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Journal of Nuclear Materials 283–287 (2000) 1033–1037

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Section 10. Plasma facing and high heat flux materials and components

Hydrogen and deuterium transport and inventory parameters through W and W-alloys for fusion reactor applications

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Abstract

The aim of this work is to measure the hydrogen/deuterium transport and inventory parameters in relevant structural and/or armour materials for the International Thermonuclear Experimental Reactor (ITER) divertor such as W and W-alloys. The W-alloys: W, W + 1% La_2O_3 and W + 5% Re have been investigated. The materials were supplied from the Metallwerk Plansee GmbH (Austria). Measurements were conducted using a time-dependent permeation method over the temperature range 673–873 K with hydrogen and deuterium pressures in the range 10–100 kPa (100–1000 mbar). The samples were also characterized using optical microscopy, SEM and energy dispersive spectroscopy (EDS) in order to investigate the composition, microstructure and morphology of the surfaces and cross-sections through the samples. © 2000 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, fueling 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.

Owing to their refractory nature and good thermal properties, W and W-alloys are considered to be alternatives to graphite as plasma-facing materials for the International Thermonuclear Experimental Reactor (ITER), especially for a divertor plate operated in the low-edge temperature (≈10 eV)/high-recycling plasma mode. W is a refractory metal having a bcc lattice and does not form binary hydrides with hydrogen. The exigencies of precise evaluations of the transport and inventory parameters of hydrogen and its isotopes through these materials are due to the fact that few determinations of these properties exist, and those that have been reported are of a questionable validity because there is no agreement among different investigations. The studies performed in the past present a large scatter of the experimental results as a consequence of the complexity of these measurements. The W-alloys: W, W + 1% La_2O_3 and W + 5% Re have been investigated in the present work.

2. Experimental

The pure W, W + 1% La_2O_3 and W + 5% Re materials consisted of disks 48 mm in diameter and 3×10^{-4}, 4×10^{-4} and 5×10^{-4} m in thickness for every alloy. The disk samples were supplied by the Metallwerk Plansee GmbH (Austria).

The method chosen for the determination of the hydrogen/deuterium transport and inventory parameters through W and W-alloys was a gas-phase technique. The permeation apparatus is constructed from standard stainless steel ultra-high vacuum (UHV) components

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PII: S0022-3115(00)00202-6

(see Fig. 1). Bakeout of the entire system was possible using a heating tape. Residual pressures lower than 10^{-6} Pa (10^{-8} mbar) prior to system bakeout at 573 K and less than 10^{-7} Pa afterwards were obtained before any experiment. High-pressure hydrogen gas, with an impurity content less than 1 ppm of H_2O or O_2, was produced by a hydrogen generator (mod. HG 200-CLAIND/RIVOIRA) joined to a hydrogen purifier. High-pressure deuterium gas, with a nominal purity of 99.7%, was taken from a cylinder. Hydrogen or deuterium gas was admitted to the sample via a control valve which, together with a pressure transducer and a Baratron with a full-scale reading of 10^3 Pa (10 mbar) (Baratron 1 in Fig. 1), enabled the pressure to be set at any value between $1–1.5 \times 10^5$ Pa (10^{-2}–1500 mbar). The sample was heated in a resistance furnace and the temperature was set at values up to 873 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 ±0.5 K. An analysis of the high-pressure gas and the permeated gas was made with a quadrupole mass spectrometer. Thus, it was possible to check for possible contaminants. The volume of the low-pressure side of the sample was measured by a gas-expansion method (Sieverts' method) using a calibrated volume (9.5×10^{-5} m^3) which was permanently attached to the apparatus. A National Instruments system (Labview) was used for the data acquisition. The disk samples were sealed between two stainless steel flanges by compression sealing using two gold 'O' rings.

2.1. Experimental procedures

After evacuating the apparatus to a UHV so that both sides of the sample were initially in contact with vacuum, one side of the sample (the 'high-pressure side') was instantaneously exposed to hydrogen or deuterium gas at a known, fixed pressure. Gas permeated through the sample and was released at the other side (the 'low-pressure side'), where it caused a pressure rise in an initially evacuated, calibrated volume. The pressure rise was measured by using two methods: a pressure-rise method (PRM) and a continuous-flow method (CFM).

2.1.1. Pressure-rise method

The pressure rise could be measured by using two Baratron capacitance manometers with a full-scale reading of 10 Pa (0.1 mbar) (Baratron 2) and 130 Pa (1.3 mbar) (Baratron 3), respectively. The calibrated volume was sealed off from the turbomolecular pump at the same time as hydrogen or deuterium gas was introduced into the high-pressure side. Since the volume was 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 rate of pressure rise could be converted into an amount of gas, in moles, permeating through unit area of the sample per second ($J(t)$). In the present work, owing to the low hydrogen permeation flux measured through W and W-alloy (see Section 4), outgassing from the walls of the sealed volume while permeation was proceeding had to be taken into account. The effect of rising pressure due to

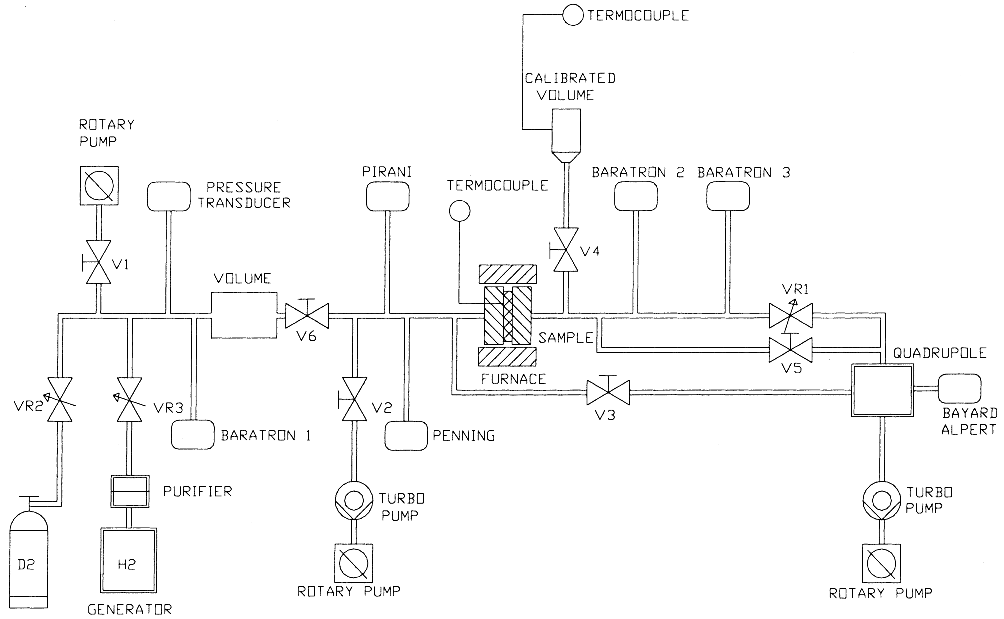

Fig. 1. Schematic of the permeation apparatus.

outgassing could be eliminated if each permeation measurement was followed by a 'blank' test under the same experimental conditions but without hydrogen or deuterium gas in the high-pressure side. The contribution due to outgassing so obtained was then subtracted from the total pressure rise to give the net contribution due to the hydrogen or deuterium permeation through the membrane.

2.1.2. Continuous-flow method

The pressure rise was also alternatively measured using a quadrupole (CFM). The mass spectrometer provided a very sensitive pressure measurement, especially when using deuterium gas. Using deuterium, it was simple to differentiate between the permeating gas and outgassing from the apparatus wall. However, owing to the necessity of running the analyzer head at total pressures less than 10^{-4} Pa, it must be constantly pumped when in operation. The continuous-flow method of measuring permeation thus involved pressurising the high-pressure side as in the pressure-rise method above, but instead of sealing the low-pressure side, it was left open and continuously pumped. The rise in partial pressure of the mass three and four (for deuterium permeation) in the evacuated part of the apparatus was then measured. The partial pressure of deuterium measured at any particular time was proportional to the permeation flux ($J(t)$), assuming that the pumping efficiency is not related to pressure. In this work, a set of calibration measurements have been conducted using both AISI 316 L and F82H steel samples, in order to determine the constant of proportionality between the partial pressure of deuterium measured by quadrupole and the permeation flux ($J(t)$).

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

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

where D (m^2 s^{-1}) is the diffusion coefficient of the membrane and K_S (mol m^{-3} $Pa^{-1/2}$) is 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 by surface reactions. At steady state (i.e. $t \to \infty$), Eq. (1) becomes $J = P/dp^{1/2}$, where $P = DK_S$ (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

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

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

The values of P and D can be obtained by least squares fitting to the experimental data for each permeation run using Eqs. (1) and (2) above for the CFM and PRM measurements, respectively. Then, having obtained the permeability P and the diffusivity D, the Sieverts' constant is determined directly from the relationship $K_S = P/D$.

4. Results

As mentioned in Section 2, the samples were sealed between two stainless steel flanges using two gold 'O' rings (2×10^{-4} m thick). This method is usually very efficient for reaching UHV because gold is very malleable. Unfortunately, one of the biggest problems when sealing the W and W-alloy samples between the two stainless steel flanges by compression sealing using two gold 'O' rings was that the samples often broke. The W + 1% La_2O_3 samples were particularly susceptible to breaking. The gold 'O' rings were also annealed in order to increase the malleability of the rings themselves. In the following, the permeation results obtained with two samples consisting of W and W+5% Re disks 48 mm in diameter and 4×10^{-4} and 5×10^{-4} m in thickness, respectively, are reported.

The hydrogen permeability for W and the deuterium permeability for W + 5% Re compared with [1–3] are presented by Arrhenius plots in Fig. 2. The results for the deuterium diffusivity and, hence, values of Sieverts' constant for W + 5% Re in comparison with [1–3] are also presented in Figs. 3 and 4, 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 about 75 600 Pa. Few data exist for deuterium- and tritium-transport parameters for W

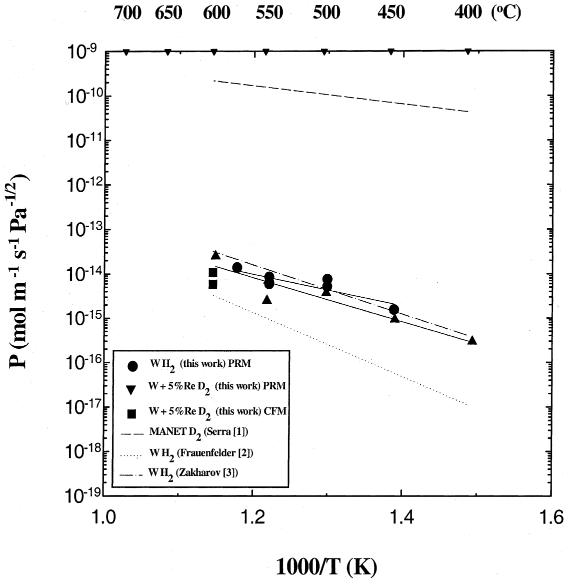

Fig. 2. Arrhenius plot of the hydrogen permeabilities for W and the deuterium permeabilities for W + 5% Re compared with [1–3].

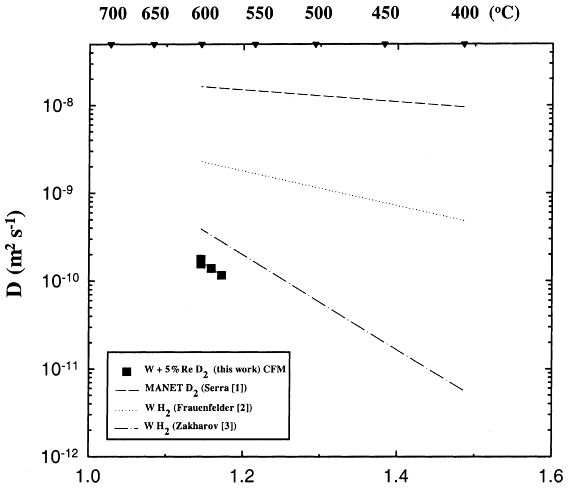

Fig. 3. Arrhenius plot of the deuterium diffusivities for W + 5% Re compared with [1–3].

and W-alloys. After a wide analysis of the existing data [4], it was observed that the H_2 and D_2 permeabilities obtained in this work for both W and W + 5% Re are in good agreement with the data [2,3]. The D_2 diffusivity obtained in this work results in good agreement with the data [3]. The data in [2] were obtained for a tungsten cylinder, manufactured by the General Electric company by rolling sintered tungsten, using mass spectroscopy and UHV techniques at a pressure of 600 Torr and temperatures between 1100 K and 2400 K. The data in [3] were obtained for: (1) polycrystalline-textured tungsten obtained from vapor phase by reducing tungsten hexafluoride with hydrogen, and (2) polycrystalline specimens of tungsten and an alloy of W + 2% Mo obtained by extrusion; again, the experiments were performed with mass spectroscopy and UHV techniques for pressures from 1–200 Torr and temperatures between 673 and 1473 K. From the deuterium-permeation data analysis in the range 610–823 K, the authors in [5] found that trapping significantly affects the deuterium transport in W, and it was estimated that trap energies vary from 130 to 150 kJ/mol and trap concentrations

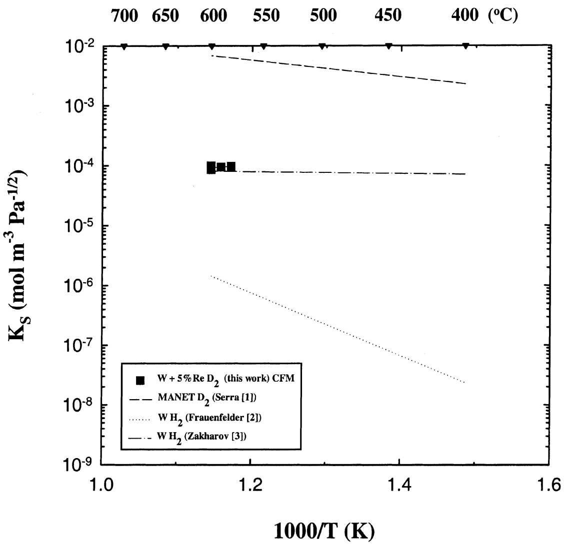

Fig. 4. Arrhenius plot of the deuterium Sieverts' constant values for W + 5% Re compared with [1–3].

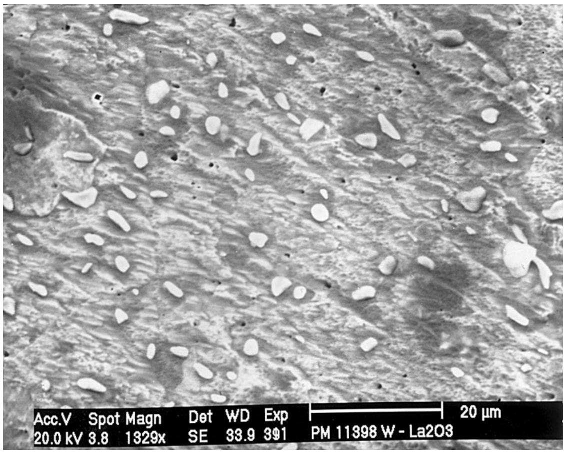

Fig. 5. SEM micrograph of the W + 1% La_2O_3 specimen.

from 6×10^{23} to 4×10^{24} sites/m^3 for unannealed and annealed tungsten, respectively. In the temperature range 673–1473 K, the trapping phenomenon can explain the differences in both the hydrogen in W diffusivity and solubility data in reference [2] (extrapolated data) vs [3].

The samples were also characterized using optical microscopy, SEM and energy dispersive spectroscopy (EDS) in order to study the composition, microstructure and morphology of the surfaces and cross-sections through the samples themselves. From optical micrographs of the W and W + 5% Re specimens, it was possible to see the microstructure of the sintered W and W + 5% Re. Furthermore, a low density of microvoids was observed. Fig. 5 shows a SEM micrograph of the W + 1% La_2O_3 specimen in which it is possible to see the lanthanum oxide distribution. EDS analysis of the three alloys indicated very low impurity levels.

5. Conclusions

The aim of this work was to measure the hydrogen/deuterium transport and inventory parameters in W and W-alloys. Measurements were conducted using a time-dependent permeation method over the temperature range 673–873 K with hydrogen- and deuterium-driving pressures in the range 10–100 kPa (100–1000 mbar). The references for H_2 and D_2 permeability, diffusivity and solubility values for W and W + 5% Re were presented. It should be pointed out that among the few existing data available, the H_2 and D_2 permeability values obtained in this work for W and W + 5% Re are in good agreement with the data [2,3] for W and the D_2 diffusivity values obtained in this work for W + 5% Re are in good agreement with the data [3] for W.

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