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Abstract

Hydrogen including a trace amount of tritium was loaded on the edge surface of an F82H rod. After the loading, the rod was held at 298 or 323 K to allow hydrogen diffuse in and release out. Tritium tracer techniques have been applied to determine hydrogen depth profiles and hydrogen release rates by using an tritium imaging plate technique and a liquid scintillation counting technique, respectively. The depth profiles were composed of a surface localized component within 200 μm of the surface and a diffused component extending over 1 mm in depth. The apparent hydrogen diffusion coefficients obtained from the depth profile of the diffused component are near the extrapolated value of the literature data determined at higher temperatures. The surface localized component, which is attributed to trapping at surface oxides and/or defects, was released very slowly to give smaller apparent diffusion coefficients than those determined from the diffused component.

Keywords: F82H, Tritium, Hydrogen, Diffusion, Trapping, Surface

1. Introduction

Low activation ferritic steels have attracted much attention for their potential wide application as structural materials in fusion reactors. In particular, the iron alloy F82H, a reduced activation ferritic/martensitic steel developed by Japan Atomic Energy Agency (JAEA), is planned to be used in a DEMO reactor in Japan. A safety concern is for possible tritium permeation through this alloy if it is used as coolant pipes or first walls of the reactor, even at locations remote from the plasma. Although hydrogen permeation and diffusion in F82H have been studied previously, the temperature range of the studies were limited to temperatures above 573 K except for two cases [1,2].

In previous work [1], we applied a tritium tracer technique to determine the apparent hydrogen diffusion coefficient in a steel (Fe with 8% Cr and 2% W (8Cr2W)) similar to F82H around room temperature (RT). Although the data agreed with the extrapolation of Serra's data [2] obtained at the temperatures above 373 K to lower temperature range, the temperature dependence showed a significant deviation to lower values for temperatures below 473 K, which is very similar to hydrogen trapping seen in hydrogen diffusion in pure Fe. This motivated us to revisit hydrogen diffusion in F82H below 473 K. The present work again used tritium tracer techniques to study hydrogen diffusion and trapping in F82H. Instead of the gaseous charging or electrochemical charging previously employed, a DC glow discharge (DCGD) method was used to load much larger amounts of hydrogen, with accompanying defect formation.

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2. Experimental

Rectangular rods of F82H (4 x 10 x 1mm³) supplied by JAEA were used, after surfaces were mechanically polished to a mirror finish. Hydrogen (H) including a tracer amount of tritium (T) with T/H=10⁻⁶ was loaded into one edge surface of the rod by the DC glow discharge (DCGD) method, while the remaining area was covered by a SS316 cathode electrode. The details of the loading were shown elsewhere [3-5]. The DCGD was conducted in a Pyrex glass tube filled with H(T) gas at 40 Pa, applying a discharge voltage of 350 V by a pulsed mode with 1 min discharge and 1 min off for 1 h. The integrated H(T) loading time was 30 min. In order to prevent H(T) diffusion into the sample during DCGD, the tube was kept at liquid N₂ temperature. After the H(T) loading, all the sample surfaces except for the H(T) loaded surface were polished to remove T contamination. This procedure took 15 min at RT and could allow some of the loaded H(T) to diffuse in and release out, which we believe to be a negligibly

small fraction. Subsequently, two experiments were conducted; i.e. measurements of released T from the surface and depth profiling of T, as schematically illustrated in Fig. 1(a) and (b), respectively. The details of the experimental methods were described in [1, 3-6]; briefly, in the case of the T release measurement, the rod was immersed in a liquid scintillation counting (LSC) solution kept at 298 or 323 K and T released from the rod was collected in the LSC solution (see Fig. 1(a)). The integrated amount of T released to the solution in 10 min was periodically measured, continuing for 10 h, which gave the T release rates [1, 6]. Then, assuming the T/H ratio in the rod was the same as that in the H(T) gas, i.e. $T/H=10^{-6}$, the T release rates were converted to H release rates, $J(t)$.

The surface distribution of T activity (T distribution profile) was determined by a tritium imaging plate (TIP) technique at liquid N₂ temperature to inhibit the H(T) migration during the procedure, as shown in Fig. 1(b) [3-5]. These measurements were made on the side surface of the T loaded rod after holding times of 15 min, 1h, 3h and 10 h at a constant temperature, either 298 or 323K. In separate work [5], we found that the T distribution profile thus obtained corresponds with the depth concentration profile of T when surface layers of around 0.1 mm thickness were removed by mechanical polishing. Figure 1(c) is one of the T distribution profiles obtained from the rod; black to white gradation from left to right indicates the T penetration from the loaded surface into the bulk. A concentration profile of H, $c(x,t)$, averaged to the rod width (y-axis) direction can be obtained by,

$$c(x,t) \propto \int_0^{y_0} I_T(x,t) dy / y_0, \quad (1)$$

where $I_T(x, t)$ is the distribution of the T activity observed on the surface (Photo-Luminescence Intensity per unit area, PSL mm⁻²) and y_0 is the width of the rod.

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3. Results

Figure 2 (a) shows sequential changes of H depth concentration profiles for the rod with the holding time of 15 min, 1 h, 3 h and 10 h at 298K after H(T) loading at 200K. The H is clearly localized in the near surface region, within 200 μm, but with some penetrating to greater depths. Therefore the surface localized component $c_1(x, t)$ was separated from the remaining deeper distribution, $c_2(x, t)$, as indicated in the figure,

$$c(x, t) = c_1(x, t) + c_2(x, t), \quad (2)$$

By integrating the profile over all depths, x_0 , the total amount of H retained in the rod was obtained,

$$M(t) = \int_{x=0}^{x_0} c(x, t) dx, \quad (3)$$

and plotted against the holding time in Fig. 3. In the figure, one can find that $M(t)$ decreased within the first 3 h and became nearly constant afterwards, which was attributed to the surface localized component (see Fig. 2(a)) and designated as M_1 . Therefore an amount of component 2, M_2 , was determined by,

$$M_2 = \int_{t=0}^{\infty} M(t) dt - M_1. \quad (4)$$

The ratio of the integrated amounts M_1 and M_2 was 2/3 or 40%/60%.

Figure 4 shows changes of the release rates of H from the rod with time at 298 and 323 K measured by the LSC technique, referred to as $J(t)$. The solid lines in the figure are numerically calculated release rates, which are discussed later. The integrated released amount, which should be equivalent to M_2 , was determined to be 9.6×10^{14} H atoms at 298 K and 4.9×10^{14} H atoms at 323 K. Considering the fugacity of H during DCGD, which is likely a GPa level of H pressure [7], and assuming the H solubility in F82H is similar to that in pure iron (Fe) at 200 K, the Sievert's law gives the H concentration of around 10^{-5} H/Fe atom ratio. Assuming the concentration of H loaded by DCGD is constant with H/Fe nearly equals to 1 within 6×10^5 layers (200 μm) of Fe, the retained amount of H in the layers is estimated to be around 10^{15} atoms, which is consistent with the observed depth of around 200 μm in Fig. 2 (a). When DCGD was stopped, the fugacity dropped immediately to the H gas pressure of around 40 Pa, and the H in the surface layers was oversaturated and hence released from the surface and diffused into deeper. Still some H was retained or trapped in trapping sites in near surface layers, such as surface oxides, grain boundaries, defects and defect clusters formed by the H loading during DCGD. Actually, about 40% of the initially retained amount of H was remained for a long time in near surface regions, as noted above.

In distinction from the surface localized component, we have tried to determine the apparent diffusion coefficients for the component 2, $c_2(x, t)$, in the depth profiles as seen in Fig. 2 (b) which shows magnified section of the H depth profiles, 20 times those given in Fig. 2(a). In the figure, one can clearly see that the H concentration extends deeper as the holding time increases from 15 min to 3 h, while that in the deeper region is almost disappeared when the rod was held for 10 h after the loading due to H release

from the rod.

The depth profiles after 1, 3 and 10 h were numerically fitted to a simple solution of the one dimensional Fick's second equation to give the H concentration profiles shown in Fig. 2 (c). Since we could not get surface boundary condition for $c_2(0,t)$ at $t=0$, because the observed depth profile $c(x,t)$ included the surface localized component, we assumed normal diffusional release of H, i.e. $c_2(0,t)=0$ ($t > 0$) and $c_2(\infty,t)=0$. Therefore both the apparent diffusion coefficient and the initial surface concentration $c_2(0,0)=c_0$ were determined as fitting parameters. The best fit gave the apparent H diffusion coefficient, $D = 5 \pm 2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ at 298 K as labeled in Fig. 2 (c). There is a large uncertainty, due to the simultaneous determination of the apparent diffusion coefficient and the initial surface concentration.

From the H release rate, apparent diffusion coefficients were also determined by fitting the solution of Fick's equation under the same initial and boundary conditions used above and the best fit results are given in Fig. 4. The apparent H diffusion coefficients thus obtained were about one order of magnitude smaller than those determined by the H depth profile, but are consistent with our previous results [1] which were determined by the H release rate.

4. Discussion

In Fig. 5, the apparent H diffusion coefficients obtained in this work are compared with literature data [1-2, 8-9]. The present values determined from the depth profiling are in agreement with the lower temperature extrapolation of Schliefer's data, as indicated by a solid line in the figure giving the temperature dependence of the diffusion coefficients as $D = 7.7 \times 10^{-6} \exp(-34.3 [\text{kJ mol}^{-1}] / RT)$, but they are much lower than extrapolation of Serra's [2] and Kulsartov's [9] data evaluated above 573 K with activation energies of 14.0 kJ mol^{-1} and 8.0 kJ mol^{-1} shown as dotted and dashed lines, respectively. However, the Serra's experimental data, which is bending to lower values below 473 K when extrapolated to RT (chained line), coincides with the present data determined from the H release rate. It is well known that diffusion data in bcc Fe are strongly influenced by trapping and/or surface oxidation, resulting in large deviations to lower values [10]. In particular, diffusion coefficients determined by thermal release and/or permeation methods are easily influenced by trapping. Actually those determined here from the H release rates should be dominated by the slow release of the surface localized component. In this respect, the diffusion coefficients determined from the depth profiling is a more direct measurement of the bulk H

diffusion, and the activation energy of 34.3 kJ mol^{-1} obtained here is the most plausible value for the bulk H diffusion in F82H near RT. Still, it seems very high compared to 14.0 kJ mol^{-1} [2] and 8.0 kJ mol^{-1} [9], indicating the influence of the surface localized H.

At present, the cause of surface localization of H is not clear, but it likely correlates with a surface oxide with large H trapping energy. In this respect, Cr, one of the alloy components, is well known to be oxidized even in a hydrogen gas atmosphere by any impurity moisture [10]. Although DCGD could introduce lattice defects in the surface layers, water vapor included in the hydrogen gas could easily react with the defects to enhance oxygen uptake. The influence of surface oxygen or surface oxides on H or T uptake is under examination.

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4. Conclusions

In order to clarify hydrogen behavior in F82H, we have applied tritium tracer techniques. Hydrogen, including a trace amount of T, was loaded on the edge of a F82H rod by DCGD at 200 K. After the loading, the rod was held at 298 or 323 K for long times to allow H diffuse in and release from the rod. During the sample holding, H depth profiles and H release rates were determined by the TIP technique and by the LSC technique, respectively.

The H depth profiles were clearly separated into two components; one that had diffused deeply into the bulk and the other highly localized in near surface regions. Correspondingly, 60% of the initially retained amount was released within first 3 h as the diffused component and 40 % remained for a long time as a surface localized component. Apparent H diffusion coefficients determined from the depth profiles in the deeper region are near the extrapolated value of the literature data determined at higher temperatures. The surface localized component was released very slowly to give smaller apparent diffusion coefficients than those determined from the diffused component. The apparent H diffusion coefficients determined by the depth profiling are more reliable than those determined by the release or permeation, because the influence of the surface localized H is mostly excluded. The surface localization of H is very likely caused by trapping at surface oxides, most probably Cr oxide, and by defects produced by DCGD.

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Acknowledgement

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Figure captions

- Fig. 1 Schematics of (a) T release experiment by the LSC technique, (b) T depth profiling experiment by the TIP technique, and (c) T distribution profile at 3h (298 K) after the loading; black to white gradation from left to right in (c) indicates T penetration from the loaded surface to the deeper into the bulk.
- Fig. 2 (a) H concentration profiles $c(x,t)$ determined by the TIP technique at 15 min, 1 h, 3 h and 10 h held at RT after the H(T) loading at liquid N₂ temperature and (b) their profiles magnified 20 times, and (c) calculated concentration profiles at respective times, assuming H was initially distributed within 200 μm in depth ($t=0$) with constant concentration and freely diffused into the depth and/or released from the surface.
- Fig. 3 Sequential changes of remaining H in the rod, $M(t)$, determined by the integration of the depth profiles. Around 60% of the initially retained H was released within a few hours and afterwards the release amount remained almost constant.
- Fig. 4 Release rates of H from the rod measured by the LSC technique, $J(t)$, at 298 and 323 K.
- Fig. 5 Comparison of hydrogen diffusion coefficients in F82H determined from the depth profiles and the release rates together with literature data [1-2, 8-9].

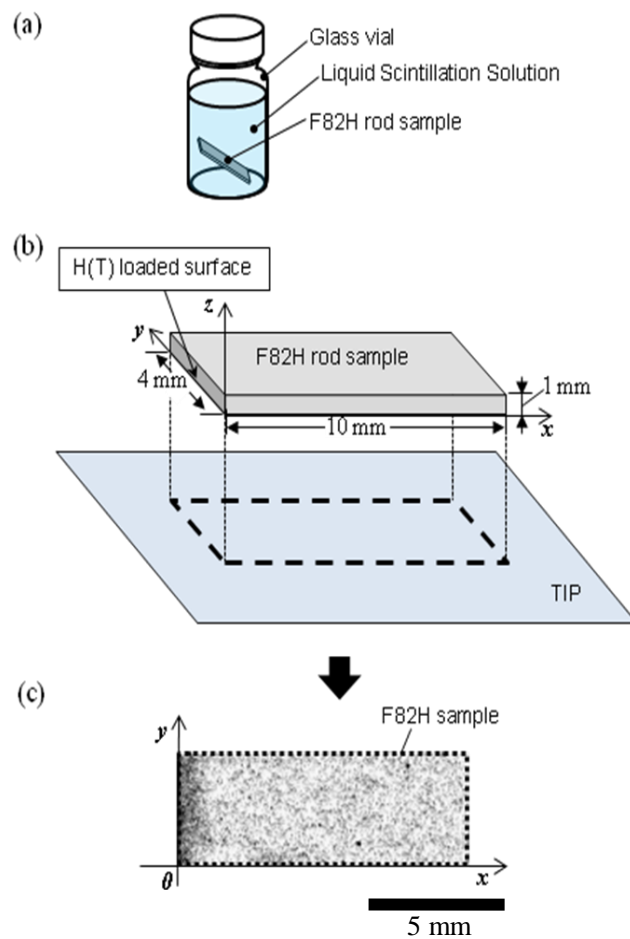


Fig. 1

T. Otsuka, one column

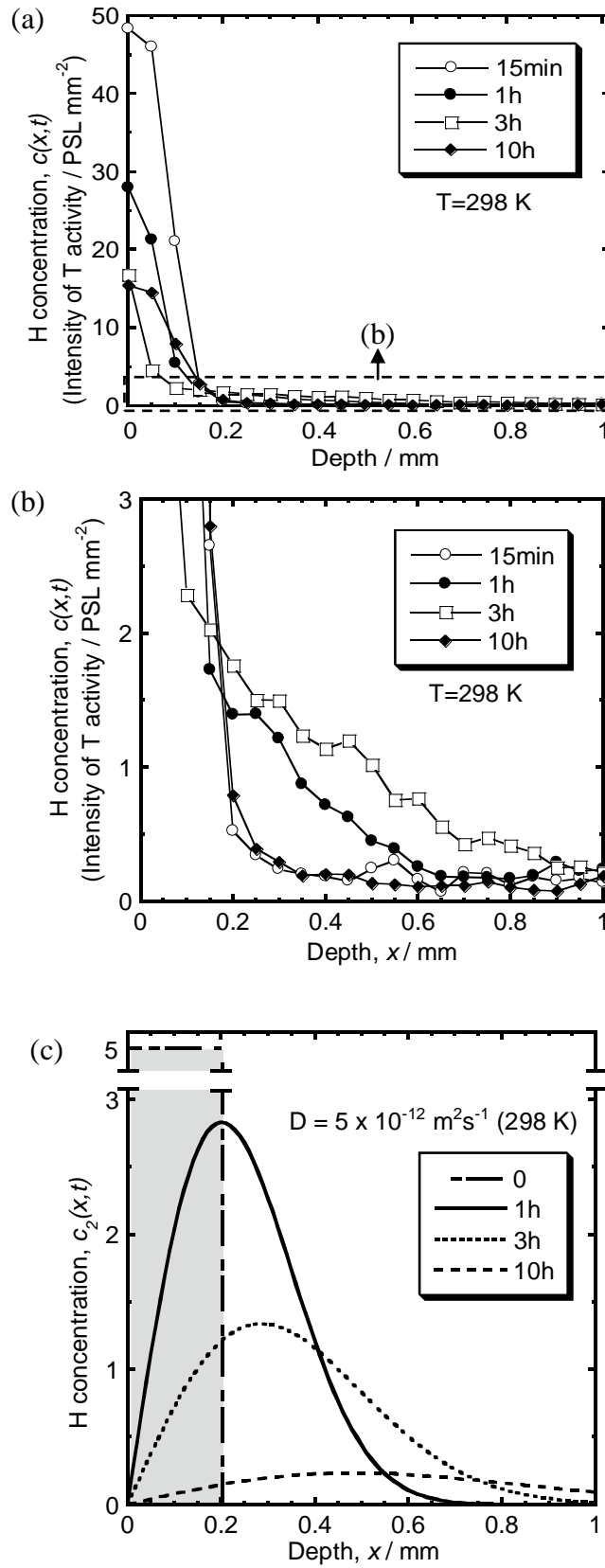


Fig. 2

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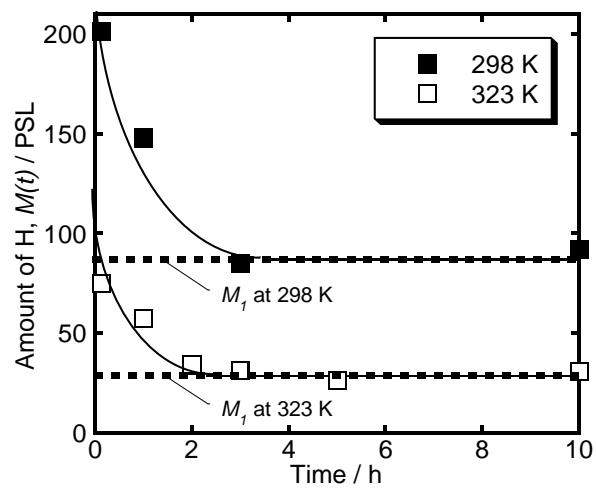


Fig. 3

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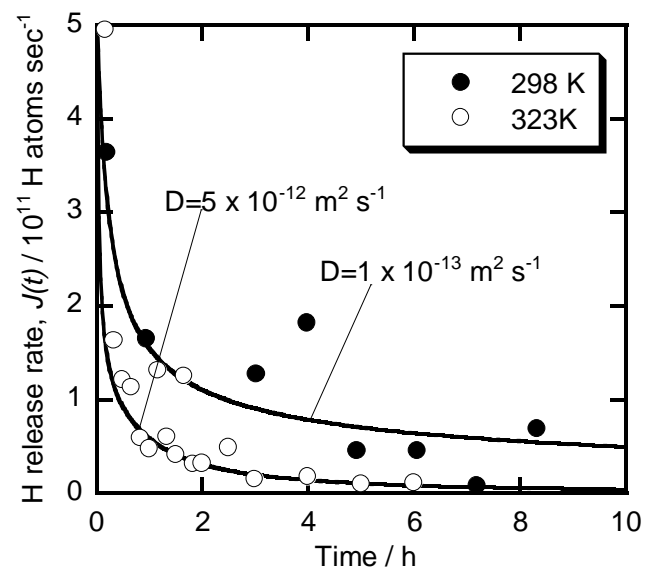


Fig. 4

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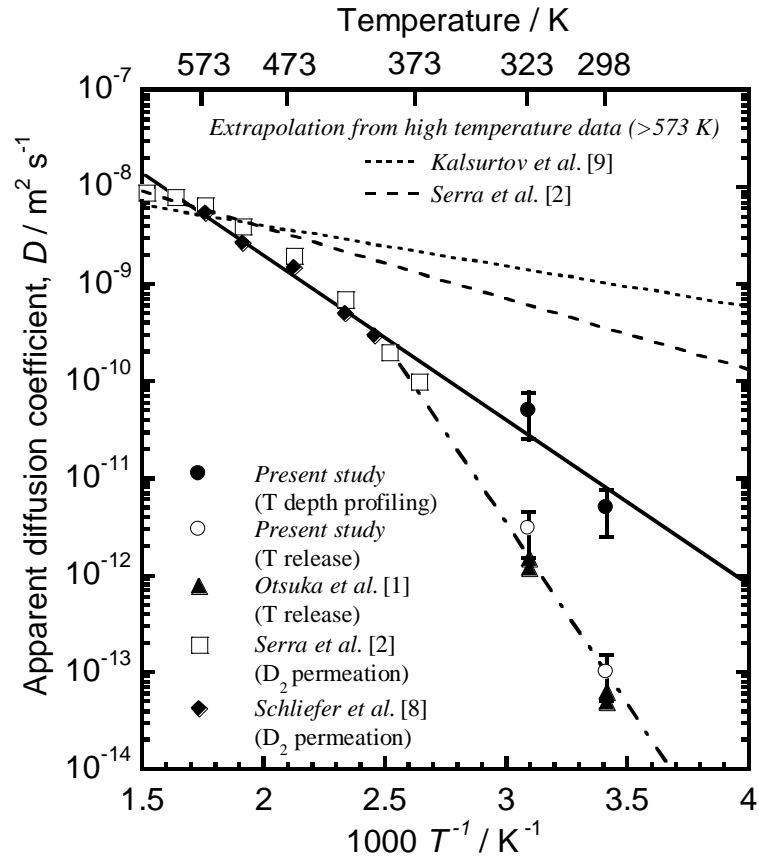


Fig. 5

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