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Hydrogen and deuterium transport and inventory parameters in a Cu–0.65Cr–0.08Zr alloy for fusion reactor applications

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Abstract

A time dependent permeation method has been used to measure the transport and inventory parameters of hydrogen and deuterium in the precipitation hardened (PH) Cu–0.65 wt% Cr–0.08 wt% Zr alloy (ELBRODUR HF). The measurements cover the temperature range from 553 to 773 K using a hydrogen or deuterium pressure in the range 1–100 kPa. The permeabilities, diffusivities and Sieverts' constant values for ELBRODUR obtained in this work were about 2 time higher, 2 times lower and between 3 and 10 time higher respectively to that of Cu (F. Reiter et al., A compilation of Tritium Material Interaction Parameters in Fusion Reactor Materials, EUR 15217 EN (1993)) in the temperature range studied. Using the measured diffusivities and Sieverts' constant values for H_2 and D_2 and a quantum-mechanical model, an extrapolation for tritium is also presented. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In considering materials for fusion reactors a detailed understanding of the transport and inventory parameters of hydrogen and its isotopes through these materials is an important issue concerning safety, fuelling and reliability. Numerical codes have been developed for the calculation of recycling, inventory and permeation of deuterium and tritium in fusion reactor design concepts in non-steady state conditions. Essential input data for these codes are the permeability, diffusivity and solubility of deuterium and tritium in the structural material involved.

The precipitation hardened (PH) Cu–0.65 wt% Cr–0.08 wt% Zr alloy, produced by Kabelmetal (Osnabrück, FRG), trade name ELBRODUR HF, is currently considered as one of the two commercially available Cu alloys that meets the International Thermonuclear Experimental Reactor (ITER) requirements to transport elevated heat fluxes to the cooling water and to withstand a large number of operating cycles [1]. Although the hydrogen transport and inventory parameters in copper are well studied [2], no data are available for ELBRODUR HF alloy.

2. Experimental

The ELBRODUR samples consisted of discs 1.6×10^{-2} m in diameter and $0.2–1.0 \times 10^{-3}$ m in thickness. The material was supplied in the form of rods in the solution treated, cold worked and aged state. The chemical composition and fabrication schedule are given in Table 1.

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 with vacuum, one side of the sample (the "high pressure side") is instantaneously exposed to hydrogen or 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 unit area of the sample ($Q(t)$) or the

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Table 1
Chemical composition of the investigated Cu–0.65Cr–0.08Zr alloy [a]

Fabrication history	Composition (wt%)	Trace element concentration (ppm)
Solution treatment at 1273 K and water quenching on 45 mm diameter extruded bar, cold drawing (44%) to 25 mm diameter rod and ageing at 733 K	Cr: 0.47, Zr: 0.19	Ag: 51, Fe: 97, Mn: 6, Ni: 60, O < 5, P: 140, Zn: 65

[a] Composition limits in wt% according to DIN 17666:0.4 < Cr < 1.1, 0.03 < Zr < 0.3, impurity level <0.15.

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^{-6} Pa (10^{-8} mbar) prior to system bakeout at 573 K and less than 10^{-7} Pa afterwards are obtained before any experiment. High pressure hydrogen or deuterium gas, with a nominal purity of 99.9999% and 99.7% respectively, 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 and 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 ±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 (9.13×10^{-5} m^3) 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. [3].

Before the membranes were inserted into the permeation measuring equipment, both sides were mechanically polished and then chemically cleaned. 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 hydrogen atoms through a membrane of uniform thickness d (m), in the case where the driving hydrogen 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 [4]

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

where D (m^2 s^{-1}) is the diffusion coefficient of the membrane and K_{s} (mol m^{-3} Pa$^{-1/2}$) 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., $t \to \infty$) Eq. (1) becomes: $J = P/d\, p^{1/2}$, where $P = DK_{\mathrm{s}}$ (mol m^{-1} s^{-1} Pa$^{-1/2}$) 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

$$\begin{aligned} Q(t) &= \int_0^t J(t')\,\mathrm{d}t' \\ &= \frac{Pp^{1/2}}{d}t - \frac{Pp^{1/2}d}{6D} - \frac{2Pp^{1/2}d}{\pi^2 D} \\ &\quad \sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-D\frac{n^2\pi^2}{d^2}t\right), \end{aligned} \tag{2}$$

$Q(t)$ is obtained experimentally from the pressure rise data, using the ideal gas law ($Q(t) = p(t)V_{\mathrm{eff}}R^{-1}T^{-1}$, $R = 8.314$ J K^{-1} mol^{-1} and V_{eff} = volume of the low pressure side of the sample).

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. Then, having obtained the permeability P and the diffusivity D, the Sieverts' constant is determined directly from the relationship $K_{\mathrm{s}} = P/D$.

Following the quantum-mechanical approach of Katz et al. [5], the ratio of the Sieverts' constant values for the hydrogen isotopes is

$$\ln\frac{K_{\mathrm{s}\alpha}}{K_{\mathrm{s}\beta}} = 3\,\ln\frac{f(\theta/\beta^{1/2}T)}{f(\theta/\alpha^{1/2}T)} - \frac{3}{2}\,\ln\frac{\beta}{\alpha} + \frac{1}{2}\,\frac{G^0_\alpha - G^0_\beta}{RT}, \tag{3}$$

where $\alpha, \beta = 1, 2, 3$ for H, D, T respectively, θ is the characteristic vibration temperature for the diffusing atom in the solid in the ground state, G^0_i are the free energies of the corresponding gas in the standard state (with $i = \alpha$ or β) and

$$f(\theta/i^{1/2}T) = \frac{\sinh(\theta/2i^{1/2}T)}{\theta/2i^{1/2}T}. \quad (4)$$

The values for the last term on the right-hand side of Eq. (3) are tabulated in Ref. [6]. The ratio of the diffusivities for the hydrogen isotopes is

$$\frac{D_\alpha}{D_\beta} = \left(\frac{\beta}{\alpha}\right)^{1/2} \left[\frac{f(\theta/\alpha^{1/2}T)}{f(\theta/\beta^{1/2}T)}\right]^3 \left[\frac{f(\theta^*/\beta^{1/2}T)}{f(\theta^*/\alpha^{1/2}T)}\right]^2, \quad (5)$$

where, as before, $\alpha, \beta = 1, 2, 3$ for H, D, T, respectively and θ^* is the characteristic vibration temperature for the diffusing atom in the solid in the activated state. Using the experimental Sieverts' constant values for hydrogen and deuterium, it is possible to determine θ by a non-linear least-squares fitting process of Eq. (3) with $\alpha = 1$ and $\beta = 2$ and then with an inversion of Eq. (3) to determine the Sieverts' constant values for tritium using the K_s experimental values for hydrogen or deuterium. At that moment, using the experimental values of diffusivities for hydrogen and deuterium and θ it is possible to determine θ^* by a non-linear least-squares fitting (Eq. (5)) and then with an inversion of Eq. (5) to determine the diffusivities for tritium.

4. Results and discussion

The results for ELBRODUR in comparison with the data for Cu [2] are presented by Arrhenius plots of effective permeability, diffusivity and, hence, values for Sieverts' constant in Figs. 1–3, respectively. The Cu tritium permeability data in [2] are essentially taken from [7]. The Cu tritium diffusivity data in [2] are an average, extrapolated from [5,8–11]. Finally, the Cu tritium values for Sieverts' constant in [2] are taken from [12].

The measurements in Figs. 1–3 were determined using a driving pressure, i.e. the pressure on the high pressure side of the apparatus, of 100 kPa (Figs. 1–3 insertion).

The Arrhenius expressions for the hydrogen and deuterium permeability, diffusivity and Sieverts' constant values obtained from a fitting to the whole temperature range are as follows:

Hydrogen

$$\begin{aligned} P_{H_2} &= 3.3 \times 10^{-7} \exp(-77510/RT) && \text{mol m}^{-1}\,\text{s}^{-1}\,\text{Pa}^{-1/2}, \\ D_{H_2} &= 5.7 \times 10^{-7} \exp(-41220/RT) && \text{m}^2\,\text{s}^{-1}, \\ K_{sH_2} &= 0.9 \exp(-38580/RT) && \text{mol m}^{-3}\,\text{Pa}^{-1/2}, \end{aligned} \quad (6)$$

Deuterium

$$\begin{aligned} P_{D_2} &= 2.6 \times 10^{-7} \exp(-76350/RT) && \text{mol m}^{-1}\,\text{s}^{-1}\,\text{Pa}^{-1/2}, \\ D_{D_2} &= 4.8 \times 10^{-7} \exp(-40370/RT) && \text{m}^2\,\text{s}^{-1}, \\ K_{sD_2} &= 0.71 \exp(-37380/RT) && \text{mol m}^{-3}\,\text{Pa}^{-1/2}. \end{aligned} \quad (7)$$

The tritium values have been calculated from the measured ratios of hydrogen and deuterium Sieverts' constants and diffusivities and applying the mentioned above quantum-mechanical method. The characteristic vibration temperature for the diffusing atom in the solid,

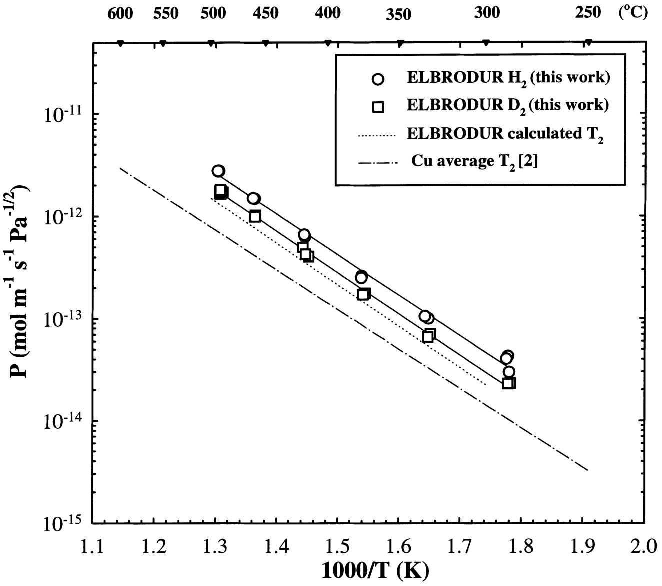

Fig. 1. Arrhenius plot of hydrogen and deuterium permeabilities for ELBRODUR compared to that of Cu [2]. The dotted line represents the calculated tritium permeabilities.

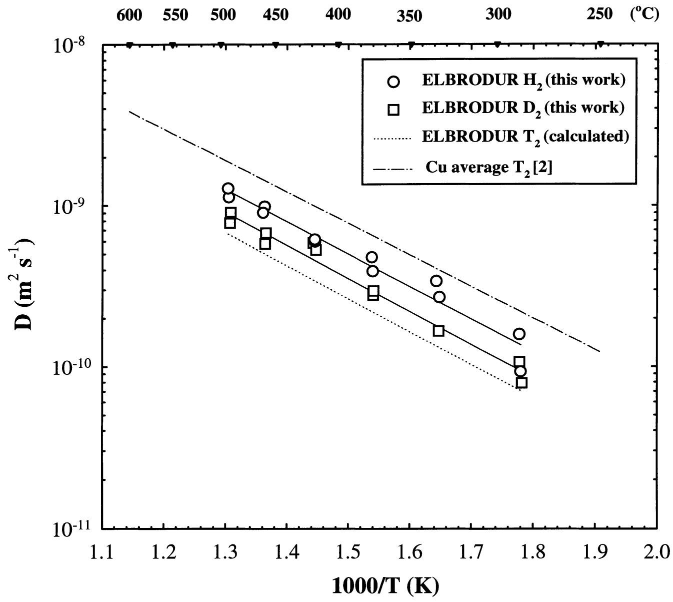

Fig. 2. Arrhenius plot of hydrogen and deuterium diffusivities for ELBRODUR compared to that of Cu [2]. The dotted line represents the calculated tritium diffusivities.

in the ground state and in the activated state, are $\theta = 1932$ and $\theta^* = 2218$ K, respectively. The quantum-statistical method has been applied directly to the experimental data points for each temperature rather than to Eqs. (6) and (7). This justifies that the activation energy is slightly different to that of deuterium and hydrogen rather than remaining the same as expected from the theory. The Arrhenius expressions for the tritium permeability, diffusivity and Sieverts' constant values are as follows:

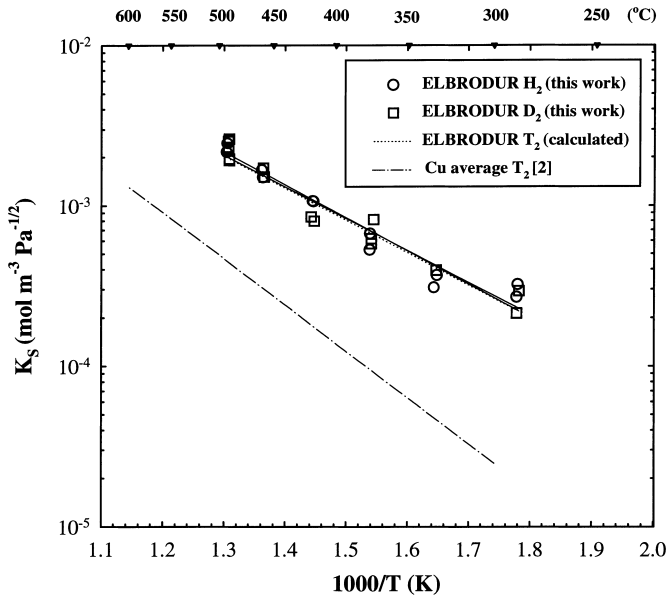

Fig. 3. Arrhenius plot of hydrogen and deuterium Sieverts' constants for ELBRODUR compared to that of Cu [2]. The dotted line represents the calculated tritium Sieverts' constants.

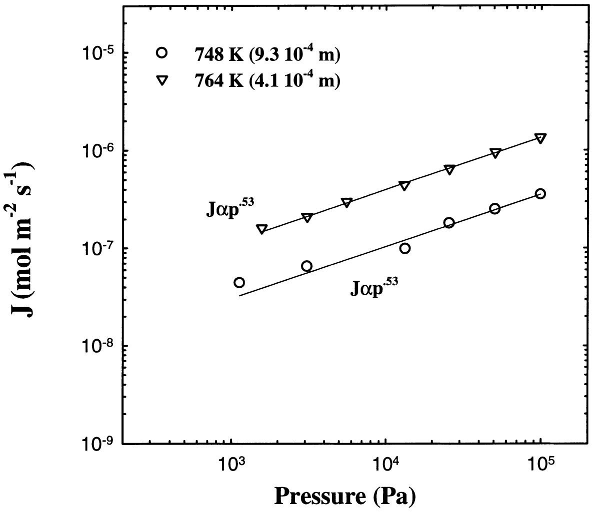

Fig. 4. The deuterium permeation rate through ELBRODUR as a function of driving pressure.

Tritium

$$\begin{aligned}
P_{T_2} &= 2.6 \times 10^{-7}\ \exp(-77660/RT) && \mathrm{mol\ m^{-1}\ s^{-1}\ Pa^{-1/2}},\\
D_{T_2} &= 3.07 \times 10^{-7}\ \exp(-39120/RT) && \mathrm{m^{2}\ s^{-1}},\\
K_{sT_2} &= 0.84\ \exp(-38540/RT) && \mathrm{mol\ m^{-3}\ Pa^{-1/2}}.
\end{aligned} \tag{8}$$

Other permeation measurements with deuterium driving pressures in the range 10^3–10^5 Pa were performed. The variation with deuterium pressure of the steady state flux J, for two membranes of 9.3×10^{-4} m and 4.1×10^{-4} m, at temperatures of 764 and 748 K respectively, is shown in Fig. 4. In the present pressure range, a half-power pressure dependence (confirming the hypothesis of a diffusion-limited permeation) of the permeation flux was observed (Fig. 4 insertion).

5. Conclusion

The hydrogen, deuterium and tritium transport and inventory parameters in ELBRODUR HF alloy were investigated using a gas phase technique employing a step change in pressure. Using the measured transport parameters for H_2 and D_2 and a quantum-mechanical model an extrapolation for tritium is also presented.

The permeabilities, diffusivities and Sieverts' constant values for ELBRODUR obtained in this work were about 2 time higher, 2 times lower and between 3 to 10 time higher respectively than that of Cu [2] in the temperature range studied.

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