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Diffusion and permeation of hydrogen in low-activation martensitic stainless steel – effect of irradiation

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Abstract

The effect of irradiation on permeation and diffusion of hydrogen in low-activation martensitic stainless steel, F82H-mod, was investigated in three experiments:

1. Permeation and diffusion of H_2 in pre-irradiated specimens, showing decrease of both the properties with increasing dose. The diffusion results were evaluated in terms of a saturable-trap-model.
2. Permeation of deuterium under simultaneous proton irradiation, showing enhancement of permeation by irradiation.
3. Diffusion of protons which were implanted to various depths in a 800 μm foil. These results were compared to H_2 gas diffusion in virgin and pre-irradiated material. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Hydrogen in structural materials is cause for concern mainly from viewpoints of material stability, e.g., problems of embrittlement [1], and environmental safety, especially tritium confinement. These problems are considered more severe in martensitic than in austenitic steels due to lower solubility and higher diffusivity of hydrogen. Up to now very little is known about possible effects of irradiation on absorption, mobility and retention of hydrogen in martensitic steels. For this reason, permeation and diffusion experiments were performed in the present study, including pre-irradiated material, permeation during simultaneous proton irradiation, and studies on implanted hydrogen.

2. Experimental details

Low-activation martensitic F82H-mod steel (7.7% Cr, 1.9% W, 0.16% Mn, 0.16% Mn, 0.09% C) from the ITER programme was mechanically cut and cold-rolled in steps of 25 μm with intermediate heat treatments to foils of about 200 and 800 μm thickness with final standard treatment (12 h:1040°C – quench; 1 h:750°C – furnace cooling). For pre-irradiation with protons, 200 μm specimens were fixed to copper heat sinks by Wood's metal, which limited specimen temperature during irradiation and unmounting to 70°C. Proton energy was 12.3 MeV, the calculated range of which is 375 μm, i.e., far above the specimen thickness. For homogeneity of damage, specimens were turned around after half the dose. Displacement doses (dpa) were calculated by using an average displacement cross-section of 3.3×10^{-25} m^2 [2]. The irradiated area of the 21.5 mm diameter specimens was limited by a 19×19 mm^2 aperture, which exceeded the open area in the permeation apparatus, defined by a 12 mm diameter gold gasket. For more details of experimental apparatus and evaluation, see [3,4].

200 μm foils and 12.3 MeV protons beams ($\leqslant 0.01$ A/m^2) were also used to measure permeation of deuterium during proton irradiation. In this case, the beam passed through an 8 mm aperture, which was slightly smaller than the 12 mm permeation area, and then through a small volume of D_2 gas at 1.5 bar [3,4]. The diffusion measurement on implanted protons were performed on ≈800 μm specimens. In this case, different implantation depths were achieved by appropriate proton energies.

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3. Permeation and diffusion in pre-irradiated specimens

Apparent permeabilities of H_2 in ≈200 μm unirradiated and pre-irradiated F82H-mod and of H_2 and D_2 in unirradiated ≈800 μm specimens are shown in Fig. 1. Included are the previous results on D_2 in 500–800 μm specimens [5] and on H_2 in 210 and 810 μm MANET-II [3]. The apparent permeabilities of unirradiated F82H-mod consistently decrease with decreasing thickness, indicating substantial surface effects. Importance of surface effects is also indicated by a pressure dependence of permeability. This can be approximated by power laws with exponents n_p (Fig. 2), which in turn do not depend on temperature but clearly increase with irradiation dose. Both these dependences on thickness and pressure were much smaller in MANET-II [3,4]. The fact that permeability in F82H is clearly higher than in MANET-II can be ascribed to its lower chromium content [6]. The apparent permeabilities of H_2 in 810 μm F82H-mod can be described by

$$P^*_{H_2} = 4.5 \times 10^{-8} \exp(-35200/RT). \quad (1)$$

For D_2, the activation energy is the same within experimental error, while the pre-factor is lower by about 10%. Apparent permeabilities of the 200 μm foils give $P^*_{H_2} = 2.2 \times 10^{-8} \exp(-41700/RT)$ for the virgin material and $P^*_{H_2} = 2.0 \times 10^{-9} \exp(-36300/RT)$ after pre-irradiation to 0.007 dpa (thin dotted lines in Fig. 1). When permeation is dominated by bulk diffusion, the apparent permeability is independent of pressure, i.e., $n_p \to 0$ (Fig. 2), while the trend towards $n_p \to 0.5$ indicates increasing importance of surface effects by pre-irradiation.

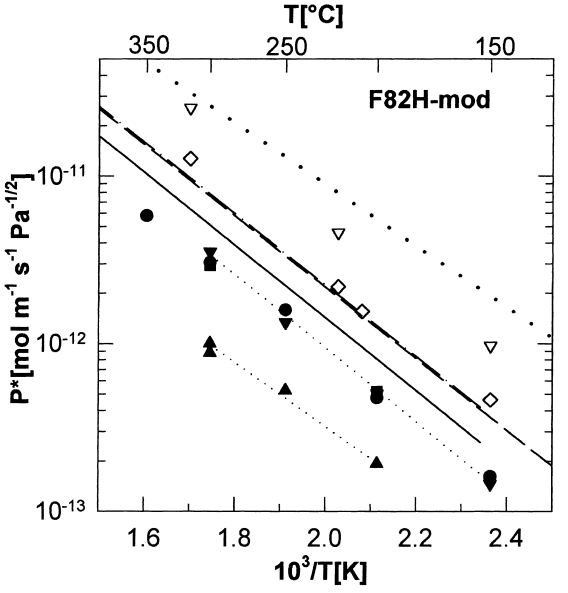

Fig. 1. Temperature dependence of apparent permeabilities of hydrogen isotopes in F82H-mod specimens of 817 μm thickness (H_2: ▽, D_2: ◇) at pressures of 1 bar and of H_2 (≈1.85 bar) in ≈203 μm specimens, pre-irradiated to doses of 0 (▼), 2×10^{-3} (●), 4×10^{-3} (■) and 7×10^{-3} dpa (▲). Included are results from D_2 in 500–800 μm F82H-mod (- -) [5], from H_2 in 210 μm (–) and 810 μm (-·-) MANET-II [3] and from H_2 in Fe (· · ·) [11].

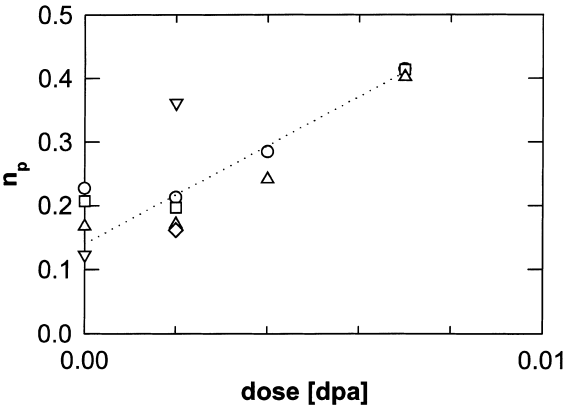

Fig. 2. Exponent of power law pressure dependence of apparent permeabilities in 203 μm F82H-mod as a function of displacement dose at 423 K (▽), 473 K (○), 523 K (□), 573 K (△) and 623 K (◇).

Diffusion coefficients D^* of H_2 and D_2 in ≈800 μm foils obtained from pressure transients at pressures of 1 bar and of H_2 in ≈200 μm pre-irradiated specimens at ≈1.85 bar are shown in Fig. 3. Similar to permeability, diffusivity also decreases with pre-irradiation dose. Diffusion coefficients of F82H-mod also slightly decrease with thickness and exceed those of MANETII. Normalised diffusion coefficients of H_2 in unirradiated and pre-irradiated (7×10^3 dpa) specimens of ≈200 μm are plotted as a function of reciprocal square root of pressure in Fig. 4. D is the asymptotic diffusion coefficient at high temperatures, given by $D = 1.8 \times 10^{-7} \exp(-14090/RT)$ [7]. The lines give tentative fits by a saturable-trap-model [8,9] which has previously been used for analysing results from MANET-II [3]. From initial slopes and asymptotic values of the curves in Fig. 4, trap concentrations n_T/n_0 (with trap density n_T and n_0 $\approx 8.3 \times 10^{28}/m^3$ the density of lattice atoms) and effective binding energies E_b of hydrogen atoms to traps can be derived. They are plotted versus reciprocal temperature in Fig. 5. E_b is practically not changed by pre-irradiation but increases with temperature. On the other hand, the trap concentration n_T/n_0 is raised by irradiation, especially at low temperatures. It should be mentioned that the applicability of the saturable-trap-model to the F82H-mod data is doubtful due to the contribution of surface effects as indicated by the pressure dependence of apparent permeabilties.

Hydrogen solubility as derived from the quotient of P^*/D^* shows a much smaller difference between

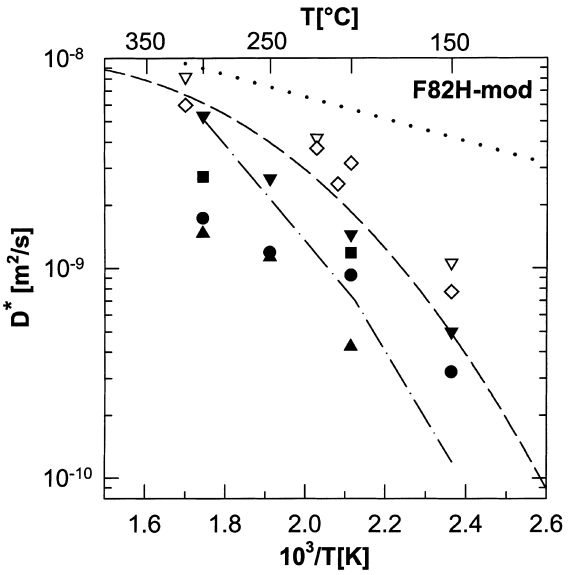

Fig. 3. Temperature dependence of diffusion coefficients of hydrogen isotopes in F82H-mod specimens of 817 μm at pressures of 1 bar (H_2: ▽, D_2: ◇) and of 203 μm thickness at pressures around 1.85 bar pre-irradiated to doses of 0 (▼), 2×10^{-3} (●), 4×10^{-3} (■) and 7×10^{-3} dpa (▲). Included are results from D_2 in 500–800 μm F82H-mod (- -) [5], from H_2 in 810 μm (-·-) MANET-II [3] and from H_2 in Fe (···) [11].

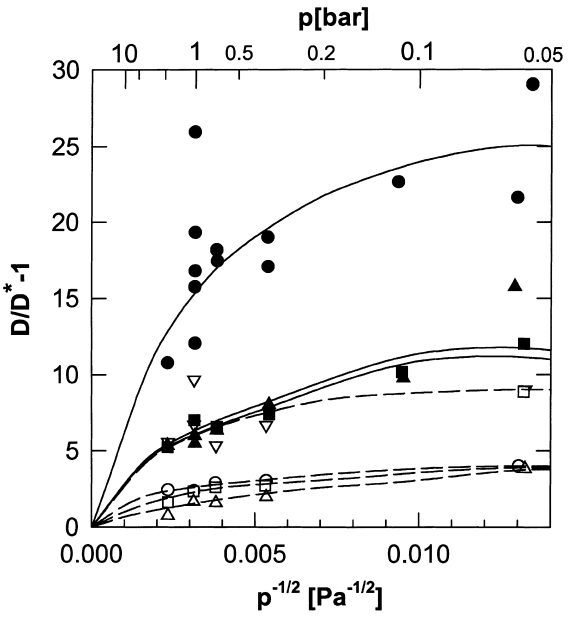

Fig. 4. Evaluation of trapping parameters from the pressure dependence of the ratio of apparent diffusion coefficients D^* to asymptotic high temperature lattice diffusivities D, according to the saturable-trap-model. Symbols indicate temperatures of 423 K (▼), 473 K (○,●), 523 K (□,■) and 573 K (△,▲). Open and filled symbols indicate unirradiated and pre-irradiated (7×10^{-3} dpa) specimens, respectively.

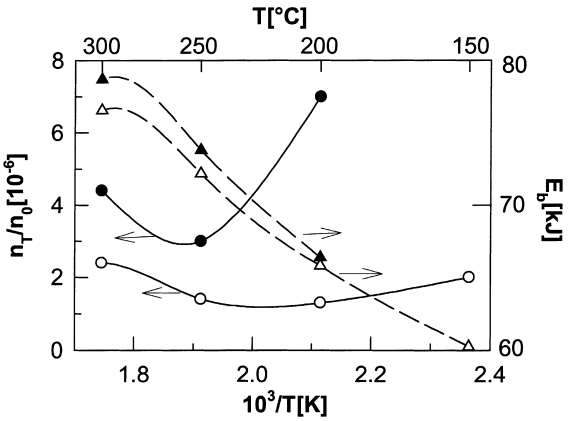

Fig. 5. Trap concentrations n_T/n_0 and effective binding energy of hydrogen to traps E_b as a function of reciprocal temperature derived from Fig. 4 for virgin F82H-mod (open symbols) and for specimens pre-irradiated to 0.007 dpa (filled), respectively.

MANET-II and F82H-mod than the P^* and D^* values themselves, see also [5].

4. Permeation during irradiation

Permeation of D_2 through a 200 μm foil of F82H-mod rises when a 12.3 MeV proton beam passes through the gas on the upstream side and the specimen. Ratios of change of permeation flux $\Delta\Phi_p$ to proton flux Φ_i at a beam density of 0.01 A/m^2 (≈500 nA) are plotted in Fig. 6 as a function of reciprocal temperature. Using $\Delta\Phi_p$ in this plot pre-supposes that permeation through the unirradiated part of the permeation specimen is not changed under irradiation. The irradiation induced increase in F82H-mod is lower than in MANET-II [3], where it was ascribed to ionisation and/or dissociation of the gas on the upstream side. It is possible that again surface effects reduce the sensitivity to irradiation of permeation through F82H-mod.

5. Diffusion of implanted hydrogen

When protons are implanted into a foil, flux to the back surface increases gradually after start of implantation and eventually reaches a constant value. The asymptotic change of flux $\Delta\Phi_p$, normalised to the implantation flux Φ_i for virgin F82H-mod is plotted in Fig. 7 as a function of relative implantation depth, i.e., range r divided by foil thickness d. Again surface effects may cause the lower fractional release $\Delta\Phi_p/\Phi_i$ in F82H-mod compared to MANET-II [3]. Diffusion coefficients D^* can be derived from the half-time $t_{1/2}$ of the transient after switching on or off the beam. According to nu-

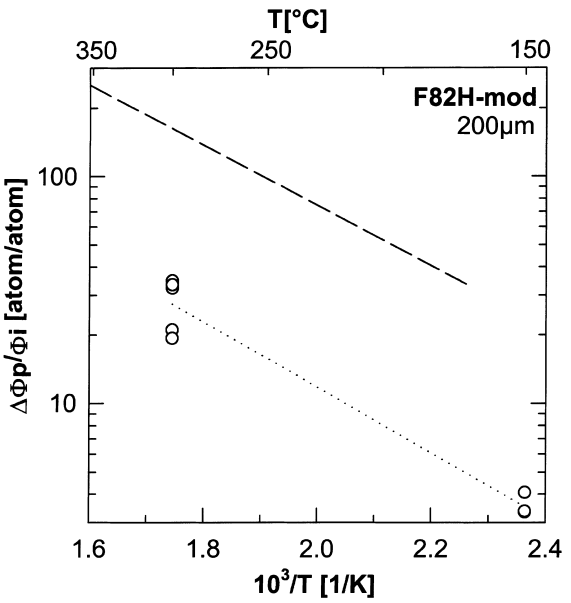

Fig. 6. Ratio of D_2 permeation flux to proton beam flux in F82H-mod as a function of temperature at a beam density of 0.01 A/m^2 and upstream pressure of 1.5 bar D_2. The dashed line gives average results for 210 and 810 μm MANET-II [3].

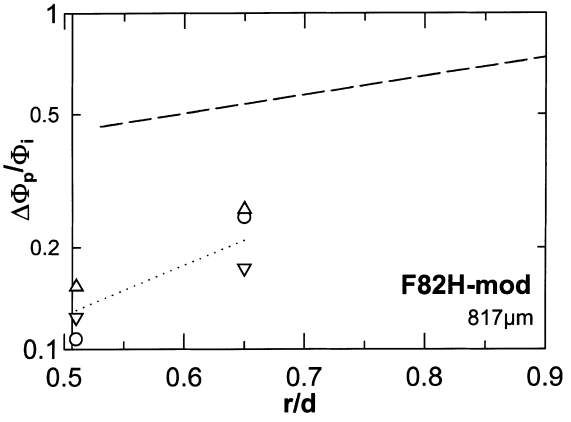

Fig. 7. Ratio of H_2 permeation flux to implantation flux as a function of relative implantation depth at ≈405 K (▽), ≈480 K (○) and 573 K (△).The dashed line gives results for 810 μm MANET-II at 573 K [3].

merical calculations [10], D^* can be approximated within about 10% by

$$D^* = \frac{d^2 \sin^2 \pi(1 - r/d)}{\pi^2 \varepsilon t_{1/2}} \quad \text{for } r/d > 0.5, \tag{2}$$

where the factor $1/\varepsilon$ takes into account permanent trapping, i.e., it approximates the total released fraction of implanted atoms ($1/\varepsilon \approx \Delta\phi_p \phi_i \cdot d/r$). D^* values from

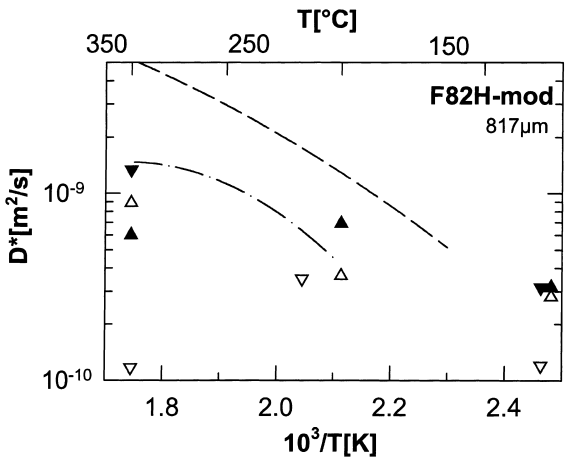

Fig. 8. Diffusion coefficients of implanted hydrogen in F82H-mod as a function of reciprocal temperature at relative implantation depth r/d ($d = 817$ μm) of 0.51 (▽,▼) and 0.65 (△,▲). Open and filled symbols indicate diffusion measurements at the beginning and the end of implantation, respectively. The dashed line gives coefficients of H_2-diffusion in ≈200 μm unirradiated (– – –) and pre-irradiated (8×10^{-3} dpa, –·–) specimens from Fig. 3.

the beginning (open) and the end (filled) of implantation are plotted in Fig. 8 as a function of reciprocal temperature. Both values coincide within experimental error, depend relatively weakly on temperature and are close to diffusion coefficients derived from gas diffusion in the pre-irradiated (0.007 dpa) specimens.

6. Summary and conclusions

1. Dependence of permeation and diffusion in F82H-mod on specimen thickness and of permeation on gas pressure indicate significant effects of surfaces, far beyond those observed in MANET-II.
2. Permeation and diffusion in F82H-mod at equal thickness are higher than in MANET-II, which can be ascribed to the lower chromium content. Differences in solubility are much smaller.
3. Permeation and diffusion of hydrogen in F82H-mod is reduced by pre-irradiation.
4. Trap concentrations, as tentatively derived from a saturable-trap-model, increase by pre-irradiation, while trap binding energies depend on temperature but practically not on damage.
5. Permeation through F82H-mod is enhanced under simultaneous irradiation, but less than in MANET-II.
6. Diffusion coefficients derived from implanted hydrogen are similar to those of gas diffusion in 0.007 dpa pre-irradiated material.

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