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Journal of Nuclear Materials 367–370 (2007) 473–477

journal of nuclear materials

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Hydrogen transport and trapping in EUROFER'97

G.A. Esteban [a,*], A. Peña [a], I. Urra [a], F. Legarda [a], B. Riccardi [b]

[a] UPV-EHU, Department of Nuclear Engineering and Fluid Mechanics/E.T.S.I., 48013 Bilbao, Spain
[b] AssociazioneEURATOM-ENEA sulla Fusione, I-00044 Frascati, Rome, Italy

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Abstract

The gas evolution permeation technique has been used to investigate the interaction of hydrogen with the reduced activation ferritic–martensitic steel EUROFER'97. The measurements were performed over the temperature range of 376–724 K with hydrogen driving pressures ranging from 5×10^4 to 1.5×10^5 Pa. The resultant diffusive transport parameters are: a diffusivity of D ($\mathrm{m^2\,s^{-1}}$) $= 4.57 \times 10^{-7}\exp(-22.3(\mathrm{kJ\,mol^{-1}})/RT)$, a permeability of ϕ ($\mathrm{mol\,m^{-1}\,Pa^{-1/2}\,s^{-1}}$) $= 1.03 \times 10^{-8}\exp(-37.4(\mathrm{kJ\,mol^{-1}})/RT)$ and a Sieverts' constant of K_s ($\mathrm{mol\ m^{-3}\,Pa^{-1/2}}$) $= 2.25 \times 10^{-2}\exp(-15.1(\mathrm{kJ\,mol^{-1}})/RT)$. The resultant trapping parameters are: a trap density of $N^{\mathrm{t}} = 1.3 \times 10^{25}\,\mathrm{m^{-3}}$ and trapping energy of $E_\mathrm{t} = 43.2\,\mathrm{kJ\,mol^{-1}}$. The possible sources of trapping are analysed and the most probable current mechanism in EUROFER'97 postulated. All the hydrogen transport parameters obtained for EUROFER'97 are compared to the available data corresponding to several steels of the same kind.

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1. Introduction

EUROFER'97 is a reduced activation ferritic/martensitic (RAFM) steel considered to be a promising candidate for fusion reactor structural components [1]. Its elevated thermo-mechanical properties and its resistance to irradiation and activation properties are well characterized [2]. It has already been fabricated on an industrial scale to test some fusion components.

In order to have a complete characterization of the material, the interaction with hydrogen (H) isotopes must be analysed and characterized because H isotope transport within a fusion material will determine H inventory retention in the fusion components, permeation through structural walls to personnel working areas or H isotope recycling to plasma. All of these issues affect the radiological safety, the fuel economy and the plasma operation of any fusion reactor and have to be evaluated beforehand when studying its feasibility.

In this work, the diffusive H transport parameters of diffusivity, Sieverts' constant and permeability in EUROFER'97 have been experimentally measured by means of the gas evolution permeation technique. The trapping phenomena (i.e. the capacity of the microstructural defects of the material to trap H atoms) have been accounted for and characterised. The results are compared with those of other steels of the same kind and the resultant values are commented on in relation to the most probable physical phenomena.

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* Corresponding author. Tel.: +34 94 601 4272; fax: +34 94 601 4159.

E-mail address: gustavo.esteban@ehu.es (G.A. Esteban).

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doi:10.1016/j.jnucmat.2007.03.114

2. Experimental

The material studied is the RAFM steel of the 9CrWVTa type EUROFER'97 [1,2]. A bulk piece of the material has been used to manufacture thin discs (0.8 mm thick with 30 mm diameter). After the normalising heat treatment, the samples have been mechanically polished and their surface cleaned before insertion into the experimental rig.

The gas evolution permeation technique has been used to characterize the material. It is a well established experimental method that has been used to characterise other fusion materials [3,4]. Here it is briefly described for the sake of completeness.

The gas permeation technique (Fig. 1) permits the measurement of H transport parameters by characterizing the permeation of H through a membrane of the material. A single run of the experiment consists of holding one surface of the specimen at a certain high H pressure level to force H permeation through the specimen to a low pressure region. Two capacitance manometers (P1 and P2) record the pressure increase in the low pressure volume. This single run is repeated for different driving pressures and temperatures achieved with the pressure controller (PC) and the resistance furnace (F) respectively.

When the high driving pressure starts forcing permeation, the H permeation flux rises progressively with time until a steady-state permeation flux is reached. The modelling of the pressure increase $p(t)$ due to the gas permeation in the low-pressure region makes it possible to obtain the H transport properties of the material.

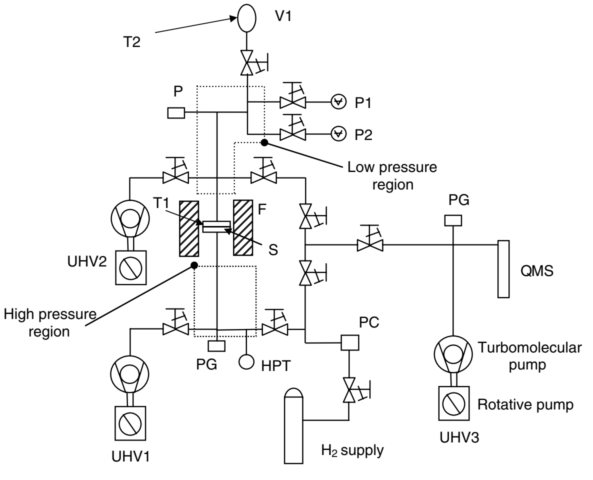

Fig. 1. Schematic view of the permeation facility. PG: penning gauge, F: furnace, PC: pressure controller, HPT: high-pressure transducer, QMS: quadrupole mass spectrometer, S: specimen, T1,T2: nickel/chromium–nickel thermocouples, P1, P2: capacitance manometers, UHV: ultra high vacuum pumping units and V1: calibrated volume.

3. Theory

The effective transport parameters of diffusivity (D_{eff}) and permeability (Φ) are evaluated for each experimental temperature using a non-linear least squares fitting the theoretical H pressure increase to the experimental increase measured with the capacitance manometers. The Sieverts' constant $K_{\mathrm{s,eff}}$ is derived from the quotient of the previous transport parameters, $K_{\mathrm{s,eff}} = \Phi/D_{\mathrm{eff}}$.

The theoretical expression for the pressure increase, $p(t)$, in the low pressure region is obtained by solving Fick's second law [5]

$$p(t) = \frac{RT_{\mathrm{eff}}}{V_{\mathrm{eff}}}\left[\frac{\Phi p_{\mathrm{h}}^{1/2}}{d}At - \frac{\Phi p_{\mathrm{h}}^{1/2}d}{6D_{\mathrm{eff}}}A - \frac{2\Phi p_{\mathrm{h}}^{1/2}d}{6D_{\mathrm{eff}}}A\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-D_{\mathrm{eff}}\frac{n^2\pi^2}{d^2}t\right)\right], \tag{1}$$

where R is the ideal gas constant (8.314 $\mathrm{JK}^{-1}\,\mathrm{mol}^{-1}$), T_{eff} and V_{eff} are the effective temperature and volume of the low pressure region, p_{h} the loading pressure, d the thickness of the sample and A the surface area of the sample.

'Trapping' is the process by which dissolved H atoms remain bound to some specific centres known as 'traps' (e.g. inclusions, dislocations, grain boundaries and precipitates). The effect of trapping on H transport is, on the one hand, the increase in the gas absorbed inventory that leads to an increase in the effective Sieverts' constant $K_{\mathrm{s,eff}}$ with respect to the lattice Sieverts' constant K_{s}. On the other hand, the dynamics of transport becomes slower, i.e. the effective diffusivity D_{eff} decreases with respect to the lattice diffusivity D. As a result the Arrhenius temperature dependence of the parameters has to be modified as follows:

$$K_{\mathrm{s,eff}} = K_{\mathrm{s}}(1 + (N_{\mathrm{t}}/N_{\mathrm{l}})\exp(E_{\mathrm{t}}/RT)), \tag{2}$$

$$D_{\mathrm{eff}} = D/(1 + (N_{\mathrm{t}}/N_{\mathrm{l}})\exp(E_{\mathrm{t}}/RT)), \tag{3}$$

where

$$K_{\mathrm{s}} = K_{\mathrm{s,0}}\exp(-E_{\mathrm{s}}/RT), \tag{4}$$

$$D = D_0\exp(-E_{\mathrm{d}}/RT), \tag{5}$$

where D_0 and $K_{\mathrm{s,0}}$ are the pre-exponential lattice diffusivity and pre-exponential lattice Sieverts' constant, and E_{d}, E_{s} the diffusion and solution energies. N_{t} (m^{-3}) is the trap site concentration, N_{l} (m^{-3}) is the lattice dissolution site concentration and E_{t} the trapping energy.

When the effective parameters for each experimental temperature have been obtained, another fitting routine is separately run with Eqs. (2)–(5) for the lattice parameters D_0, E_d, K_{s0} and E_s and trapping parameters E_t and N_t over the corresponding temperature range of influence. The value of 5.2×10^{29} sites m^{-3} is taken for the density of solution sites in the lattice N_l, assuming that the martensitic steel is close to a bcc structure where H occupies only the tetrahedral interstitial positions [6].

4. Results and discussion

A set of 17 individual tests have been carried out in the temperature range from 376 to 724 K and loading pressures from 5×10^4 to 1.5×10^5 Pa. The individual results with the respective temperature dependence (including trapping effects) are shown in Figs. 2–4 together with other steels. The Arrhenius parameters obtained for H in EUROFER'97 are

$$D(\mathrm{m^2\ s^{-1}}) = 4.57 \times 10^{-7} \exp(-22.3(\mathrm{kJ\ mol^{-1}})/RT),$$

$$\Phi\ (\mathrm{mol\ m^{-1}\ Pa^{-1/2}\ s^{-1}}) = 1.03 \times 10^{-8} \exp(-37.4\ (\mathrm{kJ\ mol^{-1}})/RT),$$

$$K_s\ (\mathrm{mol\ m^{-3}\ Pa^{-1/2}}) = 2.25 \times 10^{-2} \exp(-15.1\ (\mathrm{kJ\ mol^{-1}})/RT).$$

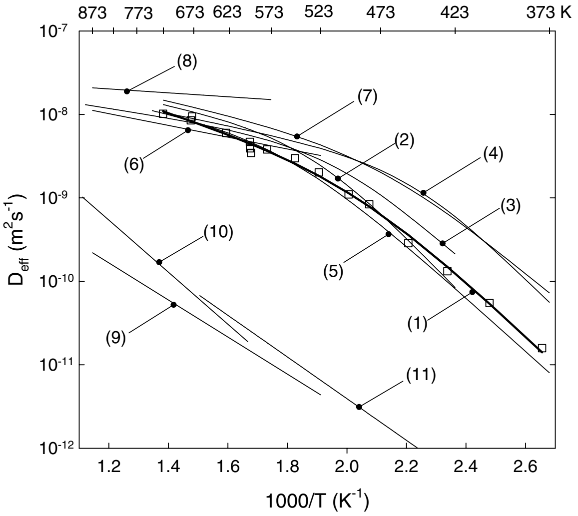

Fig. 2. Hydrogen diffusivity in EUROFER'97 compared with reference steels: (1) this work, (2) EUROFER'97 (deuterium) [7], (3) OPTIFER-IVb [8], (4) F82H (deuterium) [8], (5) and (6) MANET [8], (7) Batman (deuterium) [8], (8) α-Fe [8], (9) and (10) SS316L [8], (11) Incoloy 800 [4].

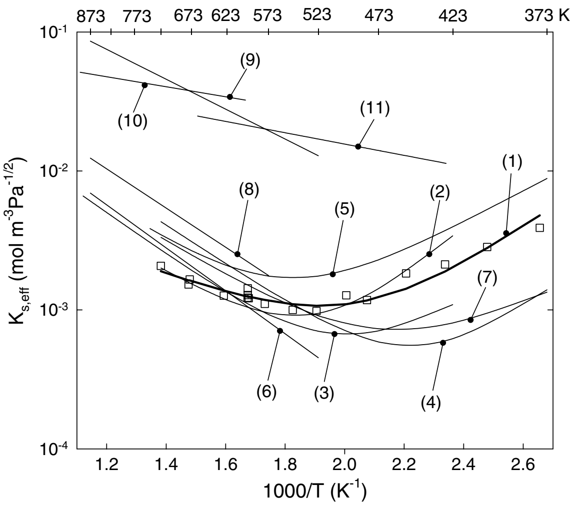

Fig. 3. Hydrogen Sieverts' constant in EUROFER'97 compared with reference steels: (1) this work, (2) EUROFER'97 (deuterium) [7], (3) OPTIFER-IVb [8], (4) F82H (deuterium) [8], (5) and (6) MANET [8], (7) Batman (deuterium) [8], (8) α-Fe [8], (9) and (10) SS316L [8], (11) Incoloy 800 [4].

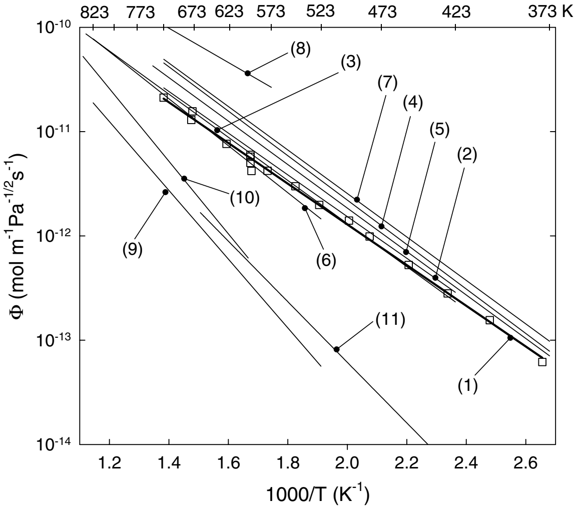

Fig. 4. Hydrogen permeability in EUROFER'97 compared with reference steels: (1) this work, (2) EUROFER'97 (deuterium) [7], (3) OPTIFER-IVb [8], (4) F82H (deuterium) [8], (5) and (6) MANET [8], (7) Batman (deuterium) [8], (8) α-Fe [8], (9) and (10) SS316L [8], (11) Incoloy 800 [4].

The trapping parameters are $N_t = 1.3 \times 10^{25}\ m^{-3}$ and $E_t = 43.2\ kJ\ mol^{-1}$.

Experiments have demonstrated that the H transport is limited by diffusive phenomena rather than surface effects, though the complete lack of surface effects can not be proven. At the end of the measuring campaign, a set of 4 tests were performed at the same temperature (597 K) and with different loading

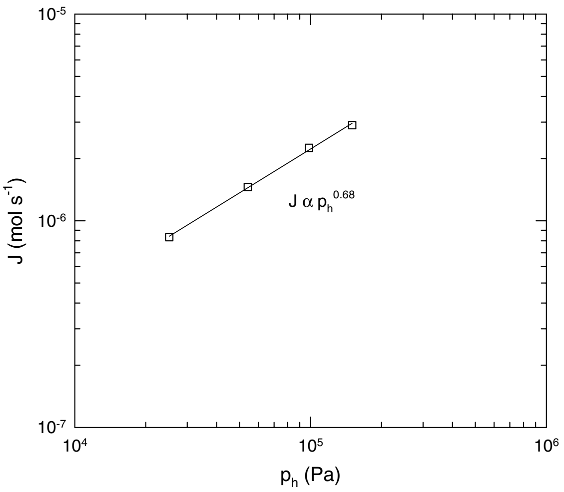

Fig. 5. Experimental hydrogen permeation flux in EUROFER’97, dependence on driving pressure.

pressures (Fig. 5). The power law relationship between the steady-state H flux (J) and the loading pressure (p_h) has an exponent of $n = 0.68$, which is closer to 0.5 (pure diffusive regime) rather than 1.0 (pure surface-limited regime). Further investigation on surface effects is in progress to get a complete description of H transport in this material.

All the transport parameters obtained for H in EUROFER’97 are within the collection of results obtained for other ferritic/martensitic steels (Figs. 2–4; Table 1). It is worth noting the similarity with the results corresponding to curves (2) and (3). These are the results for deuterium in EUROFER’97 obtained by Aiello et al. [7] and H in OPTIFER-IVb obtained by Esteban et al. [8] respectively.

Consistent with the general behaviour of ferritic/martensitic steels, EUROFER’97 is an endothermic material ($E_s > 0$) with respect to H dissolution and shows a lower Sieverts’ constant and higher diffusivity and permeability than the austenitic steels. The effect is related to the different crystal structure of the steels (bcc for the ferritic/martensitic steels, fcc for the austenitic steels).

The trapping phenomenon is noticeable at temperatures less than 623 K. In Figs. 2 and 3, the decrease in the effective diffusivity and increase of Sieverts’ constant at those temperatures is evident, presumably due to the additional H inventory retained in the trapping sites. The trapping parameters describing this phenomenon, the energy of trapping E_t and the trap density N_t, have similar values to some of the other ferritic/martensitic steels (Table 1). The value of $E_t = 43.2$ kJ/mol is close to 59 kJ/mol characteristic of high angle grain boundaries [8]. This fact indicates that the governing cause of trapping may be grain boundaries and/or the fine martensitic laths characteristic of this type of steel. Moreover, a higher trapping density N_t has been detected in EUROFER’97 in comparison to F82H, possibly due to a finer pre-austenite grain size and consequently higher internal grain boundary surface area [9].

5. Conclusions

The gas permeation technique has been used with EUROFER’97, a European candidate martensitic steel manufactured to be employed as a blanket structural material for future thermonuclear reactors. The H diffusive transport parameters have been obtained. All the results have been found congruent with the behaviour of the other ferritic/martensitic steels for fusion. The grain boundary surface area and the martensitic laths of the material have been identified as the possible origin of the H trapping effect. Further analysis on surface effects is necessary to achieve a complete description of hydrogen transport in the material.

Table 1
Experimental transport parameters for reference structural steels. (Activation energies in kJ mol^{-1})

Material	Φ_0	E_Φ	D_0	E_d	K_{s0}	E_s	N_t	E_t	$T(K)$	Refs.	Curve
EUROFER’97 (H_P)	1.03×10^{-8}	37.4	4.57×10^{-7}	22.3	0.023	15.1	1.3×10^{25}	43.2	373–723	T. W.	(1)
EUROFER 97 (H_D)	1.53×10^{-8}	38.3	1.50×10^{-7}	14.5	0.102	23.8	1.0×10^{24}	57.9	423–723	[7]	(2)
OPTIFER-IVb (H_P)	1.80×10^{-8}	39.6	5.49×10^{-8}	10.6	0.328	29.0	2.2×10^{24}	52.2	423–892	[8]	(3)
F82H (H_D)	4.03×10^{-8}	40.8	1.07×10^{-7}	13.9	0.377	26.9	1.6×10^{23}	55.9	373–723	[8]	(4)
MANET (H_P)	2.73×10^{-8}	39.9	1.01×10^{-7}	13.2	0.270	26.7	1.5×10^{25}	48.5	373–743	[8]	(5)
MANET (H_P)	2.93×10^{-8}	43.1	7.17×10^{-8}	13.5	0.409	29.6	–	–	523-873	[8]	(6)
Batman (H_D)	3.76×10^{-8}	39.9	1.90×10^{-7}	15.2	0.198	24.7	8.6×10^{24}	43.2	373–723	[8]	(7)
α-Fe (H_P)	1.97×10^{-8}	31.5	3.87×10^{-8}	4.5	0.510	27.0	4.2×10^{23}	69.0	573–873	[8]	(8)
SS316L (H_P)	1.12×10^{-7}	63.1	7.66×10^{-8}	42.5	1.468	20.6	–	–	523–873	[8]	(9)
SS316L (H_P)	3.86×10^{-7}	66.6	2.99×10^{-6}	59.7	0.129	6.9	–	–	600–900	[8]	(10)
Incoloy 800	3.94×10^{-8}	55.6	3.87×10^{-7}	47.8	0.102	7.8	–	–	427–664	[4]	(11)

Acknowledgements

This work has been funded by the University of the Basque Country. Most of the components of the experimental facility were transferred from the Joint Research Centre – Ispra site. The authors would like to thank Professor A. Perujo for making possible the transfer of the equipment and know-how to the Spanish University.

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