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Gas driven deuterium permeation through F82H martensitic steel

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Abstract

The permeation of deuterium through martensitic steel F82H is investigated in the ranges of 573–873 K and 10^2–10^3 Pa in two series of experiments with different surface conditions. The experiment is compared with diffusion calculations. The effective values of the diffusion coefficients and solubilities have been obtained. Both the 'permeation' and 'accumulation' curves are analyzed. The later can mislead in judgment about the quality of the experiment and validity of the diffusion approach.

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1. Introduction

Permeation of hydrogen through martensitic steels is widely investigated in application to the water-cooled liquid lithium–lead breeding blanket [1–23]. The data on diffusivity and solubility have been accumulated from those measurements. For this purpose, the simple diffusion approach was commonly used.

Comparison of experiment and calculations is often a weak point of the publications. We have not found examples of comparison of the permeation rate curves. Curves measured in the regime of accumulation are available; and some of them demonstrate visible disagreement.

The measurement of accumulation $Q(t)$ is a static or integral method, while the measurement of the permeation rate $J(t)$ is a dynamic or differential method. Therefore, one can expect that $J(t)$ curves are richer in features in comparison with $Q(t)$ curves. We made our experiments in the permeation mode, and calculated $Q(t)$ by integration of $J(t)$. Then we compared both curves with predictions of the standard diffusion-limited model.

2. Experimental method and calculations

The experimental details are described in [23]. The permeation was measured in the temperature range of 523–873 K and inlet pressures of 10^2–10^3 Pa by a mass spectrometer in the dynamic regime. Oil-less vacuum (10^{-7} Pa) was achieved in a baked chamber by Ti discharge pumps. A steel membrane welded between two SS tubes was heated by a resistive heater. Two series of experiments were performed with the same sample. In the first series the surface was suggested to be 'clean' while in the second one was 'contaminated' after air leakage into the vacuum chamber. No analysis of surface purity was made.

The permeation rate was calculated using the well-known formula for the diffusion-limited permeation with a constant concentration C_0 determined by the Sieverts law on the inlet surface.

$$J(t) = \frac{DC_0}{l}\left\{1 + 2\sum_{n=1}^{\infty}\left[(-1)^n \exp\left(-\frac{D\pi^2 n^2}{l^2}t\right)\right]\right\}.$$

3. Comparison of experiments and calculations

Experiments with the 'clean' surface are presented in Figs. 1–4. Hereafter the experimental points are skipped,

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so their density may not coincide in the different figures. One can see from Fig. 1 that the permeation rate slightly rises linearly for a long time after achievement the quasi-steady-state level. This increase is not a good characteristic for the experiment. It means that some conditions, possibly on the surface, are not very stable. The negative feature of Fig. 1 disappears after integration of the permeation curve: the same experimental data represented in Fig. 2 as the accumulation curve look rather good. The dashed straight line really well approximates the steady-state phase (70–400 s) and gives the diffusion coefficient $D = 9.21 \times 10^{-5}$ cm^2 s^{-1} and solubility $S = 1.02 \times 10^{16}$ molecules cm^{-3} Pa$^{-1/2}$ (set 1). Unfortunately, this set is not suitable for description of the transient phase (dashed lines in Figs. 3 and 4). This phase can be well described with another set: $D = 1.15 \times 10^{-4}$ cm^2 s^{-1} and $S = 7.79 \times 10^{15}$ molecules cm^{-3} Pa$^{-1/2}$ (set 2), as the solid lines in Figs. 3 and 4 show, but this set does not suit the steady-state phase of the accumulation curve (Fig. 2).

The reason of the effects observed is obvious. As the experimental permeation rate is not constant in the quasi-steady-state, the accumulation curve is not straight on the large time scale; but its curvature is small and even not visible in Fig. 2. Nevertheless, the curvature of $Q(t)$ is positive, and the diffusivity obtained from Fig. 2 is underestimated. Therefore, the transient phase of permeation and accumulation cannot be reproduced properly with the respective set of parameters. The increase of the diffusivity (set 2) improves the situation in Figs. 3 and 4 but worsens long-term description (solid

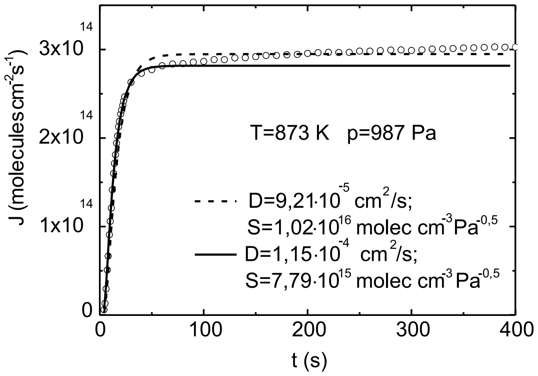

Fig. 1. Permeation rate as a function of time. Dots – measurements with a 'clean' surface. Lines – calculations for two sets of parameters. Dashed line – parameters are obtained from linearization of the accumulation curve in the quasi steady state phase (60–400 seconds) in Fig. 2. Solid line – parameters are taken to fit the experimental data on the permeation rate in the transient phase (0–70 seconds) Fig. 3.

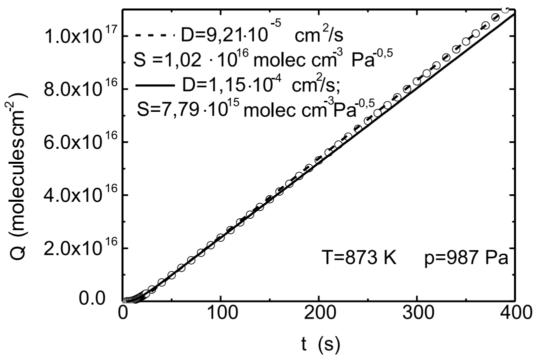

Fig. 2. Accumulation curve in the experiment with a clean surface re-plotted by integration of the permeation rate of Fig. 1. Dashed line: best linear fit in the range of 60–400 s in this figure. Solid line: the best fit of transient phase in Figs. 3 and 4.

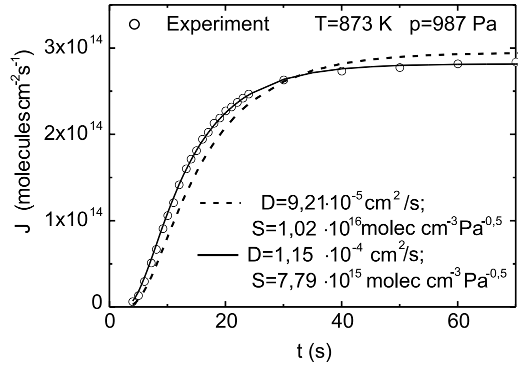

Fig. 3. Transient phase of permeation in the experiment with a clean surface (initial part of Fig. 1). Solid line: best fit in this figure (0–70 s). Dashed line: best fit of the steady-state accumulation in the range of 60–400 s in Fig. 2.

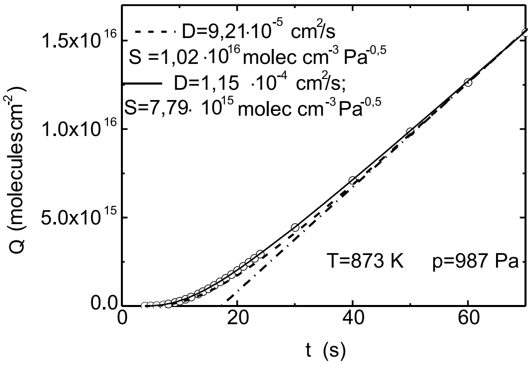

Fig. 4. Transient phase of accumulation in experiments with a clean surface (initial part of Fig. 2). Solid line: best fit of transient permeation in Fig. 3. Dashed line: best fit of the steady-state accumulation in Fig. 2. Dash-dot line: extrapolation of the linear accumulation in Fig. 2.

line in Fig. 2) because the permeability $P = DS$ in the set 2 is less than in the set 1.

This comparison shows that diffusivities and solubilities obtained from 'steady-state' and transient measurements may not coincide in general if the conditions of the experiment are not stable. Nevertheless, if the characteristic times of the instabilities are much longer than the diffusion time, the diffusion coefficient can be found with a good accuracy from the transient phase of permeation.

Experiments with the 'contaminated' surface demonstrated a significant decrease of the permeation rate and increase of the lag time. The permeation rate also increased steadily at large times, but the accumulation plot (Fig. 5) can be well approximated by a straight line in the quasi-steady-state phase of the experiment. The diffusion coefficient and solubility obtained from this approximation give a wrong description of the transient phase of the experiment (dashed lines in Figs. 6 and 7), but the change of parameters lead to a better agreement (solid lines in these figures). It is important to note that the agreement of experimental and calculated accumulation curves looks really good in Fig. 6, though we know that the permeation was suppressed by an order of magnitude due to surface contamination, and the diffusion limited regime is invalid. At the same time, differential representation of the experimental data (Fig. 7) shows that the diffusion approach disagrees with the experiment as it should be. An important conclusion follows from this comparison: accumulation analyses can mislead in judgment about quality of the experiment and validity of the diffusion limited consideration.

The temperature dependence of diffusion coefficient and solubility is shown in Figs. 8 and 9. One can see that the difference between the values obtained by fitting the accumulation and permeation curves is not large. One can see also that the values of the diffusivity and

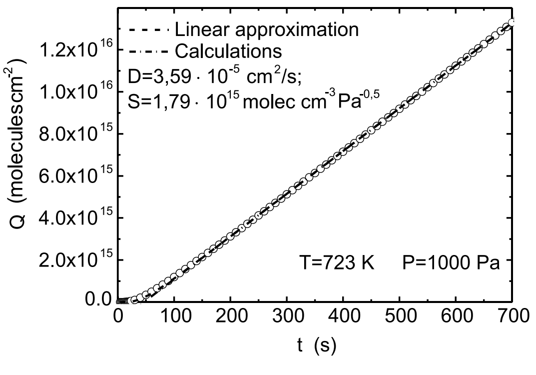

Fig. 5. Accumulation as a function of time in experiments with a contaminated surface. Dots: integration of the experimental permeation rate. Dash-dot line: linear approximation. Solid line: calculation.

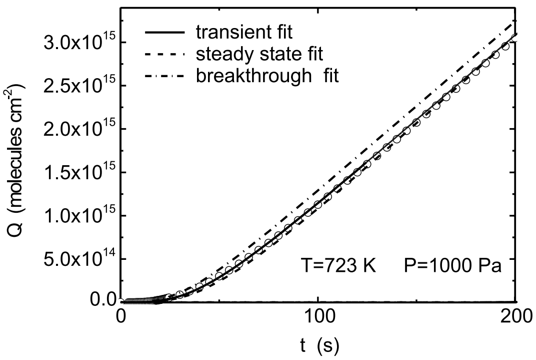

Fig. 6. Transient accumulation in experiments with contaminated surface. Solid line: 'best fit' in the time interval of this figure and Fig. 7. Dashed line: best fit of the quasi-steady-state phase in Fig. 5. Dash-dot line: fitting to initial phase of permeation in Fig. 7.

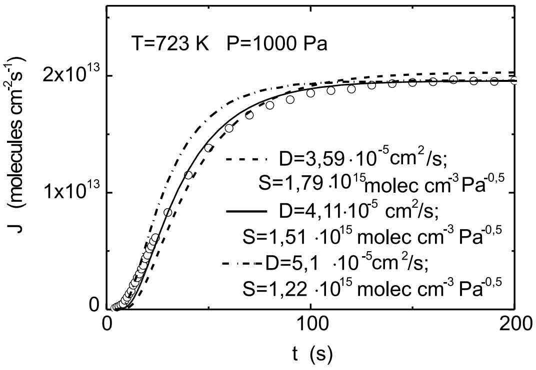

Fig. 7. Transient permeation in experiment with a contaminated surface. Solid line: 'best fit' in the time interval of this figure. Dashed line: best fit of linear accumulation in Fig. 5. Dash-dot line: fitting to an initial stage of permeation in this figure.

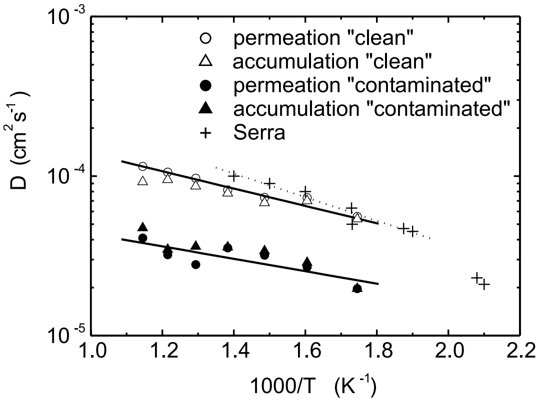

Fig. 8. Temperature dependence of the diffusion coefficient obtained in the two series of the experiments by using both the accumulation and the permeation curves.

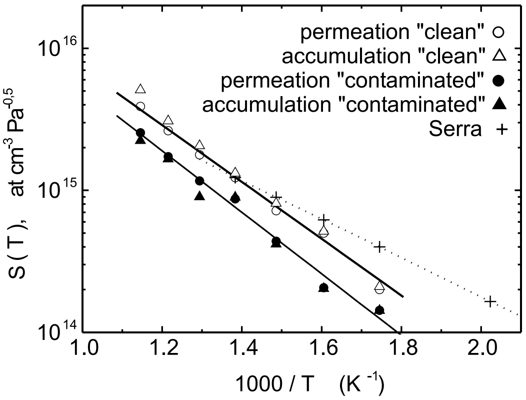

Fig. 9. Temperature dependence of the solubility obtained in the two series of the experiments by using both the accumulation and the permeation curves.

solubility obtained for the sample with the 'contaminated' surface are both less than in the experiments with the 'clean' surface by the factor of 3–4 each. This means that both *D* and *S* are underestimated if the diffusion limited approach is used for the description of experiments where surface effects are important.

4. Conclusion

Two sets of experiments on deuterium permeation through martensitic steel F82H with either 'clean' or 'contaminated' surface were performed and analyzed using a commonly accepted diffusion equation. The permeation rate was less and the lag time was longer in the second series.

Experimental data represented in the form of permeation rate and accumulation were analyzed. It has been demonstrated, that the accumulation curves can be well described by a straight line in the 'steady-state' phase of permeation though the permeation rate slightly increased in both series. It has also been demonstrated that the accumulation curve in the transient phase of experiments with the contaminated surface can be well described by the standard diffusion equation, though surface effects decreased the permeation rate by an order of magnitude.

The conclusion has been made that the analyses of accumulation curves can mislead in judgment about the quality of the experiment and validity of the diffusion limited approach.

The 'effective' values of diffusion coefficient and solubility obtained in the experiments with a 'contaminated' surface are both less than the real values if the diffusion limited model is applied.

Acknowledgement

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