PERMEATION AND THERMAL DESORPTION STUDIES

OF

DEUTERIUM DIFFUSION AND TRAPPING IN ION-IMPLANTED NICKEL

By

SAN-QIANG SHI, B.Sc., M.Sc.

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DEUTERIUM DIFFUSION AND TRAPPING IN IRRADIATED NICKEL

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- AUTHOUR: San-Qiang Shi, B.Sc. (Department of Applied Physics, University of Science and Technology in Beijing) M.Sc. (Department of Applied Physics, University of Science and Technology in Beijing)
- SUPERVISORS: Professor D. A. Thompson Professor W. W. Smeltzer Professor J. A. Davies

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Abstract

The interaction between hydrogen isotopes and irradiation defects in nickel is studied using Gas-phase Permeation and Thermal Desorption Analysis techniques. The work was motivated by the need for the understanding and control of tritium diffusion and trapping in structural materials of the first generation of D-T fusion reactors, as well as by the need for minimizing helium "ash" in the plasma. Major attention was given to the study of relationships between helium defect configuration and deuterium diffusion and trapping behavior.

Permeation results show that crystalline defects such as dislocation loops produce no measurable effect on deuterium permeation in the temperature range of 373 K - 573 K, whereas helium defects decrease the apparent diffusivity and, sometimes, the permeability of deuterium by several orders of magnitude, indicating a strong trapping effect for hydrogen isotopes. Thermal treatments at elevated temperatures of samples pre-implanted with helium ions resulted in a newly observed abnormal aging history dependence on deuterium diffusion and permeation behavior. The basic aspects of this abnormal behavior were examined and analyzed.

Thermal desorption technique was used to obtain additional information on helium trapping mechanisms: for examples, the effective binding energies of deuterium to helium defects consist of a distribution of values and are in the range of 0.4 - 0.6 eV with higher values observed when helium bubbles formed; the trapping efficiency decreases from > 1 to < 0.3 when the helium fluence increases from 1×10^{15} to $4 \times 10^{17} / \text{cm}^2$; thermal treatments of these samples resulted in a decrease in the trapping efficiency that was also dependent on the initial helium fluences. An interesting phenomenon, "H" enhancement of helium release, was observed and analyzed using the Hydrogen-Assisted Cracking model.

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CHAPTER I

Introduction

It is correct to say that all real metals contain defects. It may also be correct to say that all metal defects trap hydrogen. The same is true, of course, of all atoms dissolved in metals, but the rapid diffusion of hydrogen in metals, even at low temperatures, permits the trapping to take place at much lower temperatures than is true of any other dissolved atom.

Hydrogen-defect interactions in metals have been the subject of intensive study for over 100 years. Historically, the embrittlement of steels by hydrogen accumulating at fracture sites such as grain boundaries or crack tips has been of immense interest. Although its presence may have been suspected by makers and users of steel products long before 1873, it was in this year, according to Buzzard and Cleaves [I.1], that W.H. Johnson [I.2, 3] recorded hydrogen "embrittlement" as a form of hydrogen damage. Johnson detailed much of the problem as it exists today. This interest was extended to other metals and alloys as they became important structural materials. The ideas concerning a "hydrogen economy" have further focused attention onto the ability of some metals and alloys to store hydrogen incorporated in the lattice. Again, the hydrogen-defect

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interaction may play an important role for hydrogen storage. Finally, in the new generation of long pulse D-T (deuterium-tritium) fusion reactors, the plasma fueling and tritium inventory are greatly influenced by recycling of hydrogen isotopes in the first-wall, which is in part controlled by hydrogen trapping at irradiation damage, and at impurities such as helium. Helium as an impurity in D-T reactors is inevitable not only because it is one of the products of the fusion reaction, but also because it can be generated by nuclear reactions of neutrons or protons with atoms in the structural materials, as well as by the decay of tritium to ³He. It was found (see, e.g., the work of Wilson et al. [I.4], and Besenbacher et al. [I.5]) that the helium trap is probably the most important one in fusion reactors in terms of the trapping energy.

Besides the concern of tritium inventory, another concern in reactor design is to minimize the helium "ash" in the plasma because it decreases the burning efficiency of the D-T fuel. One possible way of doing this is to make use of the helium "self-pumping" effect [I.6]. This effect is based on the fact that helium can be strongly trapped at lattice defect sites. Consequently, it is expected that for some materials, there is a temperature range in which implanted hydrogen isotopes are released without significant helium release. In such a way, helium "ash" in the plasma can be reduced.

The present study is closely focused onto the fundamental aspects of the the relationship between helium defect configuration, and deuterium diffusion and trapping behavior in nickel. To cover different helium configurations, a wide range of helium implantation fluences and different thermal treatments of the samples are used in this work. The basic techniques employed are gas-phase permeation and thermal desorption techniques. Nickel is chosen as a base material for study because it is a well characterized material on both helium defect configuration and deuterium diffusion. Compared to stainless steels nickel oxide has little effect on hydrogen permeation. Nickel has also been used as a reference material for the study of helium ash "self-pumping" effect in limiter (or diverter) design [I.7].

In chapter II, the thermodynamics and kinetics of radiation defects in metals are reviewed. Although the theories for crystalline defects are well established, the theories for helium defects are still being developed . Nevertheless, important experimental results on helium defect formation and annealing behavior in metals are given. Chapter III introduces the fundamental theories of hydrogen trapping, and diffusion in metals. Again, the theories for hydrogen trapping at helium defects, and hydrogen diffusion in the presence of helium defects, are still being developed and proven. In chapter IV the basic experimental apparati and methods of this work are described in detail. Chapter V includes all the experimental results, analyses, and discussions. Finally, in chapter VI, conclusions are given.

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CHAPTER II

Thermodynamics and Kinetics of Radiation Defects in Metals

II.1 Introduction

Radiation damage caused by ion implantation of materials is a powerful technique for studying the characteristics of defects because this method can generally control the spatial distribution and amount of lattice defects, and introduce impurities in controlled amounts that may exceed the solubility limits. Using ion implantation, lattice defects, or crystalline defects, of structural metals have been extensively investigated and comprehensive theories of radiation damage were well established in the 1950s and 1960s. Helium defects, as a special problem of interest, have attracted many systematic experimental and theoretical studies in the past three decades. The main difficulty here is that in most cases, helium defects are in non-equilibrium states, so that helium defect configurations are highly dependent on helium introduction conditions. Any theory developed to describe defect formation and transitions has to be a non-equilibrium type, hence will be quite complicated.

In the next section, a brief summary of theories describing radiation induced crystalline defects is given. Section II.3 provides the basic experimental findings of helium defects and related theoretical results.

II.2 Crystalline defects

II.2.1 Overview

and (vacancy defects include: point Crystalline defects dimensional defects (dislocations), dimensional two self-interstitial), one defects (stacking faults and grain boundaries), and three dimensional defects such Initial defects produced during as voids and stacking fault tetrahedra, etc. irradiations are most likely to be point defects. All other higher dimensional defects are produced by the agglomeration of these point defects in different ways.

During irradiation the following processes may be involved : electronic excitations, atomic displacements and transmutations. Transmutations, which are due to nuclear reactions, are only observed with neutrons and very high energy light ion irradiation; accordingly, in many cases they are missing and will be ignored in this section. Electronic excitations are very effective for defect production in insulators, but in metallic materials, with which we are concerned here, they only heat the target. Hence the most important process for the crystalline defect production is by elastic collisions producing atomic

displacements.

When an incident ion undergoes an elastic collision with an atom in the target material, a certain amount of kinetic energy, called the primary recoil energy, is transferred to the atom. If the recoil energy is sufficient (above a threshold energy which is about 20 to 50 eV in metals) the atom will be "permanently" ejected from its original lattice position to an interstitial site, leaving behind a vacancy. This interstitial-vacancy pair is called a *Frenkel pair*. In many cases the primary recoil energy is high enough to create a cascade of atomic collisions by ejecting further atoms from their sites, resulting in more Frenkel pairs.

The spatial distribution of the defects depends on the nature of the incident particles: for electrons with energy of the order of 1 MeV one obtains isolated Frenkel pairs; for proton and neutron, especially for heavy ion irradiations one generally observes collision cascades, which one can imagine as a vacancy rich core surrounded by interstitials along the incident ion track. In this case it is easier to observe higher dimensional defects because point defects are created so close to each other within the cascade that they can more easily join together to form larger clusters.

The number of displacements per atom and per second $(dpas^{-1})$ characterizes the irradiation. It is equal to the rate of production of Frenkel pairs (not the net production). For instance an atomic fraction of 10^{-3} Frenkel pairs is produced per second by an irradiation characterized by 10^{-3} dpas⁻¹. To calculate dpas⁻¹, two steps are usually taken :

(i) given the flux of the incident particles and the collision cross sections of these particles with the atoms of target one can calculate the energy spectrum of the primary knock-on atoms. In this case it is a collision problem between different particles. When the recoil energy is larger than a threshold energy it is assumed that this atom is ejected or "displaced" from its stable position; it is not displaced if the energy is smaller than the threshold. The energy of incident particles decreases as they penetrate more deeply into the sample and the energy spectrum of primary knock-on atoms is modified. This is an important effect for ions. To calculate the ion implantation range see Lindhard et al [II.1, 2].

(ii) one calculates the number of atoms displaced by each primary knock-on atom. In this case it is a collision problem between like particles. Kinchin and Pease [II.3] gave an equation which was later modified by Sigmund [II.4] for the number of displaced atoms N(E_p) by a primary recoil energy E_p as

N (E_p) =
$$\frac{0.84 \ E_{el}}{2 \ E_{d}}$$
 (II.1)

 E_d is the threshold energy for displacements. E_{el} is the energy which is given to the lattice through elastic collision processes by the primary recoil with energy E_p ; according to Robinson [II.5] E_{el} is given by

$$E_{el} = \frac{E_P}{1 + K \cdot g(\varepsilon)}$$
(II.2)

where $K = 0.1337 Z^{2/3} A^{-1/2}$, $\varepsilon = 0.01015 Z^{-7/3} E_p$, and $g(\varepsilon) = \varepsilon + 0.4024 \varepsilon^{3/4} + 3.4 \varepsilon^{1/6}$. A and Z are the mass and the atomic number of the target. E_{el} and E_p are in eV.

Computer codes are now available which allow to calculate directly the defect production and their spatial distribution. See for instance Biersack and Haggmark [II.6], and more recently, TRIM [II.7]. A typical damage profile comparing with the ion range profile is shown in Figure II.1, according to a TRIM simulation.

It has been shown experimentally that for electron and photon irradiation, where Frenkel pairs are produced without cascades, the calculated number of defects agrees fairly well with the actual production rate, and that for neutron and ion irradiation, where defects are produced within cascades, the calculated number of defects overestimates the net production rate, and especially at high temperature. This is due to the recombination and agglomeration of point defects which are not taken into account with the above model. Another important deviation from the above model comes when the irradiation fluence reaches such high level that the cascades spatially overlap each other.

A further consideration is a model based on chemical rate theory, first proposed by Lomer [II.8], and extended by many others. An example is given here. The recombination of Frenkel pairs and annihilation of point defects on



Figure II.1 TRIM simulation of 30 keV 4 He⁺ ion-implantation in nickel. Total ions calculated = 10000, displacement energy = 25 eV, lattice binding energy = 1.5 eV, mean ion range R_P = 115.8 nm, straggling ΔR_P = 48.5 nm, vacancies created per ion = 99.

dislocations are considered. Agglomeration of defects (e.g. loop and void formation), thermal vacancy concentration and free surface effects are neglected. The rate equations for the two types of defects (v and i) in a semi infinite sample can be written as

$$\frac{\partial C_{v}}{\partial t} = K - Z (v_{i} + v_{v}) C_{i}C_{v} - L_{v}D_{v}C_{v}$$
(II.3)

$$\frac{\partial C_i}{\partial t} = K - Z (v_i + v_v) C_i C_v - L_i D_i C_i$$
(II.4)

where C_v and C_i are concentrations of vacancies and interstitials, respectively, K is the production rate for Frenkel pairs (proportional to the irradiation rate), Z recombination efficiency, v_v and v_i are the jump frequencies for vacancies and interstitials ($v_i \gg v_v$), L_v and L_i are the effective dislocation densities for vacancy and interstitial annihilation, and D_v and D_i are the diffusion coefficients for vacancies and interstitials. Usually one writes $D_v = v_v a^2$, and $D_i = v_i a^2$ where a is the lattice parameter.



Numerical integrations have been done by several authors (see for example Sharp [II.9]). One typical time evolution of defect concentrations is shown on

Figure II.2 for low temperature irradiation and a low dislocation density. As one can see, at the beginning ($0 < t < \tau_1$) defects do not react and concentrations increase. In this region $C_v = C_i$ at each time. For $\tau_1 < t < \tau_2$ recombination is the only effective mechanism of elimination. This is the quasi-steady state where $C_v = C_i \approx \left(\frac{K}{Z v_i}\right)^{1/2}$. For $\tau_2 < t < \tau_3$ diffusion to sinks becomes efficient. Because interstitials are more mobile, they are the first to be lost at sinks. Therefore C_i decreases and then C_v increases (fewer recombinations). Finally for $t > \tau_3$ we have reached the true steady state $L_i D_i C_i = L_v D_v C_v$. This simple example has shown us that the configuration of irradiation defects depends on many parameters such as implantation rate (K), initial sink densities $(L_v \text{ and } L_i)$, crystalline properties (Z, D_v and D_i), and of course, temperature. Smith and Was



[II.10] combined the chemical rate model with the rate theory of creep and swelling and took the generation of dislocation loops into account (see the computation flowchart in Figure II.3). Using this model they estimated creep strain, swelling and microstructure evolution in pure single crystal nickel during irradiation.

In the following sections a little more detailed consideration of crystalline defects is given from the thermodynamic point of view, most of which can be found in many physical metallurgy text books or the books about radiation defects in metals (see, e.g., Thompson [II.11]). Some experimental results from the literature are to be given as well.

II.2.2 Point defects

Under thermal equilibrium conditions, even in the absence of radiation a crystal cannot exist at finite temperatures in a state of complete perfection. The vibrations of the lattice constitute one form of imperfection. These may be represented as a statistical distribution of thermal energy among the atoms of the crystal, and in any such distribution there is always a finite probability of sufficient energy being concentrated by local fluctuations onto a group of atoms to form a defect in the crystal lattice.

Assume a Henrian solution in which each defect r increases the internal energy by U_f^r , the volume of the solid by $\Delta V_{f'}^r$ and the vibrational entropy by $\Delta S_{f'}^r$

Then the change of the Gibbs free energy of the system due to adding n_r defects to N_r sites at constant temperature can be written as

$$\Delta G_{\text{total}} = n_r \cdot U_f^r + n_r \cdot P \cdot \Delta V_f^r - T(n_r \cdot \Delta S_f^r + \Delta S_{\text{mix}})$$
(II.5)

where ΔS_{mix} is the mixing (or " configurational ") entropy, and P and T are the pressure and temperature, respectively.

If one defines a formation free energy ΔG_f^r as

$$\Delta G_{f}^{r} = U_{f}^{r} + P \cdot \Delta V_{f}^{r} - T \cdot \Delta S_{f}^{r} , \qquad (II.6)$$

then a statistical thermodynamic consideration results in an expression of the equilibrium number of defect r as

$$\frac{n_r}{N_r - n_r} = \exp\left\{\frac{-\Delta G_f^r}{kT}\right\}.$$
(II.7)

where k is the Boltzmann's constant.

For most purposes it is a fair approximation to take the volume of the crystal as constant, and assume $n_r \ll N_r$; then the fraction of occupancy of the defect r is

$$\theta_{\rm r} = \frac{n_{\rm r}}{N_{\rm r}} \approx \exp\left\{\frac{\Delta S_{\rm f}^{\rm r}}{k}\right\} \exp\left\{\frac{-\Delta U_{\rm f}^{\rm r}}{k\,\rm T}\right\}.$$
(II.8)

Vacancies

The simplest of all defects is the vacancy (vacant lattice site). A bond model, which is best justified for covalent crystals, can be used to estimate the vacancy formation energy U_f^{V} . However, for metals, since the valence electrons are not localized in bonds, an alternative treatment may be found. A model which regards the crystal as a continuous rigid medium has been found to give surprisingly good results and has the advantage that it is easy to extend to a cluster of vacancies in the form of a void. Suppose one creates a small cavity with $\Omega = \frac{4}{3}\pi r_a^3$ equal to that occupied by one atom in the crystal, where Ω and r_a are defined as the *atomic volume* and *atomic radius*. The formation energy U_f^V is the difference in surface energy of the crystal with and without the cavity, and if γ is the surface energy per unit area it is simple to show

$$U_{f}^{V} \approx 4\pi r_{a}^{2} \gamma \qquad (II.9)$$

This will be something of an overestimate since by postulating rigidity we have neglected the tendency of the cavity to collapse under surface tension, which will be resisted by elastic strains generated in the surrounding medium. The elastic continuum model results in a smaller radius r_0 and predicts

$$U_{f}^{V} \approx 4\pi r_{o}^{2} \gamma - 12\pi r_{o}^{2} \frac{\gamma^{2}}{\mu} + 6\pi r_{o} \frac{\gamma^{2}}{\mu}$$
 (II.10)

where μ is the shear elastic modulus. The second term is the reduction in surface

energy due to contraction by the surface tension. The third is the elastic energy stored in the solid. Now it clear why the rigid continuum model succeeds for cavities: the decrease in surface energy due to inward relaxation is partly offset by an increase in elastic energy.

Expressing (II.9) in terms of Ω gives:

$$U_{f}^{V} = (6 \sqrt{\pi} \Omega)^{2/3} \gamma$$
 (II.11)

If one takes a spherical void composed of n vacancies the volume Ω in this expression is simply replaced by $n\Omega$ and it follows that

$$U_{f}^{nv} = (6 n \sqrt{\pi} \Omega)^{2/3} \gamma = n^{2/3} U_{f}^{v}$$
(II.12)

A useful concept is that of a binding energy U_b between defects, this being the energy required to separate the cluster into its constituent defects. In the case of the divacancy, $U_b^{2V} = 2U_f^V - U_f^{2V} = 2U_f^V (1 - 2^{-1/3}) = 0.4 U_f^V$, and $U_f^{2V} = 2^{2/3} U_f^V = 1.6 U_f^V$, where $U_f^V \approx 1$ eV for many metals. It is also possible to estimate the migration energy U_m^V , using above model by considering the energy difference in two configurations. Experimentally, $U_m^V \leq U_f^V$ for most metals.

Interstitials

The formation energy of a self-interstitial U_f^i is dominated by the strain

energy associated with a large outward dilatation. Unfortunately one cannot apply the elastic continuum model here because the strain must approach the atomic radius. Various atomic models which demand a detailed knowledge of interatomic forces have been used to calculate interstitial properties. Unlike the vacancy, it appears that there are several configurations with almost the same formation energy. The three most probable types are often referred to as the *dumb-bell* (the extra atom is accommodated by sharing one lattice site with another atom), the *body-centered* (the extra atom occupies the largest interstitial space), and the *crowdion* (the extra atom is squeezed in a close packed atom row).

An useful expression for U_f^i is given approximately [II.12] as

$$U_{f}^{i} \approx \mu \Omega/2$$
 (II.13)

 U_{f}^{i} is found to be about 4 eV for Cu, but the migration energy U_{m}^{i} is very low (about 0.1 eV).

Vacancy-interstitial pairs

As being mentioned earlier, in radiation damage, interstitials and vacancies are produced in equal numbers and in many cases the interstitial is associated with a nearby vacancy, called a *Frenkel* pair, the two having been formed in the same collision event. From the continuum model one would expect that because their dilatation are of opposite sign an attractive force should exist between the members of the pair. Under thermal activation there should then be a high probability of any migration leading to annihilation, rather than the more mobile partner escaping. Within a certain short distance, annihilation would occur even in the absence of thermal activation. Annihilation is much easier for metals because of the low migration energy of point defects and the non-directionality of atomic bonding. Thus, although the formation energy of an interstitial-vacancy pair in Cu is about 5 eV the mean threshold energy for dynamic production of the pair is over 20 eV. Figure II.4 shows a computer simulation of pair stability for Cu by Gibson et al.[II.13]. The unstable zone extends along the closely-packed <110> directions. Similar results were obtained in other metals.

> Figure II.4 Stability of Frenkel pairs in (100) plane of Cu. Split interstitial is at lower left. Dotted line separates stable from unstable sites for a vacancy. Approximate threshold energies for dynamic production of three particular pairs are indicated. S, stable; U, unstable.



II.2.3 Point defect clusters

In the electron microscope it is possible to observe point defect clusters

in metals. Clusters have been seen in many forms : voids, loops with and without stacking fault, and more complex defects.

Vacancy clusters

Suppose n vacancies condense to form a flat circular void of radius r and equal in thickness to one vacancy (~ $\Omega^{1/3}$). If the disc shaped void collapses in its central region, then a vacancy type dislocation loop is formed. In this process the surface energy of the void has been converted into dislocation strain energy. As an estimation, taking μb^2 as the formation energy per unit length of dislocation line, b being the *Burgers Vector*, we have for the loop:

$$U_{\rm f}^{\rm loop} \approx 2 \pi r \,\mu b^2 \tag{II.14}$$

since $n\Omega \approx \pi r^2 \Omega^{1/3}$, then

$$U_{f}^{loop} \approx 2 \sqrt{n\pi} \Omega^{1/3} \mu b^{2} \qquad (II.15)$$

Comparing the loop with the spherical void (II.12) gives:

$$\frac{U_{f}^{loop}}{U_{f}^{void}} \propto \frac{1}{n^{1/6}}$$
(II.16)

showing that for large enough n the loop has the lowest formation energy.

Ŋ.

The collapse of the disc need not necessarily join the lattice planes in the correct manner, and the loop will then enclose an area of stacking fault. For instance, in an f.c.c. crystal the disc void may be formed by removing part of a {111} A plane. Collapse perpendicular to the plane, by a vector $\frac{1}{3}a(111)$, will lead to a *B* and *C* plane in contact. The resulting stacking fault *ABC.BCAB* in principle could be removed by a shearing in the {111} plane by a vector $\frac{1}{6}a(11\overline{2})$. This process results in a loop of full dislocation ($\mathbf{b} = \frac{1}{2}a(110)$) with no stacking fault enclosed.

The interaction forces between loops have been calculated (e.g., see Foreman and Eshelby [II.14]). The force is very anisotropic: either attractive or repulsive according to the relative positions of the loops. The interaction energy in each case falls off as r^{-3} , r being the distance between two loops. Therefore there is a chance that they will join up to form larger loops, or that they will line up in arrays.

A different type of vacancy clusters was reported in 1959 by Silcox and Hirsch [II.15], called *Stacking Fault Tetrahedra* (SFT). When viewed along a <111> direction it appears triangular, but along <110> it appears square. It is a tetrahedron of a stacking faults enclosing a region of normal crystal. The four stacking fault faces correspond to the four {111} planes and the edges lie along the six <110> axes. It is believed [II.16] that the formation of SFT proceeds from a triangular plate of vacancy loop enclosing a stacking fault on a (111) plane, with its sides along <110> directions, as shown in Figure II.5(a). The triangular dislocation then throws off a partial of the type $\frac{1}{6}a(121)$ onto each of the upright faces of the tetrahedron, leaving a dislocation of the type $\frac{1}{6}a(110)$ on the base according to

$$\frac{1}{3} a (111) \longrightarrow \frac{1}{6} a (101) + \frac{1}{6} a (121).$$
 (II.17)

The partials $\frac{1}{6}$ a<121> bow out on the upright faces and meet one another along the upright edges of the tetrahedron forming new dislocations of the same type, $\frac{1}{6}$ a<110>, that surround the base. Then the whole tetrahedron is constructed and each face covered with the same type of stacking fault.



Figure II.5 Illustrating the formation of a stacking fault tetrahedron on {111} planes from a triangular plate of vacancies.

The dislocation energy of SFT is one-third of the original value of the

vacancy loops. However, four additional stacking fault areas, with energies of γ per unit area, have been created. These additional energies impose an upper limit on the size of the tetrahedron formed (~ 50 nm).

Interstitial clusters

Interstitial clusters have most often been observed in irradiated solids. They can only have plate or needle shapes. The plate can be thought of as part of an extra plane of atoms surrounded by a dislocation loop. The most likely plane in f.c.c. metals is the (111) plane, resulting in a stacking fault on either side of the extra plate of atoms, and a dislocation loop with a b vector of $\frac{1}{3}a(111)$. If this is swept by two partial dislocations, one above and one below the plane, the stacking faults can be removed to give a loop with $\mathbf{b} = \frac{1}{2}a(110)$.

II.2.4 Annealing of crystalline defects

In metals, an important property of a lattice defect is the contribution it makes to electrical resistivity. According to Matthiessen's Law [II.11] the contributions of the individual defects to resistivity are additive and independent of temperature. Specifically, the resistivity measurement is more sensitive to point defects and small clusters than large defects since the wavelength of the conduction electrons is of the same order as the dimensions of point defects. Therefore the resistivity is a convenient index of defect concentration and has the added advantage of being relatively easy to measure with high precision.

Electrical resistivity studies of annealing of crystalline defects after irradiation were performed intensively in the 1960s and 1970s (see e.g., the review article by Schilling et al.[II.17] and by Young [II.18]). Take nickel as an example. At low temperature (\leq 70 K) the resistivity decrease is best interpreted in terms of free self-interstitial migration because of the very low migration energy. At this stage free interstitials disappear at sinks such as vacancies and interstitial clusters, dislocations, and grain boundaries.

As the annealing temperature is raised, very small interstitial loops become unstable because of high line tension, and small interstitial clusters shrink as large interstitial loops grow.

At higher temperature $(350 \sim 500 \text{ K})$, first di-vacancies, then single vacancies become mobile, and some will condense to form loops, voids or tetrahedra. Those near to the edges of a crystal may escape rather than condense. Others may condense on the existing dislocation network of the crystal causing the dislocation lines to move by the process known as *climb*. In the case of a pure edge dislocation the extra half plane of atoms is eaten away by the vacancies and the line climbs perpendicular to its Burgers vector. A pure screw dislocation can not climb but becomes a spiral when vacancies condense on it.

As the annealing proceeds to higher temperatures the vacancy type defects

emit vacancies and shrink in the process. The driving force for the emission of vacancies arises from the line tension of a prismatic loop (no stacking fault), or the stacking fault energy of the loop, or the surface energy of a void. Large interstitial loops at this stage behave as vacancy sinks rather than emitting interstitials because $U_f^i > U_f^v$ and therefore the dominant process is vacancy emission. The smallest vacancy loops will emit vacancies most readily due to the high line tension. Indeed, small loops are often seen to shrink whilst larger ones grow. Eventually the temperature will be sufficiently high for all loops to disappear and this is observed at temperatures approaching those where self-diffusion first becomes appreciable (roughly 40% of the absolute melting temperature, ~ 700 K for nickel).

Stacking fault tetrahetra have been found to have an extremely stable structure, persisting well above the self-diffusion temperature (> 65% of melting temperature for Au). The stability arises from the difficulty of vacancy emission, which involves the nucleation of jog lines on the surface of SFT.

II.3 Helium defects

II.3.1 Overview

As a result of a comparison of solubilities of various solute elements in metals, several empirical rules, called the Hume-Rothery rules have been developed [II.16]. These are (1) the atomic size factor — if the atomic diameter of the
solute atom differs by more than 15 per cent from that of the solvent atom the extent of the primary solid solution is small; (2) the electrochemical effect — if the two elements come from columns in the periodic table that are far separated the greater is the tendency for the two to form compounds rather than extensive solid solutions; (3) relative valency effect — the valency of the solute should be greater than that of solvent in order to be more likely to dissolve to a large extent in the solvent. Inert gases present a class of foreign atoms in metals for which at least one or two of the Hume-Rothery conditions are not fulfilled. Furthermore, the fact that the first ionization potentials of inert gases lie in the range 10 - 25 eV shows that the outer electrons are much more tightly bound than in other atoms, and results in their chemical inertness. Consequently, the inert gases usually have very high activation energies of solution (from a few eV to about 20 eV) and therefore extreme low solubilities in metals.

Inert gases in metals started to attract increased attention with the development of nuclear technology where the interaction between neutrons and the nuclei of fuel or structural materials not only leads to displacement damage but also to the production of foreign elements. Of the various foreign species produced, the inert gases play a particularly important role since they can cause drastic property changes, even at low concentrations. Whereas the effects of inert gases in nuclear fuels had already attracted much attention in early years of reactor development, research on (n, α) -produced helium in structural alloys did not begin until the mid-sixties [II.19]. The stimulus came from a paper by Barnes (1965) [II.20] who attributed observations of high temperature embrittlement of irradiated steels to helium bubbles in grain boundaries. About a

decade later the field recieved a strong impetus when the progress in controlled thermonuclear fusion led to intense fusion materials research. There are mainly

	Fast breeder reactors	S-15 ppm/yr		
(<i>n</i> , a)	Fusion devices	50-300 ppm/yr		
(r, He ^a)	Tritium storage	up to 100 ppm/d		
(<i>p</i> , α)	Spallation sources	up to 100 ppm/d		
ά	Implantation	up to several %/hr		

Table II.1 Typical He production rates in nuclear technology

three helium generation processes: (1) nuclear reactions such as (n, α) and (p, α) in bulk and near-surface regions of materials, (2) exposure to high fluxes of α -particles resulting in near-surface deposition of helium atoms, (3) the decay of tritium (half-life 12.3 years) to ³He in tritium-contaminated materials. It was soon recognized that these processes will produce helium defects in structural materials of fusion reactors at much higher rates than those in fast fission reactors. Table II.1 [II.19] presents 1982 estimates of the helium production rates.

Upon introduction into the bulk material, helium atoms undergo three distinct processes: transport, bubble nucleation, and bubble growth. While helium atoms have a very small solubility in normal interstitial sites of a metal lattice, they usually have very large interstitial diffusivities. For examples, the migration energies for helium atoms in interstitial sites in nickel are said to be $0.1 \sim 0.4$ eV [II.21–25], which is even smaller than that for hydrogen (0.41

eV). Therefore whenever a helium interstitial is created at room temperature, it will quickly move around until it is trapped at crystalline defects and impurities, including by other helium atoms.

In the cases of energetic neutron irradiation and helium implantation at room temperature, vacancies, self-interstitials and helium defects are created. Vacancies offer interstitial helium atoms the strongest trapping sites due to the opposite signs of stress fields around these two species. The interactions between the three fundamental defects lead to the formation of small clusters of one to three helium atoms and one to three vacancies, with sizes in the 0.2 to 0.4 nm range.

The tiny clusters formed during the transport stage are in highly non-equilibrium state and are thus very unstable. For example, a self-interstitial atom can readily replace a trapped helium atom from a vacancy site because the formation energy for a vacancy-interstitial pair is 4.5 eV while the vacancy-helium binding energy has been estimated to be about 3.6 eV in nickel [II.26]. For helium-filled cavities to grow, stable He-V complexes (HeVCs) must first nucleate. Estimates for stable He-V complexes indicate that between 3 to 10 defects must be involved for the formation of critical HeVCs [II.27]. The sizes for critical clusters are in the 0.2 to 1 nm range.

Beyond the nucleation stage, HeVCs are stable up to a temperature that is about 0.3 - 0.4 of the metal melting temperature. Thus the next phase of cavity evolution constitutes the growth phase. Growth can be accommodated by accumulating more helium atoms, absorption or creation of vacancies, or by migration and coalescence with other HeVCs. The insolubility of helium atoms in the matrix causes the helium atoms to be trapped inside small bubbles which may reach pressures exceeding fluid-solid phase transition densities (~ 100 kbar [II.28]). For these high densities, sophisticated equitions of state (EOS) of helium (analytical [II.29, 30] and numerical [II.31]) must be used since Van der Waal's gas law is invalid in this regime. Thus, even during the growth phase, the HeVCs are in a non-equilibrium state which precludes the use of classical Several attempts have been made to nucleation theory and growth models. theoretically simulate the process of the helium defect development [II.21, 32-34] by ignoring the majority of many possible interactions. The latest progress was made by Sharafat et al. [II.26] who applied a continuum two-dimensional Fokker-Planck equation of stochastic process theory, combined with a set of chemical rate equations, to evaluate the time evolution of the non-equilibrium system, i.e., the helium-defect system. Good agreement between the calculated size evolution/distribution and some experimental measurements was obtained.

Generally, the final configuration of helium defects depends on the temperature, displacement rate, helium-atom generation levels and material properties such as other impurity levels and thermal treatment history. In this thesis work, the helium implantation temperature is controled at about room temperature; the displacement rate is about 10^{-4} dpa/s; other impurities are in very small amount (~ 1 ppm); and the samples were annealed at high temperature in vacuum before implantation. The only parameters varied in this work are the implantation fluence and the temperatures for post-implantation annealing, so that

we can check the interaction between different helium defect configurations and hydrogen transport behavior.

II.3.2 Evolution of the helium defect configuration

He⁺ fluence effect

Experimental results on helium defect configurations in nickel were mainly reported by scientists at Institut für Festkörperforschung der Kernforschungsanlage, Jülich [II.35–42] since the end of 1970s. In Ehrhart et al.'s work [II.40], nickel foils of about 12 μ m thickness have been homogeneously implanted with 0 - 6 MeV ⁴He ions at room temperature. For helium concentrations ranging between 0.1 and 5 at % the implantation induced changes of the microstructure have been investigated by measurements of the electrical resistivity (ER), the foil length and the lattice parameter (Differential

Table II.2 TEM results on the microstructure of He-implanted Ni

		Dislocation	T^{*}	Loops	5	SFT	F	Bubbles
No.	с _{не} (at.%)	density/10 ¹¹ (cm ⁻²)	d _L (nm)	c _t /10 ⁻¹¹ (cm ³)	<i>d</i> _{SIT} (nm)	c _{SFT} /10 ^{-1#} (cm ⁻³)	d _H (nm)	c _B /10 ^{−04} (cm ⁺³)
1	0.21	0.5	5.1	0.022	1.5 ± 0.5	0.06	N.O.	N.O.
2	0.34	0.5	5.4	0.029	4		N.O.	N.O.
3	0.45	1.2	3.4	0.084	a	4	N.O.	N.O.
4	0.74	1.0	2.4	0.060	1.5	0.10	1.4	0.48
5	1.60	1.3	3.9	0.031	1.5	0.08	1.3	1.98
6	2.80	1.7	4	4	4	•	1.4	3.20
7	4.9	1.8	b	*	ħ		1.6	1-20

^aDefect observed but no quantitative results due to sample preparation problems. ^bHigh degree of strain contrast overlap did not allow identification of defects under the given conditions. N.O. = not observed.



Dilatometry) and by transmission electron microscopy (TEM). Table II.2 reproduces their TEM observations. One can see that clustering of irradiation induced vacancies and self-interstitial atoms leads to the formation of stacking fault tetrahedra (SFT) and dislocation loops that eventually interact to form a dislocation network at quite low implantation doses of 0.1 at % He. In addition a large number of helium-vacancy complexes is present, and small bubbles become visible in the TEM for a He concentration larger than 0.7 at %. When the helium fluence increases the bubble size does not change much while the bubble density increases steadily. The authors claimed that SFT were created by high energy collision cascades and that there was no strong dependence of the helium defect configuration on the ratio of dpa/He.

Jäger and Roth [II.35] investigated the evolution of helium defects at higher fluences. They used a multiple energy implantation technique (0.25, 0.5,



(c)

Figure II.6 Multi-energy implantation: Evolution of steady-state microstructure and He re-emission through channels: (a) bubble lattice; (b) = $2x10^{17}$ /cm², pipe-like channels at surface allow He re-emission; (c) system of interconnected channels moving its interface to greater depth.

1, 2, 4, and 8 keV) on nickel. Figure II.6 illustrates a typical evolution of the helium defect configuration as the helium fluence increases. Ordered arrays ("lattice") of small He bubbles were established when the helium fluence reached 1×10^{17} /cm². At fluences above a critical value ($\approx 2 \times 10^{17}$ /cm²), microchannels form in the regions close to the surface. With increasing dose a system of interconnected channels develops allowing He to be easily re-emitted. The interface of this porous structure is shifted to larger depth as bombardment continues. Under monoenergetic condition (8 keV) the critical dose for blistering was reached at 3×10^{17} /cm².

Annealing effect

As discussed earlier, Ehrhart et al. [II.40] reported detailed investigations on the heliun defect configuration after room temperature implantation using three different techniques, i.e., ER, DD, and TEM. They also extended the investigation to the effect of post-implantation annealing on these helium implanted nickel samples (0.1 - 5 at % He). The results are as follows:

(i) For annealing temperature below 650 K, the major change observed was due to a decrease of the electrical resistivity resulting from the recombination reactions of very small defect clusters such as Frenkel pairs, and tiny helium-vacancy clusters (few helium atoms and few vacancies).

(ii) Annealing through the region of 650 K - 790 K is characterized by the

rearrangement and growth of He-vacancy agglomerates that form bubbles large enough to become visible in the TEM. At this annealing stage, differential dilatometry showed an increase of the ratio of C_{He}/C_v for low helium fluence samples (~ 0.4 at%) and no change for higher helium fluences (~ 1 at%).

(iii) Annealing at high temperature ($T \ge 900$ K) leads to bubble growth accompanied by decrease of the bubble density and a release of the pressure in the bubbles by the absorption of thermal vacancies. These observations are in agreement with other experimental observations for Ni and stainless steel containing similar He concentrations [II.43, 44].

In following sections some basic aspects of different helium defects are summarized.

II.3.3 Small He-V clusters

The "small cluster" is generally defined as all helium agglomerates smaller than the visible limit by TEM (< 1 nm in diameter). The properties of single He atoms and small clusters in a metal lattice are the basis for any fundamental understanding of helium effects. The crucial parameters are the energies of He atoms at different sites in perfect and imperfect lattices (Figure II.7). The experimental techniques applied to investigations of small helium clusters are [II.19]: (1) direct methods such as Field Ion Microscopy, Positron Annihilation, and possibly Perturbed Angular Correlation; (2) indirect methods



Figure II.7 Some examples of energies of helium atoms in metals: E_I^S energy of solution into interstitial sites, E_I^M migration energy of interstitial He, E_V^B binding energy between He atom and vacancy, E_V^D dissociation energy from vacancy, E_{2I}^B binding energy of two He atoms in an interstitial site.

such as Thermal Desorption Analysis (TDA) and Differential Dilatometry (DD). The indirect method TDA, supported by calculations, has proven to be very useful techniques for extracting information on atomic properties of helium in metals. For example, by choosing different helium introduction parameters (implantation above or below the damage threshold energy or tritium decay, low or high temperatures, slow or fast rates, materials with different microstructures) one is in many cases able to assign the observed release peaks to certain processes and to determine the corresponding activation energies.

Theoretically, the calculation of such energies has successfully been tackled by computer simulation of model crystals in which the atoms interact via suitably chosen interatomic potentials. Since the early 1970s, virtually all atomistic calculations of inert gases in metals have emanated from two research groups: Caspers, van Veen and co-workers from Delft in the Netherlands and Wilson,

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Baskes, Bisson and co-workers at Sandia Labs., California. The initial motivation for both groups was the desire to understand the thermal desorption results of Kornelsen [II.45] and Delft group [II.46]. An extremely important result as far as athermal cluster growth processes are concerned was the observation of so-called "trap mutation" in TDA experiments on subthreshold implantations. The process is as follows: Starting with a specimen known to contain only single helium atoms in single vacancies, the specimen is further irradiated with subthreshold helium. The TDA spectra revealed that the number of helium atoms in each vacancy increases with increasing dose, but with each successive helium atom being bound less strongly to the cluster than its predecessors. This situation continues up to a mean cluster size of order He_6V in b.c.c. metals (or He_5V in f.c.c.), whereupon injection of further helium results in the observation of more energetic trapping sites for helium. The authors' initial interpretation of this observation was that after a critical number, N, of helium atoms in a one-vacancy cluster was exceeded the trap mutated to a di-vacancy, i.e.,

$$He_N V + He = He_{N+1} V_2 + I$$
 (II.18)

where I is a self-interstitial. It was further proposed that this process would continue so that at critical numbers of helium atoms the cluster would continue to release strain by creation of additional vacancies in the cluster resulting in free interstitials. Although this qualitative model seemed to account satisfactorily for the observations of the Delft group, their attempts to model this behaviour quantitatively were unsuccessful. Their computer simulation of helium clustering in Mo yielded a steadily decreasing binding energy of each successive He to an initial HeV but it did not yield trap mutation. In fact the binding energy of a 7th He to a cluster dropped to below 1 eV indicating no trapping at room temperature. Subsequent calculations by van Heugten et al. [II.47] for other metals also failed to reproduce the experimental observations. In more recent work by Wilson et al. [II.48, 49] trap mutation was observed in calculations of Ni crystallites. Intriguingly, the mutation which the calculations yielded was, in a sense, only partial in that the interstitial produced by a cluster at a critical helium density was observed to be bound to the cluster. Calculations were carried out for clusters containing up to 16 helium





Minimum energy configuration for an 11 atom helium cluster in nickel $(He_{11}V_7 I_7)$ as calculated by Wilson *et al.*.

atoms which had mutated up to 10 times and in all cases the lowest energy configuration was with the displaced nickel atoms bound to the cluster. Furthermore, instead of being distributed isotropically around the cluster the interstitials clustered together on one side of the defect. Figure II.8 illustrates such a defect, described by the authors as $He_{11}V_7*I_7*$. A similar recent theoretical result for He in Mo was given by Caspers et al. [II.50], and they found that the precise value of helium filling which gave rise to trap mutation was highly dependent on the potentials used in the computer simulation.

II.3.4 Helium bubbles

For any surface, the surface free energy $\gamma(T)$ at a temperature T is given by:

$$\gamma(T) = \sigma(T) - TS_s \qquad (II.19)$$

where $\sigma(T)$ is the surface internal energy and S₁ is the surface entropy. $\gamma(T)$ is often referred to as the surface tension.

For a helium bubble of radius R whose pressure is in equilibrium with its surface tension the pressure is given by the well-known expression:

$$P = \frac{2\gamma}{R}$$
(II.20)

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The surface tension at room temperature $\gamma(300 \text{ K})$ and that at the melting point $\gamma(T_m)$ can be related via the expression [II.28]:

$$\gamma(300 \text{ K}) \sim \gamma(T_m) \cdot \left[\frac{\Omega_m}{\Omega_{300 \text{ K}}}\right]^{2/3}$$
 (II.21)

where $\Omega_{\rm m}$ and $\Omega_{300\rm K}$ are the atomic volumes at the melting point and room temperature respectively. This expression yields, for most metals, values of surface tension at room temperature ~ 8 % higher than the liquid metal values.

Using values of $\gamma(300 \text{ K})$ and the equation of state for high pressure helium suggested by Mills et al. [II.29], Donnelly calculated the equilibrium pressures and densities of helium atoms in bubbles for some metals (see Table II.3) [II.28].

	R = 10 Å		R = 20 Å		R = 30 Å	
Element	Pressure (kbar)	Density (Hc/V)	Pressure (kbar)	Density (He/V)	Pressure (kbar)	Density (He/V)
Al	20	1.28	10	0.98	7	0.85
v	41	1.40	20	1.10	14	0.96
Fe	39	1.14	19	0.89	13	0.78
Ni	38	1.05	19	0.83	13	0.72
Cu	28	1.02	14	0.80	9	0.67
Zr	30	2.07	15	1.62	10	1.38
Nb	40	1.76	20	1.39	13	1.19
Mo	48	1.62	24	1.28	16	1.11
Ag	18	1.27	9	0.97	6	0.81
Er	20	2.38	10	1.83	7	1.58
W	53	1.71	26	1.35	18	1.18
Au	23	1.45	12	1.14	8	0.97

Table II.3Equilibrium pressures and densities for helium bubbles of three different
radii in a number of metals.

An overpressurized bubble has a pressure in the range between the equilibrium pressure given in equation (II.20) and an upper limit, P_{max} , determined by stress relief mechanisms operating in the material around the bubble. There are three possible stress relief mechanisms which may operate: self-interstitial creation, dislocation loop punching, and interbubble fracture.

(i) Self-interstitial creation From an energetic point of view the creation of individual self-interstitial atoms (SIA) by bubble overpressure is certainly less likely than the creation of a cluster of interstitials essentially because when a cluster of interstitials (or dislocation loop) is created the binding energy is recovered. Trinkhaus et al. [II.27] have examined this process and an important conclusion reached was that SIA emission would dominate over helium emission if the criterion

$$\left(\left(\Omega / \Omega_{\text{He}} \right) \cdot yz - \mu_{g} \right) \ge 2\gamma \Omega / \text{RkT}$$
(II.22)

is met. Ω and Ω_{He} are the atomic volumes of metal and helium atoms respectively, y and z are the parameters related to the helium density in the bubble, μ_g is the chemical potential of helium in the gas phase. Using this expression the authors estimated that for a 20 Å bubble at room temperature in Ni, SIA emission is the preferred mechanism for densities of the order of or greater than 0.7 He/V. At densities less than 0.7 He/V, where helium emission dominates, the pressure is sufficiently low that neither process is liable to operate. Glasgow and Wolfer [II.51] derived an expression for the pressure required to create a SIA:

$$P_{SIA} = 2\gamma/R + U_{f}^{i}/\Omega + U_{m}^{i}/\Omega + (kT/\Omega) \cdot \ln(\phi/AR)$$
(II.23)

where U_f^i and U_m^i are the formation and migration energies of SIA, as being defined earlier; ϕ is the arrival rate or generation rate of helium and A is a constant. The authors further found that the overwhelming contributor to the pressure was the formation energy term. A reasonable approximation to the pressure for SIA emission is thus given by

$$P_{SIA} \approx 2\gamma/R + U_f^i/\Omega$$
 (II.24)

in agreement with the calculations of Trinkhaus [II.27]. The formation energy is given in equation (II.13), which results in a simple expression for P_{SIA} as

$$P_{SIA} \approx 2\gamma/R + \mu/2 \tag{II.25}$$

Taking values of γ and μ of metals, equation (II.25) yields values of P_{SIA} in Table II.4, in the range of 100 – 800 kbar. As pointed out above, these values are greater than the pressure required for loop punching but all estimations of pressures are based on a bubble in an otherwise undamaged lattice. It is, however, possible that in the highly damaged lattice which exists after helium irradiation there may be impediments to the punching of loops which may not impede SIA creation. Finally, the values of U_f^i given in equation (II.13) are those for a free SIA. For a SIA bound to a helium cluster in Ni, Wilson et al. [II.48] have calculated a binding energy of 2 eV so that the effective U_f^i and thus P_{SIA} for a bound interstitial may be ~ 30 % less than for a totally dissociated SIA. (ii) *Dislocation loop punching* The punching of dislocation loops as a means of stress relief was first discussed by Seitz in 1950 [II.52]. Observations of such loops resulting from stress relief around inclusions have since been made in a variety of materials.

	Table	II.4
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	R = 10 Å		<i>R</i> =20 Å		R = 30 Å		SIA emission	
Element	Pressure (kbar)	Density (He/V)	Pressure (kbar)	Density (He/V)	Pressure (kbar)	Density (He/V)	Pressure (kbar)	Density (Hc/V)
AI	91	2.11	46	1.70	30	1.47	125	2.33
v	165	2.18	82	1.75	56	1.55	237	2.43
Fe	233	2.01	116	1.62	78	1,43	390	2.36
NI	230	1.86	114	1.50	77	1.32	380	2.18
Cu	136	1.71	68	1.37	45	1.20	241	2.04
Zr	136	3.36	68	2.70	45	2.37	164	3.56
Nb	154	2.70	77	2.17	51	1.91	200	2.93
Мо	373	3.07 -	186	2.48	124	2.19	598	3.56
Ag	100	2.24	50 🐃	1.80	33	1.57	143	2.50
Er	116	4.24	58	3.40	39	3.00	135	4.44
W	488	3.42	243	2.75	163	2.43	793	3.97
Au	108	2.40	55	1.94	36	1.69	148	2.65

Maximum pressures and densities for helium bubbles of three different radii determined using simple loop punching expression . Also tabulated in the final two columns are the pressures and densities for SIA emission (neglecting equilibrium bubble contribution)

According to Trinkhaus's analysis [II.27], the simple expression

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$$P = 2\gamma/R + \mu b/R \tag{II.26}$$

is probably accurate in the range of 2 < (R/b) < 10, where b is the Burger's vector. For larger bubbles, the expression

$$P = 2\gamma/R + \frac{\mu b}{2\pi(1-\nu)} \ln \frac{R_L}{r_o}$$
(II.27)

is the best approximation, where v is Poisson's ratio, and R_L and r_o are the radius of the loop and the core radius of the dislocation respectively.

(iii) Interbubble fracture This mechanism has been described by Evans [II.53,54] to explain blister formation and is simple to describe for the case of a single plane of overpressurized bubbles at some depth below the surface of a semi-infinite medium. The tensile stress perpendicular to the surface of each bubble will combine to give a resulting tensile stress perpendicular to the bubble containing plane and tending to seperate the material at this plane. The pressure at which such a process occurs is obviously dependent on bubble concentration, C, as well as the fracture stress of the material. Taking the fracture stress equal to $\mu/2\pi$, the fracture pressure, P_F, for this simple planar case is given by:

$$P_{\rm F} = 2\gamma/R + \frac{\mu}{2\pi} \left[(\pi R^2 C^{2/3})^{-1} - 1 \right]$$
(II.28)

This expression is plotted in Figure II.9 along with curves for the other pressure limiting mechanisms. The pressures in this Figure are excess pressures to which the equilibrium pressure must be added to obtain total pressures. The maximum pressures and densities expected for cases where pressure is limited by loop punching have been calculated by Donnelly [II.28] for three different radii using equation (II.26) and these values are tabulated in Table II.4. The inclusion of the "ln" term in equation (II.27) will result in a decrease in pressures by a factor of ~ 2 .



Figure II.9 Loop punching and other possible limits to maximum bubble pressure plotted as pressure (in units of shear modulus) versus bubble radius (in units of Burger's vector). Also shown is the equilibrium pressure as a function of bubble radius. Where applicable, parameters used (b, μ , γ) are for Ni.

Under such high pressures at room temperature, helium would be in solid state. Indeed, diffraction experiments have been performed for xenon, argon and krypton bubbles in Al, Cu, Au and Ni [II.55–57]. In all cases, electron diffraction patterns indicated that the bubbles contained the inert gas as a room temperature, f.c.c. solid, epitaxial with the metal substrate. Unfortunately, light elements such as helium are weak scatterers of both X-ray and electrons so that such an experiment would be unlikely to succeed. Because of the high stress fields created around bubbles by high pressures and by the generated dislocation loops, strong interactions between bubbles were observed in the form of ordered arrays of bubbles of uniform size whose spacing can be obtained using diffraction techniques. Such bubble (and void) lattices were first reported by Mazey et al. [II.58] in molybdenum, later in copper, nickel, stainless steel and titanium [II.28].

II.3.5 Helium release

Thermal desorption analysis (TDA) of helium implanted into metals by ion bombardment has been the subject of active investigations (e.g., [II.59–65]) which covered a wide range of fluences from 10^{15} to 10^{19} /cm² and a large range of implantation energies. Amounging these studies, Zelenskij et al. [II.65] employed a high resolution apparatus which enabled them to examine in detail the TD spectra for Ni sample (99.9 wt%) implanted at T = 300 K with 20 keV He ions to various fluences. Figure II.10 reproduces some of their results. The heating rate was 4.2 K/sec (in this thesis work the heating rate is in a range of 1.5 – 3 K/min). The multi-peak structure of helium release is seen. When helium fluences are below 2.7x10¹⁷ /cm², no helium release was observed at T < 1100 K. In a range between 4.5 – 6.3x10¹⁷ /cm², helium started to release at T < 400 K. As the implanted samples were heated to ~ 1700 K, almost all helium desorbed.

From thermal desorption results, a helium diffusion coefficient can be

Figure II.10 TDA spectra of He implanted into Ni to various fluences.

extracted, i.e., the apparent (or effective) helium diffusivity after helium ion implantation. Some experiments have revealed activation energies which correspond to vacancy mechanisms for helium diffusion in Au, Ag, Al [II.66] ($D_0 \approx 0.1 - 1$ cm^2/sec , $E_m \approx 1.35 - 1.70$ eV) but for helium in nickel an unusually low activation energy (0.81 eV) has been found [II.25], suggesting a dissociative mechanism (where helium atoms move alternately between vacancies and interstitial sites). Based on a literature survey the measured apparent activation energy of helium diffusion in nickel can vary from below 1 eV to above 3 eV. It seems to this author that the actual measured value is very much dependent on the helium ion implantation conditions such as temperature and damage level.

II.4 Summary of defect annealing in nickel

CHAPTER III

Thermodynamics and Kinetics of Hydrogen Trapping and Diffusion in Metals

III.1 Introduction

The laws of thermodynamics guarantee the impurity of all solids at attainable temperatures. This arises because the addition of small amount of impurity in a system results in a large increase in the entropy, and therefore a decrease in the free energy. Hydrogen (and its isotopes), as a special impurity in metals, has been of immense interest because the presence of hydrogen impurity may be associated with many striking mechanical effects — especially embrittlement of many metals.

Random solid solutions of hydrogen in metals might exist if the metal were a single crystal free of defects, and if the dissolved hydrogen were in dilute enough solution. However, all real solids contain defects which may interact with hydrogen, and the mutual interaction of dissolved hydrogen atoms may permit clusters to form. The interaction between hydrogen and defects, which has been called " trapping ", serves to both increase the effective solubility and decrease the effective diffusivity in a solid. Darken and Smith [III.1] were apparently the first investigators to report the trapping effects in cold worked steels. Later on, an important step was made by McNabb and Foster [III.2], who described solutions of the diffusion equation with accompanying trapping at one kind of trap. The general formulation of McNabb and Foster is the foundation of later researches. Oriani [III.3] applied a local equilibrium theory to McNabb and Foster's formulation and evaluated comprehensively the relevant trapping parameters.

In this chapter, an overview of theoretical and experimental studies of hydrogen trapping and diffusion phenomena is given, with emphasis on hydrogen - helium interaction.

III.2 Trapping

III.2.1 Non-saturable traps

One class of trapping models is characterized by the equilibrium relation,

$$C_{T} = \alpha \cdot C_{0}^{m}$$
, (m = 1, 2, 3, ...) (III.1)

where C_T is the concentration of trapped solute, C_0 is the concentration of solute dissolved in normal lattice, and α is a constant related to the trapping parameters such as trapping energy. These traps are non-saturable since the trapped hydrogen concentration increases without limit as C_0 increases. A simple example of this type is when hydrogen is trapped as molecules in internal voids, where m = 2.

III.2.2 Saturable traps

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There is an important class of trapping sites, such as dislocations, impurities, vacancies, and internal interfaces, where plausible physical arguments suggest that the capacity of the traps for hydrogen is finite. In these models the trapped hydrogen concentration saturates as the lattice hydrogen concentration is increased.

Suppose that in an unit volume of a solid, there are n_1 hydrogen atoms trapped in N_1 trapping sites, and n_0 distributed in N_0 normal sites. Assuming each trapping site can only accommodate one hydrogen atom, then one can use the same strategy as in Chapter II, section II.2.2, and find the relationship between these two states of hydrogen in equilibrium as

$$\frac{n_1}{N_1 - n_1} = \frac{n_0}{N_0 - n_0} \exp\left\{\frac{\Delta G_f^0 - \Delta G_f^1}{k T}\right\}.$$
 (III.2)

People usually define a trapping (or binding) energy E_b as

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$$E_{b} = \Delta G_{f}^{0} - \Delta G_{f}^{1} , \qquad (III.3)$$

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and define n_i as the number of hydrogen in sites of type i per unit volume, then the concentration of i-th type of hydrogen $C_i = n_i$, therefore the equation (III.2) becomes

$$\frac{C_{1}}{N_{1}-C_{1}} = \frac{C_{0}}{N_{0}-C_{0}} \exp\left[\frac{E_{b}}{kT}\right],$$
 (III.4)
$$C_{1} = \frac{\frac{C_{0}N_{1}}{N_{0}-C_{0}} \exp\left[\frac{E_{b}}{kT}\right]}{1 + \frac{C_{0}}{N_{0}-C_{0}} \exp\left[\frac{E_{b}}{kT}\right]},$$
 (III.5)

or,

and, of course,
$$C_{\text{total}} = C_0 + C_1$$
. (III.6)

Generally, if the system contains more than one type of trapping site, and if the interactions between sites can be ignored, then for each type of site, the local equilibrium requires that

$$\frac{C_{i}}{N_{i}-C_{i}} = \frac{C_{0}}{N_{0}-C_{0}} \exp\left(\frac{E_{b}^{i}}{k T}\right)$$
(III.7)

and

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$$C_{\text{total}} = \sum_{i} C_{i}$$
, (i = 0, 1, 2, ...). (III.8)

These two equations provide a practical method to evaluate the binding energy and the trap density of certain type of trap by measuring the solubility of hydrogen under equilibrium with a hydrogen gas phase of pressure P. Because the normal solution C_0 can be determined by Sievert's law,

$$C_0 = S \cdot \sqrt{P} = S_0 \exp\left(\frac{-E^S}{kT}\right) \sqrt{P} . \quad (III.9)$$

where E^S is the activation energy for H solution, $S = S_0 \exp(-E^S/kT)$ is known as the Sieverts constant or *Solubility* constant. Sievert's law is valid in a large range of gas pressures. Departures from equation (III.9) occur either for a monoatomic gas (e.g., He), or at an extremely low pressure of a diatomic gas where $C_0 = S \cdot P$ holds, or when the concentration of hydrogen in the solid exceeds a level of the order of one atomic percent [III.4], where H-H interactions become important.

The gas phase equilibrium method has produced many trapping parameters in many systems for different defects. Other sensitive techniques include: internal friction, resistivity, Mössbauer spectroscopy, positron annihilation, neutron scattering, magnetic aftereffects and nuclear magnetic resonance [III.5]. All these techniques are mainly used for the studies of equilibrium properties of trapping. There is another large group of studies in which a kinetic trapping process is involved, such as permeation, and thermal desorption techniques. An overview of principles in these non-equilibrium techniques will be presented in section III.3. The experimental results on the binding energy of hydrogen to different defects in nickel are listed in Table III.1.

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Table III.1 Experimental values of

hydrogen-defect binding energies in nickel

Experimental t echnique	Defect	E _b (eV)	Ref.
Desorption	dislocation	~ 0.1	[111.6]
Channelling	vacancy	0.43	[111.7]
	self-interstitial	0.25	[III.8]
Gas-phase equil.	void/He bubble	0.52	[III.9]
Desorption	Ti, Fe imp.	≤ 0.1	[111.6]
Nuclear reaction	N, O, C imp.	≤ 0.2	[III.10]

Besides these experimental measurements, theoretical calculations of binding energies and the corresponding equilibrium positions of hydrogen isotopes at defects in metals from atomic view point have also drawn attention. Among them, the effective-medium theory [III.11, 12, 13] is the most successful one. Some details about this theory will be given, since this theory is useful for understanding general trapping effects, especially a chemisorption-type trapping model [III.14, 15] for hydrogen trapped at He defects in metals.

The basic approach is to replace the host with an effective medium with an electron density equal to that seen locally by the embedded hydrogen atom. In this theory, the binding energy E_b is mainly determined by the energy, $\Delta E_{eff}^{hom}(\bar{n})$, of the hydrogen atom in the average homogeneous electron gas of density \bar{n} . Figure

III.1 shows the calculated curve of ΔE_{eff}^{hom} as a function of \overline{n} for hydrogen and helium. It is evident that there is a minimum point (maximum E_b) at low electron density for hydrogen atoms. This minimum value is called an optimum electron density that a hydrogen atom prefers to sit in.

Figure III.2 gives a qualitative picture of what happens when a hydrogen atom interacts with a metal. Imagine hydrogen atoms being taken from far outside a metal surface to the surface and through the crystal as indicated in Figure III.2(a). The electron density that a hydrogen atom will sample along this path is indicated in Figure III.2(b), and one can construct a first approximation to the energy variation using Figure III.1. This is shown in Figure III.2(c). It is seen that the first minimum in the energy vs. position curve is just outside the surface at a position where the density is equal to the optimum density in Figure This point is so called Chemisorption Point for III.1 for the first time. hydrogen atom. Closer to the surface the density becomes higher than the optimum, so the energy will again increase, going through a maximum within the first layer of atoms where the density has a maximum. For most metals typical interstitial site electron densities are higher than the optimum density and therefore the energy is basically linearly related to the electron density at the position of the hydrogen. Changes in the electron density arising from defects and impurities will of course also change the binding energy. In Figure III.2 the example shown is a vacancy. In the center of the vacancy the electron density is so low that the energy curve increases again, while the best trapping sites for hydrogen are the optimum density locations which are close to the edge of the vacancy.

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Figure III.1 ΔE_{eff}^{hom} as a function of average electron density \overline{n}_0 in atomic units as a_0^{-3} , a_0 being the Bohr radius. The similar curve for helium impurity is shown for comparison, indicating that the rare-gas atom interacts repulsively with any host.[III.15]

Theoretical calculations using effective medium theory for different metals agree very well with experimental results [III.8]. Figure III.3 shows some examples.

Figure III.3 Measured (open symbols) and calculated (filled symbols) binding energies using the effective-medium theory [III.8].

III.2.3 Trapping by He defects

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In Chapter II it was shown that He defects could have different configurations. Therefore trapping mechanisms may depend on the configuration, although there is little work on the trapping mechanism of small He-vacancy complexes in the literature. This may be due to the fact that the He-vacancy complex itself is complicated enough for studying. On the other hand, several hydrogen trapping mechanisms by He bubbles have been suggested. One model is called *the Chemisorption-type Trapping Model* [III.14, 15]. In this model, the He bubble wall is treated as a free surface, where hydrogen atoms can be adsorbed. The binding energy to the bubble then is the energy difference between the energy of solution and the energy of chemisorption. The electron density at the bubble surface depends on the surface orientation and the density of hydrogen coverage and therefore does the binding energy. For nickel (100) and (111) surfaces and for low hydrogen coverage, the binding energy E_b is predicted as 0.66 eV using effective medium theory [III.15].

Another model is called *the Stress Field Trapping Model* [III.16, 17, 18]. This model is based on the idea that He bubble growth is controlled by a self-trapping mechanism in which helium atoms are attracted towards the bubble, and metal atoms are rejected from the bubble, creating dislocation loops. Therefore helium bubbles are usually associated with a very high internal pressure which results in high stress field (tensile stresses) around them. From Chapter II, equation (II.5), we know the usual form of ΔG_{total} includes a P· ΔV^{f} term. This concept could be generalized to include shear terms present in a solid. Let

$$\Delta G_{\text{total}} = n \cdot \Delta U_{\text{f}} - T \cdot \left(n \cdot \Delta S_{\text{f}} + \Delta S_{\text{mix}} \right) - n \cdot \Delta W , \qquad (\text{III.10})$$

where ΔW is the work done by an existing stress, while the other terms are independent of the stress. Following the process described earlier, one can get an equation similar to equation (III.2)

$$\frac{C_T}{N_T - C_T} = \frac{C_0}{N_0 - C_0} \exp\left[\frac{\Delta W}{k T}\right]$$
(III,11)

where C_T and N_T are the density of trapped hydrogen atoms in the strain field and the density of trapping sites, respectively. Here it is clear that the binding energy $E_b = \Delta W$. This term can be estimated [III.19] by

$$E_{b} = \Delta W \approx V_{H} \sigma_{h} , \qquad (III.12)$$

where $V_{\rm H}$ is the volume of hydrogen atom in metal, and $\sigma_{\rm h}$ is the hydrostatic component of the stress tensor, which is defined in plastic-elastic theory [III.20] for cubic lattices as

$$\sigma_{h} = \frac{1}{3} \sum_{i} \sigma_{ii} = \frac{1}{3} \left[\sigma_{xx} + \sigma_{yy} + \sigma_{zz} \right], \quad (III.13)$$

$$\sigma_{\rm ii} (r) \propto \sigma_0 \left[\frac{r_0}{r} \right]^3$$
, $(r \ge r_0)$, (III.14)

and

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where σ_0 is a constant related to the bubble pressure and properties of the materials, r_0 is the bubble radius and r is the distance from the bubble centre. Elastic theory shows that σ_h must be zero for a spherical inclusion in an isotropic elastic medium. Therefore, by equation III.12, E_b must be zero. Abramov [III.21] suggested that the lattice around a small helium bubble is anisotropic and assumed $\sigma_h \propto 1/r^3$. For iron, Abramov and Eliezer [III.17] gave a value of the maximum binding energy at the bubble surface as 0.71 eV for a He bubble with 350 kbar internal pressure and $r_0 = 0.5$ nm. Therefore, one can find

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$$E_{b} = 0.71 \left(\frac{r_{0}}{r}\right)^{3} eV.$$

According to the experimental observations in this study (section V.3.5), this authour suggests a "crack tip" trapping mechanism around an overpressurized helium bubble. It is assumed that small helium bubbles are not spherical but polyhedral in shape. The joining edge between two adjacent faces could be seen as a "crack tip" (see Figure III.4). Plastic-elastic theory predicts a non-zero hydrostatic stress zone at the front of such tips. Then

$$\sigma_{\rm h} \propto 1/r^{\alpha}$$
, and $0.5 < \alpha < 3$ (III.15)

where the 0.5 is for one dimensional stress and 3 is for spherical stress. Since a polyhedral inclusion is more like a spherical one, α should be close to 3.

Figure III.4 "Crack Tip" Trapping

The Stress Field Trapping Model does not consider the effect of hydrogen-hydrogen interaction near bubble surfaces. This actually can be done by

putting in an interaction term in the equation (III.10), such as,

$$\Delta G_{\text{total}} = n \cdot \Delta U_{\text{f}} - T \cdot \left(n \cdot \Delta S_{\text{f}} + \Delta S_{\text{mix}} \right) - n \cdot \Delta W + \varepsilon \cdot N_{\text{p}} , \qquad (\text{III.16})$$

here ε is the interaction energy between the H-H pair, and N_p is the density of H-H pairs. According to the B-W approximation, if Z is the number of the first nearest neighbour sites, then N_p is given by [III.22]

$$N_{p} = \frac{Z \cdot C_{T}^{2}}{2 N_{T}}$$
 (III.17)

Therefore the equation (III.11) becomes

$$\frac{C_{T}}{N_{T}-C_{T}} = \frac{C_{0}}{N_{0}-C_{0}} \exp\left\{\frac{\Delta W + \varepsilon \cdot Z \cdot (\frac{C_{T}}{N_{T}} - \frac{C_{0}}{N_{0}})}{k T}\right\}.$$
 (III.18)

Figure III.5(a) shows theoretical plots of the equilibrium distributions of trapped hydrogen around the bubble for different ε . The value of $\varepsilon = -0.044$ eV (repulsive) is taken for iron [III.23]. One can see that hydrogen atoms occupy a high percentage of trapping sites at locations close to the bubble surface and that the occupancy drops down quickly as r increases, resulting a thin trapping layer around the bubble. The equilibrium distribution of C_T is slightly decreased near the bubble surface by the repulsive interaction between hydrogen atoms. Figure III.5(b) shows the effect of C_0 on the trapping. The effective trapping radius for any given occupancy is increased when C_0 increases.

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Figure III.5 (a) Hydrogen profiles around a helium bubble calculated using Strain Field Trapping Model and assuming different C_0 . Here $r_0 = 0.5$ nm, maximum binding energy at bubble surface = 0.71 eV, interaction energy between hydrogen = -0.044 eV, T = 300 K.

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Figure III.5 (b) Hydrogen profiles around a helium bubble calculated using Strain Field Trapping Model and modified with H-H interaction. Here $r_0 = 0.5$ nm, maximum binding energy at bubble surface = 0.71 eV, T = 300 K, and $C_0 = 10^{-5}$ (atomic ratio).
There are two features of interest in this model. One is that the binding energy E_b is a function of r, which means that the value of E_b is a continuous distribution of values with the maximum at the bubble surface. Another point is that if the internal pressure were reduced in some way (e.g., annealing, helium escaping) the binding energy should decrease.

Both the Chemisorption-type Trapping Model and the Strain Field Trapping Model can produce us a rough estimation of the trapping efficiency which is defined as the ratio of trapped hydrogen atoms to helium atoms in the bubble. Assume $r_0 = 0.5$ nm, and assume that one rejected host atom is replaced by one helium atom. Then there are about 65 helium atoms in one bubble, and about 40% of them are at the bubble surface. If one assumes that the maximum amount of chemisorped hydrogen atoms is approximately the same as that of the " surface " helium, then the maximum trapping efficiency is about 0.4. On the other hand, since the trapping layer predicted by Strain Field Trapping Model is so thin (about one or two atomic layers), then the trapping efficiency is more or less the same as in the other case.

The binding energy is some what different between these two models. The chemisorption model predicts discrete values, while the strain model predicts a distribution. One may calculate an average binding energy, $\langle E_b \rangle$, using the following equation

$$\langle E_{b} \rangle = \frac{\int_{v}^{C} C_{T} E_{b} dV}{\int_{v} C_{T} dV} , \qquad (III.19)$$

where V is the volume around a helium bubble. This method yields a value of 0.52 eV for iron when $r_0=0.5$ nm and the maximum binding energy is 0.71 eV.

Experimentally, the binding energy of hydrogen isotopes to helium defects has been measured using both thermal equilibrium methods and kinetic methods.

Using the gas phase equilibrium method, Wampler and Myers [III.9] determined the deuterium trap strengths in nickel pre-implanted with 30 keV ⁴He or 750 keV ³He to a fluence of ~ 10^{17} /cm². The technique they used to detect the content of trapped deuterium is the *Nuclear Reaction Analysis* (NRA), using D(³He,p)⁴He. They assumed that a 0.43 eV trap existed after ion-implantations, based on previous work. They found that, in order to get a better fit to all experimental data, a second type of traps with a binding energy of 0.52 eV has to be assumed.

Most of experiments on helium trapping effects are kinetic type. Many scientists have made contributions in this area. Besenbacher et al.[III.24] used NRA technique combined with temperature ramping of samples pre-implanted with helium and deuterium ions to study the kinetic release of deuterium from radiation defects. They measured the retention of trapped deuterium in the damaged layer while heating the sample at a constant rate. Figure III.6 shows typical retention curves from experiments on nickel. The solid lines are the calculation results from a set of kinetic diffusion equations assuming three types of traps, i.e., 0.24, 0.43 and 0.55 eV. They claimed that the 0.55 eV trap is due to helium bubbles (~ 1 nm in diameter). They observed that the measured release curves were

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Table III.2 The measured binding energies (eV) [III.26]

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Metal	He bubble	Vacancy	
Fe	0.78	0.53	
Ni	0.52	0.43	
Cu		0.42	
Pd	0.29	0.23	
Al	0.52	≤0.52	
Stainless steel	0.42	0.23	
Inconel	0.42		١,
Metglas	≈0.5		

slightly broader than predicted, perhaps indicating a narrow distribution of high trapping energies. Frank et al [III.25] did similar experiments on krypton-implanted nickel and they had to assume five types of traps to explain the results. Results of helium trapping on some other materials are listed in Table III.2.

Another type of kinetic measurements is to measure the release rate during the temperature ramping, instead of measuring the retention. This is called the *Thermal Desorption Analysis* (TDA) using Mass Spectrometers. This method is more sensitive than the retention method, because it can detect smaller quantities of gases and it measures the desorption rate which is directly related to the diffusion and trapping mechanisms, while retention is equal to the total trapped hydrogen minus an integration of the desorption rate. Wilson and Baskes used TDA technique in steels and found an insufficient fit for helium trapping if assumed only one type of traps exists [III.27].

An overview of the kinetic diffusion theories will be given in next section.

III.3 Diffusion with traps

III.3.1 Fundamentals

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The movement of solute during the approach to equilibrium is most often

described by employing Fick's laws. Fick's first law states that the flux of solute J at any point r and time t is given by

$$\mathbf{J}(\mathbf{r},t) = -\mathbf{D}(\mathbf{r}) \cdot \nabla \mathbf{C}(\mathbf{r},t)$$
(III.20)

where D(r) is the diffusion coefficient at position r which characterizes the rate of solute flow in the solid. D is, in general, a tensor. However, in isotropic mediums D is directional independent. For Henrian's solutions D is independent of solute concentration and is usually found to follow an Arrhenius relationship, i.e. $D = D_0 \exp(-E_D/kT)$ where D_0 and E_D are constants.

Mass conservation requires that the change of solute concentration due to diffusion obeys the Fick's second law, i.e.,

$$\frac{\partial \mathbf{C}(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{J}(\mathbf{r},t) = \nabla \cdot \left[\mathbf{D}(\mathbf{r},t) \cdot \nabla \mathbf{C}(\mathbf{r},t) \right]$$
(III.21)

The solute distribution at any moment is described by solving Fick's second law with appropriate initial and boundary conditions.

For one-dimensional and isotropic diffusion, Fick's second law becomes simple,

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$$\frac{\partial C(x,t)}{\partial t} = D(t) \frac{\partial^2 C(x,t)}{\partial x^2}$$
(III.22)

When traps exist in the diffusion field, the above formula should be

modified. McNabb and Foster [III.2] assumed that the trapped solutes do not join the diffusion process unless they escape from traps. So they added another " source " term in to Fick's second law, so that

$$\frac{\partial C_0(x,t)}{\partial t} = D(t) \frac{\partial^2 C_0(x,t)}{\partial x^2} - \frac{\partial C_T(x,t)}{\partial t}$$
(III.23)

or when there are different types of traps,

$$\frac{\partial C_0(x,t)}{\partial t} = D(t) \frac{\partial^2 C_0(x,t)}{\partial x^2} - \sum_{i \ge 1} \frac{\partial C_i(x,t)}{\partial t}$$
(III.24)

where C_0 , C_T and C_i are as defined as in early section,

and,
$$C_{\text{total}} = C_0 + \sum_i C_i$$
 (III.25)

III.3.2 The trapping term

Questions come from how to estimate the trapping terms in equation (III.24). Many researchers, like McNabb and Foster [III.2], adopted chemical rate theory and wrote

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$$\frac{\partial C_i}{\partial t} = \text{trap rate} - \text{detrap rate} \qquad (III.26)$$

The problem then became the solution of two partial differential equations simultaneously. Some numerical computer codes are available based on equations (III.24) and (III.26), such as DIFFUSE [III.28], that of Gervasini and Reiter [III.29], or the group of Myers et al. [III.8]. In these codes, each C_i is associated with one discrete binding energy and a trapping density that characterize the trapping sites.

Another way to approach this problem is to make use of a special property that the diffusion rate of hydrogen atoms is so fast in most metals, that in many diffusion cases, a local equilibrium distribution of hydrogen in different trapping sites can be presumably maintained. Therefore one should first concentrate on setting up a thermal equilibrium relationship between C_0 and C_i , or C_i expressed as a function of C_0 . Then using the transform, $\frac{\partial C_i}{\partial t} = \frac{\partial C_i}{\partial C_0} \frac{\partial C_0}{\partial t}$,

one can produce a new equation:

$$\frac{\partial C_0(x,t)}{\partial t} = \frac{D}{1 + \sum_{i} \frac{\partial C_i}{\partial C_0}} \frac{\partial^2 C_0(x,t)}{\partial x^2}$$
(III.27)

The term $\frac{D}{1 + \sum_{i=0}^{n} \frac{\partial C_{i}}{\partial C_{0}}}$ can be seen as an effective diffusion coefficient that

characterizes diffusion with traps.

Oriani used the local equilibrium relationship (III.4) combined with

equation (III.27) for a single trap class and found an effective diffusivity [III.3]

$$D_{eff} = D \cdot \left[1 + \frac{\frac{N_1}{N_0} \exp\left[\frac{E_b}{k T}\right]}{\left\{1 + \frac{C_0}{N_0} \exp\left[\frac{E_b}{k T}\right]\right\}^2} \right]^{-1}$$
(III.28)

where $N_0 \gg C_0$ is assumed. It is easy to prove from equation (III.4) that at low trapping occupancy, i.e., $C_1 \ll N_1$,

$$D_{eff} = D \cdot \left[1 + \frac{N_1}{N_0} \exp\left(\frac{E_b}{k T}\right) \right]^{-1}$$
(III.29)

Although no such attempt has yet been published, it is possible to make a similar calculation of the effective diffusivity for helium trapping using, say, the equation (III.11). However, this equation is only for one bubble. To calculate the total trapped hydrogen, C_{TT} would require an equation like

$$C_{TT} = N_b \cdot \int_V C_T \, dV \tag{III.30}$$

where N_b is the bubble density per unit volume, and V is the small volume around one bubble within which the majority of trapping occurs. Then one can substitute $\partial C_{TT}/\partial C_0$ into equation (III.27) and solve the equation numerically.

The local equilibrium assumption provides a great advantage over the

chemical rate theory, because the application of chemical rate theory is a time-consuming problem on computer calculations. In contrast, the local equilibrium analysis is so simple that one can always measure an apparent diffusivity and compare to the effective diffusivity calculated using even a small calculator.

The difficulties with the local equilibrium theory are: (1) it is not always easy to construct an analytical relationship between C_0 and C_i ; and most importantly, (2) in many cases where either the transition of diffusion states is too fast, or the detailed diffusion process is unknown (e.g., shape of the potential energy in the diffusion field varies from site to site, see [III.30] for example), it is safer to use a flexible chemical rate approach.

III.3.3 DIFFER — a new attempt

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Besides the standard chemical rate and local equilibrium approaches, Riehm [III.31] developed a new numerical method to solve the diffusion problems with trapping. He basically assumed that the trapped hydrogen atoms do not join the diffusion process and used the local equilibrium theory mentioned earlier but in an implicit way. The computing procedure of his code " DIFFER " is, first to calculate the change of C_0 in a small time interval Δt , using the simple form of Fick's second law (i.e. the equation (III.22)); let this change be equal to the change of total hydrogen concentration C_{total} ; then use the equations such as (III.7) and (III.8) to calculate a new C_0 , to be the input value for the next time

step of the diffusion calculation.

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This method has yielded nearly identical results when compared to the chemical rate approach [III.10]. The limit of this method is the fact that the analytical solution of C_0 does not exist when more than two types of traps are present. Even for two types of traps, the solution is very complicated (Riehm [III.31]). The thermal desorption experiments in this work have been interpreted using DIFFER.

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CHAPTER IV

Experimental Methods and Apparatus

IV.1 Sample preparation

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The samples used were pure nickel foils (99.99 at.%) supplied by Johnson Matthey Ltd., with impurities mainly Cu (5 ppm by weight), Pb (3 ppm), and Cr, Fe, Mg, Si, Ag, Al, and Ca, each about 1 ppm or less. The foil thickness is 25 μ m. These foils were annealed at 1173 K in a 10⁴ torr pure hydrogen gas environment for 20 hours, prior to the ion implantation. After annealing the Ni surface was visibly brightened and the average grain size is about 25 μ m (etching solution : 50% HNO₃ + 50% CH₃COOH).

Ion implantation was performed in a 10^{-6} torr vacuum system with a liquid nitrogen trap in front of the sample holder. The ion beam was rastered in both vertical and horizontal directions across an area of 25 cm² to ensure uniform fluences. In order to avoid beam heating effects the sample holder was water cooled and the ion beam current density maintained at less than 0.5 μ A/cm² except for the highest helium fluence (4x10¹⁷/cm², beam current 2 μ A/cm²). The sample temperature during the implantation was measured to be room temperature.

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Some samples were implanted with Ni⁺ ions of 90 keV, in order to check the effect of crystalline defects on deuterium diffusion. Other samples were implanted with ⁴He⁺ ions at various fluences, in order to cover different helium defect configurations. Table IV.1 summarizes the implantation parameters of this work. In this table, the profiles of helium ions and radiation damage are calculated using TRIM simulations [IV.1]. The displacement energy used in these simulations is 25 eV. The peak concentration of helium is calculated using a formula (see, e.g., [IV.2]), $\frac{\text{net } f \text{ luence}}{2.4 \Delta R_p \rho_{Ni}}$, where ρ_{Ni} is the atomic density of a nickel crystal, and ΔR_p is the ion range straggling.

After ion-implantation, some samples were vacuum annealed at 703 K or 923 K, for one hour, in order to check the annealing effects. The lower annealing temperature of 703 K was chosen to enable short range rearrangement of helium-vacancy complexes [IV.3]. The higher temperature (923 K) annealing was reported to be the condition for helium bubble migration and growth (Chernikov et al. [IV.4]).

IV.2 Permeation apparatus and method

IV.2.1 The vacuum systems

An ultra-high vacuum apparatus, depicted in Figure IV.1, consists of two independent vacuum systems which are separated by the test foil. The "upstream" side vacuum system is pumped with a liquid nitrogen trapped mercury diffusion pump, having a base pressure 10^{-7} torr. The "downstream" side vacuum chamber is

Ions	Dose	Peak	Radiation	Defect
	(ions/cm ²)	(at%)	(dpa)	configuration
Ni	10 ¹⁴		0.3	· · · · ·
$R_{p}= 25 \text{ nm}$	10 ¹⁵		3	
$\Delta R_{p} = 12 \text{ nm}$	10 ¹⁶		30	
	10 ¹⁷		300	
⁴ He	1x10 ¹⁵	0.09	0.09	no bubbles
$R_p = 115 \text{ nm}$	3.5x10 ¹⁵	0.31	0.3 J	observed
	8x10 ¹⁵	0.70	0.7	bubbles become visible, d ≈ 1nm
	5x10 ¹⁶	4.4	4.4	d ≈ 1.6 nm
	1x10 ¹⁷	7	7	d ≈ 2 nm
15 keV $R_{p} = 66 nm, 2$	4x10 ¹⁷ AR _P = 31 nm	33	43	blisters and micro-channels
³ He	16			
30 keV	1x10 ¹⁰	0.87	0.7	bubble $\approx 1 \text{ nm}$
17 keV	$4x10^{17}$	36	35	blisters and
$R_{p^{=}}$ 68 nm, Δ	micro-channels			

Table IV.1 Implantation Parameters



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ų: P pumped with a turbomolecular pump, having a base pressure 10^{-9} torr at room temperature, and 10^{-8} torr when the sample is at elevated temperature.

Deuterium gas is introduced from the upstream side where it is maintained at a pressure p_1 (generally about 60 to 100 torr), and permeates through the foil to the downstream side. The downstream side is continuously pumped, and the permeation rate is determined by measuring the partial pressure p_2 of D_2 gas in that vacuum chamber.

IV.2.2 Flux calibration and measurement

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In order to obtain an accurate deuterium permeation flux measurement, two calibrated leaks were purchased from Vacuum Instruments (Ronkoma, New York) which provide known constant deuterium gas leak rates at magnitudes of 10^{12} and 10^{15} molecules/second, respectively.

 D_2 partial pressures are measured with a Leybold (San Jose, California) quadrupole mass spectrometer equipped with an electron multiplier. The sensitivity is quoted by the manufacturer as being able to measure partial pressure down to 10^{-13} torr, which is equivalent to a deuterium flux of 10^{10} molecules/cm²/sec.

IV.2.3 Sample mounting, heating and temperature measurement

A standard method was used to mount the thin nickel foil for permeation

experiment (see Figure IV.2): the sample was sandwiched between two copper gaskets which were sealed with knife-edges between two stainless steel flanges. The effective area of the sample for permeation is about 2 cm². Since some measurements involved very small permeation fluxes $(10^{10} \sim 10^{11} \text{ molecules/cm}^2/\text{sec}$ at 350 K) the copper gaskets were annealed and very carefully polished to a mirror finish, in order to get the best seal possible.



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Figure IV.2 Sample mounting, heating and temperature measurement in permeation experiments.

Sample heating is accomplished via Thermocoax heating wire (Philips Electronics, Mahwah, New Jersey). The thermocoax wire consists of a Nichrome heating core surrounded by packed MgO powder for electrical insulation, and housed in an Inconel sheath. The wire was spot-welded to the end of mounting tube close to the sample.

During permeation experiments, the sample was heated by passing an A.C. current through the heating coils. The sample temperature was measured with a chromel-alumel thermocouple attached close to the sample-copper gasket join. A digital temperature controller, calibrated at ice and steam points, provided a temperature display. The temperature drift was kept within ± 2 °C during the measurements.

IV.2.4 Typical permeation experimental procedures

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When the sample has been mounted and all vacuum seals are made, a leak check is performed by introducing He gas into the upstream side and testing the He signal at the downstream side. Sometimes if a small leak around the sample-copper gasket area exists, then increasing the sample temperature to about 370 K will seal the leak.

Usually, the sample and vacuum systems are pumped for 1-3 days in order to reduce the residual gas. Prior to a permeation experiment power is applied to the heater and the temperature is allowed to stabilize, with both sides of the sample being pumped throughout. The upstream side vacuum valves are then shut. As soon as D_2 gas is introduced to the upstream side of the sample, the computer controlled mass spectrometer starts to monitor the permeation flux at the downstream side, saving the data in a computer at user-specified time intervals.

Generally a series of experiments is performed at various temperatures, in order to determine the activation energies and pre-exponentials of the diffusion and permeation coefficients, or to test the trapping effect. For pure nickel foil (25 μ m) without any ion-implantation it takes a few minutes for deuterium permeation flux to reach the steady state at 370 K and a few seconds at 570 K. This is the temperature range over which the experiments reported in this work were conducied. After each measurement the sample temperature is usually raised to 520 K or higher to degas the deuterium absorbed in the sample and tube, with both sides of the sample being pumped. For a pure nickel sample a half hour of this degassing procedure is sufficient to reduce the outgassing flux below the detectable limit.

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IV.3 Thermal desorption apparatus and methods

IV.3.) Introduction

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The basic procedures in thermal desorption experiments are (i) to introduce a known gas into the sample, and (ii) to measure the gas desorption rate from the sample as a function of time at a controlled temperature. In this way, a mathematical ana¹ysis of the desorption spectrum will yield information on various adsorption and desorption parameters, such as the number of adsorbing sites, the activation energies of desorption from different sites, and the order of the desorption reaction.

Prior to the thermal charging and desorption experiments, some nickel foils pre-implanted with helium ions were annealed in $-3x10^{-8}$ torr vacuum for 1 hour at 703 K or at 923 K, in order to change the helium defect configuration in the samples.

IV.3.2 Deuterium charging

There are various ways to charge deuterium into the nickel samples. Ion-implantation of deuterium is a method which is frequently used for studying fusion reactor first wall problems (see, e.g., [IV.5]). In the present study, in order to avoid the radiation defects introduced other than by helium implantation, another nondestructive charging method should be considered. Electro-chemical charging [IV.6] has been tried for nickel samples without ion-implantation and showed a significantly higher deuterium concentration than the solubility limit of pure nickel, indicating that some lattice defects have been created during the charging process. Therefore the alternative method of gas phase charging [IV.7], seems to be more appropriate.

In the gas phase charging method, two points are important: the charging

temperature and quenching the sample after charging. The charging temperature should be high enough to load a sufficient amount of deuterium in a reasonable short time. On the other hand, the charging temperature must not be too high, or the helium defect configuration may change. A charging temperature of 423 K has been chosen in this study since, after annealing at this temperature, there were no apparent changes in permeation behaviour (see section V.4).

The Ni sample temperature must be decreased quickly after charging in order to prevent deuterium from escaping. This was done by quenching the sample in liquid nitrogen. This quenching procedure may not be necessary for materials with very low deuterium diffusion coefficient, such as Be.



Figure IV.3 The system for deuterium charging and quenching.

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The deuterium charging and quenching system is illustrated in Figure IV.3. A chromel-alumel thermocouple is attached to the sample. Before charging the whole s_3 stem is usually pumped to 10^{-6} torr at 423 K. High purity deuterium gas is then introduced into the system and kept at 70 torr for about 2 hours. At the end of charging, the heating power is surned off and the tube with the sample is immersed in a liquid nitrogen Dewar. It takes less than 10 seconds for the temperature to drop to below 273 K. Usually the charged sample is aged at room temperature to let the untrapped deuterium (dissolved in normal lattice interstitial sites) diffuse out. A pure nickel sample without implantation was charged with deuterium in this way and then tested by thermal desorption. It was shown that aging at room temperature for 2 hours is sufficient to degas the untrapped deuterium. Therefore the samples for thermal desorption experiments in this work were aged for at least 2 hours at room temperature after deuterium charging.

IV.3.3 Sample holder

The design of the sample holder is critical for high quality thermal desorption measurements. First, the materials of the holder should have smaller deuterium diffusivity and solubility than that of the material investigated in order to minimize the absorption effect of deuterium by the holder in thermal desorption experiments. Oxygen-free copper has been chosen to be the holder material for this purpose in present work. Secondly, the holder should be carefully designed to obtain uniform and accurate temperature control over the

whole sample during the temperature ramping. It has been checked for a common sample holding method in which the nickel foil is clipped onto a copper heater surface. The sample temperature was 20 K lower than the temperature of heater surface during a ramping (5K/min) to 750 K, which is unacceptable. The final design of the holder is shown in Figure IV.4. A slit (~ 0.25 mm wide, 1.2 cm deep and 3 cm long) was cut into an oxygen-free copper cylinder, and the nickel foil is inserted in. A thermocouple is attached to the core of the holder from a hole



Figure IV.4 The sample holder for thermal desorption experiments.

close to the slit. Thermocoax heating wire is tightly wrapped around the holder. Temperature calibration was made by attaching a second thermocouple to the nickel

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foil. The temperature readings from these two thermocouples are the same to within 1 K in the temperature range from 300-700 K and within 3 K difference up to 800 K.

IV.3.4 Temperature controller

The key part of the temperature controller is a model 808 digital controller (Eurotherm Corporation, Reston, Virginia). During the temperature ramping, the controller sets a temporary temperature frequently according to the ramping rate specified by operator, compares this temperature set point with the measured value from thermocouple, and adjusts the output heating power to the sample holder. The control accuracy quoted from manufacture is ± 1 K. The ramp rate is selectable from 0-99 K/min. For maximum flexibility and control, a three-level output power supply was built for the digital controller (see Figure IV.5). These three power levels are: 18 Volts, maximum current 10 Amps; 36 Volts, maximum current 10 Amps.

IV.3.5 Typical thermal desorption experimental procedures

The ultra-high vacuum chamber (downstream side) for permeation experiments is used in thermal desorption experiments. Therefore the flux calibration using the mass spectrometer is the same as in permeation experiments. After the sample is inserted in the holder slit and vacuum sealed into the chamber, the system is usually pumped to about 10^{-7} torr. A ramp rate is set up on the temperature



Figure IV.5 The temperature control system: three-level power supply.

controller, and the power level is chosen. At the beginning of the desorption experiment, a final temperature at which the ramping process stops is set on the controller. This operation starts the temperature ramping immediately. The computer controlled mass spectrometer can be turned on at any time desired. The thermal desorption data as a function of time will be saved in computer automatically. A data analysis program " TDA " has been writen. By running this program, the desorption parameters such as the total amount of desorption and the desorption activation energy are obtained.

IV.4 Sample preparation for TEM

The defect morphology of some ion-implanted nickel samples was investigated using Transmission Electron Microscopy (TEM). These samples were first cut into small disks of 3 mm in diameter. Then the electro-chemical polishing was conducted from one side of the disk (the unimplanted side) at 10 volts. The other side of the disk, the ion-implanted side, was covered by Lacomit Varnish (soluble in acetone) during the polishing. The polishing solution was 33 volume % of nitric acid in methanol at 250 K.

CHAPTER V

Results and Discussions

V.1 Introduction

The main purpose of this work is to study the role of helium related defects on deuterium diffusion and trapping behavior. The defect configurations were varied using a wide range of implantation fluences, as well as annealing at high temperatures.

Two different experimental techniques are used in this study. Permeation experiments can provide information on *apparent diffusivity*, *permeability* and *solubility* of deuterium in materials, while thermal desorption experiments can yield detailed information on *binding energies* and *trapping efficiencies* of deuterium to defects.

Before annealing, permeation experiments show a "normal" behavior of deuterium diffusion and permeation, which can be approximately explained by Oriani's trapping theory [V.1]. However, after annealing of samples pre-implanted with helium, a strong history dependence of deuterium diffusion and permeation behavior was observed, which is called "abnormal" behavior in this thesis. Thermal desorption experiments yield additional information on the interaction of deuterium with helium defects, which is helpful for understanding the permeation results. In the next section, the "normal" results of permeation experiments are given. This is followed by the results of thermal desorption experiments. Finally, the "abnormal" behavior of deuterium permeation will be described in detail.

V.2 The normal behavior of permeation experiments

V.2.1 Introduction to rise-time analysis

A generalized rise-time experiment may be described as follows: a planar membrane, of thickness l and initially uniform solute concentration C_0 , is subjected at time t = 0 to conditions which maintain its surfaces at concentration C_1 (at x = 0) and C_2 (at x = l). Solving Fick's second law equation (III.21), the time evolution of the solute concentration is then given by [V.2]

$$C(x,t) = C_{1} + (C_{2}-C_{1})\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{C_{2}\cos(n\pi) - C_{1}}{n}\sin\left(\frac{n\pi x}{l}\right)\exp\left(-\frac{Dn^{2}\pi^{2}t}{l^{2}}\right) + \frac{4C_{0}}{\pi}\sum_{m=0}^{\infty}\frac{1}{2m+1}\sin\left(\frac{(2m+1)\pi x}{l}\right)\exp\left(-\frac{D(2m+1)^{2}\pi^{2}t}{l^{2}}\right), (V.1)$$

where D is the diffusion coefficient, n and m are integers.

For the present type of permeation experiment (described in Chapter IV), we have $C_0 = C_2 = 0$. Therefore, equation (V.1) becomes

$$C(x,t) = C_1(1-\frac{x}{l}) - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_1}{n} \sin\left(\frac{n\pi x}{l}\right) \exp\left(-\frac{Dn^2 \pi^2 t}{l^2}\right).$$
 (V.2)

In a permeation experiment, the quantity measured is the flux, ϕ , through the downstream face, which is given by

$$\phi = A \cdot J = -A \cdot D \cdot \frac{\partial C}{\partial x} \Big|_{x=l}, \qquad (V.3)$$

where A is the sample area for permeation and $J = -D \cdot \frac{\partial C}{\partial x}$. Then it is readily shown to yield

$$\phi(t) = \frac{A D S \sqrt{P_1}}{l} \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left[-\frac{Dn^2 \pi^2 t}{l^2}\right] \right\}, \quad (V.4)$$

Here we used the equation $C_1 = S \sqrt{P_1}$ according to Sievert's law, where S is the solubility and P_1 is the gas pressure on the upstream side of the foil. If the gas is monoatomic rather than diatomic, then $C_1 = S P_1$ should be used. Or, as indicated in section III.2.2, if the diatomic gas has an extremely low pressure, or when the concentration of hydrogen in the solid exceeds a level of the order of a few atomic percent, then $C_1 = S P_1$ may be appropriate. It has been verified [V.3] that Sievert's law holds in these experiments.

The permeability K is defined as the product of diffusivity D and

solubility S, i.e.,

$$K = D \cdot S \tag{V.5}$$

and it is easy to show that

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$$\phi(t = \infty) = \frac{A K \sqrt{P_1}}{l}$$
(V.6)

This equation is used to determine the permeability K, where ϕ (t = ∞) is the steady state flux, or the maximum flux in permeation experiments.

To measure the diffusivity D (and therefore obtain the solubility S), one can use several methods. One of them is to integrate the permeation flux and get the total amount of diffusant, Q, at the time t, i.e.,

$$Q(t) = \int_0^t \phi(t) dt.$$
 (V.7)

As $t \Rightarrow \infty$ (at steady state), the graph (Figure V.1) of Q against t tends to the line Q = ϕ (t = ∞) $\left(t - \frac{l^2}{6D}\right)$, which has an intercept, t_{lag} , on the t-axis given by

$$t_{\text{lag}} = \frac{l^2}{6 \text{ D}} \tag{V.8}$$

t_{lag} can be measured in permeation experiments. Therefore, one can obtain the parameter D.



Figure V.1 The definition of t_{lag} . ϕ and Q are defined by equations (V.4) and (V.7), respectively.

For a two layer membrane, if the initial and boundary conditions are the same as above except $l = l_1 + l_2$, then solution of the Fick's second law is very complicated (see, e.g. [V.4]). One finds ϕ (t = ∞) and t_{lag} [V.5] as follows,

$$\phi(t = \infty) = \frac{A K \sqrt{P_1}}{l} = \frac{A K_1}{l_1} \frac{\sqrt{P_1}}{\frac{l_2 K_1}{l_1 K_2} + 1}$$
 (V.9)

where K is the apparent permeability of the whole foil, K_1 and K_2 are the permeabilities of the first and second layer, respectively. Also,

$$\iota_{\text{lag}} = \left[\frac{l_1}{K_1} + \frac{l_2}{K_2}\right]^{-1} \left\{\frac{l_1^2}{D_1} \left[\frac{l_1}{6K_1} + \frac{l_2}{2K_2}\right] + \frac{l_2^2}{D_2} \left[\frac{l_2}{6K_2} + \frac{l_1}{2K_1}\right]\right\} (V.10)$$

In the case where $K = K_1 = K_2$, one can determine D_2 by knowing D_1 .

Before presenting the experimental results, we should mention the experimental procedure again. The permeation experiments generally start from low temperature (i.e., ≈ 373 K), and proceed to higher temperatures, unless a special task is desired. Between two successive measurements, the sample was allowed to outgas deuterium at 460 ~ 520 K for more than one hour.

V.2.2 Samples pre-implanted with Ni⁺

Before doing any helium related studies, pure Ni samples pre-implanted with Ni⁺ ions were investigated in order to check if implantation induced crystalline defects affect deuterium permeation. The results are summarized in Figure V.2. It can be seen that the values of permeability observed (Figure V.2a) are consistently higher than the literature values summarized by Völkl and Alefeld [V.6]. The values of apparent diffusivity are close to literature data (Figure V.2b). Although high densities of crystalline defects (such as small dislocation loops) were observed in the implanted samples using TEM (see examples in Figure V.3), there is no significant difference in both the apparent permeability and diffusivity from that of the samples without any ion-implantation.

These results may be due to the facts that: (a) the damaged layer is very thin (~ 25 nm) in comparison to the thickness of the membrane and (b) the binding energies of deuterium atoms to crystalline defects such as dislocation loops are too small (< 0.2 eV, see section III.2.2, Table III.1) to have any measurable effects at this temperature range (370 K ~ 570 K). Individual free vacancies have a larger binding energy (0.43 eV [V.7]) for deuterium atoms, but at T > 373 K temperature, the vacancy concentration decreases due to diffusion (1.4 eV for single vacancy migration [V.8], 0.9 eV for divacancies [V.9]) and annihilation with interstitial loops and clusters.

The effect of 700 K annealing is checked on these samples as well. Figure V.4 gives an example. Again, there is no measurable annealing effect observed.



Figure V.2 (a) Measured permeabilities of deuterium in nickel samples pre-implanted with 90 keV Ni^+ at room temperature. The dpa were obtained using TRIM [V.13].

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Figure V.2 (b) Measured apparent diffusivities of deuterium in nickel samples pre-implanted with 90 keV Ni⁺ at room temperature. The dpa were obtained using TRIM [V.13].

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Figure V.3 TEM observation of radiation defects, beam direction is close to <111> direction: (a) nickel pre-implanted with 90 keV Ni⁺ to a fluence of 1×10^{14} /cm² (0.3 dpa). The dots with black and white contrast are small vacancy type dislocation loops. (b) nickel pre-implanted with 90 keV Ni⁺ to a fluence of 1×10^{16} /cm² (30 dpa). The black dots and pairs of lobes are dislocation loops.

1000 Å

(b)

1000 Å

 $\langle \gamma_{n,\pm}\rangle = -\gamma^n$

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(a)

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Figure V.4 The comparison of before and after 700 K annealing for the sample pre-implanted with 90 keV Ni⁺ to a fluence of $10^{14}/\text{cm}^2$ (0.3 dpa). (a) permeabilities; (b) apparent diffusivities.
This example was chosen because the radiation damage (0.3 dpa) in this sample is in the comparable range as the helium implanted samples (see section IV.1, Table IV.1). This check is important since in a later section we will see a significant annealing effect on the samples pre-implanted with helium ions.

V.2.3 Samples pre-implanted with He⁺: the normal behavior

Nickel foils implanted with four different helium fluences were investigated in permeation experiments with the helium implanted layer on the downstream side. These unannealed samples all appear to behave "normally", except for the samples pre-implanted with 3.5×10^{15} He⁺/cm², for which the permeation behavior starts to be "abnormal" after ~ 460 K annealing. The "normal" results are given in Figure V.5. The data for the sample pre-implanted with 3.5×10^{15} He⁺/cm² were chosen from "quick" measurements which means the aging time between two measurements is about one hour. As one can see, there is no measurable difference in the apparent permeability for all helium fluences and the permeability agrees with the unimplanted nickel. However, the apparent diffusivity of deuterium decreases as the He⁺ fluence increases. The decrease in diffusivity saturates when the He fluence reaches ~ 1×10^{16} /cm², i.e., peak He concentration reaches ~ 0.7 at%. As the measurement temperature is increased, the difference in apparent diffusivity decreases and approaches that of unimplanted nickel.

If we use the two-layer model given in section V.2.1 (equation V.10), to estimate the apparent diffusivity in the helium implanted layer by assuming no



Figure V.5 (a) Normal trapping behavior : measured permeabilities of deuterium in nickel samples pre-implanted with 30 keV 4 He⁺ at room temperature.

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Figure V.5 (b) Normal trapping behavior : measured apparent diffusivities of deuterium in nickel samples pre-implanted with 30 keV 4 He⁺ at room temperature.

change in permeability, we can then create Table V.1 for the two high fluence samples. Here D_1 and D_2 are the diffusivities in the perfect nickel layer and the helium implanted layer, respectively. Also shown in Table V.1 is the ratio of solubilities of the helium implanted layer to the perfect layer using equation (V.5).

Table V.1 Calculated ratios of D_2/D_1 and S_2/S_1 for samples pre-implanted with 8×10^{15} and 5×10^{16} He/cm²

T (K)	D ₂ /D ₁	s ₂ /s ₁
370	2.3x10 ⁻⁶	4.3x10 ⁵
450	1.0x10 ⁻⁵	1.0x10 ⁵
530	1.6x10 ⁴	6.3x10 ³

One can see that the apparent diffusivity in the helium implanted layer is lower by 4 ~ 6 orders of magnitude! To the author's knowledge, this is the first time in the literature that the apparent diffusivity of deuterium atoms in helium implanted nickel has been estimated directly from experimental measurements. Figure V.6 shows theoretical calculations made according to a simple trapping model described in Chapter III, equation III.29, assuming a binding energy of 0.55 eV and trap densities equal to helium peak concentrations. This model predicts that at higher temperature when the time for diffusion through helium layer (~ 100 nm) is comparable to the time for diffusion through the whole sample thickness (25 μ m), the delay effect due to helium defects will apparently disappear, this is

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Figure V.6 Theoretical calculations of apparent diffusivities of deuterium in nickel using equation III.28 and the Two-Layer model (equation V.10).

consistent with experimental observations of normal permeation behaviour in this The theoretical calculations can only show the general trend. study. The quantitative disagreement may be expected because this model was noted to be only suitable for low occupation of trapping sites, while thermal desorption experiments to be reported later show a very high coverage (or trapping efficiency) of $0.4 \sim 1.5$. Furthermore, the calculation using a single value of binding energy may not be adequate for different helium fluences. Later thermal desorption experiments show that the effective binding energy varies between 0.4 \sim 0.6 eV from sample to sample and reaches a maximum value at the fluence of 8×10^{15} He/cm². This point will be discussed in more detail in the thermal desorption Nevertheless, this simple model is not too bad in predicting the section. deuterium diffusion behavior if reasonable parameters are chosen.

V.2.4 Summary of the normal behavior in permeation

Nickel ion implantation apparently has no effect on deuterium permeation in the temperature range of 370 K to 570 K. This may be due to low binding energies of deuterium atoms to crystalline defects such as dislocation loops.

Helium ion implantation can decrease the apparent diffusivity of deuterium in helium implanted layers by $4 \sim 6$ orders of magnitude in this temperature range without changing the apparent permeability, which implies a few orders of magnitude increase in the apparent solubility of deuterium in the implanted layer. A simple trapping model can approximately show the trend when suitable parameters are chosen.

V.3 Thermal desorption

V.3.1 Introduction

As discussed in section III.2.3, thermal desorption analysis (TDA) is a more sensitive technique for studying diffusion processes, trapping effects and Particularly, in the study of trapping effects, the gas-surface interactions. desorption peak temperature (T_p) is a direct indication of trapping strength: a high T_p corresponds to a high binding energy. However, the quantitative analysis of the desorption spectrum to extract the diffusion coefficients and surface or bulk trapping parameters (binding energy and trap density) is complicated and usually possible only by making some simplifying assumptions. Redhead [V.10] and Carter [V.11] demonstrated similar theories to analyze the desorption data during linear or reciprocal temperature variation, but assumed that the gas atoms are adsorbed on the sample surfaces, i.e. no diffusion process being taken into Later, Farrell and Carter [V.12] suggested a model which includes account. diffusion processes from bulk. However, their model did not take trapping effects In the present study, the computer code DIFFER (see section into account. III.3.3) is used to analyze the desorption spectra.

Before each deuterium desorption experiment, deuterium was charged into nickel samples at 423 K, in 70 torr of D_2 gas phase for about two hours. At this

temperature, permeation experiments show that it will take about one minute for the deuterium permeation flux to reach the maximum (steady state) in pure nickel with a thickness of 25 μ m. Although the helium layer slows down the diffusion process by 5 orders of magnitude as indicated in Table V.1, the helium layer is so close to the surface (~ 100 nm) that the 2-hour-charging time should be sufficient to establish the equilibrium state.

The solubility of deuterium in a normal nickel lattice is about $4x10^{16}$ atoms cm⁻³·Pa^{-1/2} at 423 K. This is 20 times higher than the room temperature value of $2x10^{15}$ atoms cm⁻³·Pa^{-1/2}. Later reported desorption experiments show that most of the trapped deuterium will be released at temperatures below 423 K. This implies that at this charging temperature there will be a thermal balance between trapping and non-trapping sites so that not all of the traps are filled with deuterium. The quenching process after charging allows the over-saturation of deuterium atoms in normal lattice sites to migrate into the empty traps. An estimation using the equation (III.5) shows that for a trap density 5 at% and a binding energy 0.5 eV nearly 100 % of traps may be filled by charging plus quenching process.

Molecular deuterium (D_2) and ⁴He atoms are both mass 4 species as seen by the mass spectrometer and hence not discriminated. But the detection sensitivity for D_2 of the quadrupole mass spectrometer is higher by a factor of -2 than the sensitivity for helium, as quoted by the manufacturer. Most samples used in this study were implanted with ⁴He ions rather than ³He ions because (1) ⁴He is much less expensive, (2) from the literature no difference is expected and (3) no ⁴He was observed, in this study, to release at below 950 K if no hydrogen isotopes were charged in nickel samples pre-implanted with 30 keV helium ions to fluences of $1 \times 10^{15} - 1 \times 10^{17}$ /cm². Therefore it was not expected that helium atoms could be released at low temperatures when hydrogen isotopes are charged. After a new phenomenon, named in this thesis, the *enhanced helium release*, was observed, it was realized that using ³He ions may help to clarify some problems. Therefore some samples with ion-implanted ³He were also prepared for study.

During the thermal desorption experiments, the sample temperature is linearly increased with time and the mass 4 (sometime both mass 4 and mass 3) signals are regularly collected by the mass spectrometer to obtain a desorption spectrum. At least four samples for one helium fluence were used in these measurements and the desorption spectra obtained for identical samples peaked within a few degrees of each other, indicating good repeatability for such measurements. From the thermal desorption spectra two parameters may be determined: deuterium *binding energy*, and *trapping efficiency* to the helium defects. An interesting phenomenon, *enhanced He release due to the presence of hydrogen isotopes*, was observed. These three subjects will be presented in turn.

V.3.2 Binding energy

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Figure V.7 shows typical calculation results of DIFFER for 1 and 2 types of traps compared with the actual deuterium desorption measurement for a sample which had been pre-implanted with 5×10^{16} ⁴He/cm². In the computer calculations,



Figure V.7 Comparison of simulated deuterium thermal desorption curves using DIFFER with experimental results on nickel pre-implanted with 30 keV 4 He⁺ to a fluence of 5×10^{16} /cm². Ramp rate = 1.5 K/min. The dashed curve is calculated assuming a single trap class ($E_{b} = 0.52 \text{ eV}$, $C_{trap} = 4.4$ at%). The solid curve uses two types of traps ($E_{b1} = 0.5 \text{ eV}$, $C_{trap1} =$ 2.64 at%; $E_{b2} = 0.6 \text{ eV}$, $C_{trap2} = 1.76 \text{ at\%}$)

the total trap density was arbitrarily chosen to be equal to the helium concentration, the total amount of trapped deuterium was taken as the measured value (Q_T) , and helium depth profile was determined using TRIM [V.13].

An important difference between DIFFER calculations and experimental curves is the shape of the desorption curves: DIFFER predicts a relatively slow increase on the low temperature side of the peak and a steeper decrease on the high temperature side; but the shape of experimental curves is just opposite, i.e. a more rapid increase on the low temperature side and a somewhat slower decrease on the high temperature side.

Assuming a single trap (0.52 eV) the calculated curve (dashed line in Figure V.7) is seen to be narrower than that measured, resulting in a higher peak desorption rate. A 2-trap calculation (the solid curve) is a better fit but the measured data still extends to higher temperature. One may expect to get even better fits by assuming a larger number of traps extending to higher binding energies and lower trap densities. This kind of observation implies that the traps have a distribution of binding energies rather than one discrete value as usually given in literature.

Very little attention has been given to the subject of distributions of binding energies at He defects. Wilson et al. [V.14] in 1978 have made a similar observation on one stainless steel sample pre-implanted with helium ions when trying to fit the data with a single binding energy to their own computer model. Unfortunately they did not give a detailed discussion on this matter. In 1989 Frank and co-workers [V.15] published experimental data from krypton-implanted nickel. They had to assume five different traps in order to model the experimental data. They claimed that there actually appears to be a continuum of binding energies, instead of discrete values, although the mechanism behind such observation was not given. According to these observations it may be concluded that the traps created by inert gas implantation vary in configuration so that using a single binding energy to describe them as is done in most studies of this kind (see section III.2.3, Table III.2) may not be appropriate.

Considering the trapping mechanisms given in section III.2.3 one should recognize that the concept of a distribution of binding energies is more reasonable. After helium implantation to such high fluence ($\geq 1 \times 10^{15}/\text{cm}^2$) there must be a distribution of different sizes of helium-vacancy clusters. The surface configuration and strain field around a helium-vacancy cluster should depend on the size of the cluster. Therefore both a chemisorption model and a strain model (see section III.2.3) will predict a distribution of binding energies to deuterium. It is one of the major subjects of this thesis work to experimentally study the relationship between helium defect configuration and the binding energy.

In this work, it is assumed that different helium implantation fluences produce different helium defect configurations (for example, the average size of helium clusters varies with fluence), and that annealing at elevated temperature will further change the defect configuration, as has been previously reported in the literature (see section IV.1, Table IV.1 and section II.4). In order to compare results between samples, an *effective binding energy*, E_b^{eff} is defined by

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setting the peak release temperature (T_p) in a single trap calculation at the temperature where 50 % of trapped deuterium has been released. Therefore the values of E_b^{eff} obtained in this manner have only relative rather than absolute meaning.

The depth profiles of traps used in DIFFER calculations were chosen as helium implantation profiles predicted by TRIM (see section IV.1, Table IV.1). Once the depth profile is fixed, there are four input parameters that control the result of a DIFFER calculation: (i) the total amount of trapped deuterium, this is chosen as the measured value (Q_T) ; (ii) the total trap density, this is chosen as the helium peak concentration (CHe, see section IV.1, Table IV.1); (iii) the temperature ramping rate, this is taken as the experimental value ($\beta = 1.5 - 3$ Figure V.8 typically K/min in most cases); and (iv) the binding energy. illustrates how the binding energy (E_b) affects the desorption peak temperature (T_p) when all other parameters are fixed. The simulations indicate a peak temperature difference of 35 - 40 K per 0.1 eV change in binding energy. After taking a temperature error $(\pm 3 \text{ K})$ into account, it is reasonable to conclude that this method can distinguish 0.03 eV difference (about 10 K in temperature) in E_b^{eff} when comparing between desorption spectra. It is interesting to note that if one plots T_p as a function of E_b , the relation looks linear (see Figure V.9a). Also shown in Figure V.9 are DIFFER calculation results of the relationships between T_p and trapping density C_{He} (Figure V.9b) and between T_P and ramp rate β (Figure V.9c). Figure V.9d gives an example for varying the amount of trapped deuterium C_{H} if other parameters (i.e., E_{b} , C_{He} , and β) are fixed. The solid curves in Figure V.9 are the best fit curves to the calculated data.



Figure V.8 DIFFER simulation of binding energy effect on deuterium TD spectra



Figure V.9 Examples of DIFFER calculation results. Solid curves are the best fit curves: (a) $T_P \sim E_b$; (b) $T_P \sim \ln C_{He}$; (c) $T_P \sim \ln\beta$; (d) $T_P \sim -C_H$, where C_H is the concentration of trapped hydrogen.

⁴ He fluence (ions/cm ²)	Hepeak no concentration (at%)	o anneal (eV)	703K anneal (eV)	923K anneal (eV)
1x10 ¹⁵	0.09	0.45	0.52	0.52
3.5x10 ¹⁵	0.31	0.46	0.51	0.49
8x10 ¹⁵	0.70	0.56	0.52	0.50
5x10 ¹⁶	4.4	0.52	0.52	C.50
1x10 ¹⁷	7.1	0.52		0.50*
4x10 ¹⁷	33	0.50		0.48

Table V.2 The effective binding energy estimated using DIFFER $E_{h}^{eff}(\pm 0.03 \text{ eV})$

* annealed at 800 K.

The estimated values of E_b^{eff} for all samples are shown in Table V.2. Referring to the experimental observations given in Table IV.1, we know that helium defects were not observable in TEM in the two low helium fluences cases, which implies that helium atoms are in small He-Vacancy complexes. Helium bubbles become visible in TEM (~ 1 nm) when the helium concentration reaches about 0.7 at%. Then bubble size increases slightly as helium fluence increases.

First, if one looks at the "no anneal" column, results of E_b^{eff} suggest that small He-V clusters produced in the two low fluence cases before annealing have lower E_b^{eff} . Another interesting point which has not been reported in the literature is that these low E_b^{eff} are close to the value for the single vacancy trapping mechanism (0.43 eV, see Table III.2). While helium bubbles have higher

 E_b^{eff} as is evident in Table V.2 when helium bubbles are formed by higher implantation fluences. At the fluence of $8 \times 10^{15} \text{He/cm}^2$ where bubbles just reach ~ 1nm in diameter, E_b^{eff} reaches a maximum and then decreases as the bubble size increases.

Secondly, let's look at the annealing effects on E_b^{eff} as illustrated in Table V.2. Annealing at 703 K or 923 K causes an increase in E_b^{eff} for the two low It has been found experimentally (see section II) that after helium fluences. annealing at these temperatures helium bubbles (> 1nm) are formed for low fluence helium ion-implantation. Therefore the results of E_b^{eff} suggest again that helium bubbles have higher binding energies for deuterium atoms. After bubbles are formed, annealing generally causes a slight decrease in E_b^{eff} . There is a fairly stable region ($\geq 5 \times 10^{16}$ He/cm²) in which E_b^{eff} does not change until the annealing temperature reaches the bubble growth and migration temperature (~ 900 K, see section II.4). Later analysis of trapping efficiency indicates very little change in the region of $5 \times 10^{16} \sim 1 \times 10^{17}$ He/cm². Accordingly one may conjecture that, in this region, the He defect configuration is stable. For the highest He fluence $(4x10^{17} \text{ He}^+/\text{cm}^2)$ where microchannels and blisters have been established (see section II and next section for SEM pictures), the He was seen to begin to release at about 350 K and continue to high temperature (see Figure V.10). The multi-peak structure is usually seen in the literature (e.g., see section II.3.5, Figure II.10), although there is no clear explanation yet to this structure. Qualitatively, one could assume that higher temperature release peaks correspond to deeper helium traps. The total helium release in Figure V.10 is about 1.5×10^{17} By taking this release to obtain a residual helium concentration, a He/cm².



Figure V.10 ⁴He thermal desorption from nickel pre-implanted with 15 keV ⁴He⁺ to a fluence of $4x10^{17}/\text{cm}^2$. No hydrogen isotopes has been charged.

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smaller E_b^{eff} (0.48 eV) is calculated for the samples after 923 K annealing. An analysis to be presented in the next section demonstrates that the trapping efficiency shows a significant decrease which may be explained by the possibility that some helium defects are no longer trapping centers for deuterium after annealing, since the strain around the bubbles is released by helium atom release according to the Strain Trapping Model (section III.2.3), and may be due to the fact that more deuterium escape paths have been created during annealing. In the next section one also will see that Scanning Electron Microscopy (SEM) indeed reveals a high density of holes formed on the sample surface after high temperature annealing and helium release.

V.3.3 Trapping efficiency

It was found in this work that another parameter, trapping efficiency, is also closely related to the change of helium defect configuration. This parameter is defined as the ratio of trapped deuterium atoms (Q_T) to helium atoms (C_{He}) in nickel, i.e., $\frac{Q_T}{C_{He}}$. It should be noted that C_{He} may not be equal to the density of trapping center in general. But the true density of trapping center for deuterium in the helium implanted layer is an unknown parameter which should relate to C_{He} in someway. The total trapped deuterium atoms can be measured from thermal desorption experiments by integrating the desorption curves. The reproducibility involved in measuring Q_T is about 15% for low dose samples ($\leq 8 \times 10^{15} \text{He/cm}^2$) and 10% for high dose samples (5×10^{16} and $1 \times 10^{17} \text{He/cm}^2$). The errors come from a statistical analysis of many identical experiments. Although the accuracy is not great, the general trend is clear.

Table V.3 Trapping Efficiency
$$\begin{pmatrix} Q_T \\ C_H \end{pmatrix}$$

⁴ He fluence	He peak	Q	Q _T /C _{He} (± 10~15%)		
(ions/cm ²)	concentration (at%)	no anneal	703K anneal	923K anneal	
1x10 ¹⁵	0.09	1.2	0.4	0.4	
3.5x10 ¹⁵	0.31	1.3	0.6	0.3	
8x10 ¹⁵	0.70	1.5	0.84	0.8	
5x10 ¹⁶	4.4	0.64	0.4	0.4	
1x10 ¹⁷	7.1	0.4		0.4*	
4x10 ¹⁷	33	0.25		0.08	

* annealed at 800 K.

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Table V.3 summarizes trapping efficiencies for every helium fluence. The "no anneal" column reveals: (1) small He-V clusters in the cases of two low helium fluences have high trapping efficiency (>1), possibly due to the *relatively* high trapping density; (2) similar to the result of E_b^{eff} , the trapping efficiency reaches a maximum at the fluence of 8×10^{15} He/cm² where helium bubbles just become visible in TEM (~ 1nm in diameter); (3) then the trapping efficiency decreases as the fluence increases.

Annealing generally causes a decrease in trapping efficiency as seen in Table V.3. In many cases the value is around 0.4, which is consistent with the

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theoretical estimation given in section III.2.3 for a helium bubble about $1 \sim 2$ nm in diameter. For low dose samples, the trapping efficiency decreases significantly due to annealing, which indicates a significant change in helium defect configuration. Again, as discussed earlier, there is a stable region $(5 \times 10^{16} \sim 1 \times 10^{17} \text{ He/cm}^2)$ where the helium defect configuration does not change significantly by annealing.

At the highest helium fluence, i.e. 4×10^{17} He/cm², the situation is rather special. Scanning Electron Microscopy (SEM) reveals helium blisters on the sample surface; no blisters are seen at lower helium fluences. Figure V.11 compares the microstructures of one sample before and after annealing at 923 K. It can be seen that about 20 % of blister caps are broken off during the implantation (Figure V.11(a)). The helium content within the samples after ion-implantation, measured by melting the materials, was shown to be $(3.5 \pm 0.3) \times 10^{17}$ He/cm². Therefore helium actually starts to release at low temperature (see Figure V.10). This poor surface structure may be the reason of low deuterium trapping efficiency (0.25) before annealing. After 923 K annealing, about 1.5x10¹⁷He/cm² have been released. A high density of small holes (small black points in Figure V.11(b)) appeared. The large black spots are the craters left after the blister caps broke off. Figure V.12 shows SEM pictures with higher resolution on the same samples as in Figure V.11. The annealed sample was then charged with deuterium and further thermal desorption showed an even lower trapping efficiency (0.08) by the residual helium defects.





Figure V.11 SEM studies of surface morphology of nickel pre-implanted with 15 keV, $4x10^{17}$ He⁺/cm² at T < 323 K. (a) just after ion-implantation, blisters are evidence and about 20 % of blisters are broken. (b) after 923 K annealing, large black circles used to be blisters, small black spots are holes.





Figure V.12 SEM studies of the same samples as in Figure V.11 but higher resolution: (a) just after helium implantation; (b) after 923 K annealing.

Figure V.13 to Figure V.17 present typical desorption spectra for samples pre-implanted with 1×10^{15} to 1×10^{17} e/cm², respectively. The peak shifting (experimental error within ± 3 K) in each figure before and after annealing is mainly due to the changes in E_b^{eff} as discussed in an earlier section. For example, in the case of low fluence $(1 \times 10^{15} \text{ He/cm}^2 \text{ in Figure V.13})$, annealing at 703 K causes the desorption peak to move to the high temperature side, indicating a formation of higher binding energy traps by the annealing process. At high helium fluences $(8 \times 10^{15} \text{ to } 1 \times 10^{17} \text{ He/cm}^2 \text{ in Figure V.15}$, V.16 and V.17), annealing treatments start to shift the desorption peak to the low temperature side, which implies a removal of high binding traps.

The width of the desorption spectra is another indicator of the helium defect configuration. The full width at half maximum (FWHM) of five non-annealed samples (from 1×10^{15} to 1×10^{17} He/cm², see the "circle" curves in Figure V.13-17) are about 20 K, 30 K, 40 K, 75 K, and 100 K, respectively. The increase in the peak width may indicate a continual broadening of the distribution of helium defect sizes, therefore a broadening of distribution of binding energies. In other words, at low helium fluences, there are no "big" He-V clusters. While at high helium fluences, besides many "big" He-V clusters, there may be also a lot of small clusters.

Figure V.18 shows the desorptions from nickel pre-implanted with ${}^{3}\text{He}^{+}$ to a fluence of $4 \times 10^{17}/\text{cm}^{2}$. The reason for using ${}^{3}\text{He}$ ions is to separate the mass 4 peak (D₂) from mass 3 peaks (${}^{3}\text{He}$) in the desorption spectra, in order to obtain



Figure V.13 Deuterium thermal desorption from nickel pre-implanted with 30 keV 4 He⁺ to a fluence of 1×10^{15} /cm².



Figure V.14 Deuterium thermal desorption from nickel pre-implanted with 30 keV 4 He⁺ to a fluence of 3.5×10^{15} /cm².



Figure V.15 Deuterium thermal desorption from nickel pre-implanted with 30 keV 4 He⁺ to a fluence of 8×10^{15} /cm².



Figure V.16 Deuterium thermal desorption from nickel pre-implanted with 30 keV 4 He⁺ to a fluence of 5×10^{16} /cm².



Figure V.17 Deuterium thermal desorption from nickel pre-implanted with 40 keV 4 He⁺ to a fluence of 1×10^{17} /cm² at room temperature.



Figure V.18 Deuterium and ³He desorptions from nickel pre-implanted with 17 keV ³He⁺ to a fluence of $4x10^{17}/\text{cm}^2$ at room temperature, and then charged with deuterium at 423 K in D₂ gas phase for 2 hours.

the trapping parameters (E_b^{eff} and $\frac{Q_T}{C_{He}}$, see values in Table V.2 and V.3). Some samples used for ⁴He release experiments were charged with deuterium again and followed by deuterium desorption experiments. One typical result is given in Figure V.19 showing a 0.08 trapping efficiency based on an experimental estimate of about $2x10^{17}$ /cm² of residual ⁴He still left in the sample.

To conclude this section, the important experimental observations are:

(1). when the size of He defects is small, the trapping efficiency is high (\geq 1), and reaches a maximum when helium bubbles about 1 nm in diameter are formed. Then the trapping efficiency decreases as the bubble size increases;

(2). annealing generally decreases trapping efficiencies;

(3). there is a fluence region $(5 \times 10^{16} \sim 1 \times 10^{17} \text{ He/cm}^2)$ where the He defect configurations are quite stable because the changes of trapping efficiency are small after annealing;

(4). at the highest He concentration, where blisters were formed, the trapping efficiency decreases; further annealing causes a significant decrease in the trapping efficiency.

V.3.4 Summary and discussion of E_b^{eff} and $\frac{Q_T}{C_{He}}$ results

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Figure V.20 summarizes the measurements of effective binding energy (E_b^{eff}) and trapping efficiency $(\frac{Q_T}{C_{He}})$. Different helium defect configurations were given according to Table IV.1 in section IV.1.



Figure V.19 Desorption from nickel pre-implanted with 15 keV 4 He⁺ to a fluence of 4×10^{17} /cm². After He desorption up to 960 K, followed by deuterium charging at 423 K, the deuterium desorption shows a trapping efficiency ~ 0.08.





Figure V.20 Summary of measurements of effective binding energy E_b^{eff} and trapping efficiency $\frac{Q_T}{C_{He}}$. The helium configuration is approximately corresponding to the helium implantation fluence. The error for E_b^{eff} is 0.03 eV, and for $\frac{Q_T}{C_{He}}$ is about 10–15%.

At low helium fluences, where most of the helium atoms are in small helium-vacancy complexes (He_mV_n), E_b^{eff} is smallest. It may be significant that the measured binding energies (about 0.45 eV) are close to the binding energy of deuterium atoms to single vacancies in nickel (~ 0.43 eV) [V.7]. Therefore the trapping mechanisms in both cases may be similar. The trapping efficiency $\frac{Q_T}{C_{He}}$ is high (> 1) in this range, which may be due to relatively higher densities of the trapping centers since the size of helium clusters is small and may be due to the trapping at vacancy type defects that survived during the implantation process.

A combination of chemisorption-type and strain field trapping models (section III.2.3) may be appropriate to explain the results in the bubble region. Both models suggest a distribution of binding energies for bubble trapping. Both models predict higher binding energies for deuterium trapped at helium bubbles than that at vacancies. This may explain why E_b^{eff} increases when helium bubbles Particularly, if the bubble size (~ 1 nm) is small, the internal are formed. pressure is large ($p \propto 1/R$) and so is the local strain, therefore E_b^{eff} should be higher, according to the strain field trapping model. This might explain why E_h^{eff} reaches a maximum when bubbles just start to form. Then as the bubble size increases the internal pressure decreases, therefore E_b^{eff} decreases. On the other hand, after annealing at 923 K where most of strain may be released, bubbles are still traps for deuterium as suggested by the chemisorption trapping model. Both chemisorption-type and strain field trapping models predict a trapping efficiency of about 0.4 for bubbles with ~ 1 nm in diameter (see section III.2.3), which is consistent with our measurements.

At a very high helium concentration, microcracks and interconnected channels between bubbles (even blisters) are established (see section II.3.2). The smaller E_b^{eff} and significant decrease in $\frac{Q_T}{C_{He}}$ before and after annealing can be understood when it is considered that there may be more paths for deuterium (and for helium) escaping and that strain fields are partially reduced by helium release.

V.3.5 " H " enhanced He release

An unexpected phenomenon observed in desorption experiments is named in this thesis as the *Enhanced Helium Release* (EHR) due to hydrogen isotope charging.

Figure V.21 gives an example for the highest helium fluence $(4\times10^{17}$ ⁴He/cm²). The circle curve represents the helium desorption from a sample without any post-implantation annealing or hydrogen charging. The cross curve is the thermal desorption data for another identical sample after charging with hydrogen (H₂) at 423 K for 2 hours. The first helium release peak (at ~ 450 K) is smaller in the cross curve because some of the helium atoms were released during hydrogen charging. The high temperature peaks in both curves are similar in shape but higher for the sample charged with hydrogen, resulting in a 15 % increase in the total amount of ⁴He release compared to that of the sample without hydrogen charging. Similar phenomena were observed for samples pre-implanted with ³He to the same fluence. Deuterium charging seems to have a stronger enhancement effect



Figure V.21 ⁴He thermal desorption with, or without hydrogen charging from two nickel samples pre-implanted with 15 keV, 4×10^{17} He⁺/cm².
on helium release, and appears to shift the helium release peaks to lower temperature [V.16].

At lower helium fluences ($\leq 1 \times 10^{17}$ He/cm²), if the samples were not charged with hydrogen isotopes, then no helium release peak is seen at temperatures up to 950 K. After being charged with deuterium, many of these samples, especially the samples pre-implanted with fluences $\geq 8 \times 10^{15}$ He/cm², showed a second mass-4 release peak at about 550 K beside the deuterium release peak. Figure V.22 gives two examples. This peak is usually very small but within the resolution of the mass spectrometer. Sometimes it was necessary to repeat the desorption experiments several times in order to have this peak appear. Occasionally, more than two peaks appear around 550 K. One possible explanation for the low intensity of mass 4 peaks may be due to some deuterium contamination in the charging chamber. An alternative explanation is that the 550 K peak is a combination of ⁴He and D₂. But for both explanations it is hard to understand why deuterium would be trapped to such a high temperature where the binding energy would be larger than 1 eV. It is also hard to understand why this deep binding is not always observed.

In order to clarify these problems a set of nickel samples were implanted with 30 keV ³He ions to a fluence of 1×10^{16} /cm². Then similar thermal desorption experiments were conducted. Both mass 4 signal (D₂) and mass 3 signal (mainly ³He) were collected during these measurements and a higher temperature ramping rate (10 K/min) was used in order to possibly enhance the phenomenon. Without charging deuterium, no mass 3 peaks were observed up to 700 K. After deuterium



Figure V.22 Small mass 4 release peaks at 550 – 600 K from nickel preimplanted with 30 keV helium and after deuterium charging. (a) a sample pre-implanted with 8×10^{154} He⁺/cm²; (b) samples pre-implanted with 1×10^{15} ⁴He⁺/cm². Large low temperature peaks are deuterium desorptions.

charging the desorption experiments show mass 3 release peaks at around 550 K. Figure V.23 gives an example: the "circle" curve is the mass 4 signal due to D_2 , the "cross" curve is the mass 3 signal most likely due to ³He release. It is clear that there is no further deuterium release above ~ 480 K, which indicates that there is no high binding traps (> 1eV) in the helium-implanted nickel samples. Therefore, the peaks at 550 ~ 600 K observed in Figure V.22 are most likely to be ⁴He release peaks.

To summarize these observations, two points may be significant:

(1). hydrogen isotopes may enhance the helium release in nickel;

(2). no high binding traps (>1eV) for deuterium were observed in helium-implanted nickel.

There is a possible reason for the Enhanced Helium Release (EHR) after charging hydrogen isotopes. In history, a phenomenon called *Hydrogen-Assisted Cracking* (HAC) has resulted in many intensive studies (see a review article [V.17]). In this phenomenon, "H" (not in hydride form) causes crack formation and growth, particularly in the presence of sustained loads. This form of hydrogen damage is observed most often in iron and steels, primarily quenched and tempered, precipitation hardened, or otherwise high in strength. Alexander R. Troiano's 1960 paper [V.18] is the most widely referenced paper on HAC. In his theory, Troiano suggested that the electrons from the hydrogen ions would enter the d bands of the metallic cores, and that "the increase of the electron concentration of these bands produces an increase in repulsive forces between metallic cores, or, in other words, a decrease in the cohesive strength of



Figure V.23 Thermal desorptions of deuterium and ³He from a nickel sample pre-implanted with 30 keV ³He to a fluence of 1×10^{16} /cm², followed by deuterium charging at 423 K for 2 hours.

the lattice". This electrostatic repulsive force reduces the additional stress required for atomic separation, and cracks may grow.

In the helium implanted layer, the high density of the dislocation network $(\sim 10^{11}/\text{cm}^2)$, combined with high densities of helium-vacancy complexes and bubbles $(10^{17} \sim 10^{19} /\text{cm}^3)$ in present study) result in a high stress field. Very often, dislocations, even microcracks, connect with bubbles because of the very high internal pressure. After helium ion-implantation, this type of defect configuration is in a stable state. During hydrogen charging, hydrogen isotopes attracted to these high strain fields (such as the tips of these microcracks, see Figure III.4) may destroy the local stress balance which may result in crack propagation, gas void formation and dislocation motion. Quenching after charging and repetition of desorption experiments may help to develop microchannels from bubbles to the sample surface. Once these channels are created, low temperature helium release may occur. The chance to create open channels by the HAC process should be small for low He fluences, therefore the amount of low temperature release is small in these cases.

Clearly, much more investigations are needed. The EHR phenomena should be important in helium "self pumping" studies as mentioned in chapter I. The intention of such studies is to establish suitable materials and the conditions necessary for capturing the helium "ash" in limiters (and diverters) in fusion reactor whilst allowing the recycling of tritium and deuterium. Therefore EHR should be avoided.

V.4 Annealing effects on permeation : abnormal behavior

The previously mentioned phenomenon of "abnormal" permeation will be discussed in detail. The "abnormal" behavior is often characterized by an extremely low apparent diffusivity of deuterium. It is important to note at this point that all "abnormal" behavior appeared after a certain annealing of samples and all anneals were performed under vacuum condition (~10⁻⁶ torr). This vacuum condition has been proved to have no effect on deuterium permeation through nickel [V.19]. In fact, Auger Electron Microscopy showed normal surfaces on both sides of nickel membranes. A typical example is given in Figure V.24. The upstream side of the sample seems to present a slightly higher oxide peak compared to the surface before permeation. This is reasonable because the upstream side is at a relatively poor vacuum (~ 10^{-6} torr at elevated temperatures). Sputtering profile analysis on this surface is given in Figure V.25. It shows that the thickness of the oxide layer is less than 20 Å, which is about the normal oxide thickness on nickel and is too thin to cause such abnormal behavior.

This phenomenon was so unexpected and confused that it took a long time for investigations. Even now, some essential problems are still unclear. On the other hand, the effect of this phenomenon is so strong that it is important to be reported. The basic objective of the next section is to state the experimental observations (no matter how confused they are). The results will be given in the order of helium fluences, starting from high helium fluence $(5x10^{16}\text{He/cm}^2)$ to low fluence $(1x10^{15}\text{He/cm}^2)$. The method described in section V.2.1 is used to

Figure V.24 Auger nickel spectrums from pre-implanted with 30 keV, (a) the $\frac{z}{z}$ 1x10¹⁵ He/cm². helium implanted surface before permeation, **(b)** the upstream side surface without helium implantation but after permeation and annealing. (c) (a) but after same as permeation and annealing.





Figure V.25 Auger sputtering profile of the nickel surface pre-implanted with 30 keV, 1×10^{15} He/cm² and after permeation and annealing. The oxide layer is estimated to be less than 20 Å.

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calculate the apparent diffusivity for every sample, although this method is only applicable to ideal cases. Therefore the values of apparent diffusivity given in the next section represent only the delay time for reaching the steady state – the maximum permeation flux.

In section V.4.2 the "general conditions and characters" of this phenomenon are summarized from the author's view point and followed by a discussion about possible mechanisms behind this phenomenon. It is no doubt that more work should be done in order to have a thorough understanding of this phenomenon.

V.4.1 Observations

Figure V.26 shows the permeation results from a sample pre-implanted with $5x10^{16}$ He/cm². The apparent diffusivity measurements are quite repeatable even after 700 K annealing for 1.5 hours. But after an additional 740 K anneal in vacuum for 2 hours, the first measurement carried out at 533 K shows an extremely low diffusivity. Figure V.27 shows the permeation curve taken at 533 K. As one can see, there was an initial slow rising stage up to ~ $2.5x10^4$ seconds, followed by a sudden increase of the permeation flux, then a more gradual increase up to the steady state flux, which is the same flux as in the normal behavior. In order to confirm this surprising result, a few more measurements around this temperature were taken using the same procedure, i.e., (1) annealing and pumping out deuterium at 740 K for 1.5 hours and then (2) cooling the temperature for permeation





Figure V.27 An abnormal behavior : one rise-time permeation flux measurement at 533 K after 740 K annealing for 2 hrs.

experiments. The results were "normal" again.

Figure V.28 gives the results of samples pre-implanted with 8×10^{15} He/cm². Before 700 K annealing the apparent diffusivities are consistent in three different runs (one run means a whole set of measurements from 373 K to 573 K). But after annealing at 700 K for 1 hour, the apparent diffusivity became very dependent on the aging history before permeation measurements. The permeation experiments were started from low temperature (~ 370 K) to high temperature (~ 570 There are three points (A, B, C) on the "normal" line which are the K). measurements with relatively short aging time (about 2 hours) from the previous measurement at corresponding temperatures before permeations. According to thermal desorption experiments such aging time is sufficient for outgasing trapped deuterium from the previous measurement. The other points were measured after at least 6 hours aging at corresponding temperatures. The apparent diffusivities at these temperature points are more than one order of magnitude lower, compared to the "normal" behavior. Very surprisingly, three points (D, E, F) taken after an additional aging at room temperature for more than 15 hours, resulted in even lower apparent diffusivities, see points D, E, F in Figure V.28. One can see the actual permeation curves for points D and F from Figure V.29. Again, there is a long induction period followed by a sudden jump to the maximum flux.

After these studies, the helium layer of the sample was turned to the upstream side, facing the deuterium gas phase. Then permeation experiments were conducted again from low temperature to high temperature. The results show that



Figure V.28 Measured apparent diffusivities of nickel pre-implanted with 30 keV, 8×10^{15} He/cm². Some of star points are marked by letters.

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Figure V.29 Abnormal behaviors : two rise-time permeation flux measurements at, (a) 557 K (F point in figure V.28); (b) 377 K (D point in figure V.28).

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not only is the apparent diffusivity reduced, but also the permeability is decreased by 1 - 2 orders of magnitude, compared to the "normal" behavior. These can be seen in Figure V.30. By changing the side, one actually changed the local deuterium concentration at the helium layer. Putting the helium layer at upstream side results in an increase of deuterium concentration in this layer because this is the side that is facing the gas phase. The apparent differences of "D" and "K" in different arrangements (upstream or downstream) may imply a concentration dependence (repulsive interaction between deuterium atoms) of deuterium permeation through the helium damaged layer.

Diffusivity results of the sample pre-implanted with 3.5×10^{15} He/cm² are given in Figure V.31. As usual, the measurements were started from low temperature. After each measurement at low temperature, the sample was allowed to age at about 400 K overnight for pumping out deuterium. Before the measurement at the point "A" in Figure V.31, the sample was aged at 460 K for 4 hours. After this measurement abnormal behavior starts to show up. Above 435 K, the the apparent diffusivity was scattered over two orders of magnitude, depending on the aging history. There are basically three groups of data. The circle points are "quick" measurements before which the aging times were less than 2 hours at corresponding temperatures. The triangle points are the results of aging for 6 – 10 hours at 450 – 530K. The lowest apparent diffusivities were measured after aging at room temperature for more than 15 hours (the star points). Figure V.32 shows two examples of actual permeation curves for two star points in Figure V.31. Once more, there is a long slow rising period followed by a sudden jump.



Figure V.30 Measured permeabilities (a) and apparent diffusivities (b) from nickel pre-implanted with 30 keV, 8×10^{15} He/cm². The diamond points are measured when the helium layer is on upstream side (facing deuterium gas phase). All other points are measured when the helium layer is on downstream side (facing vacuum).

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Figure V.31 Measured apparent diffusivities of nickel pre-implanted with 30 keV, 3.5×10^{15} He/cm².

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Figure V.32 Abnormal behaviors : two typical rise-time permeation flux measurements at 533 K and 553 K for the sample pre-implanted with 30 keV, 3.5×10^{15} He/cm².

For the lowest helium fluence, i.e., 1×10^{15} He/cm², samples had to be annealed at 700 K in order to see "abnormal" behavior. Figure V.33 gives the results. This time, the measurements were all taken after sample degasing at about 520 K for 2 hours followed by aging at room temperature for more than 15 hours. As one can see, the apparent diffusivity is 1 - 3 orders of magnitude lower, compared to the "normal" behavior. Figure V.34 shows a typical permeation curve for a 540 K measurement, which has the similar shape as before. One interesting point is that the apparent diffusivity becomes even lower at high temperatures, so that the trend of D is showing a " \cap " shape. This " \cap " shape also appears when the "abnormal" behavior occurs in Figure V.28 and Figure V.31.

V.4.2 Summary and discussion

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The general conditions for "abnormal" behavior to occur are as following: 1. after annealing : samples with 5×10^{16} He/cm², after anneal at 740 K for 2 hours, only for the first measurement; 8×10^{15} He/cm², after anneal at 700 K for 1 hour; 3.5×10^{15} He/cm², after anneal at about 460 K for 4 hours; 1×10^{15} He/cm², after annealed at 700 K for 2 hours;

2. the longer the aging time at elevated temperature, the stronger the effect;

3. long time aging at room temperature generally enhances the effect.

The general properties of this phenomenon are :

1. the permeation curve consists of three stages, (1) a relatively long time slow-rising period, (2) a sudden jump in the permeation flux, and then (3)

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Figure V.33 Measured apparent diffusivities of nickel pre-implanted with 30 keV, 1×10^{15} He/cm².



Figure V.34 Abnormal behaviors : one typical rise-time permeation flux measurement at 540 K for the sample pre-implanted with 30 keV, 1×10^{15} He/cm².

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approaching to the maximum flux;

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2. The apparent diffusivity curve develops a " \cap " shape in the "log D — 1000/1" graph, which means at high temperature the effect seems even stronger;

3. Permeation appears to be deuterium concentration dependent in the helium layer.

Since the surface analysis indicates normal carbon contamination and nickel oxide and these impurities show no effect on deuterium permeation in pure nickel samples, then there might be some kind of internal process responsible for the abnormal behavior. There may be a number of possible explanations for the abnormal behavior: (a) some high binding energy traps (much higher than 0.5 eV) might be formed after annealing; (b) deuteride formation; (c) the diffusion field in the helium layer is changing during the permeation due to the HAC mechanism (see section V.3.5).

The possibility (a) is not favored by thermal desorption experiments since TDA results show no indication of high binding trap formation.

Deuteride formation might be based on the assumption that the local concentration of deuterium near helium bubbles is possibly very high (~ 1:1 of deuterium to nickel atoms, according to helium trapping models, see Chapter III). But this assumption can not explain why the effect is stronger at higher temperature, since normally nickel hydride is not stable at elevated temperatures when the hydrogen pressure is low [V.20]. This assumption also can not explain why there is a sudden jump in the permeation curve, which means a sudden disappearance of any effect from deuterides.

The HAC process may be used to explain some of the properties and conditions of the abnormal behavior. We know that the helium layer is under high stress from bubbles and other defects. Annealing at ~ 700 K can not remove the stress in whole, but can cause some local rearrangements of defects. Furthermore, the sample itself is pressed by deuterium gas from the upstream side (~ 200 g on ~ 2 cm² area) during the permeation, which introduces an external stress to the foil (~ 25 µm thick). Helium bubbles are likely overpressurized. The dislocations and microcracks generated by such internal stress are in a stable state. In such circumstances, deuterium atoms might trigger HAC processes or even deuterium bubble formation that slows down the diffusion process of deuterium. These microscale processes would continue as deuterium atoms diffuse to these high stress locations (such as the crack tips), resulting in a slow-rising period of permeation, until the entire layer reached a new stable state, after which, the permeation behavior would immediately revert to normal, causing a sudden jump in the permeation flux. Similar phenomena by dislocation motion and formation were reported in electro-chemical permeation experiments [V.21] where the sample was being deformed under a tensile load during the permeation.

If the dislocation pinning is so strong that the HAC process cannot be started, then permeation will be "normal". This might be the reason why samples showed normal behavior before annealing. After the abnormal behavior appears, the cooling procedure and long time aging at room temperature might restore stresses in the material, so that the abnormal behavior was enhanced. The " \cap " shape of apparent diffusivity data may be explained as follows: At low temperatures, apparent D values are mainly determined by the low jumping rate of deuterium in the damaged layer. At high temperatures, the HAC process is relatively easily triggered, so the low apparent D values are mainly due to HAC disturbances.

There were no significant increases indicated in the binding energy by thermal desorption experiments, because the dislocations and microcracks created in the HAC process have low binding energy to hydrogen isotopes (about 0.2 eV). Voids have a higher binding energy (~ 0.5 eV, see section III.2.2) for deuterium atoms. But during the outgasing and cooling processes most of the deuterium trapped by these defects will escape.

The low apparent diffusivity and low permeability measured when the helium layer was on the upstream side may be due to a combination of HAC processes and a "blocking" effect that involves a high local deuterium concentration around helium bubbles and helium-vacancy complexes. These deuterium-rich regions, or "quasi-deuteride" regions, might effectively reduce the volume of the total diffusion field, so that the apparent permeability was reduced.

No detailed picture of how HAC could actually slow down the permeation process can be given so far. It might be some processes closely related to the dislocation movement and void formation. The actual picture of the abnormal behavior in the microscopic scale might be an interactive or dynamic type, not a static type. In other words, defects would attract deuterium atoms, in the meantime, deuterium atoms would cause a change in the defect configuration. The morphology study of helium bubbles and voids using TEM before and after deuterium charging may be useful to understand this problem.

CHAPTER VI

Conclusions

Deuterium diffusion and trapping behavior in polycrystalline nickel pre-implanted with Ni⁺, 4 He⁺ and 3 He⁺ ions to various fluences were studied under different thermal treatments using gas phase permeation and thermal desorption techniques. The basic observations and conclusions are :

1. Crystalline defects introduced by Ni ion-implantation in nickel have no measurable effects on deuterium diffusivity and permeability in a temperature range of 370 K - 573 K.

2. For a normal trapping behavior, helium related defects decrease the apparent diffusivity of deuterium by a few orders of magnitude in this temperature range, but do not change the apparent permeability.

3. Deuterium permeation may be concentration dependent due to helium defects, since the apparent permeability of deuterium is dependent on whether or not the helium implanted layer

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faces the deuterium gas phase.

4. "Abnormal" diffusion behaviour revealing a strong aging history dependence was observed when samples containing helium defects were annealed. This is assumed to be due to an internal process such as Hydrogen-Assisted Cracking (HAC) and void formation.

5. The binding energy of deuterium to helium defects consists of a distribution of values rather than one or two discrete values. The effective binding energies of deuterium to helium defects are in the range of $0.4 \sim 0.6$ eV, with higher values observed when He bubbles are formed. Small helium-vacancy complexes have lower binding energies for deuterium, similar to a value of 0.43 eV for the binding of deuterium to single vacancies.

6. The trapping efficiency $\left(\frac{Q_T}{C_{He}}\right)$ decreases from > 1 to < 0.3 when He fluences increase from 10^{15} to $4x10^{17}/cm^2$.

7. Annealing generally causes a decrease in the trapping efficiency. Annealing at 703 K causes a larger decrease in trapping efficiency from >1 to 0.4 for samples with low He⁺ fluences, probably due to rearrangement of helium-vacancy complexes. For samples with 30 keV He⁺ implantation to

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fluences of $5 \times 10^{16} - 1 \times 10^{17} / \text{cm}^2$, the configuration of helium defects is stable until the annealing temperature reaches the bubble growth and migration temperature (~ 900 K).

8. At low helium concentration where helium atoms are in small He-V complexes, the trapping behaviour is similar to vacancy trapping. When helium bubbles are formed a combination of chemisorption-type trapping and strain field trapping may be appropriate to explain the thermal desorption results.

9. Hydrogen isotopes interact with helium defects, resulting in the enhancement of helium release: a 15% increase in helium desorption after hydrogen charging is observed for the highest helium fluence $(4x10^{17}/cm^2)$; small hydrogen enhanced helium release peaks at low temperature (550 – 650 K) occur at lower helium fluences. A possible reason for the enhancement is discussed in terms of the HAC process.

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