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# Influence of traps on the deuterium behaviour in the low activation martensitic steels F82H and Batman

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### Abstract

A time dependent permeation method is used to measure the permeability, diffusivity and solubility of deuterium in the low activation martensitic steels F82H and Batman. The measurements cover the temperature range from 373 to 743 K which includes the onset of deuterium trapping effects on diffusivity and solubility. The results are interpreted using a trapping model. The number of trap sites and their average energies for deuterium in F82H and Batman steels are determined.

#### 1. Introduction

The martensitic steel DIN 1.4914 (MArtensitic for NET, MANET) is a Nb bearing steel which has better swelling resistance, lower sensitivity to helium embrittlement and more suitable thermophysical properties than the austenitic stainless steel AISI 316L [1]. MANET is a candidate material for the first wall and structure for the demonstration fusion reactor DEMO. The martensitic steels F82H and Batman (Japanese and Italian, respectively) belong to the 7–10% Cr martensitic steel class that have undergone some modification in order to achieve better low-activation characteristics compared with those of MANET. These reduced activation martensitic (RAM) steels are still undergoing development and characterization from the point of view of their mechanical and physical properties.

In considering materials for fusion reactors a detailed understanding of the permeability, diffusivity and solubility of hydrogen and its isotopes through these materials is of crucial importance. The trapping of hydrogen isotopes in iron and steels (hydrogen may be trapped at particular defect sites such as inclusions, precipitates, grain boundaries or dislocations), has been invoked to explain differences in measured diffusivities in these materials during hydrogen isotopes absorption and desorption experiments at temperatures below 550 K. Furthermore, the retention of tritium in the structural materials of a fusion reactor will be affected by trapping and the consequent increase in the tritium inventory could affect adversely the prospects for breeding. The knowledge of the trapping parameters is required in fusion reactors in order to evaluate and control tritium retention in walls and structures when operated with deuterium/tritium plasmas. Numerical codes have been developed for the calculation of inventory, permeation and recycling of deuterium and tritium in fusion reactor design concepts in non steady state conditions [2-5]; two of the essential input data for these codes are the trapping parameters such as the number of trap sites and their average energies.

There has also been a continuing interest by many authors in the hydrogen trapping behaviour in metal, because its relation with the resistance or susceptibility to hydrogen embrittlement of steels. The specific causes of this phenomenon remain controversial, but there seems to be general agreement that hydrogen transport within the steel is a controlling factor and that modification of the transport rate by trapping is one of the most promising routes to improve hydrogen compatibility.

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Although the governing hydrogen transport and inventory parameters (permeability, diffusivity and solubility) in MANET are well known at temperatures above 570 K [6-8], no data are yet available for F82H and Batman steels. In addition, the solubilities and diffusivities of hydrogen in these steels are likely to be strongly influenced by trapping at temperatures below 570 K. The objectives set for this work are to measure the deuterium transport parameters (permeability, diffusivity and solubility) and to obtain experimental values for the number of trap sites and their average energies for deuterium in the F82H and Batman steels.

Measurements of permeation rates of deuterium in F82H and Batman specimens were performed using a gas permeation technique. Measurements were conducted over the temperature range 373-743 K with deuterium driving pressures in the range 0.5-100 kPa (5.0 to 1000 mbar).

#### 2. Experimental

The F82H and Batman samples consisted of discs 48 mm in diameter and 0.5-0.8 mm in thickness. They were supplied by ENEA (fusion division). In Table 1 the compositions of these steels are given. The membranes were machined from a slab of material and underwent the following heat treatment in order to produce a fully martensitic phase: austenising at 1313 K for 38 min, quenching to room temperature, tempering at 1023 K for 1 h, slow cooling to room temperature.

The method chosen for the permeation measurements during the current investigation was a gas-phase technique where, after evacuating the apparatus to a ultra high vacuum, so that both sides of a sample are initially in contact

Table 1

Chemical composition of F82H and Batman (wt%)

	F82H	Batman	
C	0.09	0.12	
Cr	7.8	8.67	
Ni	0.04	0.02	
Мо	< 0.01	0.01	
V	0.16	0.2	
Nb	< 0.01	0.002	
Si	0.13	0.025	
Mn	0.18	0.52	
S	0.003	0.002	
Р	0.004	0.006	
В	< 0.001	0.0064	
N	0.006	0.0057	
Co	-	0.01	
Та	0.02	_	
Al	< 0.01	0.0084	
Cu	< 0.007	0.0048	
W	2	1.43	
Ti	< 0.02	0.07	
Fe	balance	balance	

with vacuum, one side of the sample (the 'high pressure side') is instantaneously exposed to deuterium gas at a known, fixed pressure. Gas permeates through the sample and is released at the other side (the 'low pressure side'), where it causes a pressure rise in an initially evacuated, calibrated volume. The pressure rise is measured using a Baratron capacitance manometer with a full scale reading of 100 Pa (1 mbar). Since the volume is calibrated, either the pressure rise could be converted into an amount of gas in moles permeating through a unit area of the sample (Q(t)) or the rate of pressure rise could be converted into an amount of gas in moles permeating through unit area of the sample per second (J(t)). The permeation apparatus is constructed from standard stainless steel UHV components. Bakeout of the entire system is possible using heating tapes. Residual pressures lower than 10<sup>-6</sup> Pa

 $(10^{-8} \text{ mbar})$  prior to system bakeout at 573 K and less than  $10^{-7}$  Pa afterwards are obtained before any experiment. High pressure deuterium gas, with a nominal purity of 99.7%, is taken from a cylinder and admitted to the sample via two pressure controllers which enable the pressure to be set at any value between 0.1-150 kPa (1.0 to 1500 mbar). The sample is heated by a resistance furnace and the temperature may be set at values up to 773 K by a temperature controller with a thermocouple held in a well drilled into one of the flanges holding the sample, allowing a temperature stability of  $\pm 1$  K. An analysis of the high pressure gas and the permeated gas are made with a quadrupole mass spectrometer. Thus it is possible to check for possible contaminants and to distinguish permeation from outgassing. The volume of the low pressure side of the sample is measured by a gas expansion method (Sieverts' method) using a calibrated volume  $(9.13 \times 10^{-5})$ m<sup>3</sup>) which is permanently attached to the apparatus. A microcomputer interfaced to the equipment via a digital voltmeter is used for data storage and later processing. A detailed description of the method and the apparatus chosen for the present permeation measurements is given in Ref. [9]. Before the membranes were inserted into the permeation measuring equipment, both sides were mechanically polished. Thus, only oxide layers resulting from exposure to air at room temperature should be present.

#### 3. Theory

It is possible to obtain an expression for the permeation flux J (moles of gas  $m^{-2} s^{-1}$ ) of deuterium atoms through a membrane of uniform thickness d (m), in the case where the driving deuterium pressure is increased instantaneously from zero to p (Pa) (always very much higher than the pressure on the low pressure side) and where the initial concentration throughout the solid is zero (i.e., the experimental conditions used for the present work). Here J(t) is given by the one-dimensional solution of Fick's law and can be expressed as [10]

$$J(t) = \frac{DK_{S} p^{1/2}}{d} \times \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^{n} \exp\left[ -D \frac{n^{2} \pi^{2}}{d^{2}} t \right] \right], \qquad (1)$$

where D (m<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient of the membrane and  $K_s$  (mol m<sup>-3</sup> Pa<sup>-1/2</sup>) its Sieverts' constant. It is also assumed that the diffusion coefficient D is independent of concentration within the experimental range and no surface effects are present, i.e., the rate limiting process is diffusion through the material rather than surface reactions. At steady-state (i.e.,  $t \rightarrow \infty$ ) Eq. (1) becomes:  $J = P/dp^{1/2}$ , where  $P = DK_s$  (mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1/2</sup>) is defined as the permeability of the material. The total amount of gas, Q(t) moles of gas, which has permeated after time t, is given by

$$Q(t) = \int_0^t J(t') dt' = \frac{Pp^{1/2}}{d}t - \frac{Pp^{1/2}d}{6D} - \frac{2Pp^{1/2}d}{\pi^2 D}$$
$$\times \sum_{n=1}^\infty \frac{(-1)^n}{n^2} \exp\left(-D\frac{n^2\pi^2}{d^2}t\right). \tag{2}$$

Q(t) is obtained experimentally from the pressure rise data, using the ideal gas law  $(Q(t) = p({}^{t})V_{eff}R^{-1}T^{-1})$ .

As shown in Fig. 1, the values of P and D can be obtained by least squares fitting to the experimental data for each permeation run using Eq. (2) above. It is possible also to obtain P from the steady state behaviour and D from the so-called time lag  $t = d^2/6D$ , the time at which a line fitted to the asymptotic region of the pressure rise curve intersects the time axis [11,12]. Then, having obtained the permeability P and the diffusivity D, the Sieverts' constant is determined directly from the relationship  $K_{\rm S} = P/D$ .

Internal trapping is a process that delays the flow of deuterium in a solid via the capture and release of deuterium atoms by sites other than the ordinary solution ones. For a single type of trapping site uniformly distributed throughout the solid, it is assumed that the deuterium atoms in the solid are distributed either in the ordinary or lattice sites characterized by the normal enthalpy of solution  $E_s$  (J mol<sup>-1</sup>), or in the extraordinary or trapping sites with an energetically favoured environment for occupancy by the deuterium, with respect to an atmosphere of gaseous deuterium with which the metal may be brought into contact. As shown in Fig. 2,

$$E_{\rm t} = E_{\rm s} + \Delta E \tag{3}$$

represents the energy difference between a normal and a trapping site.  $\Delta E$  represents the energy change between a gas-phase and a trapped hydrogen atom. Generally the majority of sites are lattice sites. It should be noted that,



Fig. 1. Rate of pressure rise in sealed volume due to deuterium permeation through F82H steel at 382 K. The upstream deuterium pressure side was  $10^5$  Pa. The solid line represents the least squares fitting to the experimental data using Eq. (2). The broken line represents an estimation of the pressure rise using Eq. (2) and the lattice diffusivity  $D_1$  (assuming no trapping). It is evident that, the trapping affects the diffusivity (longer time lag) and leaves the permeability unaffected (same slope). In the insertion, the first 400 s are depicted.

contrary to the convention adopted by Oriani [13], here the energy  $E_t$  has been defined as positive to avoid possible confusion.

Exchange between these two states occurs through a reversible reaction with rate constants  $k_A$  (s<sup>-1</sup>) for trapping and  $k_B$  (s<sup>-1</sup>) for detrapping [14]. The trapping rate,  $k_A$ , is defined as to  $\nu \exp[(-E' - E_d)/RT]$ , whereas the detrapping rate  $k_B$  is equal to  $\nu \exp[(-E_t - E_d - E')/RT]$  [15]. The term  $E_d$  is the energy barrier between normal lattice sites, while that between a normal site and a trap-



Fig. 2. Energy model for trapping sites. The energies  $E_s$  and  $E_d$  are related to solution in the solid (enthalpy of solution) and lattice diffusion, respectively, whereas E' and  $E_t$  are related to trapping.

ping site is taken to be increased by a further energy E'.  $\nu$  $(s^{-1})$  is the vibrational frequency for trapped deuterium and R is the molar gas constant (8.314 J  $K^{-1}$  mol<sup>-1</sup>). These rate constants are assumed to vary with temperature, but not with the concentrations  $c_1 \pmod{m^{-3}}$  and  $c_t \pmod{m^{-3}}$  $m^{-3}$ ) of deuterium atoms in the lattice and in the trapping sites, respectively. If  $C_1 = c_1 2 N_A / N_1$  and  $C_t = c_1 2 N_A / N_t$ are the fractions of available sites occupied in the lattice and in traps, respectively,  $(N_1 \text{ and } N_1 \text{ are the number of } N_1 \text{ are the number of } N_1 \text{ are the number of } N_1 \text{ and } N_2 \text{ are the number of } N_1 \text{ are the number of } N_1 \text{ and } N_2 \text{ are the number of } N_1 \text{ and } N_2 \text{ are the number of } N_2 \text{ are the numb$ lattice and trapping sites per unit volume, respectively and  $N_{\rm A}$  is Avogadro's number), the variation in time of  $C_{\rm t}$  is the difference between a trapping and a detrapping term. The former is proportional, through  $k_A$ , to  $C_1$  and to the fraction of unoccupied trapping sites  $1 - C_t$ . The latter is similarly proportional to  $C_1$  multiplied by a correction factor representing the fraction of available solution sites,  $1 - C_1/C_s$ , where  $C_s$  is the saturation concentration. The rate equation is

$$\frac{\partial C_{t}}{\partial t} = k_{\rm A} C_{\rm I} (1 - C_{\rm t}) - k_{\rm B} C_{\rm t} \left( 1 - \frac{C_{\rm t}}{C_{\rm s}} \right). \tag{4}$$

Here, the irreversible trapping sites, which are described by setting  $k_{\rm B,i} = 0$ , are not considered, because  $T \ge 373$  K during the present investigation. Irreversible means that the traps are so deep that the time constants for release are too long to be measured during an experiment. Irreversible traps have been defined by Oriani [13] as traps where  $E_t > 67$  kJ/mol and thus,  $k_{\rm B,i} \approx 0$  at room temperature. The continuity equation becomes

$$\frac{\partial(c_1 + c_t)}{\partial t} + \frac{\partial J}{\partial x} = 0.$$
 (5)

It is evident that the effect of trapping is to increase the deuterium uptake by providing additional sites to accommodate deuterium and to increase the time necessary for deuterium to move into the solid, therefore creating an apparent decrease of the diffusivity. In other words, the effective diffusion coefficient  $D_{eff}$  measured when trapping is present is smaller than  $D_1$ , where  $D_1$  is the diffusivity of deuterium in the lattice (see Fig. 1). On the other hand, trapping does not affect the steady state permeation through the membrane. The steady state permeation flux J across the membrane is always given by Eq. (1) and does not depend on the trapping parameters  $N_i$ ,  $k_A$  and  $k_B$ . Then we can write Fick's first law for the flux J in terms of the occupied lattice sites exclusively:

$$J = -D_1 \frac{\partial c_1}{\partial x}.$$
 (6)

The diffusion equation for a system exhibiting trapping can be written as

$$\frac{\partial c_1}{\partial x} = D_1 \frac{\partial^2 c_1}{\partial x^2} - \frac{\partial c_t}{\partial t}.$$
(7)

The system of Eqs. (4) and (7) is nonlinear owing to the product  $C_1C_t$  and can only be solved numerically.

At equilibrium  $(\partial/\partial t = 0)$ , the effect of trapping on the solubility can be found by Eq. (4):

$$C_{t,eq} = \frac{k_A C_{1,eq}}{k_B + (k_A - (k_B / C_s) C_{1,eq}}.$$
 (8)

For low mobile concentration and low trap occupation, i.e., if  $C_1 < 1$  and  $C_t < 1$ , at equilibrium, Eq. (4) becomes

$$C_{\rm t,eq} = \frac{k_{\rm A}}{k_{\rm B}} C_{\rm l,eq} \tag{9}$$

and the total concentration  $c_{eq}$  is then

$$c_{\rm eq} = c_{1,\rm eq} + c_{\rm t,eq} = c_{1,\rm eq} \left( 1 + \frac{N_{\rm t} k_{\rm A}}{N_{\rm l} k_{\rm B}} \right)$$
(10)

or, using the definition of  $k_{\rm A}$  and  $k_{\rm B}$ ,

$$c_{\rm eq} = c_{1,\rm eq} \left[ 1 + \frac{N_{\rm t}}{N_{\rm l}} \exp\left(\frac{E_{\rm t}}{RT}\right) \right]. \tag{11}$$

If an effective Sieverts' constant is defined as  $K_{\text{S,eff}} = c_{\text{eq}}/p^{1/2}$ , since the permeability is not affected by trapping,  $(P = D_1 K_{\text{s,l}} = D_{\text{eff}} K_{\text{S,eff}}$  and  $K_{\text{S,l}} = c_{1,\text{eq}}/p^{1/2})$ , the effective diffusivity is

$$D_{\rm eff} = D_1 \frac{K_{\rm S,1}}{K_{\rm S,eff}} = \frac{D_1}{\left[1 + (N_t/N_1)\exp(E_t/RT)\right]}.$$
 (12)

Eqs. (11) and (12) are the relations for the effective concentration and diffusivity arrived at in Oriani's work [13]. It can be seen from Eq. (12) that at high enough temperatures  $D_{\rm eff} \approx D_1$ , but when the temperature is decreased,  $D_{eff}$  starts to fall below the value of  $D_1$ . Note that the temperature at which this occurs depends on both  $E_{t}$ and  $N_t/N_1$ . Eventually the exponential dependence starts to dominate the denominator and again an Arrhenius behaviour is obtained, but with an activation energy increased by  $E_t$ . Eqs. (11) and (12) describe correctly the transition region and the region where, although most of the deuterium is in the traps, only a small fraction of the traps are filled. Here, it should be noted that if all traps have been filled, i.e.,  $C_t \rightarrow 1$ , the total concentration gradient again becomes identical to the gradient of  $c_1$  and the effective diffusion coefficient approaches  $D_1$ .

#### 4. Results and discussion

All permeation measurements described in this section are performed using a deuterium gas with the following impurity content:  $H_2O = 2$  vppm,  $O_2 = 2$  vppm and  $N_2 =$ 20 vppm. The results for F82H and Batman in comparison with MANET II [8] are presented by Arrhenius plots of effective diffusivity, permeability and, hence, values for Sieverts' constant in Figs. 3–5, respectively. The measurements in these figures were determined using a driving pressure, i.e., the pressure on the high pressure side of the apparatus, of 100 kPa. Besides, other permeation measure-



Fig. 3. Arrhenius plot of deuterium diffusivities for F82H and Batman.

ments with deuterium driving pressures in the range  $30-10^5$  Pa were performed, but no significant difference in *D*, *P* and  $K_S$  values, at any temperatures of the present temperature interval (373-743 K), were observed.

Occasionally during the permeation measurements, a small decrease of permeability and diffusivity values was noted, especially at high temperature (743 K). Every time this phenomenon has been observed, due to a build-up of an oxide on the surface during the permeation, the sample has been taken out of the rig and both its sides have been mechanically polished. In fact, the input and output surface conditions must be rigorously controlled to preclude surface impedance to permeation that can affect the determination of diffusivity and permeability values, especially at low temperatures. It is evident from the results shown in



Fig. 4. Arrhenius plot of deuterium permeabilities for F82H and Batman.



Fig. 5. Arrhenius plot of deuterium Sieverts' constants for F82H and Batman.

Fig. 3 that the measured diffusion coefficients for all the martensitic steels, in the lower part of the present temperature interval (373-523 K), drop sharply below the broken lines representing the data at higher temperatures (633-743 K). Therefore, it may be assumed that, in this high temperature range, the trapping effect becomes negligible and  $D_{\rm eff}$  becomes  $D_1$ . Thus, the increase in the activation energy of  $D_{\rm eff}$  at lower temperatures is most probably a result of trapping as predicted by Eq. (12). It can be seen also that the values of permeability can be described by an Arrhenius straight line in the present temperature interval. This result arises from the fact that the values of permeabilities have been estimated from the steady part of the time dependent increase of pressure on the low pressure side of the sample, i.e., when the trapped population has reached equilibrium and, thus, does not affect any further the flux of deuterium through the sample. The contrasting behaviour of the independently measured values of P and D<sub>eff</sub> provides remarkably convincing proof of the applicability of Oriani's model to the present investigation.

As expected, few differences in the hydrogen transport lattice parameters are found among these metals because they belong to the same class of martensitic steels. The Arrhenius expressions for the deuterium permeability obtained from a fitting to the whole temperature range, lattice diffusivity  $D_1$  and lattice Sieverts' constant values  $K_{S,I}$  are as follows:

F82H:

$$P = 3.9 \times 10^{-8} \exp(-40710/RT)$$
  
(mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1/2</sup>),  
$$D_1 = 1.07 \times 10^{-7} \exp(-13950/RT) \text{ (m}^2 \text{ s}^{-1}\text{)},$$
  
$$K_{S,1} = 0.377 \exp(-26880/RT) \text{ (mol m}^{-3} \text{ Pa}^{-1/2}\text{)};$$
(13)

Batman:

$$P = 4.7 \times 10^{-8} \exp(-40980/RT)$$
(mol m<sup>-1</sup> s<sup>-1</sup> Pa<sup>-1/2</sup>),  

$$D_1 = 1.9 \times 10^{-7} \exp(-15190/RT) \text{ (m}^2 \text{ s}^{-1}\text{)},$$

$$K_{S,1} = 0.198 \exp(-24703/RT) \text{ (mol m}^{-3} \text{ Pa}^{-1/2}\text{)}.$$
(14)

The values of  $E_t$  and  $N_t/N_1$  may be estimated, using Eq. (14), by a non-linear least square fitting of the experimental data  $D_{\rm eff}$  onto the theoretical curve Eq. (12). In Fig. 3, either for F82H or for Batman, the fit is the curve that links the data of both temperature regimes. For such evaluation the following hypotheses have been made:

— The concentration of lattice sites is  $5.2 \times 10^{29}$  m<sup>-3</sup>, this value is based on the assumption that, in bcc iron, there are 6 tetrahedral lattice sites per host atom [16,17].

— The diffusivity of the lattice has been taken to be equal to the diffusivity obtained using the data at high temperatures (T > 573K) where the trapping effects are negligible.

The evaluation of the trapping sites and their binding energy was made using the diffusivity data. The values obtained for these two parameters are reported in Table 2. An estimation of the trapping parameters was also done using the solubility data. However, this is less accurate because the solubility is not measured directly by the experimental procedure but is obtained by combining permeability and diffusivity data. Using Eq. (8) with  $C_1 \ll 1$ there is an estimation of  $C_t$ ,  $C_1$  and  $c_1/c_t$  values based on data of Fig. 3 in Table 3. It is evident from the table that, at high temperatures T > 573 K,  $c_1 \gg c_t$  and therefore, this supports the approximation made for  $D_1$ , i.e.,  $D_1$  is obtained from the high temperature range only.

Some published results [18] for the trapping energy in various types of trap in ferritic steels are given in Table 4. In the grain boundary category, the traps with an activation energy of 59 kJ/mol relate to high-angle grain boundaries, whereas the traps with an activation energy of 32 kJ/mol to low-angle grain boundaries [15]. The interfaces between the second phase particles and the matrix in which they have been precipitated have the highest trapping energy, whereas the second largest values are for grain boundaries and the least effective traps are interstitial N and C atoms or substitutional Cr, Mo, V and Mn atoms. It is worth noticing that, substitutional elements which are located to

 Table 2

 Trapping parameters for MANET II [8], F82H and Batman.

	MANET II	F82H	Batman
$\overline{N_{t}}$	$1.5 \times 10^{25}$ sites/m <sup>3</sup>	$1.6 \times 10^{23}$ sites/m <sup>3</sup>	$8.6 \times 10^{24}$ sites/m <sup>3</sup>
$E_t$	48 500 J/mol	55938 J/mol	43175 J/mol
$E_{\rm d}$	13210 J/mol	13950 J/mol	15190 J/mol

Table 3

Estimation of  $C_t$ ,  $C_1$  and  $c_1/c_t$  values based on the data of Fig. 2.  $C_1$  and  $C_t$  are the fractions of available sites occupied in the lattice and in traps, respectively.  $c_1/c_t$  is the ratio between the deuterium atoms in the lattice and traps sites

Temp. (K)	F82H			Batman		
	C <sub>t</sub>	C	$c_1/c_t$	$\overline{C_{t}}$	<i>C</i> <sub>1</sub>	$c_1/c_1$
373	0.6	$2.4 \times 10^{-8}$	0.1	0.027	$2.5 \times 10^{-8}$	0.056
473	0.18	$1.5 \times 10^{-7}$	2.6	0.008	1.4×10 <sup>-7</sup>	1.1
573	0.058	$4.9 \times 10^{-7}$	27	0.003	$4 \times 10^{-7}$	7.1
673	0.024	$1.1 \times 10^{-6}$	149	0.002	$8.7 \times 10^{-7}$	27.1
773	0.012	$2.1 \times 10^{-6}$	535	0.001	$1.5 \times 10^{-6}$	73.5

the right of iron in the periodic of the elements (Ni) should repel hydrogen when present in solid solution, while elements to the left of iron should trap hydrogen. This is confirmed by the literature [21], which indicate that substitutional Ni atoms are repulsive trap in an iron lattice. Single vacancies should only exist in significant quantities in irradiated materials. A number of authors [27,28] has suggested that lattice defects that have a coherent interface with the surrounding matrix such as dislocations and fine precipitates in the early stages of formation, have a lower trapping energy than, for example, fully coarsened second phase particles which have incoherent boundaries with the metal lattice. After the heat treatment was applied to the present samples, the main trapping places are probably grain boundaries, interstitial atoms and particle interfaces but since the calculated  $E_t$  value for F82H and Batman are less than any of the literature values in Table 4 for high-angle grain boundaries or precipitates and higher than

Table 4

Trapping energies for hydrogen in ferritic steels and iron alloys

Type of trap	Trapping energy (kJ/mol)	Ref.	
Single vacancy	50, 46.6 and 78.3	[19,20]	
Atomic traps			
Substitutional Cr atoms	26.1	[21]	
Substitutional Mo atoms	27	[21]	
Substitutional V atoms	27	[21]	
Substitutional Mn atoms	10.6	[21]	
Interstitial C atoms	3.3	[22]	
Substitutional Ni atoms	-11.6	[21]	
Interstitial N atoms	12.5	[22]	
Grain boundaries	59, 32	[15,23]	
Second phase particles (surfaces)			
AlN	65	[24]	
$\epsilon$ carbide (Fe <sub>2-3</sub> C)	65	[25]	
MnS	72	[25]	
Dislocation	20 to 30	[26]	

those for interstitial atoms and low-angle grain boundaries, it is difficult to indicate which trap is predominant. Here it is useful to compare the present measurements with the work of Benamati et al. [29] on the hydrogen diffusivity of MANET II using Devanathan's electrochemical technique. These investigators calculated a trapping energy of 22.4 kJ/mol. However, these authors failed to measure the trapping energies of traps such as fully coarsened particles since, in the low temperature region of their investigation (278-343 K), such traps were considered to be irreversible because of their depths, i.e., the detrapping rate was too low to allow equilibrium between the trapped and nontrapped populations to occur during a measurement. In the present work, such measurements are possible and they seem to suggest that in F82H and Batman the trapping is more likely to be associated with the lath boundaries (martensitic laths), with fine coherent Fe<sub>3</sub>C precipitates and with dislocations.

#### 5. Conclusion

The effect of trapping on the diffusivity, solubility and permeability of deuterium in F82H and Batman was investigated using a gas phase technique employing a step change in pressure. The data were fitted very well using Oriani's model and the trapping parameters such as the number of trap sites and their average energies were determined. The surfaces of samples were kept under control for the presence of oxide layers.

The trapping process in both F82H and Batman is very pronounced in the low temperature range up to 523 K. The results obtained can be used as a reference for future evaluation of the effects of the presence of hydrogen in steels damaged by radiation.

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