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Theoretical examination of the trapping of ion-implanted hydrogen in metals

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Theoretical analysis of the defect trapping of ion-implanted hydrogen in metals has been extended in two respects. A new transport formalism has been developed which takes account not only of the diffusion, trapping, and surface release of the hydrogen, which were included in earlier treatments, but also the diffusion, recombination, agglomeration, and surface annihilation of the vacancy and interstitial traps. In addition, effective-medium theory has been used to examine multiple hydrogen occupancy of the vacancy, and, for the fcc structure, appreciable binding enthalpies relative to the solution site have been found for occupancies of up to six. These extensions have been employed to model the depth distribution of ion-implanted hydrogen in Ni and Al during linear ramping of temperature, and the results have been used to interpret previously published data from these metals. The agreement between theory and experiment is good for both systems. In the case of Ni, the two experimentally observed hydrogen-release stages are both accounted for in terms of trapping at vacancies with a binding enthalpy that depends upon occupancy in accord with effective-medium theory.

I. INTRODUCTION

When hydrogen is ion-implanted into metals at concentrations not exceeding several atomic percent, its subsequent migration is usually inhibited by trapping at radiation defects created during the implantation. This phenomenon has been extensively investigated, both because it can be used to obtain fundamental information on hydrogen-defect interactions and because the effect is important to plasma-wall interactions in fusion reactors. Such studies have encompassed numerous alloys and pure-metal hosts, the latter including Be, Al, V, Fe, Ni, Cu, Zr, Pd, Ag, Ta, and Pt. (See, for example, Refs. 1–6 and citations therein.) Experiments typically begin with the implantation of hydrogen at cryogenic temperatures, followed by a heating schedule during which hydrogen release from the implanted region is observed by such methods as gas detection and nuclear-reaction analysis. The binding enthalpy of the hydrogen-defect pair is then deduced from the temperature rise necessary to produce the release. In some cases supporting configurational information is obtained from ion-channeling experiments.

We have previously analyzed data from a number of experiments like the above, taking into consideration the predictions of effective-medium theory along with other information on the properties of hydrogen and defects in metals. This led to a proposed hierarchy of traps.[5–7] In particular, relatively strong binding of the hydrogen is believed to occur at monovacancies and small vacancy clusters, and as a result these traps dominate the behavior of the system. The interaction with single self-interstitials and small interstitial clusters is weaker, but it was suggested that these entities may influence the evolution at higher hydrogen concentrations where the vacancy traps are saturated. Dislocations, formed by more extensive agglomeration of irradiation defects, are considered relatively unimportant in the implanted region because the associated traps are thought to be even weaker and less numerous.

The present paper is concerned with further advances in the analysis and interpretation of hydrogen-implantation experiments and with the resulting broader implications for hydrogen behavior. We begin by reporting two theoretical developments which allow an improved description of the thermally activated evolution: The first is an expanded transport formalism which more realistically treats hydrogen migration in the presence of mobile defect traps, and the second is a detailed theoretical calculation of the binding of multiple hydrogen atoms to the monovacancy. These developments provide the basis for a refined mathematical model of the implanted system. This model is then applied to two representative hosts, Ni and Al, and comparison is made with previously reported hydrogen-release data.[8,9] The results of these calculations provide several new insights into trapping mechanisms and their influence upon hydrogen redistribution. In the particular case of Ni, a stage of hydrogen release that previously was tentatively associated with detrapping from self-interstitial atoms is assigned herein to release from multiply occupied vacancies. The remainder of the present section provides additional background, and in subsequent sections each of the above topics is developed in turn.

The migration of ion-implanted hydrogen in metals has until now been described in terms of diffusion through a static field of traps, even though the relatively high mobility of point defects has long been recognized. (See, for example, Refs. 2, 5, 10 and 11.) This approximation is attractive because it greatly simplifies the mathematics of the analysis. Moreover, as will be demonstrated, such a model can often provide a fairly accurate description of hydrogen release even when the temperature of that release is somewhat above the temperature where the unoccupied defect traps become mobile. This is the situation for monovacancy traps in several metals. In other instances, however, one is concerned with the coupling of the hydrogen to defects whose migration enthalpy is substantially less even than that of the untrapped hydrogen; this is frequently the case for trapping by self-interstitial atoms. Then, as we shall show, the static-trap approximation can lead to a severe overestimation of the hydrogen-release temperature for a given trap-defect binding enthalpy. In these circumstances it is desirable to employ a transport formalism which takes account not only of the hydrogen diffusion and trapping, but also the evolution of the defect microstructure. This is accomplished by the expanded formalism to be presented in the present paper.

Although the concept of several hydrogen atoms being trapped at the same monovacancy has been advanced previously,[12] a realistic theoretical treatment of the interactions has not been available. In the present paper this effect is addressed using effective-medium theory.[13] This approach has previously been employed to calculate the binding enthalpy and lattice position for a single hydrogen attached to the monovacancy in Al, Fe, Ni, Cu, and Pd;[7,9] in each case the resulting enthalpy is in good agreement with an experimentally measured trap strength for the particular metal, and, for Fe, Ni, Cu, and Pd, the predicted lattice site of the hydrogen conforms to the results of ion-channeling analysis.[6] The validity of the theoretical method is further supported by its success in two other areas, namely the prediction of binding enthalpies and atomic configurations for hydrogen on metal surfaces[13] and the calculation of hydrogen heats of solution in metallic matrices.[14] Based on these findings we feel justified in using the effective-medium approach to address the more complicated issue of multiple occupancy of the monovacancy. The specific objectives are to determine whether more than one hydrogen can be trapped, and, if so, to calculate the binding enthalpies. Since vacancy defects are believed to be the dominant matrix traps for implanted hydrogen in pure metals, this matter is important to the interpretation of the thermal evolution of such systems.

Certain of the qualitative conclusions of this work have been mentioned in previous papers.[5,6]

II. TRANSPORT FORMALISM

The objective is to develop a system of equations with which to describe the time-dependent distribution of ion-implanted hydrogen in metals during thermally activated evolution. Among the physical processes which should be included in the formalism are the diffusion, trapping, and surface release of hydrogen, and the migration, agglomeration, and annihilation of defect traps; hydrogen immobilization by hydride formation and by the precipitation of hydrogen bubbles are important primarily at concentrations above several atomic percent, and these effects will not be considered here. As indicated in the Introduction, previous transport models have made the simplifying assumption that the hydrogen migrates through a field of fixed traps.[2,5,10,11] Consequently, one important extension to be pursued in the present paper is the incorporation of the evolution of the defect microstructure during annealing. A second, less complicated generalization is the provision for multiple occupation of traps with a binding enthalpy dependent upon occupancy.

The defect microstructure initially produced by ion irradiation and its subsequent alteration during annealing are far too complicated to be exactly described by any tractable array of differential equations. For example, the beginning spatial distributions of monovacancies and monointerstitials are highly nonrandom, due both to the complicated structure of ion cascades (see, for example, Ref. 15) and to the statistical proximity of Frenkel-pair constituents.[16,17] As a result it would be very difficult to express accurately the initial rates of reaction among the point defects in terms of their average concentrations. Furthermore, the thermally activated evolution from point defects to ripening clusters, and from there to dislocations and voids, and finally to a perfect lattice, may involve hundreds of structurally distinct defect entities, each with a concentration dependent upon time and depth.[16,17] It is therefore necessary to simplify the treatment of defect behavior while retaining those features most relevant to the behavior of implanted hydrogen. To this end we will deal only with the trapping which occurs at point defects, and only those defect-defect interactions which most directly influence the concentrations of monointerstitials and monovacancies will be included.

In the present analysis we assume always a locally random distribution of monovacancies and monointerstitials. This simplifying approximation is believed to provide an adequate description of the system after correlated recombination occurs between those closely spaced vacancies and interstitials that are created in the same atomic displacement. Since such correlated recombination takes place at temperatures much lower than those where hydrogen detrapping occurs,[17] there is no inherent difficulty in initiating the mathematical formalism at the completion of this process; it is necessary simply to adjust appropriately the concentrations of the point defects.

Three entities are assumed in the formalism to be mobile, namely monointerstitials, monovacancies, and hydrogen. Various other species such as di-interstitials and divacancies are believed to diffuse as well,[16,17] but their migration is not necessary to reproduce the principal features of the point-defect evolution. The migrating monointerstitials are permitted to recombine with vacancies, to bind hydrogen and thereby become immobile, to be annihilated at the surface, and to form interstitial clusters of up to five. Monovacancies can recombine with either monointerstitials or interstitial clusters, bind hydrogen, and undergo surface annihilation; however, the clustering of vacancies is not essential to the limited purposes of the present analysis, and consequently this process is omitted for simplicity. Due to considerations which will be discussed in Sec. III, provision is made for the trapping of up to four hydrogen atoms at the monointerstitial and up to six at the monovacancy; trapping is also expected to occur at interstitial clusters, but this effect is beyond the scope of the present work. Hydrogen is released at the metal surface through second-order recombination to form gas molecules.

In the above model there are seventeen distinct entities whose concentrations vary with time and depth, namely hydrogen in the solution site, the monovacancy with zero to six hydrogens attached, the monointerstitial with zero to four hydrogens attached, and interstitial clusters containing from two to five host atoms. For each of these species, indexed as $i=1-17$, the local concentration C_i is given by a partial differential equation having the generalized form

$$\frac{\partial}{\partial t}C_i(x,t)=D_i\frac{\partial^2}{\partial x^2}C_i+4\pi N_h\sum_{j,k}\alpha_{ijk}(D_j+D_k)R_{jk}\left[C_jC_k-C_iz\frac{P_jP_k}{P_i}\exp\left[-\frac{Q_i}{k_BT}\right]\right],\quad i=1,2,\ldots,17 \tag{1}$$

where

$$D_i=D_{0i}\exp(-Q_{Di}/k_BT)\ . \tag{2}$$

The first term on the right-hand side of Eq. (1) describes the diffusion of species i, whereas the second term sums the increases and reductions in C_i that result from various interactions involving the migrating hydrogen, monovacancies, and monointerstitials. Here the concentrations are expressed as atomic fraction, D_i is the diffusion coefficient of species i, N_h is the atomic density of the host, α_{ijk} is a dimensionless integer of order 1 which takes account of the positive or negative change in the number of species i resulting from one reaction of species j and k, and R_{jk} is the effective separation within which this reaction occurs. One example of the reactions included in the formalism is the recombination of a diffusing monointerstitial with an immobile monovacancy containing four hydrogens; this process removes the defects and introduces four hydrogen atoms into solution. As another illustration, a mobile monovacancy encountering a cluster of three interstitials will undergo recombination, leaving only a di-interstitial. The second term within the summed square brackets in Eq. (1) describes the reverse of the exothermic reaction under consideration. It is taken to be nonzero only for the transfer of hydrogen from a defect trap to solution; other reactions, such as vacancy-interstitial recombination and interstitial clustering, are so exothermic as to be effectively irreversible at the temperatures of interest. In this reverse term, C_i is the concentration of the product of the reaction, and z is the number of interstitial hydrogen solution sites per host atom. The quantities P are the respective degeneracies of the two initial and one final hydrogen states. Finally, Q_i is the decrease in the total enthalpy of the implanted system resulting from the reaction; it can be regarded as the binding enthalpy of hydrogen to the defect trap.

The mathematical approach to interacting diffusing species embodied in Eq. (1) is similar to that which we used previously to describe hydrogen diffusion within a field of fixed traps.[5,11] Indeed, when only the hydrogen is mobile, Eq. (1) reduces to the earlier formalism. Despite this similarity, however, the new treatment is sufficiently more complicated to warrant further explanation, particularly with regard to the reaction terms on the right-hand side of Eq. (1). The assumptions inherent in these terms are that species i and j react at a rate proportional to the product C_iC_j of their respective concentrations and that the appropriate prefactor is as derived elsewhere for diffusion-limited kinetics.[18] The last term within the summed square brackets is then chosen to conform to thermodynamic equilibrium among species i and j and their reaction product when the square-bracketed expression is set equal to zero; this means in effect that the net reaction rate goes to zero as equilibrium among the species is approached. The condition for equilibrium was derived by averaging over a canonical ensemble of the states of a system containing species i and j and their product at concentrations small compared to one. To provide further insight into the meaning of the ratio of degeneracies P_jP_k/P_i, it is instructive to write this quantity as $\exp(\ln P_j+\ln P_k-\ln P_i)$, whereupon one has the more familiar exponent of an entropy difference.

The system of equations given by Eq. (1) was solved numerically using methods described elsewhere.[19] Rather than treating the implantation process itself, which would have entailed creation terms on the right-hand sides of the differential equations, we elected simply to initiate the calculations after all of the hydrogen atoms, monovacancies, and monointerstitials were in place and after the completion of correlated recombination. Surface release of hydrogen was incorporated via the boundary condition

$$L(t)=K_L[N_hC_H(x\to 0,t)]^2\ , \tag{3}$$

where L is the number of hydrogen atoms released as molecules per unit area and time, K_L is a phenomenological temperature-dependent parameter referred to as the recombination coefficient,[20] and the hydrogen concentration is that in solution within the matrix just beneath the surface. We have found this relation to be valid for a number of metals and various surface preparations.[5,20] For the monovacancies and monointerstitials a zero-concentration boundary condition was imposed at the surface.

III. TRAPPING OF MULTIPLE HYDROGEN ATOMS BY POINT DEFECTS

We have used effective-medium theory[13] to calculate the enthalpies for two, three, four, five, and six hydrogen atoms trapped at the monovacancy in Ni. The methods were essentially the same as those used previously to treat single occupancy of the vacancy in Ni, Al, Fe, Cu, and Pd.[7] These earlier calculations yielded excellent agreement with experiment,[5,6] both in absolute magnitude and in the relative variations among the hosts, and this tends to support the validity of the present application of the same theory. For vacancies with more than one hydrogen atom, we incorporated the hydrogen-hydrogen interactions simply by including the electron density from each hydrogen atom at the positions of the others, as suggested by Nordlander and Hölmstrom for the similar problem of hydrogen-hydrogen interactions on a metal surface.[21] Due to the simplicity of the approach and because the zero-point energies were estimated only from harmonic fits to the potential, the accuracy of the results for multiple occupancy is expected to be less than that for a single hydrogen in the vacancy. Nevertheless, we believe that the calculations provide a good semiquantitative indication of the trends in the enthalpy. The results are given in Fig. 1, where we have plotted as a function of occupancy the change in the total enthalpy of the system when one of the hydrogen atoms moves from the vacancy to a solution site; this quantity is in effect the binding enthalpy for the last hydrogen entering the vacancy, and each of the given values corresponds to a particular Q_i in Eq. (1). The value for an occupancy of one is larger by 0.09 eV than that reported in Ref. 7 due to recent refinements in the treatment of the octahedral solution site to which the binding enthalpies are referenced.[14] The trapped hydrogen atoms are predicted to occupy positions between the vacancy center and the adjacent octahedral interstitial positions, and the existence of six such sites then determines the maximum occupancy. The repulsion among the hydrogen atoms results in equilibrium positions that are displayed further from the vacancy center than in the case of single occupancy.

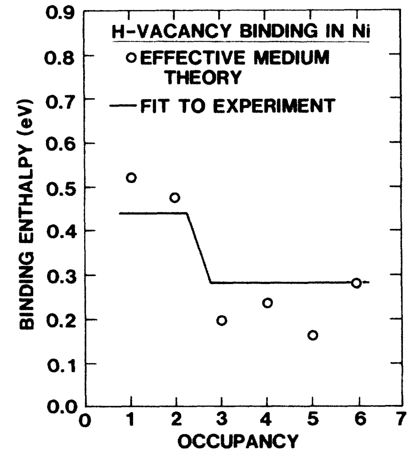

FIG. 1. Theoretically predicted and experimentally fitted binding enthalpies for one to six hydrogen atoms trapped at the monovacancy in Ni. The plotted quantity is defined as the total increase in enthalpy when one hydrogen moves from the vacancy to a solution site.

It is seen in Fig. 1 that the binding enthalpies for the first two hydrogen atoms in the vacancy are virtually the same, whereas the trapping is substantially weaker for occupancies from three to six. This is readily understood in terms of the atomic configurations for the various cases. Thus, the first two atoms lie on opposite sides of the vacancy toward opposing octahedral interstitial sites, and the resulting separation is such that repulsion effects are relatively unimportant. For occupancies greater than two, however, some hydrogen atoms are necessarily positioned about the vacancy center with only a 90° separation, and the resulting interactions reduce the binding enthalpies.

It may be noted that the occupancy of vacancies by multiple hydrogen atoms discussed here is analogous in several respects to the predicted and observed trapping behavior of He in metals. (See, for example, Ref. 22 and the review in Ref. 1.) Generally speaking, however, neither the specific conclusions regarding the inert gas nor the theoretical methods used to obtain these conclusions should be directly transferred to hydrogen. The binding enthalpies for the He are greater by an order of magnitude, so that the probability of multiple occupancy is much greater, and the theoretical predictions are far less sensitive to uncertainties of tenths of an electron volt. Moreover, the simple two-body potentials used to treat He interactions are not suitable for the more complicated interactions involving hydrogen.

A single hydrogen atom bound to the self-interstitial [100] dumbbell in Ni was previously shown from effective-medium theory to occupy one of the four near-octahedral interstitial sites about the axis of that dumbbell. The predicted binding enthalpy was 0.17 eV.[7] Although multiple occupancy of this defect trap has not yet been treated, we anticipate that appreciable binding will occur with up to four hydrogens, each filling one of the near-octahedral positions. For the modeling of the present paper a rough estimate of the four binding enthalpies is sufficient, and consequently all are assigned the value 0.17 eV.

IV. APPLICATIONS TO NICKEL AND ALUMINUM

In this section we use the formalism described in Sec. II, together with the theoretical results of Sec. III, to model the behavior of Ni and Al hosts that are first ion-implanted with hydrogen at low temperatures and then subjected to linear temperature ramping. Comparison is made between these calculations and our previously reported implantation experiments in which nuclear-reaction analysis was employed to measure the amount of retained hydrogen as a function of increasing temperature.[8,9] One objective of the analysis is simply to assess the applicability of the new theoretical methods to the implanted system. Another is to re-examine the mechanistic interpretations of the observed trapping behavior which we proposed on the basis of a simpler analysis, one which assumed fixed traps and only one trapped hydrogen per vacancy.[5,6] Finally, in the case or Ni, trap binding enthalpies are refined by fitting the new formalism to the experimental data.

Before considering the relatively complicated behavior of the implanted hosts, it is useful first to treat a simpler system, an infinite host initially containing uniform concentrations of monovacancies, monointerstitials, and hydrogen. Such a calculation serves effectively to illustrate certain features of the thermally activated evolution. Moreover, in the absence of hydrogen, the validity of the mathematical model can be assessed by comparing its predictions with the extensively documented behavior of irradiated bulk metals during warming.[16,17,23] Figure 2 shows the results of several model calculations for Ni and Al. Here the two systems begin at a temperature of 20 K with 10^{-4} atomic fraction of both monovacancies and monointerstitials, and the temperature increases at a constant rate of 1 K/min for the Ni and 2 K/min for the Al. When hydrogen is present its concentration is 10^{-3}. For simplicity we assume that up to six hydrogen atoms can be trapped at the Ni monovacancy with a constant binding enthalpy of 0.43 eV taken from the experiments of Ref. 8, neglecting for the present the dependence of the binding upon occupancy. Up to four hydrogens are taken to be trapped about the monointerstitial dumbbell with a constant binding enthalpy of 0.17 eV.[7] Additional properties of the hydrogen and defects which were used in the calculation are summarized in Table I, together with the references from which they were obtained. It may be noted in Table I that the assigned values for certain of the interaction distances are somewhat arbitrary. The error in these quantities, however, is unlikely to be greater than a factor of 2, and the consequences of such an uncertainty are unimportant for the present modeling.

In these and all subsequent calculations for Ni and Al, the relative degeneracy P of the hydrogen in its octahedral-interstitial solution site is arbitrarily set equal to one. The degeneracies of the various trapped states are then assigned by counting in each case those equivalent configurations which maximize the number of hydrogen atoms separated by 180° about the defect center. Thus, as the population of the six near-octahedral sites about the vacancy increases from zero to six, one has $P=1$, 6, 3, 12, 3, 6, and 1 in succession. Similarly, as the four sites about the self-interstitial [100] dumbbell accumulate from zero to four hydrogens, $P=1$, 4, 2, 4, and 1. The inherent assumption in this evaluation of the degeneracies is that the entropy of hydrogen at a particular near-octahedral trapped position is not very different from the entropy at the octahedral solution site.

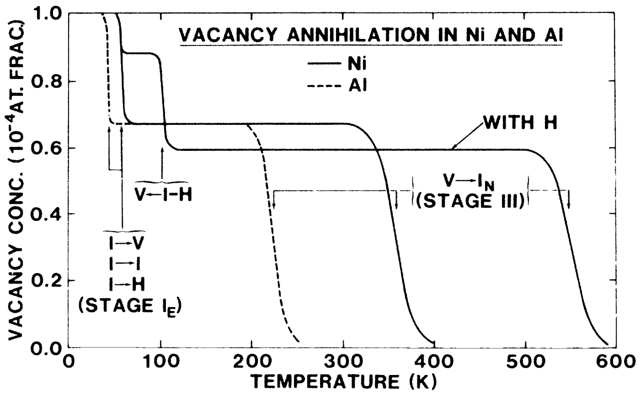

FIG. 2. Model calculations for temperature ramps of Ni and Al containing uniform concentrations of monovacancies, monointerstitials, and hydrogen. The initial concentration of both defects is 10^{-4} atomic fraction throughout, whereas hydrogen is present at a concentration of 10^{-3} atomic fraction for one of the three curves and absent otherwise. The ramp rate is 1 K/min for Ni and 2 K/min for Al.

TABLE I. Properties of hydrogen and defects used in the model calculations.

Parameter	Nickel Value	Nickel Ref.	Aluminum Value	Aluminum Ref.
H diffusion prefactor (mm^2/s)	0.48	24	11	25
H diffusion activation energy (eV)	0.408	24	0.424	25
Vacancy diffusion prefactor (mm^2/s)	92	26[a]	11	27[a]
Vacancy diffusion activation energy (eV)	1.1	28	0.62	28
Interstitial diffusion prefactor (mm^2/s)	0.20	17[b]	2.6	17
Interstitial diffusion activation energy (eV)	0.15	17	0.115	17
Vacancy-interstitial interaction distance (nm)	1.25	17[b]	1.43	17
Interstitial-interstitial interaction distance (nm)	1.25	17[c]	1.43	17[c]
H-defect interaction distance (nm)	0.62	d	0.71	d

[a] Approximated by the prefactor for self-diffusion.

[b] Equated to the value for Cu.

[c] Approximated by the vacancy-interstitial interaction distance. Same value used for the interstitial-interstitial cluster interaction.

[d] Approximated as one-half the vacancy-interstitial distance.

For Ni with no hydrogen, the calculated concentration of monovacancies is seen in Fig. 2 to decrease in two distinct stages, one at about 60 K and the other at 360 K. For Al the corresponding stage temperatures are approximately 45 and 225 K. In both metals the first of the reductions occurs when monointerstitials become mobile, leading to both vacancy-interstitial recombination and the formation of interstitial clusters; the first of these processes causes the drop in vacancy concentration seen on the plot. In terms of the widely used notation for defect recovery in irradiated metals as measured through electrical resistivity,[16,17,23] the above events correspond to stage I_E, which denotes the effects of interstitial mobility that occur after the correlated-recombination events of stages $I_A - I_D$. The second reduction in the number of vacancies occurs when the vacancies become mobile and annihilate at interstitial clusters, and in the present simplified model this removes all defects from the material. Again applying the notation from resistivity recovery, one at this point has stage III.

From the above results it is apparent that the mathematical model of Sec. II does exhibit the processes principally responsible for the removal of monovacancies and monointerstitials. Moreover, the calculated temperatures for recovery stages I_E and III are in good agreement with those observed via resistivity recovery.[23] Consequently we consider the formalism adequate for the present purpose, that being a semiquantitative examination of the influence of defect evolution on hydrogen trapping by monovacancies and monointerstitials.

The introduction of hydrogen into the calculation for Ni is seen in Fig. 2 to modify substantially the predicted temperature dependence of the vacancy concentration: A new stage is introduced at about 100 K, and the highest-temperature stage is shifted upward by about 190 K. The first of these effects results from the fact that, when the monointerstitials begin to migrate at 60 K, some become trapped at the then immobile hydrogen. The interstitial-hydrogen entities subsequently break apart at 100 K, whereupon the released interstitials undergo annihilation with vacancies and thereby produce the observed further reduction in the vacancy concentration. The upward temperature shift of the final Ni stage in the presence of hydrogen is simply a consequence of hydrogen trapping at the vacancies, which prevents their migration to the interstitial clusters until detrapping occurs.

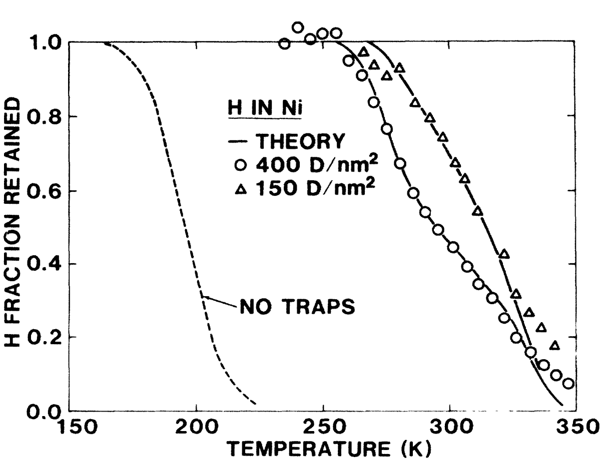

FIG. 3. Temperature-ramp data for Ni ion-implanted with the indicated fluences of hydrogen. The theoretical curves were calculated as discussed in the text. The ramp rate is 1 K/min.

Having examined the behavior of our mathematical model for a uniform bulk system, we turn now to a consideration of Ni that has been ion-implanted with hydrogen in the near-surface region. Figure 3 shows previously published data from temperature-ramp experiments;[8] here the deuterium isotope of hydrogen was ion-implanted at temperatures below 90 K, and during subsequent temperature ramping at 1 K/min the retained fraction of the deuterium was monitored by nuclear-reaction analysis. The implantations were performed at an energy of 10 keV, for which the calculated projected range is 81 nm and the rms range spread 35 nm; at the higher implanted fluence of 400 nm^{-2} in Fig. 3, the measured peak concentration is about 3 at. %. The surface was shown not to retard significantly the release of hydrogen in these experiments.

The trapping of the hydrogen by implantation defects is evidenced in Fig. 3 by the difference of about 100 K between the measured release temperatures and that calculated for no trapping. In the case of the data from the larger implantation fluence, two distinct stages are apparent, one centered at about 280 K and the other at 330 K; this is indicative of at least two trap strengths within the system. Our previous analysis of these and other data from Ni, in which we assumed that all traps are immobile, yielded 0.24 and 0.43 eV for the respective binding enthalpies expressed relative to the solution site.[8] Subsequently, calculations utilizing effective-medium theory gave 0.17 eV for a single hydrogen bound to a monointerstitial in Ni and 0.43 for one hydrogen within the monovacancy, and this prompted the hypothesis that the two point defects are responsible for the observed detrapping stages:[7] the vacancy mechanism was proposed with a relatively high degree of confidence, whereas the suggestion of trapping by interstitials was made only tentatively. Although unattached monointerstitials become mobile well below the hydrogen detrapping stages, as seen in Fig. 2, this fact does not by itself disprove the hypothesis because, as pointed out previously, trapped hydrogen can be expected to retard the defect migration. The key question for the earlier interpretation is then whether the immobilization persists to sufficiently high temperatures to account for the observed detrapping stage at 280 K.

The mobile-defect calculations already presented in Fig. 2 for uniform concentrations make it doubtful that monointerstitial traps can account for the observed hydrogen-detrapping stage at 280 K; although the immobilization effect discussed above does occur, it delays the migration of the interstitials only to about 100 K. Furthermore, as will be seen, virtually the same finding emerges from a treatment of the implanted system. Hence, in the light of these new calculations, one is left with an observed detrapping stage in Ni whose origin is unexplained. This then leads us to consider multiple occupation of the monovacancy trap as a possible explanation since, from the theoretical results of Sec. III, lower binding enthalpies are expected at the higher occupancies.

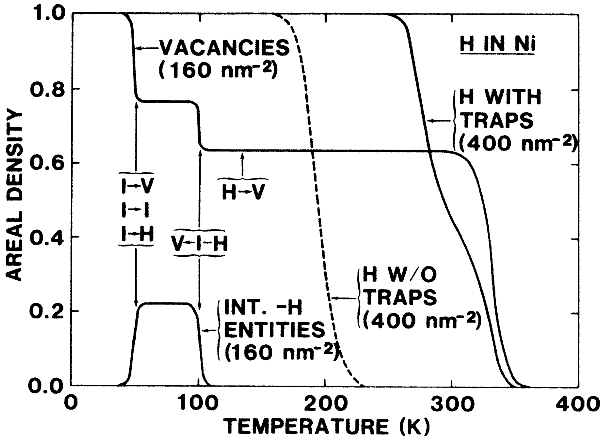

FIG. 4. Additional detail from the model calculations of Fig. 3 for Ni. The areal densities of the three species are normalized to the values in parentheses beneath the respective labels, and the schematic notation for the interactions uses *V* for monovacancies, *I* for monointerstitials, and H for hydrogen.

Our approach in assessing the possible role of multiple occupancy of the vacancy in Ni is first to adjust the hydrogen binding enthalplies to produce agreement with the experimental data. In view of the predictions of effective-medium theory plotted in Fig. 1, we make the simplifying assumption that the binding enthalpy has one value for the first two hydrogens and a second, smaller value for occupancies of three through six. It is further assumed that up to four hydrogens can be trapped about the monointerstitial, each with a binding enthalpy equal to the previously reported theoretical value for a single hydrogen, 0.17 eV.[7] The calculation is begun at a temperature of 20 K, and at that point the hydrogen depth profile is taken to be a Gaussian function having the theoretically predicted mean depth and rms spread of 81 and 35 nm, respectively. The equal initial concentrations of monovacancies and monointerstitials are approximated as constant from the surface to 120 nm and zero at greater depths; the amplitude of this distribution is then adjusted to produce agreement with the experimentally observed amplitudes of the hydrogen-detrapping stages. Other properties of the defects and hydrogen are as given earlier in this section.

The results of the above calculations are shown as solid curves through the data in Fig. 3, and the fit to experiment is seen to be good. The adjusted initial concentration of monovacancies and monointerstitials is 1.5 at. % for the higher of the implanted hydrogen fluences and 0.9 at. % for the lower. The two extracted binding enthalpies are 0.44 and 0.28 eV, respectively, and these are plotted as solid lines in Fig. 1. Agreement with the predictions of the effective-medium theory is quite satisfactory. This is especially true when we note that it is the relatively larger effective-medium value for an occupancy of six which should be compared with the lower of the two fitted binding enthalpies. Such is the case because, in a physical system having the theoretical binding enthalpies plotted in Fig. 1, the trap populations would tend to shift from occupancies of three, four, and five to those of one, two, and six so as to minimize the local free energy. In view of this consistency we are led to refine our earlier picture of the trapping behavior: The higher-temperature release stage is attributed as before to vacancy traps, but now the lower-temperature stage is tentatively associated with higher occupancies of the vacancy rather than with interstitial traps.

Figure 4 provides additional information from the above model calculations. The plotted quantities are the total areal density of hydrogen remaining within the implanted region, the areal density of monovacancies, and the areal density of monointerstitials with one or more hydrogen atoms attached. In each case the plotted quantity is normalized to the value given in parentheses beneath the label. Also included for comparison is a plot of retained hydrogen for the case where there are no traps. The first step in the evolution of the system occurs at about 50 K, when the monointerstitials achieve appreciable mobility and either annihilate with monovacancies, form interstitial clusters, or become attached to the initially solutionized hydrogen. Then, at approximately 100 K, the interstitial-hydrogen entities dissociate, and further annihilation and clustering of the interstitials takes place; at this point all of the hydrogen is again in solution. This particular result provides further confirmation that the monointerstitial trap probably is not responsible for the observed hydrogen-detrapping stage at 280 K. The next change takes place at about 140 K, when the hydrogen becomes sufficiently mobile to move to the vacancy traps. The final steps in the evolution occur in the vicinity of 300 K, where the two hydrogen-detrapping stages are followed shortly by the annihilation of mobile vacancies at the interstitial clusters.

It may be noted that some of the events depicted in Fig. 4 for the ion-implanted system occur at temperatures significantly lower than in the uniform and infinite material modeled in Fig. 2; such events include the initial stage of interstitial migration and annihilation and the migration and annihilation of vacancies following their detachment from hydrogen atoms. These temperature shifts are consequences, primarily, of two differences between the systems: In the case of the uniform infinite material the concentration of the interacting entities is orders of magnitude lower, and there is no release of hydrogen from the matrix.

We turn now to a consideration of implanted hydrogen in Al. This system differs from Ni in at least one respect which might qualitatively change the results of the modeling, namely the onset of monovacancy mobility at a temperature below that where hydrogen release is observed; thus, the calculated temperature ramp for Al represented in Fig. 2 exhibits the effects of vacancy diffusion at about 220 K, whereas ion-implanted hydrogen in Al is experimentally observed to be released only at about 340 K for a similar ramp rate. Hence, if monovacancy traps are responsible for the single observed release stage as we have previously proposed, then the vacancies must be immobilized by the hydrogen to more than 100 K above the normal onset of diffusion.

Model calculations for hydrogen-implanted Al, obtained using the formalism of Sec. II, are represented in Fig. 5. The initial conditions correspond to our previously reported experiments[9] in which Al was ion-implanted with hydrogen at 15 keV to a fluence of 80 nm^{-2}, yielding a calculated range of 220 nm and a rms spread of 59 nm. The binding enthalpies for one to six hydrogens in the monovacancy are all set equal to the value for the first hydrogen as obtained from effective-medium theory, 0.52 eV.[9] This neglect of hydrogen-hydrogen repulsion effects is partially justified by two considerations: First, such effects are expected to be smaller in Al than in Ni because of the more open lattice, and, second, the experimental data for Al were obtained at a substantially lower hydrogen concentration, where the degree of multiple occupancy is expected to be less. The initial concentration of monovacancies and monointerstitials was again approximated by a step function, constant from the surface to 280 nm and zero at greater depths, and the amplitude was such that the integrated areal density equaled the implanted hydrogen fluence. The modeling of hydrogen release is insensitive to the value used for the initial defect concentrations because, in Al, excess vacancies become mobile and annihilate before the onset of hydrogen detrapping. Variations in the strength of the hydrogen-interstitial interaction also have little effect, and consequently the corresponding binding enthalpy was simply equated to the plausible value of 0.2 eV, which is approximately the effective-medium prediction given above for Ni. Other properties of the hydrogen and defects in Al were taken from the literature and are summarized in Table I.

Also shown in Fig. 5 is a plot of hydrogen retention which was obtained assuming no mobility of the defect traps; this is actually the curve which we previously fitted to our Al data,[9] and the extracted value of the trap binding enthalpy is identical to the result from effective-medium theory for vacancy trapping, 0.52 eV. Since the same trap strength was used in the new calculations, one has in Fig. 5 a rather direct comparison between the old and new modes of data analysis. The half-amplitude temperatures for the two calculated release curves differ by only about 10 K out of 340 K, which would translate into a difference in fitted binding enthalpies for the same data of about 0.03 eV. This essentially negligible disparity is due in part to two compensating changes as one goes from the old model to the new: Introducing vacancy mobility reduces the calculated release temperature, whereas the inclusion of multiple occupancy has the opposite effect.

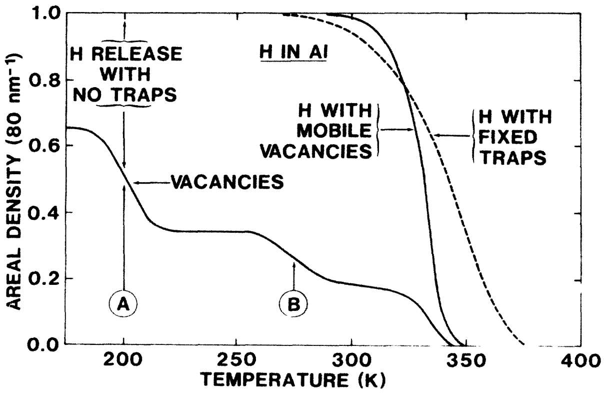

FIG. 5. Model calculations for Al ion-implanted with hydrogen to a fluence of 80 nm^{-2}. The curve for immobile traps is reproduced from Ref. 9, where a simplified treatment was used. The ramp rate is 2 K/min. Processes reducing the vacancy concentration in regions A and B are discussed in the text.

The integrated areal density of vacancies is plotted in Fig. 5 to exhibit other steps in the evolution of the implanted system. At the temperature where the plot begins, 175 K, several processes have already taken place, including vacancy-interstitial annihilation, interstitial clustering, formation of interstitial-hydrogen entities, breakup of these entities, and the migration of the hydrogen to the remaining vacancy traps. At the temperature region labeled *A*, those vacancies not immobilized by trapped hydrogen become mobile and annihilate at interstitial clusters. In region *B* the vacancy concentration is reduced further by a process in which temporarily unoccupied vacancies migrate sufficiently to undergo annihilation, and this shifts the remaining vacancy traps toward higher occupancy. Finally, with the onset of hydrogen release from the specimen, the remaining vacancies are annihilated at the interstitial clusters, thereby returning the lattice to a defect-free condition.

V. DISCUSSION

A principal goal of this study was to develop an extended mathematical formalism for the diffusion and defect trapping of ion-implanted hydrogen in metals, one taking account of the thermally activated evolution of the defect microstructure.[16,17] Because this problem is prohibitively complicated for a complete analytical treatment, a number of simplifications were introduced in describing the defect behavior. First, the system was taken initially to contain only monovacancies and monointerstitials in addition to the hydrogen in solution, and the point defects were assumed to be randomly distributed within the matrix. This ignores both the complicated structure of ion cascades and the occurrence of correlated recombination of Frenkel pairs. Second, the clustering of interstitials was included but the agglomeration of vacancies was not. Third, the diffusion of all species other than the two point defects and hydrogen was neglected, despite the probable mobility of such entities as divacancies and di-interstitials. Fourth, all interstitial clusters were presumed to be completely stable except for their progressive annihilation by impinging vacancies, thereby ignoring the well-established ripening of these clusters in the temperature range between recovery stages I and III. Finally, the trapping of hydrogen by interstitial clusters was not included.

In view of the above simplifications, the mathematical formalism of this paper should not be regarded as a means of accurately modeling irradiation damage in metals. However, it does include the principal processes which are believed to affect the concentrations of monovacancies and monointerstitials following the completion of correlated recombination in recovery stages $\mathrm{I}_A - \mathrm{I}_D$.[16,17] Moreover, in the absence of hydrogen this formalism was shown to reproduce accurately the temperatures of those recovery stages where most uncorrelated annihilation of monovacancies and monointerstitials occurs. Consequently, we believe that our calculations provide a reliable semiquantitative indication of the influence of defect mobility on the trapping of hydrogen by monovacancies and monointerstitials. This is especially true when, as in the case of Ni, the hydrogen-release data provide an independent estimate of the concentration of the defect traps.

We have elected in the present paper not to deal with hydrogen trapping by clusters of vacancies and interstitials, focusing instead on the binding to point defects. This reflects our limited goal of examining here those simpler mechanisms which can be realistically treated in the transport formalism and for which the effective-medium theory can be applied with fair accuracy. The application of this restricted analysis to implantation experiments is justified in our view by the probability that monovacancy traps dominate in a majority of such studies. For example, the observation that hydrogen concentrations up to several atomic percent can be trapped with binding enthalpies in the range of 0.5 eV would be difficult to explain in terms of extended trapping entities such as defect clusters and dislocations. In addition, channeling analysis of ion-implanted hydrogen generally shows the trapped configuration to have high symmetry, again suggesting a simple defect. Moreover, channeling results from a number of hydrogen-implanted metals conform well to the predictions of effective-medium theory for the location of hydrogen within the monovacancy.[6] Nevertheless, before leaving this subject two qualifications should be made. The first is that some trapping by vacancy clusters probably occurs in most hydrogen-implanted systems; indeed, in the case of Fe, there is a final, low-amplitude release stage which we attribute to this mechanism.[11,29] The second qualification is that, if the binding of hydrogen to interstitial clusters in Ni is similar to that predicted by effective-medium theory for the monointerstitial trap,[7] then such immobile clusters might lead to a detrapping stage close to that which we attribute to multiple occupancy of the vacancy. This contribution is believed to be much smaller than that of the vacancies, however, at the large trapped concentrations of several atomic percent.

We have concluded on the basis of results from effective-medium theory that up to six hydrogen atoms can be trapped by the monovacancy in Ni, and that the binding enthalpies for the last four hydrogens are significantly reduced from those for the first two. These predictions are in good agreement with hydrogen release data for hydrogen-implanted Ni, and, in particular, the calculated lower binding enthalpies for the higher occupancies provide an explanation for the first of the observed detrapping stages which previously was tentatively associated with monointerstitial traps. Another attractive feature of multiple occupation of the vacancy is that it reduces the defect concentrations necessary to account for the observed trapping at higher implanted fluences of hydrogen. For example, the implanted hydrogen concentrations for the Ni experiments analyzed in Sec. IV were as high as 3 at. %, whereas the fitted initial vacancy concentration had the plausible value of 1.5 at. %.

The transport formalism employed in the present paper is a relatively complicated one involving seventeen partial differential equations with numerous parameters. For this reason it is important to emphasize that there is little arbitrariness or even adjustability in the calculations. All of the physical processes included in the model are well established, and the semiquantitative formulation of these processes is straightforward and unambiguous. Moreover, in fitting to the experimental data from Ni only three parameters were adjusted, two trap binding enthalpies and the initial concentration of point defects; all other quantities were evaluated from independent information. Even the adjusted quantities could not be varied arbitrarily, since the binding enthalpies were compared with the predictions of effective-medium theory. Based on these considerations we attach substantial significance to the good agreement between theory and experiment.

Our previous experimental studies of the trapping of ion-implanted hydrogen in metals have included work on Al, Fe, Ni, Cu, and Pd.[5,6] In each case trap binding enthalpies were extracted from the temperature-ramp data using a transport formalism which neglected the mobility of the point-defect traps and which permitted only single occupancy of these traps. Therefore, having examined the implications of defect mobility and multiple occupancy for trapping in Ni and Al, it is desirable to extend such analyses to the remaining hosts. This work is in progress and will be reported in detail elsewhere, together with additional experimental results, but certain trends are emerging. In particular, our earlier conclusions regarding the trapping of the first hydrogen within the monovacancy remain essentially intact; the observed detrapping stages attributed to this mechanism were correctly assigned, and the neglect of vacancy mobility had minimal effect on the extracted binding enthalpies, even when the detrapping stages occurred at temperatures above the onset of vacancy mobility. In the case of the fcc metals, however, our more tentative association of the first of the two detrapping stages with monointerstitial traps no longer seems viable. Pending the completion of effective-medium calculations for the remaining metals, multiple occupancy of the vacancy as discussed herein for Ni seems the most probable mechanism for these lower-temperature stages.

VI. CONCLUSION

The trapping of ion-implanted hydrogen in metals is, in principle, a very complicated phenomenon, one involving the interaction of a mobile solute with the innumerable, densely packed, and evolving constituents of ion-irradiation damage. Nevertheless, the present work, in conjunction with our previous studies, promises a considerable capability for interpreting and even predicting the trapping behavior when low-temperature implantation is followed by thermally activated redistribution. This is possible in large part because trapping by a single entity, the vacancy, seems often to dominate the behavior of the system. It will be important in future research to examine the broader applicability of the methods of this paper, with regard not only to the range of metals and alloys which can be treated, but also the acceptable variations in temperature and irradiation conditions. As one example, it is desirable in connection with plasma-wall interactions in fusion reactors to provide an improved description of the behavior of hydrogen when it is ion-implanted at elevated temperatures.

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