Hydrogen trapping in helium damaged metals: a theoretical approach

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A model which explains the trapping of hydrogen around or near helium bubbles is presented. According to this model, hydrogen atoms are attracted toward the bubbles due to positive stresses created by the very high pressure (350 kbar) existing inside the bubbles. The extreme trapping energy of hydrogen atoms around helium bubbles has been theoretically calculated and found to be 0.71 eV atom^{-1}. It is shown that most of the hydrogen atoms are trapped in a very small volume located very close to the bubble surface. The total hydrogen quantity was found to be in the range of 45–76 atoms per bubble for a wide range of hydrogen atom concentration, C_∞. The good agreement between the theoretical results and data based on many experimental measurements reinforces the assumptions underlying the very basis of the suggested mechanism. The model proposed in this study can lead to better understanding of failure mechanisms.

1. Introduction

In the operation of fusion devices, hydrogen recycling between the plasma and the first wall is an important factor. Hydrogen isotopes are introduced into the first wall through a combination of energetic implantation and thermally activated processes. Such recycling influences plasma fueling and tritium inventory in the reactor and this fact has motivated a widespread interest in the controlling mechanisms. Since hydrogen isotopes entering at the surface, could lead to hydrogen embrittlement, the above mentioned processes will also affect the lifetime of reactor components.

In fusion devices, helium is formed in the first wall by severe α bombardment and by tritium decay. In such a device, helium is also formed by a (n, α) reactions whose origin is from the high fluence of very high energetic neutrons ($\cong$ 14 MeV).

Early experiments show that helium is strongly trapped at radiation-produced defects in metals [1]. Theoretical models for self-trapping of helium atoms in metals, clusters formation, and nucleation of helium bubbles have been intensively developed during the last years [2, 3]. The calculations based on those models are in agreement with experimental measurements of helium implantation or decay of dissolved tritium [4, 5].

Since there are many sources from which hydrogen can be introduced to the pre-damaged metal (e.g. gaseous hydrogen or its isotopes, aqueous solutions, and hydrogen ion bombardment), the synergestic effects caused by the presence of both helium bubbles and hydrogen atoms in the lattice, should be considered.

It is well established that hydrogen may be trapped at particular defect sites such as inclusions, participates, grain boundaries, dislocations or helium bubbles. Direct evidence such as that obtained by auto-radiography techniques [6, 7] and indirect evidence as in permeation experiments [8] or deuterium depth profile measurements [9, 10] are numerous. These results even have allowed the drawing of various classifications of possible trap types in steel [11–13].

The purpose of the study present here is to suggest a model which explains trapping of hydrogen around or near helium bubbles. A detailed calculation based on the suggested model will describe the distribution of hydrogen around the bubbles. Since hydrogen trapping controls the distribution of hydrogen around the bubbles, understanding the trapping mechanism can lead to failure prediction [14].

2. Trapping mechanisms

Many studies [15–19] have been recently conducted to characterize the shape and dimension of the bubbles as well as to determine the helium density inside the bubbles. Transmission electron microscopy (TEM) observations [15–18] show a microstructure which contains many small spherical bubbles in diameter range of 1–2 nm. It was shown [16] that the helium gas bubbles lie on a superlattice having an fcc structure with principal axes aligned with those of the

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TABLE I Trapping energy of hydrogen atoms in various defects in iron

Trapping energy (eV)	Defects
0.03–0.10	Interstitials
0.25–0.31	Dislocations
0.40–0.50	Vacancies
0.60–0.70	Clusters
0.90–1.00	Inclusions (TiC)
0.70–0.90	Helium bubbles

metal matrix. The lattice constants base on diffraction from the superlattice plans for S.S. and nickel were found to be $\cong 6.5$ nm. Other experimental works [17, 19] estimate the density of helium inside the bubbles to be 2×10^{23} atoms cm^{-3}. Using the equation of state of helium to a very high pressure [20], we have found the pressure inside the bubbles to be about 3.5×10^{10} N m^{-2} (350 kbar), for which helium should be solid at room temperature.

Hydrogen trapping near or around helium bubbles was reported by various workers [15, 18, 21]. Linear ramp thermal desorption measurements and other experimental studies, show that the interaction energy between hydrogen atoms and helium bubbles is in the range of 0.7–0.9 eV $atom^{-1}$. It should be mentioned that these values are the extreme values measured and actually there is a spatial distribution of binding energies. This trapping energy measured is very strong relative to other defects such as vacancies, clusters, etc. (Table I).

Some workers [15, 21] have attempted to explain the trapping of hydrogen around helium bubbles and to relate it to a chemisorption-like interaction at the walls of the bubbles or to the strains surrounding the isolated bubbles. However, a detailed and quantitative model which can help to understand this trapping and to estimate the binding energy and other trapping parameters have not yet been established.

In this paper we suggest a model for hydrogen trapping around helium bubbles. According to this model hydrogen atoms are attracted towards the bubble due to positive stresses (tensile stresses) which exist around the bubble [22]. These high stresses resulted from the very high pressure (350 kbar) which exists inside the bubble.

The various stages which constitute the process of hydrogen trapping around helium bubbles are summarized in Table II. Table II also describes the experimental techniques used to obtain the data which was mentioned.

3. Theoretical analysis

In order to calculate the trapping energy of the hydrogen atoms around the helium bubbles we must first consider the stress field situation around the over-pressurized bubbles. Helium bubbles growth is controlled by self-trapping mechanisms in which helium atoms are attracted toward the bubble and metal atoms are rejected from the bubble. In this case which differs from the case of growth caused by pressure rise we cannot use a simple plastic theory for the calculation of the stress field near the bubble surface. We suggest a simplified, but consistent, analysis of this complex problem by using some assumptions.

First, we will examine the hydrostatic component of the stress tensor which is defined as

$$\sigma_h = 1/3\Sigma\sigma_{ii} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad (1)$$

where σ_{ii} are the three principal stresses (σ_{xx}, σ_{yy}, σ_{zz}) at a given point. From equilibrium consideration the hydrostatic stress, σ_h, in the bubble surface or actually, in the material-free surface which bounds the bubbles, is equal to the pressure which exists inside the bubble, i.e. $\sigma_{h(r=r_0)} = 3.5 \times 10^{10}$ N m^{-2} (r is the distance from the bubble centre, and r_0 is the bubble radius). We should mention that this is an approximate value since we neglect the anisotropy resulted from the lattice structure of the solid helium.

From the solution of plastic–elastic problem in the case of a spherical cavity [23] we can learn that each of the principal stresses around the bubble is given by the equation

$$\sigma_{ii(r)} = \sigma_{ii_{(r_0)}} \cdot (r_0/r)^3 \quad (2)$$

By substituting Equation 2 in Equation 1 we see that

TABLE II The various stages which constitute the process of hydrogen trapping around helium bubbles

Stage	Causes	Experimental techniques	Reference
(a) Helium production	α particle bombardment Irradiation (high energy neutrons) Tritium decay in container walls	Depth profiling using nuclear reaction analysis (NRA)	21
(b) Bubbles formation	Helium atoms migrate to create clusters and small bubbles (self-trapping mechanism)	TEM Vacuum ultra-violet Electron energy loss	15–18 19 17, 19
(c) Hydrogen sources	Gaseous $H_2(D_2, T_2)$ Aqueous solutions Hydrogen ions bombardment	Deuterium profiling using NRA	21
(d) Hydrogen trapping	Positive stresses (tensile stresses) around the bubbles	D_2 profiling (NRA) Surface release rate	10, 15, 18 21

that

$$\sigma_{h(r)} = \sigma_{h(r_0)} \cdot (r_0/r)^3 \quad (3)$$

This equation indicates that the stress field driving the trapping decays rapidly with the distance from the surface of the bubble. This fact enables us to neglect the effects of bubble–bubble interaction on the stress state of the matrix.

The interaction energy between the stress tensor in a certain point and hydrogen atom is given by [24]

$$\delta E = V_H \cdot \sigma_h \quad (4)$$

where V_H is the partial molar volume of hydrogen in the metal discussed.

Equation 4 can be used only when

$$\sigma_h/E \ll 1 \quad (5)$$

where E is the elastic modulus. In our case $\sigma_h/E = 0.17$ so we can use Equation 4.

The partial molar volume of hydrogen atoms in iron is $V_H = 2\,\text{cm}^3/\text{g}$ atom [25, 26]. We can also use this value for deuterium since the difference between the partial molar volume of these two isotopes is negligible (less than 10% from the measured value) [27]. This fact will allow us to compare our theoretical calculations with data obtained from experiments which were conducted with deuterium.

This model enables us to calculate the distribution of hydrogen around the bubbles as a function of the distance from the bubble. A similar study has been conducted for the case of hydrogen trapping near dislocations [25]. In the above mentioned study the calculations have been made by using Boltzmann approximation

$$C_r = C_\infty \exp(\delta E/kT) \quad (6)$$

where C_r is the hydrogen concentration at point r in which the hydrostatic stress is $\sigma_{h(r)}$ and C_∞ is the hydrogen concentration under conditions of $\sigma_h = 0$, T is the temperature and k is Boltzmann's constant.

An attempt to use the above approximation in our case will lead to wrong results because of the high binding energy involved. This fact forces us to use the accurate Fermi–Dirac equation

$$\frac{C_r}{1 - C_r} = \frac{C_\infty}{1 - C_\infty} \exp(\delta E/kT) \quad (7)$$

If we define an undimensional radius $r^* = r/r_0$ and substitute Equations 3 and 4 in Equation 7 gives

$$\frac{C_{r*}}{1 - C_{r*}} = \frac{C_\infty}{1 - C_\infty} \exp\left[\frac{A}{(r^*)^3}\right] \quad (8)$$

where $A = \delta E_{(r_0)}/kT$, and by applying simple arithmetic

$$C_{r*} = \frac{C_\infty \exp[A/(r^*)^3]}{1 + C_\infty\{\exp[A/(r^*)^3] - 1\}} \quad (9)$$

The trapped hydrogen quantity from the bubble surface to a point r, Q_r, can be calculated by integration of the concentration distribution function

$$Q_r = C_M \int_{r_0}^{r} C_r 4\pi r^2 \, dr \quad (10)$$

where $A = \delta E_{(r_0)}/kT$, and by applying simple arithmetic

$$Q_{r*} = 4\pi r_0^3 C_M \int_1^{r*} C_{r*}(r^*)^2 \, d(r^*) \quad (11)$$

where C_{r*} is defined by Equation 9 and where C_M is the metal atom concentration which is needed to convert the value of Q_{r*} to a number of atoms (for iron: $C_M = 8.48 \times 10^{22}$ atoms cm^{-3}). It is obvious that we can get also the total hydrogen content per bubble by integration from $r^* = 1$ to $r^* \to \infty$.

4. Results and discussion

Considering all the assumptions discussed above, and substituting the given values of V_H and σ_h in Equation 4 we get: $\delta E = 68.7$ kJ/g atom $= 0.71$ eV atom^{-1}.

The above result is the extreme trapping energy of hydrogen atom at the walls of a helium bubble. The results of the calculations performed using Equations 9 and 11 are given in Figs 1–3.

Fig. 1 shows the distribution of hydrogen concentrations as a function of the distance from the bubble surface, for several values of C_∞. It is shown that hydrogen concentration falls rapidly from a very high value and dropped to the same order of C_∞ as r^*

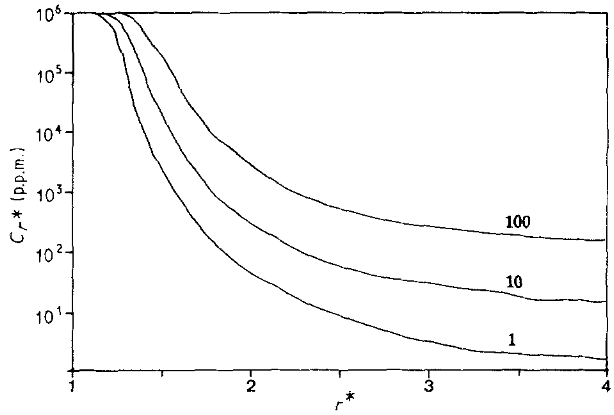

Figure 1 Hydrogen concentration against the undimensional radius r^*, for $C_\infty = 1$, 10 and 100 p.p.m.

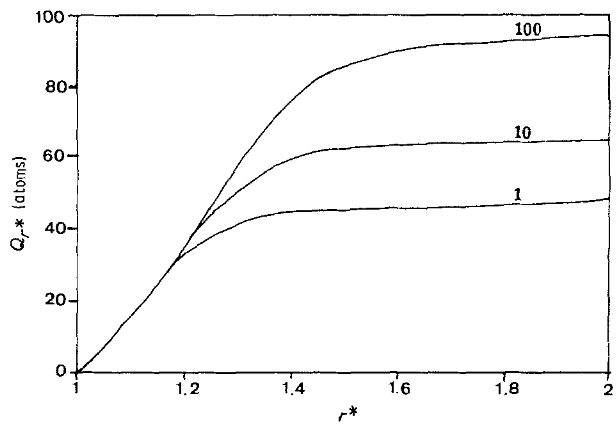

Figure 2 Hydrogen quantity against the unidimensional radius r^*, for $C_\infty = 1$, 10 and 100 p.p.m. The bubble radius was taken as $r_0 = 0.5$ nm.

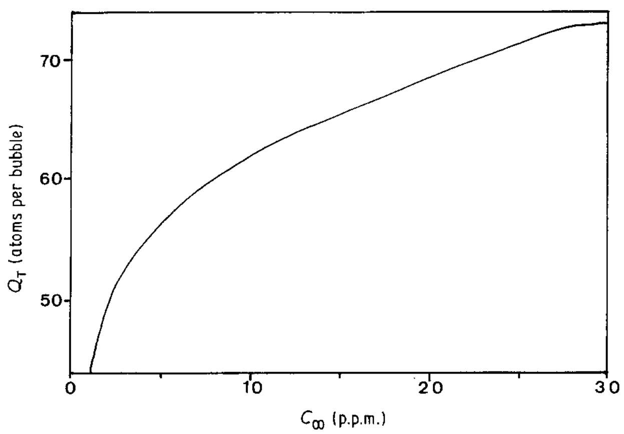

Figure 3 The total hydrogen quantity per bubble. Q_T against C_∞, in the case when $r_0 = 0.5$ nm.

reaches a value of only 4 (for $r_0 = 0.5$ nm this value will give $r = 2$ nm).

Calculations based on experimental measurements [16] show that the minimum bubbles spacing is $\cong 4.5$ nm. It is concluded that we can refer to a 1 nm diameter bubble as an isolated bubble and to neglect the effects of bubble–bubble interactions, as we actually assumed in Section 3.

The hydrogen quantity as a function of r^*, for the same values of C_∞ as in Fig. 1, is given in Fig. 2, for the case when $r_0 = 0.5$ nm. From the curves shown in this figure we can see as expected that most of the hydrogen atoms are trapped in a very small volume located very close to the bubble surface. The unidimensional radius r^* from which the hydrogen quantity is almost unchanged is effected by C_∞ and its values are 1.3, 1.4 and 1.5 for $C_\infty = 1$, 10 and 100 p.p.m., respectively.

The effect of C_∞ on the total hydrogen quantity around a 1 nm helium bubble is shown in Fig. 3. From this curve it is concluded that for a very wide range of C_∞ the total hydrogen quantity is in the range of 45–76 atoms per bubble; a result which is very consistent with experimental measurements [18].

Our conclusions show that the average hydrogen concentration in the volume which contains the helium bubbles is 4×10^3 p.p.m. in the case when C_∞ is only 1 p.p.m. The last result strongly shows that hydrogen trapping around helium bubbles must be treated as a massive factor and not only as a local and negligible one.

5. Conclusion

1. Hydrogen atoms are attracted towards helium bubbles and trapped around them due to positive stresses created by the very high pressure (350 kbar) existing inside the bubbles.

2. The extreme interaction energy between hydrogen atoms and helium bubble has been theoretically calculated and found to be 0.71 eV atom^{-1}.

3. Most of the hydrogen atoms are trapped in a very small volume located very close to the bubble surface.

4. The total hydrogen quantity was found to be in the range of 45–76 atoms per bubble for a very wide range of C_∞.

5. The good agreement between the theoretical results and data based on many experimental measurements reinforces the assumption underlying the very basis of the suggested mechanism.

6. The model proposed in this study can lead to better understanding of failure mechanisms.

Acknowledgement
The authors are indebted to R. Frenkel for his help in performing the numerical calculations.

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Received 21 March and accepted 28 July 1988