The diffusivity and solubility of deuterium in a high chromium martensitic steel

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Abstract

The permeability, diffusivity and solubility of deuterium in the martensitic stainless steel MANET II have been studied in the temperature range 194–465°C by applying a time dependent gas-phase permeation technique. It was found that the temperature dependence of diffusivity and solubility could not be described by a simple Arrhenius expression over the entire temperature range investigated. At lower temperatures (below about 330°C) the diffusivity was found to be greatly reduced by the effects of trapping. Oriani's model has been applied to obtain the trapping energy and number density of the traps as well as the relative amounts of deuterium dissolved at lattice and trap sites. It is suggested that the most likely sites for trapping are at interfaces between the martensitic laths and between second phase particles and the surrounding metal matrix.

1. Introduction

MANET, a modified form of the high chromium martensitic steel DIN 1.4914, was originally developed for possible use as a structural material in the NET fusion project. Although it is no longer being considered for this application, this type of high chromium martensitic steel has been selected as a reference material for breeder blanket components in the demonstration power reactor DEMO [1]. The material has been made available in a number of very similar forms (MANET I, MANET II, etc.) which differ only slightly in composition. Such heat-treatable high chromium martensitic steels have strengths comparable or even superior to austenitic stainless steels at temperatures up to approximately 500°C. The main advantage that these particular types of steels has over austenitic stainless steels is a greater resistance to the effects of radiation damage, particularly irradiation-induced void swelling and high temperature helium embrittlement. A major problem for the designers of fusion reactors is the necessity to control both the leakage of tritium by diffusion and the total inventory of dissolved tritium in steel components at elevated temperature [2]. For this reason it is important to obtain parameters such as the permeability, diffusivity and solubility of hydrogen isotopes in candidate materials for fusion reactor components. A number of studies of these parameters have been carried out for MANET [3,4]. However, little attention has so far been paid to the effects of trapping of hydrogen isotopes at lattice defects such as grain boundaries and second phase particles, despite the fact that trapping can have a very great effect on the total solubility and the effective diffusivity of hydrogen isotopes in steels, particularly at temperatures below approximately 300°C.

The aim of the present paper is to give a more detailed explanation of the behaviour of deuterium diffusing through a steel with a martensitic structure. The microstructure here plays an important role mainly because of the increased concentration of crystal defects such as lath boundaries which provide trapping sites and which, in turn, cause an excess solubility of hydrogen and its isotopes at certain temperatures. In particular, it was intended to obtain values of the trapping energy and density of trap sites in MANET II steel using the theory of Oriani [5]. To achieve this, both the permeability and diffusivity were

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measured simultaneously over the temperature range which covers the onset of trapping.

2. Material and experimental technique

The chemical composition of the investigated steel is given in Table 1. A flat disk with thickness 0.5 mm and diameter 48 mm was machined from a sheet of the material supplied by Forschungszentrum Karlsruhe. It was heat treated in vacuum following the regime recommended by the producer (Saarstahl) in order to produce a tempered fully martensitic structure. The annealing process involved heating at 970°C for 2 h, austenizing at 1075°C for 30 min, quenching to room temperature and final tempering at 750°C for 2 h. The surfaces of the sample were abraded using a sequence of finer and finer grades of SiC abrasive paper and then mechanically polished in two stages with 6 μm and 1 μm diamond paste. The specimen was rinsed and then degreased by a proprietary solvent and ethanol before insertion into the permeation equipment.

Deuterium permeation rates through the sample were measured with a pressure of 5×10^4 Pa in the temperature range 194–465°C following the procedure described in detail by Forcey et al. [3]. Briefly, the method is a gas phase technique where the sample is held at a steady controlled temperature between two initially evacuated volumes. Into one volume (the 'high pressure side') deuterium is introduced at a fixed pressure. Gas permeates though the sample into the 'low pressure side' where the resulting pressure increase is measured. The main parameters measured are the steady-state permeation rate and the time-lag, which is the characteristic time from the start of the experiment for steady-state conditions to be approached.

For the steady-state permeation through a single layer barrier assuming that the rate limiting process is diffusion through the material rather than surface reactions, the relation between the permeation rate and the diffusion coefficient of the permeating gas is given by Richardson's law:

$$J = (Dk_s/d)(p_h^{1/2} - p_l^{1/2}) \ (\mathrm{mol \ m^{-2} \ s^{-1}}), \qquad (1)$$

where J is the permeation rate of gas per unit area; d is the thickness of the specimen; D is the heterodiffusion coefficient of the gas in the material (or diffusivity); k_s is

Sieverts' constant; and p_h, p_l are the gas pressures on the high and low pressure sides of the sample, respectively. P, the permeation coefficient (or permeability) of the material, is defined by $P = Dk_s$ (in units mol m^{-1} s^{-1} Pa$^{-1/2}$). Usually experiments are performed with the conditions $p_h \gg p_l$ so Eq. (1) becomes

$$J = Pp_h^{1/2}/d. \qquad (2)$$

Using the experimental method with a step change in pressure on the high pressure side [3], the diffusion coefficient D could be experimentally obtained from the measured time lag t_l and the thickness d:

$$t_l = d^2/6D. \qquad (3)$$

The concentration of the dissolved deuterium (or solubility), c, in equilibrium with the gas at pressure p is given by the following equation:

$$c = k_s p^{1/2} \ (\mathrm{mol/m^3}). \qquad (4)$$

In the present experiments, P and D are measured and Sieverts' constant determined by the expression $k_s = P/D$. Under many conditions P, D and k_s are found to vary with temperature in an Arrhenius manner. However, when trapping occurs, D and k_s may deviate from the Arrhenius expression.

The parameters of the trapping process can be estimated applying Oriani's model [5]. Here, the diffusivity calculated from the measured time lag is an effective value (D_{eff}) because it gives the relation between the deuterium flux and the gradient of the total concentration of the dissolved gas, c, through the sample thickness. Since the total concentration, c, includes the amount of gas atoms dissolved in the lattice interstices (c_L) plus the amount in the trapping sites (c_T), then when trapping is present D_{eff} is smaller than the intrinsic diffusivity of the metal lattice without traps. This model has been previously applied to the trapping of hydrogen in carbon steel [6]. The trapping of hydrogen isotopes may be understood by the consideration of the potential energy wells for the lattice interstices and trapping sites. Typically the energy of the ion dissolved in a trapping site will be lower by an amount ΔE_T in comparison with its energy when it is dissolved in a normal lattice position. ΔE_T is the so called trapping energy and depends on the character and parameters of the lattice defects or second phase particles acting as traps (note that in the present paper, contrary to the convention

Table 1
Chemical composition of MANET II (wt%); the balance is Fe

C	Cr	Ni	Mo	V	Nb	Si	Mn	S	P	B	N	Others
0.11	10.3	0.65	0.58	0.19	0.14	0.18	0.85	0.004	0.005	0.007	0.030	Al 0.012 Co 0.006 Cu 0.010 Zr 0.014

adopted by Oriani, the trapping energy will be defined as a positive value). Darken and Smith [7] assumed that during diffusion, a local equilibrium exists between the ions dissolved in normal lattice sites and in traps. This equilibrium may be characterised by an equilibrium constant K. Assuming that: both types of sites constitute finite populations; there is no interaction between the occupied sites; and only a small proportion of the lattice sites are occupied (i.e., $\theta_L \ll 1$), Oriani [5] suggested the following expression for K:

$$K = \frac{\theta_T}{\theta_L(1 - \theta_T)}, \tag{5}$$

where θ_L, θ_T are the fractions of the available sites occupied in the lattice and in the traps, respectively.

Now, if N_L and N_T represent the number density of lattice and trapping sites respectively, then $c_L = N_L\theta_L$ and $c_T = N_T\theta_T$ and the relation between the experimentally obtained effective diffusivity (D_{eff}) and the diffusivity in the lattice (D_L) is given as

$$D_{eff} = D_L \frac{dc_L}{dc} = D_L\left[1 + N_T N_L K/(N_L + Kc_L)^2\right]^{-1}$$
$$= D_L c_L / \left[c_L + N_T\theta_T(1 - \theta_T)\right]. \tag{6}$$

Assuming that the frequencies of vibration in both lattice and trap sites are identical, then neglecting the entropy factors, the following expression for K may be written:

$$K = \exp(\Delta E_T/RT) = \frac{\theta_T}{\theta_L(1 - \theta_T)}. \tag{7}$$

where R ($= 8.314$ J mol^{-1} K^{-1}) is the gas constant.

This expression for K may be used for solution of Eq. (6). For the case when only a small fraction of traps are occupied ($\theta_T \approx 0$), then Eq. (6) becomes

$$D_{eff} = D_L\left[1 + (N_T/N_L)\exp(\Delta E_T/RT)\right]^{-1}. \tag{8}$$

A similar expression can be written for the relation between the total solubility, c, on the high pressure side of the sample as determined by the experiment and the lattice solubility c_L:

$$c = c_L\left[1 + (N_T/N_L)\exp(\Delta E_T/RT)\right]. \tag{9}$$

It follows from Eq. (8) that at high enough temperature $D_{eff} \approx D_L$, but when the temperature is decreased, D_{eff} becomes smaller than D_L. The temperature at which it occurs depends both on ΔE_T and N_T/N_L. It also follows from Eqs. (8) and (9) that the permeability should be unaffected by trapping since the solubility and diffusivity are increased and decreased, respectively, by the same factor.

3. Experimental results and discussion

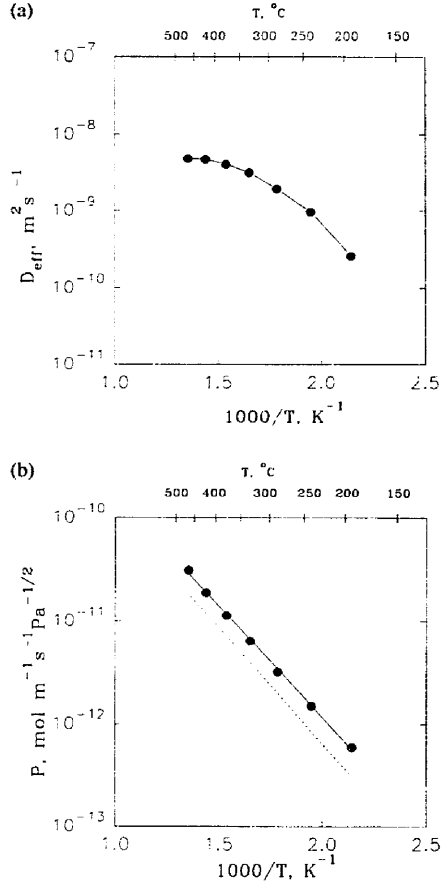Fig. 1 shows Arrhenius plots of the diffusivity and permeability calculated from the experimental data using

Fig. 1. The effective (measured) diffusivity (a) and permeability (b) of deuterium through MANET II steel. The solid line in (b) represents a fitted Arrhenius expression. The broken line is data for MANET I from Forcey et al. [3].

Eqs. (2) and (3). In Fig. 1(b) the permeability of MANET I from Forcey et al. [3] is plotted to compare with the present data. From Fig. 1(a), it is obvious that D_{eff} cannot be characterised by an Arrhenius expression with a single activation energy over the entire temperature range investigated. In the lower temperature region, the apparent activation energy for diffusion is greater than at higher temperature, behaviour which follows that predicted by trapping models such as Oriani's [5]. In contrast, Fig. 1(b) shows that the temperature dependence of the permeability, P, is well described by an Arrhenius expression $P = 2.57 \times$

$10^{-8} \exp(-41562/RT)$. As was stated above, the permeability is a parameter related to the steady state permeation process and, thus, does not depend on trapping. The contrasting behaviour of the permeability and effective diffusivity points to the trapping effect as being the most likely explanation for the observed results since other phenomena such as surface effects, which could also reduce the effective diffusivity would cause the permeability to deviate from the Arrhenius expression in the same way.

From Eq. (8) it follows that if the temperature dependence of the lattice diffusivity D_L is known, then by

Table 2
Values of the trapping energy ΔE_T, trap fraction N_T / N_L and the density of traps N_T

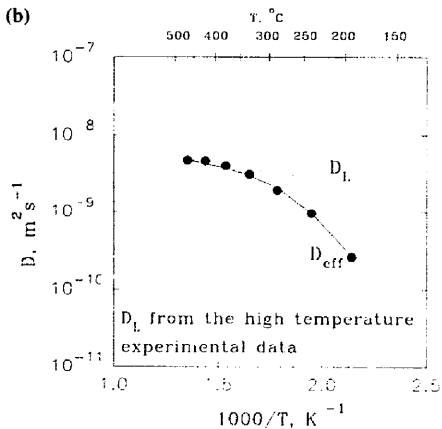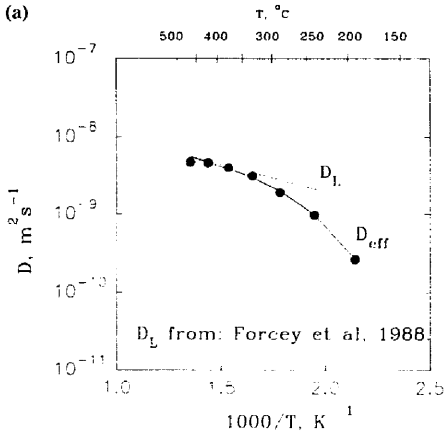| ΔE_T (kJ/mol)	N_T / N_L	N_T (m^{-3})	Calculated using D_L from:
59.3 (± 4 kJ/mol)	1.1×10^{-6}	5.7×10^{23}	Forcey et al. [3]
61.3 (± 3 kJ/mol)	1.2×10^{-6}	6.2×10^{23}	present high temperature experimental data

Fig. 2. The diffusivity data fitted (solid line) using the expression in Eq. (8). The broken lines represent the lattice diffusivity taken from Ref. [3] (a), and from extrapolating the high temperature data (b).
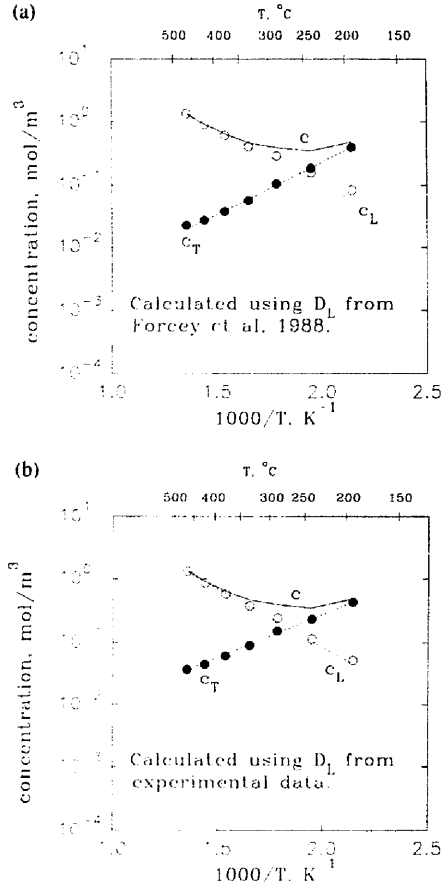

Fig. 3. The solubility of deuterium in the lattice c_L, in the traps c_T, and total solubility c, on the high pressure side of the sample (in contact with a deuterium pressure of 5×10^4 Pa). The values of c_L and c_T were calculated from trapping parameters obtained (a) using the lattice diffusivity taken from Ref. [3], and (b) using D_L from extrapolating the high temperature data.

applying a fitting procedure to the experimentally measured D_{eff}, the parameters ΔE_T and N_T/N_L can be obtained. In the absence of published data specifically for D_L in MANET II, in the present paper two different expressions have been used for D_L.

(a) $D_L = 5.07 \times 10^{-8} \exp(-13490/RT)$. This expression has been taken from the measurements of Forcey et al. [3] on the diffusivity of hydrogen through the very similar material MANET I (after correcting for the isotope effect by dividing the pre-exponential term in the original expression by $\sqrt{2}$);

(b) $D_L = 4.3 \times 10^{-8} \exp(-12999/RT)$. This expression is obtained by fitting an Arrhenius expression to the three highest temperature points in Fig. 1(a) (where it is reasonable to assume $D_{eff} \approx D_L$).

Fig. 2(a) and (b) show Arrhenius plots of the experimentally obtained effective diffusivities together with the D_L plots drawn according to the two above expressions. It can be seen in Fig. 2(a) that as temperature increases, the experimental data approach the line representing D_L taken from Ref. [3], suggesting that using this lattice diffusivity should give reasonable results for the trapping parameters. In both cases, the solid line between the experimental points is the curve fitted to the D_{eff} data using Eq. (8) with fitting parameters ΔE_T and N_T/N_L. It is obvious that both expressions for D_L lead to good fits to the experimental D_{eff} data. The fitted parameters ΔE_T and N_T/N_L are given in Table 2 where it can be seen that both approaches give very similar results.

A review of the relation between the values of ΔE_T and the character of the traps has been made by Forcey et al. [6]. Possible trap sites in metals include grain boundaries, second phase particles, interstitial impurity atoms, and dislocations. MANET II steel has a typical martensitic microstructure made up of a high density of thin laths and thus contains a high density of lath boundaries which could act as trapping sites. A typical value for the trapping energy of high angle grain boundaries in ferritic steels is

59 kJ/mol [8] whereas that for the interfaces between relatively coarse (effective size ≥ 10 microns) particles and the surrounding matrix is about 65 kJ/mol [9]. Other traps such as dislocations and impurity atoms have trapping energies below 30 kJ/mol [6]. The values of ΔE_T obtained in the present study of approximately 60 kJ/mol (± 4 kJ/mol) are consistent with those expected for trapping sites at grain boundaries and at the surfaces of coarse second phase particles. Thus, considering the measured trapping energy and the structure of the steel, the most obvious candidates for trapping sites are the interfaces between the martensitic laths, which represent a type of grain boundary. However, since there is a lack of published data specifically on the trapping energy of martensitic lath boundaries it is not possible at this stage to be certain about this point. Experiments performed by the SEM showed the presence of second phase particles with a size of about 10–15 microns. Characteristic X-ray microprobe analysis revealed that they probably are complex metallic carbides enriched with niobium. Therefore it may be assumed that beside the lath boundaries which may be the dominant trapping sites, the interfaces between the carbide particles and the surrounding matrix also contribute to the trapping effect.

In order to calculate the number density of traps from the ratio N_T/N_L, a value for N_L must be assumed. MANET retains its martensitic structure over the entire temperature range employed for the present measurements [10]. Hence a value of 5.2×10^{29} m^{-3} may be taken for N_L from the assumption that the martensitic steel is close to a bcc structure, where the deuterium should occupy only the tetrahedral interstitial positions [11,12]. The total solubility, c, at the high pressure side of the sample has been calculated from the experimental data according to Eq. (4) with the deuterium pressure 5×10^4 Pa. Then using the fitted parameters ΔE_T and N_T/N_L and applying Eq. (9), the amount c_L of the dissolved deuterium at different temperatures in the martensitic lattice has been estimated.

Table 3

Temperature dependence of total deuterium solubility, c, lattice solubility, c_L, and concentration of trapped deuterium, c_T, on the high pressure side of the sample (where the deuterium pressure is 5×10^4 Pa)

Temperature (°C)	c (mol/m^3)	Calculated using D_L from Forcey et al. [3]		Calculated using D_L from the high temperature experimental data	
		c_L (mol/m^3)	c_T (mol/m^3)	c_L (mol/m^3)	c_T (mol/m^3)
194	0.48	0.08	0.40	0.05	0.43
240	0.35	0.16	0.19	0.11	0.23
287	0.39	0.29	0.11	0.24	0.15
332	0.47	0.41	0.06	0.38	0.09
377	0.64	0.61	0.04	0.58	0.06
421	0.91	0.88	0.03	0.86	0.04
465	1.36	1.33	0.02	1.32	0.04

The amount c_T dissolved only in the traps has been calculated from $c_T = c - c_L$. The results obtained are shown in Fig. 3 and Table 3 (the calculations were performed twice using the two slightly different trapping parameters given in Table 2 – both sets of results are given). It is obvious that when displayed on an Arrhenius plot, both the solubility in the lattice, c_L, and the solubility in the traps, c_T, can be represented by straight lines with a negative and positive gradient, respectively. As a result, the total solubility, c, has a more complicated dependence on the temperature, changing slope from negative to positive as the temperature is decreased.

4. Conclusions

(1) The permeability and apparent diffusivity of deuterium in the martensitic stainless steel MANET II have been studied in the temperature range 194–465°C applying a time dependent gas-phase permeation method. The permeability, P, is well described by the Arrhenius expression $P = 2.57 \times 10^{-8} \exp(-41\,562/RT)$.

(2) The trapping process has been found to be very pronounced in the low temperature range (up to 330°C). The trapping parameters (trapping energy ΔE_T and density of trapping sites N_T) have been calculated using the model of Oriani [5]. The trapping energy was found to be 60 kJ/mol (± 4 kJ/mol), which is consistent with trapping occurring at grain boundaries, which may point to the interfaces between laths being the dominant traps. Alternatively, the surfaces of second phase particles also have trapping energies around the measured value.

(3) The solubility of deuterium in terms of the total amount and amount dissolved in the lattice and traps has been calculated and plotted for the temperature interval 194–465°C. It has been shown that the dependence on the temperature of the total solubility cannot be described by a simple Arrhenius expression.

(4) Because of the relatively high contribution of the volume of boundaries to the total volume, the trapping

effect of the lath boundaries must not be neglected when calculating tritium inventories in MANET components for fusion reactors. Second phase particles may also cause trapping. It should also be noted that in an operating fusion reactor, trapping sites such as point defects (vacancies and interstitials), voids, and helium clusters and bubbles, which are generated in structural materials by fast neutron irradiation, are likely to have a significant effect on the tritium inventory and diffusion rate. More research on the trapping parameters of such defects needs to be carried out if the behaviour of tritium in fusion reactors is to be accurately predicted.

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