



Hydrogen isotope diffusive transport parameters in pure polycrystalline tungsten

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Abstract

An experimental time-dependent isovolumetric gas-phase desorption technique has been used to obtain the diffusive transport parameters diffusivity (D), Sieverts' constant (K_s) and permeability (Φ) as well as the trapping parameters trap site concentration (N_t) and trapping energy (E_t) of hydrogen isotopes (protium and deuterium) in tungsten. The study was performed in the 673 to 1073 K temperature range and with driving pressures from 1.3×10^4 to 10^5 Pa. The characteristic protium oscillation temperatures in the ground state $\theta = 893$ K and in the excited state $\theta^* = 2467$ K were calculated using the approximation of the ideal harmonic vibration of hydrogen isotope atoms in a unique type of solution site. The extrapolated tritium transport parameters obtained using these oscillation temperatures were: D ($\text{m}^2 \text{s}^{-1}$) = $5.34 \times 10^{-10} \exp(-11.2/RT)$, K_s ($\text{mol m}^{-3} \text{Pa}^{-1/2}$) = $2.25 \times 10^{-2} \exp(-27.8/RT)$, Φ ($\text{mol m}^{-1} \text{Pa}^{-1/2} \text{s}^{-1}$) = $1.20 \times 10^{-11} \exp(-3.9/RT)$, E_t (kJ mol^{-1}) = 100.5, N_t (sites m^{-3}) = 2.3×10^{23} . © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Besides other refractory materials, tungsten (W) has been identified as a suitable candidate plasma facing material for limiters and divertors of thermonuclear fusion reactors [1,2]. The excellent thermomechanical and physical properties of W (good thermal conductivity, high temperature strength, high energy threshold for physical sputtering, high melting point and low vapour pressure) makes it very attractive for its consideration as plasma facing high heat flux material. Furthermore, W does not form hydrides or co-deposits with tritium (H_T) at reference fusion wall operating conditions. The characterisation of the behaviour of the hydrogen (H) isotopes transport in W is needed in order to quantify

major fusion reactor design issues as safety, breeding feasibility, fuel economy and plasma stability. The slow transport kinetics of H isotopes in W make the experimental measurement of the H transport parameters arduous (long measurement times may be required and a certain measuring accuracy must be assured in order to avoid background noise). This feature is probably responsible for the lack of reliable H transport data in W. The existing results [3–6] show an enormous dispersion.

This work reports the results from an isovolumetric gas-phase desorption experiment (IDE) undertaken with protium (H_P) and deuterium (H_D) in W, in the temperature range from 673 to 1073 K and gas partial pressures from 1.3×10^4 to 10^5 Pa. The diffusive transport parameters (permeability Φ , effective diffusivity D_{eff} and effective Sieverts' constant $K_{s,\text{eff}}$) and the trapping parameters (the trap density N_t and the trapping activation energy E_t) of the H isotopes are obtained.

2. Review of existing data

Table 1 reports the main H diffusive transport data in W available in the literature [3–9]; the lattice Sieverts'

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Table 1

Experimental Sieverts' constants (K_{s0} , pre-exponential, E_s , solution energy), diffusivities (D_0 , pre-exponential, E_d , diffusion energy) and trapping parameters (N_t , trapping site density, E_t , trapping energy) of hydrogen in tungsten

Material	K_{s0} (mol m ⁻³ Pa ^{-1/2})	E_s (kJ mol ⁻¹)	D_0 (m ² s ⁻¹)	E_d (kJ mol ⁻¹)	T (K)	Ref.
Sintered and rolled cylinder	1.48	101.0	4.1×10^{-7}	37.7	1100–2400	[3]
Filament ribbon	1039 (at 2713 K)	267.9	7.2×10^{-8}	173.7	1510–1902	[4]
Poly and monocrystalline W tubes	1.22×10^{-4}	2.9	6.0×10^{-4}	103.4	400–1200	[5]
1 mm diameter commercial wire	–	–	8.1×10^{-6}	82.9	1055–1570	[6]
Single crystal	–	–	3.0×10^{-10}	24.1	300–900	
Wrought	–	–	1.5×10^{-10}	24.1	300–900	[7]
	E_t (kJ mol ⁻¹)	N_t (sites m ⁻³)				
<i>Single crystal</i>						
Natural traps	48.2	3.8×10^{26}				
Ion induced (1.5, 8 keV D ⁺)	120.6	1.0×10^{28}			300–900	[7]
<i>Wrought</i>						
Natural traps	48.2	6.3×10^{26}				
<i>Pure W rolled 0.3 mm foil</i>						
Weak defects	53.0	–			350–750	[8]
Ion induced (1.5, 8 keV D ⁺)	96.5	–				
<i>Polycrystalline</i>						
Unannealed	150.5	4.4×10^{24}				
Annealed at 1273 K	137.0	1.6×10^{24}			610–823	[9]
Annealed at 1673 K	129.3	8.2×10^{23}				

constant and diffusivity pre-exponentials K_{s0} and D_0 and the respective activation energies for solution (E_s) and diffusion (E_d) are tabulated together with the characteristic trapping parameters (the trap density N_t and the trapping energy E_t).

Frauenfelder [3] modelled the H degassing from a previously loaded specimen obtaining the H diffusivity and solubility in rolled sintered W (gas loading pressure 8×10^4 Pa and temperatures between 1100 and 2400 K). The use of the gas evolution technique in [3] presents some accuracy drawbacks: (1) the neglect of H desorbed and pumped-out from the specimen between loading and release phases and (2) the ('3 min') transient flash heating to reach the desired constant temperature level. Moore and Unterwald [4] evaluated the H transport parameters in a hot W filament (1200–2500 K) studying the atomisation phenomenon of hydrogen molecules. Zakharov and Sharapov [5] measured the permeation of H through a tube of tungsten (with a sealed end) from 673 to 1473 K and pressures from 1.3×10^2 to 2.6×10^4 Pa. The specimen was polycrystalline W and was manufactured by vapour–gas phase W hexafluoride reduction. Ryabchikov [6] modelled the H degassing rates of previously up-to-saturation loaded commercial wires, evaluating diffusivities in the temperature range 1055–1570 K. Franzen et al. [7] modelled the H trapping in and release from specimens previously implanted with

H⁺. They studied two types of W specimen, single crystal and wrought, in the temperature range 300–900 K obtaining the H diffusivity and characterising the trapping phenomenon for differentiated natural and ion-induced traps. An analogous work on the trapping characteristics was developed by Pisarev et al. [8] studying ion implantation of H_D in tungsten from 350 to 750 K. From the thermodesorption peak analysis two activation energies for trapping were evaluated. Anderl et al. [9] used an ion driven permeation technique in polycrystalline W to study H_D transport and trapping phenomena. They used diverse specimens of the same material (polycrystalline tungsten foils manufactured by powder metallurgy) annealed at different temperatures. They noticed the effect of the heat treatment, i.e., the microstructure configuration, on the trapping energy.

3. Experimental

3.1. Specimens

The sample material was pure unalloyed polycrystalline W. The specimens consisted of four cylinders with 6 mm diameter and 60 mm height. The specimen dimensions were defined in this manner to make feasible the H transport study using the approximation to an

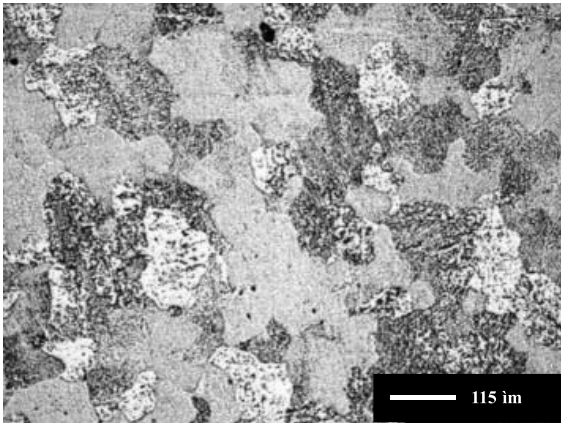


Fig. 1. Optical micrograph of the 'as-received' tungsten used in the experiment.

infinite long cylinder geometry. The specimens were cut by means of spark erosion from a rod (6 mm diameter) of material containing a minimum of 99.98% W. Each batch tested consisted of four specimens to provide a larger signal-to-noise ratio for the experiments. The specimens were used as-received without any heat treatment. Fig. 1 shows the polycrystalline microstructure of the material.

In order to remove residual oxides, the specimens were etched in a 20% KOH solution. Subsequently, the surface was mechanically polished and degreased. Finally, the specimens were dried in a vacuum furnace (100°C) before insertion into the experimental rig. These processes eliminate any impurity left on the surface that might affect the penetration of H into the bulk of the material.

3.2. Measuring procedure

The details for the IDE rig and measuring procedure are given elsewhere [10–12]. The specimens are placed in the measuring chamber having a constant volume. The chamber is loaded (loading phase), not necessarily up to saturation, at given hydrogen pressure and temperature for a time τ_l . During a short time τ_p , the fast pumping of the chamber (pumping phase) induces the hydrogen release from the specimens to the chamber (release phase).

A single experimental measurement (Fig. 2) consists in the recording of the pressure signal for the release period τ_r . Each measurement is followed by a blank run, under the same experimental conditions, (i.e., same loading pressure, specimens temperature and times τ_l , τ_p , τ_r), without specimens, to account for the contribution of the inner wall outgassing of the experimental vessel. The 'net' pressure release curve is then obtained by point-to-point pressure subtraction. This procedure must be performed at each experimental temperature in

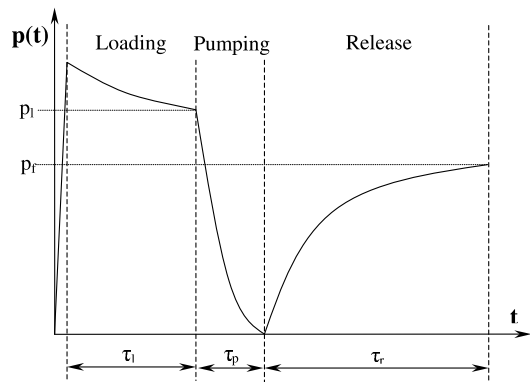


Fig. 2. Experimental phases in a single isovolumetric desorption run. The pressure $p(t)$ and time scales are different for each phase in order to appreciate their pressure profiles; τ_l , τ_p and τ_r are loading, pumping and release times, respectively; p_l and p_r the pressures measured in the experimental chamber at the end of the loading and release phases, respectively.

order not to evaluate erroneous transport parameters produced by the wall-outgassing.

4. Modelling

At high working temperatures, hydrogen in W exhibits a very low solubility and slow migration kinetics (Fig. 3). Consequently, in order to avoid very long cost-effective experimental times and stability problems in the measuring devices, non-stationary models are used [13,14]. The release rate model solves the diffusion equation in an infinite cylinder geometry linking all the three phases (loading, pumping and release) and provides transient gas concentration profiles for each single phase (Fig. 4).

The effective transport parameters D_{eff} and $K_{s,\text{eff}}$ are evaluated for each experimental temperature using a

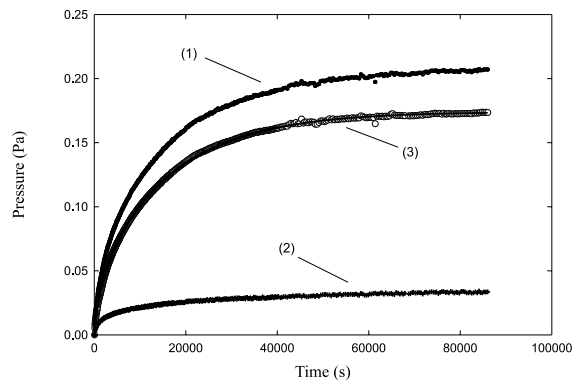


Fig. 3. Pressure increase in an experimental measurement: (1) run with specimens, (2) blank run, (3) effective pressure increase and fitting.

molar Gibbs energies of the isotope diatomic gas molecules at the reference state (298 K, 1 bar) [19], and $f(x)$ the vibration partition function defined by $f(x) = \sin h(x/2)/(x/2)$. θ and θ^* are the characteristic vibration temperatures of H_p oscillation in the ground and excited state (i.e., in the bottom of the potential well and the top of the diffusion barrier); they are related to the vibration frequencies ν and ν^* (s^{-1}) by $\theta = h\nu/k$ and $\theta^* = h\nu^*/k$, where h is the Planck constant ($6.6260755 \times 10^{-34}$ J s) and k is the Boltzmann constant (1.380658×10^{-23} J K^{-1}).

5. Results

The effective H_p and H_D Sieverts' constants and effective diffusivities are obtained from modelling the desorption curves. They are depicted in Figs. 5 and 6 together with the resultant fitting regressions and the extrapolated H_T transport parameters. The derived permeabilities are shown in Fig. 7.

The complete set of H_p transport parameters have been calculated as:

$$D \text{ (m}^2 \text{ s}^{-1}\text{)} = 5.68 \times 10^{-10} \exp(-9.3/RT),$$

$$K_s \text{ (mol m}^{-3} \text{ Pa}^{-1/2}\text{)} = 2.90 \times 10^{-2} \exp(-26.9/RT),$$

$$\Phi \text{ (mol m}^{-1} \text{ Pa}^{-1/2} \text{ s}^{-1}\text{)} = 1.65 \times 10^{-11} \exp(-36.2/RT),$$

$$N_t \text{ (m}^{-3}\text{)} = 2.0 \times 10^{23},$$

$$E_t \text{ (kJ mol}^{-1}\text{)} = 86.6.$$

The complete set of H_D transport parameters are:

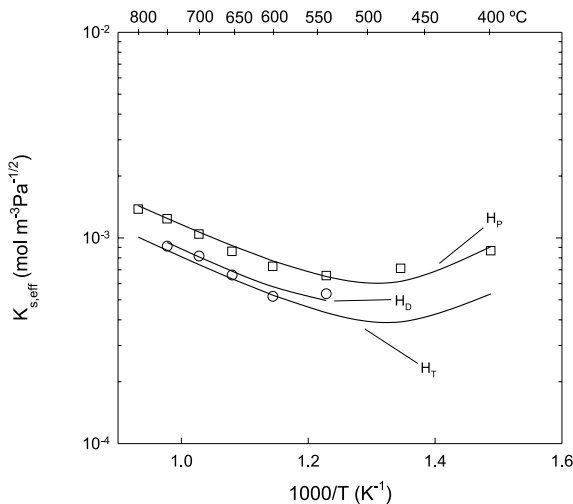


Fig. 5. Arrhenius plot of the Sieverts' constant of the hydrogen isotopes in tungsten. The tritium effective Sieverts' constant has been derived from protium values by applying Ebisuzaki's theory [18].

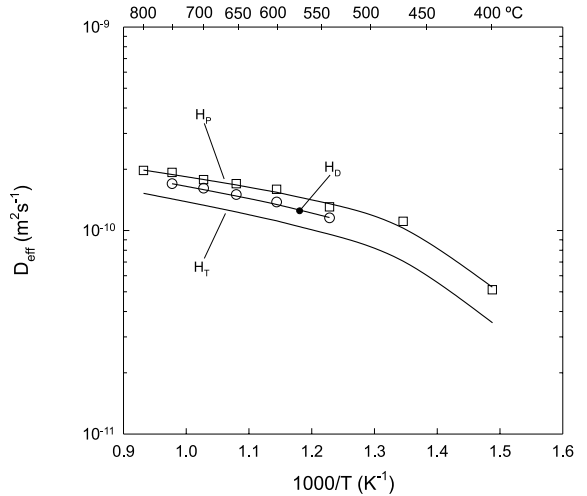


Fig. 6. Arrhenius plot of the effective diffusivity of the hydrogen isotopes in tungsten. The tritium effective diffusivity has been derived from protium values by applying Ebisuzaki's theory [18].

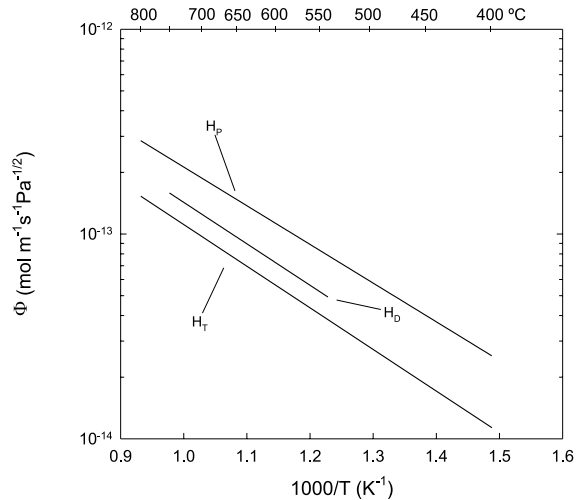


Fig. 7. Arrhenius plot of the permeability of the hydrogen isotopes in tungsten.

$$D \text{ (m}^2 \text{ s}^{-1}\text{)} = 5.49 \times 10^{-10} \exp(-10.0/RT),$$

$$K_s \text{ (mol m}^{-3} \text{ Pa}^{-1/2}\text{)} = 2.75 \times 10^{-2} \exp(-28.7/RT),$$

$$\Phi \text{ (mol m}^{-1} \text{ Pa}^{-1/2} \text{ s}^{-1}\text{)} = 1.51 \times 10^{-11} \exp(-38.7/RT),$$

$$N_t \text{ (m}^{-3}\text{)} = 1.0 \times 10^{23},$$

$$E_t \text{ (kJ mol}^{-1}\text{)} = 93.7.$$

The calculated [18] characteristic protium oscillation temperatures are:

$$\theta = 893 (\pm 178) \text{ K},$$

$$\theta^* = 2467 (\pm 227) \text{ K}.$$

Table 2

Transport parameters of hydrogen isotopes in tungsten and their corresponding standard deviations (in parenthesis)

	Protium	Deuterium	Tritium
$D_0 \times 10^{10}$ (m ² s ⁻¹)	5.68 (±0.04)	5.49 (±0.03)	5.34 (±0.70)
E_d (kJ mol ⁻¹)	9.3 (±0.6)	10.0 (±0.4)	11.2 (±3.1)
$K_{s0} \times 10^2$ (mol m ⁻³ Pa ^{-1/2})	2.90 (±0.03)	2.75 (±0.08)	2.25 (±0.40)
E_s (kJ mol ⁻¹)	26.9 (±1.0)	28.7 (±2.2)	27.8 (±4.1)
$\Phi_0 \times 10^{11}$ (mol m ⁻¹ Pa ^{-1/2} s ⁻¹)	1.65 (±0.02)	1.51 (±0.04)	1.20 (±0.40)
E_ϕ (kJ mol ⁻¹)	36.2 (±1.7)	38.7 (±2.7)	38.9 (±4.2)
N_t ($\times 10^{-23}$) (sites m ⁻³)	2.0 (±1.2)	1.0 (±0.4)	2.3 (±1.9)
E_t (kJ mol ⁻¹)	86.6 (±23.5)	93.7 (±12.3)	100.5 (±31.3)

The complete set of H_T transport parameters are:

$$D \text{ (m}^2 \text{ s}^{-1}\text{)} = 5.34 \times 10^{-10} \exp(-11.2/RT),$$

$$K_s \text{ (mol m}^{-3} \text{ Pa}^{-1/2}\text{)} = 2.25 \times 10^{-2} \exp(-27.8/RT),$$

$$\Phi \text{ (mol m}^{-1} \text{ Pa}^{-1/2} \text{ s}^{-1}\text{)} = 1.20 \times 10^{-11} \exp(-38.9/RT),$$

$$N_t \text{ (m}^{-3}\text{)} = 2.3 \times 10^{23},$$

$$E_t \text{ (kJ mol}^{-1}\text{)} = 100.5.$$

All the activation energies are expressed in kJ mol⁻¹ and the ideal gas constant, R , equals 8.314 J K⁻¹ mol⁻¹.

The standard deviation obtained for each parameter is tabulated in Table 2 for confidence intervals estimation. The source of errors comes from experimental pressure and temperature deviations (0.08% for pressure and 0.1% for temperature being the reference accuracy for the measuring devices).

6. Discussion

The H atomic dissolution in tungsten (Sieverts' law) is verified (Fig. 8) and the diffusive regime is confirmed because diffusivities measured at the same temperature and different pressures do not depend on pressure (Fig. 9).

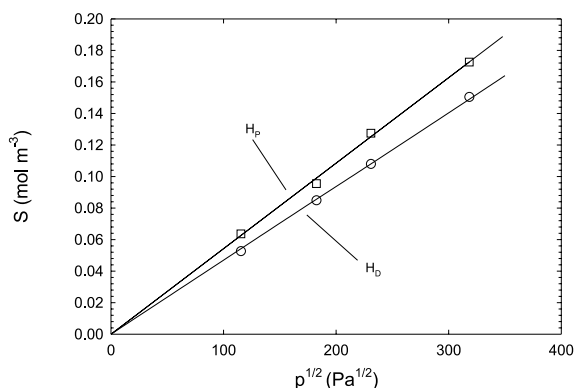


Fig. 8. Solubilities of hydrogen in tungsten at 873 K and different loading pressures. Sieverts' law is fulfilled.

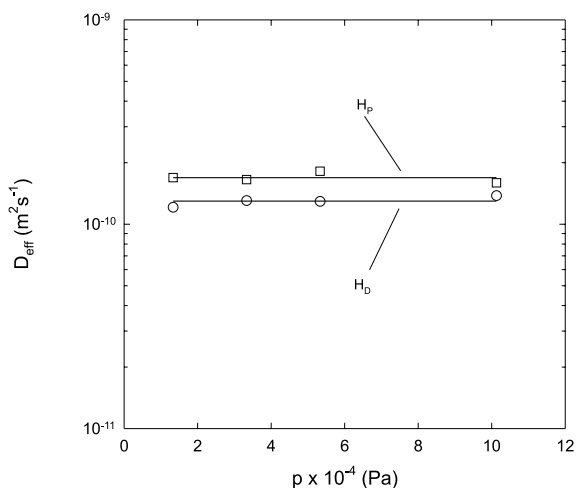


Fig. 9. Effective diffusivities of hydrogen in tungsten at 873 K and different loading pressures. The surface effect is negligible.

Trapping effects on experimental diffusivity and Sieverts' constant values may be noticed (Figs. 5 and 6) below approximately 873 K. The experimental values obtained for the trapping energies (86.6 kJ mol⁻¹ for H_P , 93.7 kJ mol⁻¹ for H_D) appear to be too high for dislocation or grain boundary traps. However, trapping phenomena with high trapping energies have been previously reported for polycrystalline W [9]. H–H bonding in H clusters nucleated at the structural defects of W was proposed as an explanation for such high trapping energy values. This hypothesis could also explain the results obtained for trapping in the present experiment.

With regard to the isotope effect, a net increase in the effective transport parameters has been noticed when diminishing the mass of the isotope; for effective diffusivity, mean factors $D_{\text{eff}}(H_P)/D_{\text{eff}}(H_D) = 1.13 (\pm 0.07)$ and $D_{\text{eff}}(H_D)/D_{\text{eff}}(H_T) = 1.70 (\pm 0.91)$ have been evaluated instead of the corresponding classical values 1.41 and 1.22. The fact that the mean increase of effective diffusivity is higher when changing isotope from H_D to H_T than from H_P to H_D may be the consequence of experimental deviations because both confidence

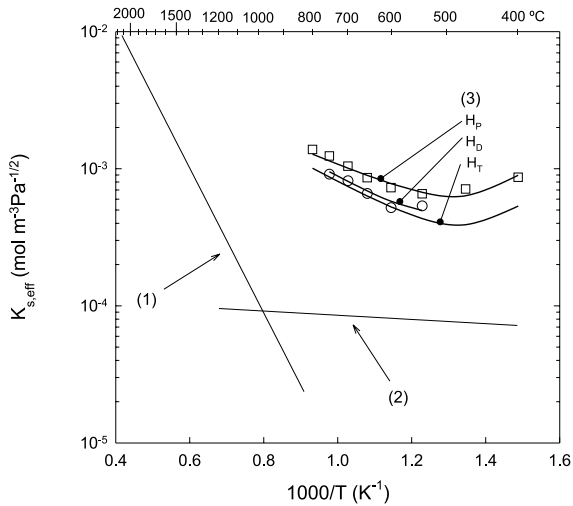


Fig. 10. Effective Sieverts' constant of hydrogen in tungsten: (1) Frauenfelder [3], (2) Zakharov et al. [5], (3) this work.

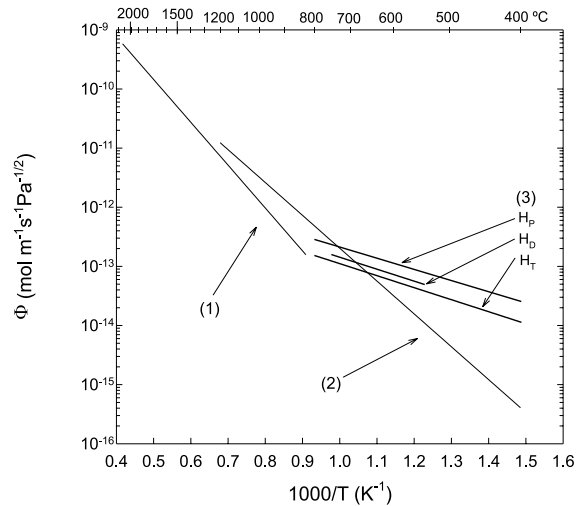


Fig. 12. Permeability of hydrogen in tungsten: (1) Frauenfelder [3], (2) Zakharov et al. [5], (3) this work.

intervals overlap. For effective Sieverts' constant the mean isotopic ratios have been evaluated as $K_{s,eff}(H_p)/K_{s,eff}(H_D) = 1.29 (\pm 0.09)$ and $K_{s,eff}(H_D)/K_{s,eff}(H_T) = 1.10 (\pm 0.60)$.

In Figs. 10–12 the obtained diffusive transport parameters are compared with the results reported elsewhere. The broad dispersion existing amongst all the results may be explained as follows. In the experiments using W specimens at high temperatures [3,4,6] the H atomisation phenomenon may imply an underestimation of the evaluated molecular H inventories. Conse-

quently, the transport properties obtained by modelling such molecular inventory may be inaccurate. The experiments using H ion implantation [7,8] to load the W specimens provoke ion-induced traps, so that the effective transport parameters may depart from those obtained only in presence of natural traps. The microstructure of each used specimen may influence the H transport within the bulk of tungsten. Moreover, depending on the manufacturing technique and subsequent heat treatment, the specimens show a particular microstructure with different grain sizes and different dislocation densities; these are sources of internal stress in the material where H may be trapped and even nucleate to form clusters. Other sources of variation may be the non-consideration of temperature transitory periods and long pumping-down stages before the release phase study [3].

In terms of activation energies, the energy of diffusion E_d reported here (9.3 kJ mol^{-1} , H_p , 10.0 kJ mol^{-1} , H_D , 11.2 kJ mol^{-1} , H_T) is the lowest compared to other referenced values. The solution energy evaluated here (26.9 kJ mol^{-1} , H_p , 28.7 kJ mol^{-1} , H_D , 27.8 kJ mol^{-1} , H_T), approximates closer to that reported in [5] rather than the high values obtained in [3,4]. With regard to the trapping effect, the trap density values and the high trapping energies obtained approximate well to the results obtained in [10].

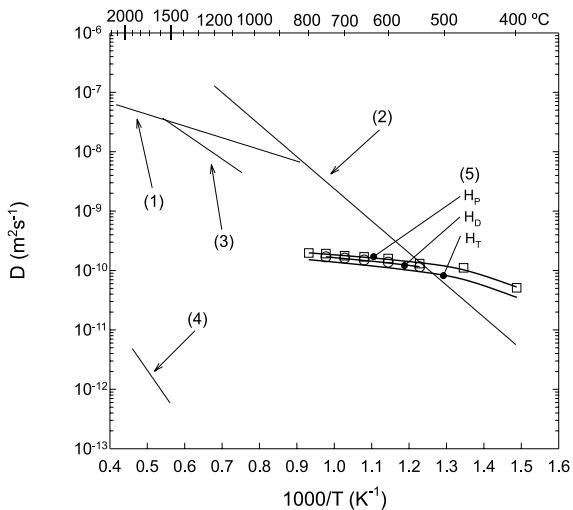


Fig. 11. Effective diffusivity of hydrogen in tungsten: (1) Frauenfelder [3], (2) Zakharov et al. [5], (3) Ryabchikov [6], (4) Moore and Unterwald [4], (5) this work.

7. Concluding remarks

Hydrogen isotopes transport characteristics in polycrystalline W have been measured using an isovolu-

metric desorption technique. A net reduction in both Sieverts' constant and diffusivity has been noticed as the mass of the isotopes increased. The trapping phenomenon has been noticed below 873 K and the characteristic trapping parameters evaluated. The possibility of H clusters nucleation at structural defects has been identified as the most probable phenomenon explaining the high trapping energies obtained.

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