV, three different core radii and number of sites in the core. Further experimentation at bulk concentrations of 100 ppm, 500 ppm and 1000 ppm determines the core radius and number of sites as shown in Figure 4. The curves illustrate the total number of hydrogen atoms trapped as a function of bulk concentration. At 5500 ppm, all curves pass through Heusers et. al. [2] 2.6H/Å experimental value. The ratio of the cross sections between 5500 and 1000 ppm is 3, and between 5500 and 100 ppm is 5. Based on these theoretical results, the cross sections at these low concentrations should be measurable. The experiments at low concentrations will

determine the number of sites and core radius when compared with the theoretical calculations shown in Figure 4. Table (1) shows the numerical results at 5500 ppm for different core radii along with the SANS measurements. Figure 5 displays the effect of the temperature. At low temperature (77 K) the deuterium atoms trapped per unit length of dislocation line increase by a factor of 10, which means that the SANS cross section can measure by a factor of one hundred as it is directly proportional to the square of deuterium density. With the decrease in temperature, the number of hydrogen atoms trapped increases. The hydrogen atoms become trapped even in the low strain field region. At 5500 ppm for 77 K, 22 hydrogen atoms per Angstrom trapped compared with 2.6 hydrogen atoms per Angstrom at 300 K.

At 77 K, the core contribution is independent of the binding energy and number of sites. Furthermore, the amount of hydrogen atoms in the bulk of the sample is negligible compared with the number of hydrogen atoms at the dislocation. At room temperature, about 30% of the total hydrogen concentration goes to the dislocation. The temperature effect is dominant in the modified Fermi-Dirac equation (8).

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Table 1
Comparison of Numerical with Experimental Results at 5500 ppm Bulk Concentration

Type of work	core radii, binding energy , sites	Total H/A
SANS measurements		2.6
Numerical	r=0.69b, E=0.3eV, 3sites	2.55
	r=1.00b, E=0.3eV, 4sites	2.66
	r=1.70b, E=0.3eV, 5sites	2.59

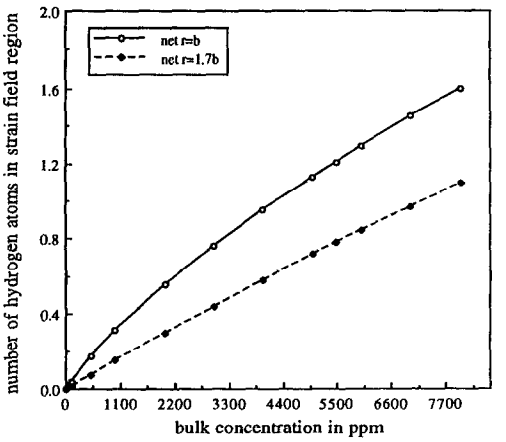

FIG. 1. Hydrogen trapping in elastic field region of edge dislocation as a function of bulk concentration

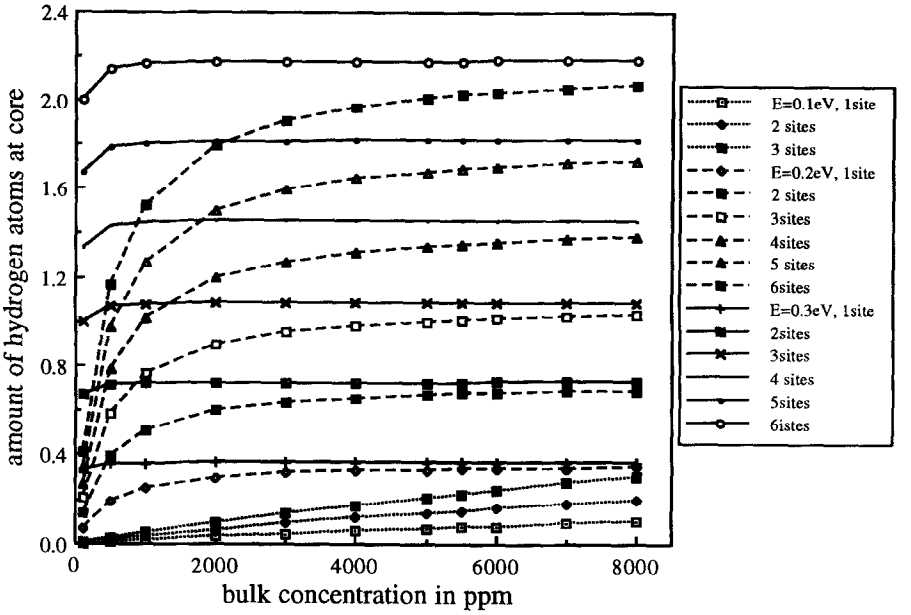

FIG. 2. Effect of binding energy and number of sites on hydrogen trapping at core

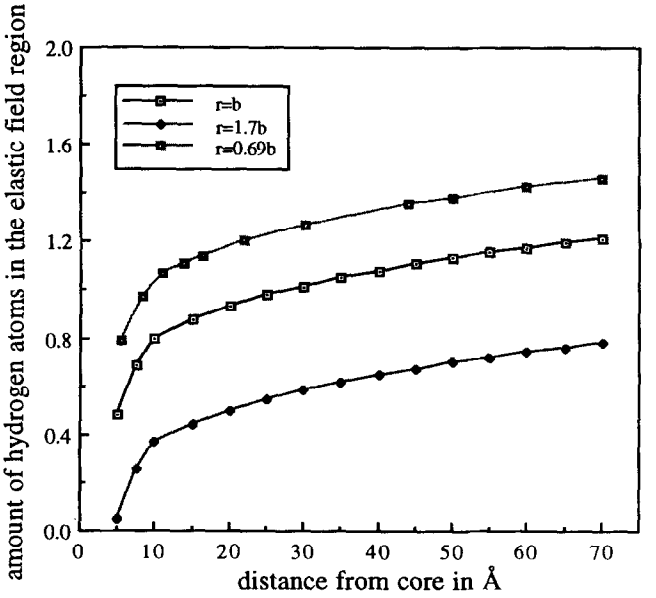

FIG. 3. The effect of outer cutoff radius on the number of H/Å of dislocation line in the elastic field region

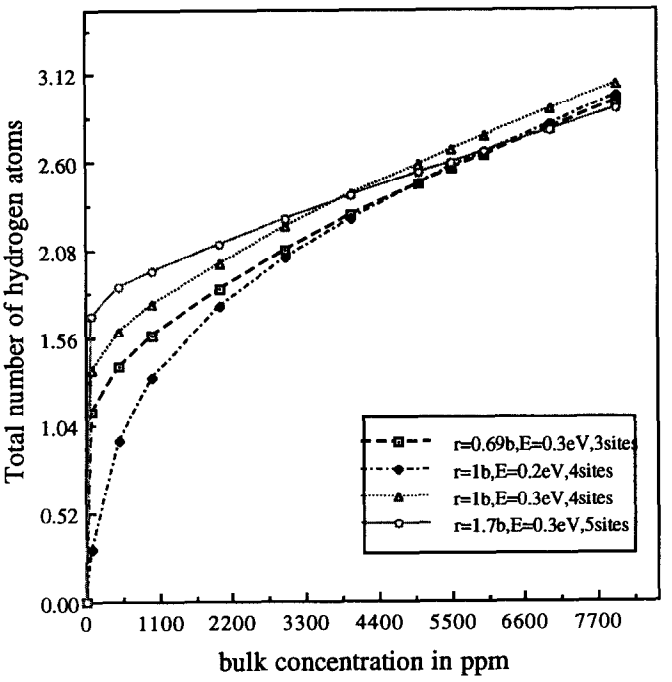

FIG. 4. Calculated total hydrogen atoms trapped as a function of core radii, binding energy, and number of sites

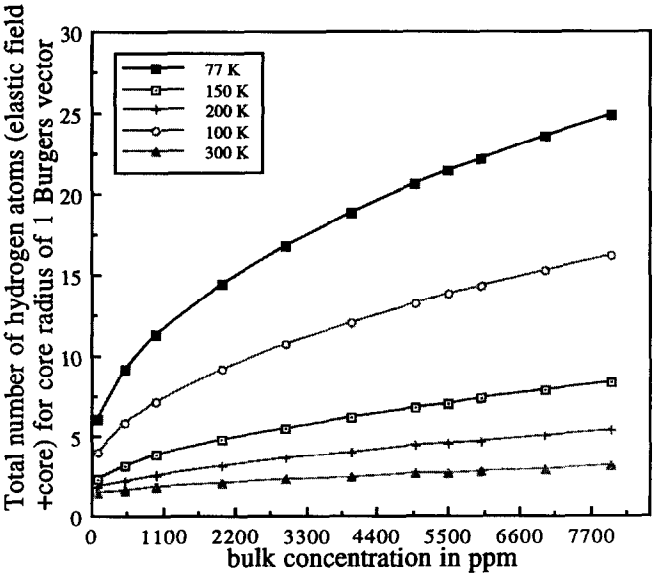

FIG. 5 Effect of operating temperature on the amount of hydrogen trapping