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Retention and release behaviors of plasma-loaded hydrogen in ferritic steels

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In order to understand retention and release behaviors of plasma-loaded hydrogen in ferritic steels, hydrogen depth profiles were examined by means of a tritium imaging plate technique (TIPT). Hydrogen release was strongly affected by trapping effect in bulk and/or barrier effect of surface oxide layers during long term storage in air at room temperature (RT) and even heating in vacuum. Helium (He)-DC glow discharge (DCGD) treatment at high temperature played a role in removing surface oxide layers and made quick hydrogen release by normal diffusion.

Keywords: tritium imaging plate technique, ferritic steel, hydrogen, diffusion, He-DC glow discharge

1. Introduction

Ferritic/martensitic steels are candidate materials in a Japanese DEMO reactor [1]. Tritium removal from the steels is one of safety issues in the reactor. Tritium removal methods such as thermal heating and inert-gas DC glow discharge (DCGD) have been proposed [2-4]. However, hydrogen release mechanism during these removal processes is not fully clarified due to lack of information on hydrogen behaviors in bulk of the steels. In the previous work, hydrogen depth profiling method using a tritium imaging plate technique (TIPT) has been proposed [5] to examine hydrogen penetration and retention behavior in a reduced activation ferritic/martensitic steel (F82H). In the present study, TIPT has been applied to investigate changes of hydrogen depth profiles after removal processes to understand release behavior of plasma-loaded hydrogen from the ferritic steels.

2. Experimental

The sample used here was a disc of a ferritic steel, SS430, with a diameter of 10 mm and a thickness of 3~6 mm. The compositions of SS430 were 16Cr, 0.4Mn, 0.09Ni, 0.04C in wt-% and balanced Fe. The sample surfaces were mirror finished by 0.06 μm colloidal silica to remove working stains. Fig. 1 shows a schematic experimental apparatus for hydrogen loading by DCGD method [6, 7]. Hydrogen (H) including a trace amount of tritium (T, T/H = 1.3×10^{-4}) was loaded to one edge surface of the sample through a hole (ϕ = 5 mm) in a mask made of molybdenum. The operating gas pressure of DCGD was about 80 Pa and the applied DC voltage was set to be 400 V.

The loading was conducted at 373 K for 2~3 h to allow hydrogen diffusion into the bulk. After the loading, the sample was rapidly cooled down to RT.

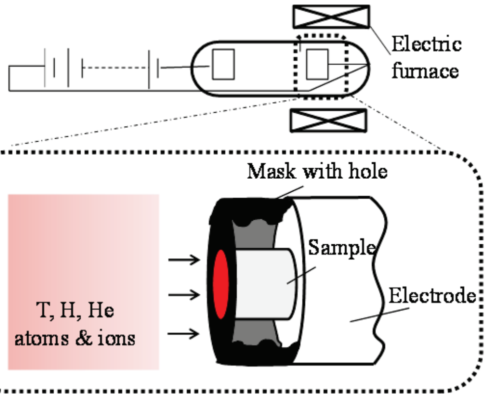

Fig. 1 Schematics of the experimental apparatus for hydrogen loading by DC glow discharge method and He-DCGD method.

After the loading, three removal processes were conducted to release plasma-loaded hydrogen from the sample. The first method was long term storage in air at RT for 1 year. The second one was heating treatment in vacuum at 473 K for 1 h. The third one was helium (He)-DCGD treatment at 473 K for 1h in which the experimental apparatus was used as shown in Fig. 1. After these removal processes, hydrogen concentration profiles on the surface and in the bulk of the sample were observed by TIPT [6]. Surface profiling was conducted on the plasma-loaded surface side at RT for 1 h as schematically shown in Fig. 2 (a). Subsequently, the sample was cut into two halves by a diamond wire saw to examine a cross-section surface perpendicular to the plasma-loaded surface. The depth profiling was conducted on the cross-section surface for 24 h as shown in Fig. 2 (b).

The resolution in the hydrogen depth profile was 50 μm, corresponding to a minimum reading size of the TIP scanning apparatus (BAS2500).

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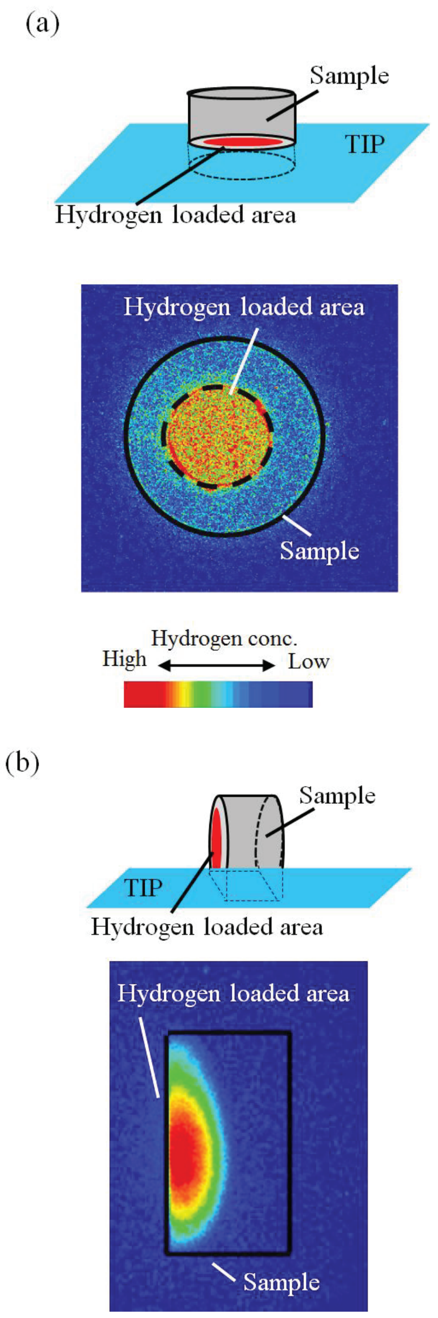

Fig. 2 (a) Schematic of surface profiling and (b) depth profiling on the cross-section surface.

3. Results

Figure 3 shows the hydrogen depth profiles just after the loading at 373 K for 2 h and how the hydrogen depth profile changed after long term storage in air at RT. In the figure, one can clearly see that the hydrogen penetration reached a maximum around 0.25 mm in depth and decreased towards the loading surface and penetrated towards a deeper region (2 mm). After isothermal storage in air at RT, the amount of hydrogen in the bulk was reduced by release at RT, but some fraction of hydrogen remained and penetrated up to 3 mm in the bulk.

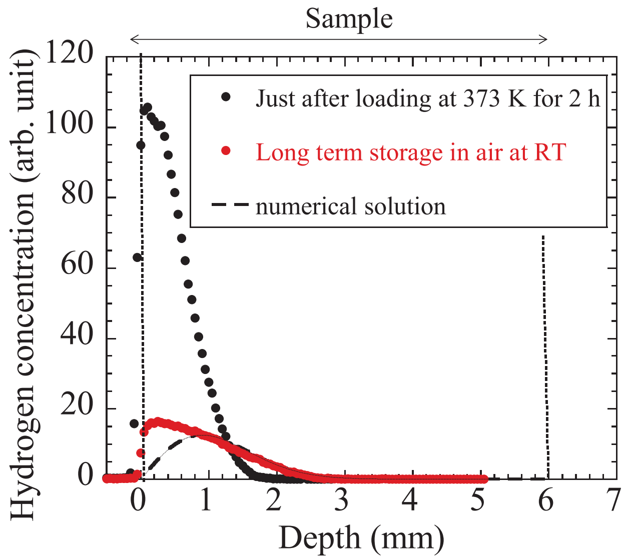

Fig. 3 Hydrogen depth profiles loaded at 373 K for 2 h and long term storage in air at RT for 1 year.

Figure 4 shows changes of the hydrogen depth profiles after the loading at 373 K for 3 h and subsequent heating in vacuum at 473 K for 1 h. The figure indicates that hydrogen concentration at the surface was still high and most of hydrogen remained in the bulk to penetrate up to 3 mm in the bulk.

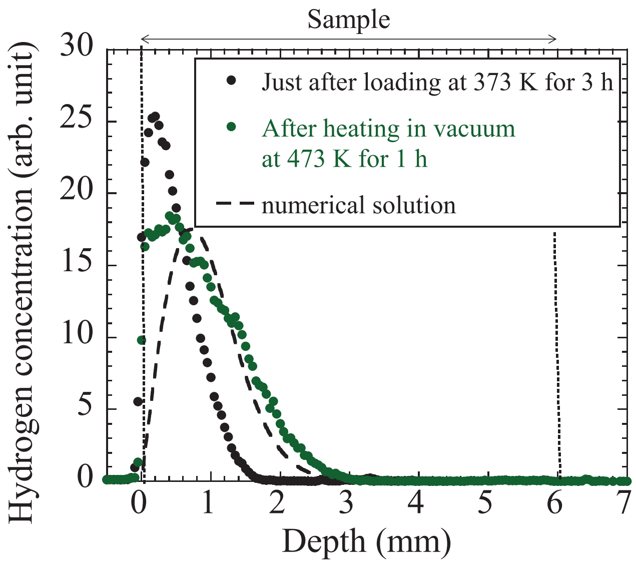

Fig. 4 Hydrogen depth profiles after heating in vacuum at 473 K for 1h

Figure 5 shows changes of the hydrogen depth profiles after the loading at 373 K for 3 h and subsequent He-DCGD treatment at 473 K for 1 h. The data for the He-DCGD treatment are multiplied by 10. The hydrogen concentration at the surface became almost zero and the amount of hydrogen in the bulk significantly decreased in comparison with that only by heating in vacuum (Fig. 4) in spite of the same treatment temperature.

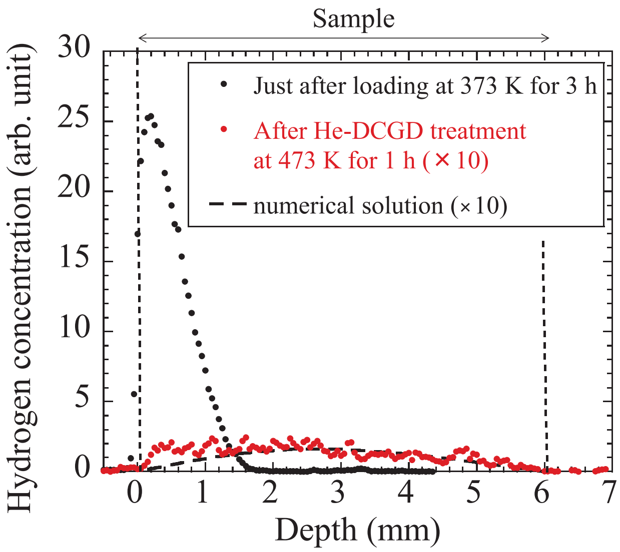

Fig. 5 Hydrogen depth profiles after He-DCGD treatment at 473 K for 1 h.

4. Discussion

Fig. 6 summarizes the hydrogen diffusion coefficients for F82H determined in our previous works compared with the literature data [5, 6, 8, 9]. The literature data were examined by means of the hydrogen gas permeation method and the hydrogen release method. These data in its Arrhenius plot were likely to reduce the diffusion coefficient as temperature is decreased bend downwards than expected from the extrapolated values from higher temperature data to lower temperatures below 473 K as shown Fig.6. The reasons of the bend, which could be attributed to a surface effect and/or a trapping effect in the bulk as known in pure Fe [10]. Our results were in good agreement with extrapolated curve from the higher temperature data of literature as shown in Fig.6. This indicates that the surface effect and/or trapping effect is negligible on hydrogen diffusion even at lower temperatures due to excess injection of energetic hydrogen by the DCGD resulting in higher driving force to saturate hydrogen trapping sites at the surface and even in the bulk of F82H such as lattice imperfections, dislocations and grain boundaries. Hydrogen loaded by plasma exposure penetrated into the bulk by normal interstitial diffusion.

In Figs. 3-5, assuming that changes of hydrogen depth profiles were caused by hydrogen diffusion during long term storage in air at RT, heating in vacuum and He-DCGD treatment, the hydrogen concentration profiles were numerically analyzed on a basis of the Fick's diffusion equation (hereinafter referred as a numerical solution). The hydrogen diffusion coefficient for SS430 was determined as a fitting parameter. The best fit results were shown in Figs. 3-5 as a broken line. The obtained diffusion coefficients for SS430 are summarized in Fig. 6. The value obtained from the profile changes during isothermal storage in air at RT was much lower than that determined from the depth profiles just after the loading. Although the microstructures are different between F82H and SS430 except for the main αFe content, hydrogen release from the ferritic steels would be much influenced by the surface effect and/or the trapping effect due to low driving force.

The value obtained from the profile changes during thermal heating in vacuum was two orders of magnitude smaller than that obtained from the profile changes during the He-DCGD treatment. At high temperatures, SS430 would be easily oxidized even in vacuum due to higher Chromium contents [11]. Comparing these profiles in Figs. 4 and 5, it was found that hydrogen release by annealing at higher temperature was strongly affected by trapping effect in the bulk and/or barrier effect of surface oxide layers during long term storage in air at RT and even heating in vacuum [12]. The diffusion coefficient for SS430 by the He-DCGD treatment was almost the same as that by normal diffusion of hydrogen in F82H. This indicates that the He-DCGD treatment would play a major role in making quick hydrogen release by normal diffusion by removal of surface oxide layers.

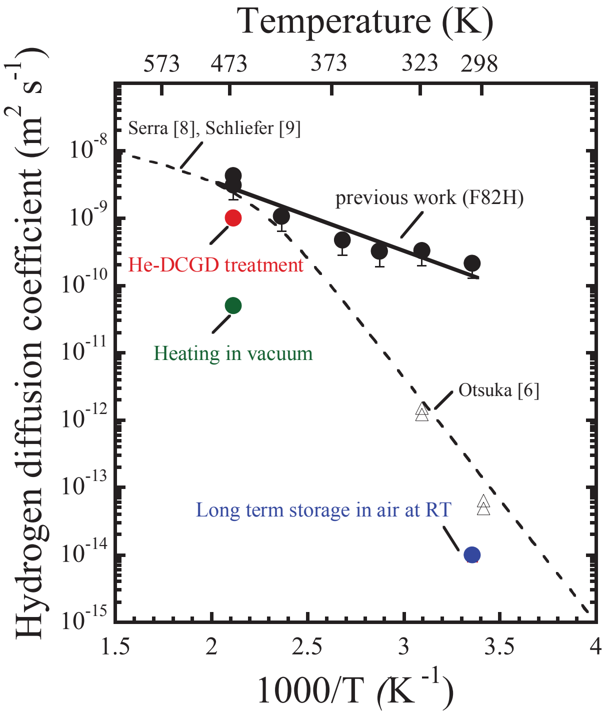

Fig. 6 Comparison of hydrogen diffusion coefficients in ferritic steels determined in the present study together with literature data [5, 6, 8, 9].

5. Conclusions

Hydrogen depth profiles in the ferritic steels were examined by TIPT to understand retention behavior of plasma-loaded hydrogen and its release behavior during long term storage in air at RT, heating in vacuum and

He-DCGD treatment.

Hydrogen loaded by plasma exposure at higher temperature penetrated into the bulk by normal interstitial diffusion and remained for a long time by trapping in the microstructures at RT. Such hydrogen was not easily released by diffusion due to trapping effect in the bulk and/or barrier effect of surface oxide layers during long term storage in air at RT and even heating in vacuum. He-DCGD treatment at higher temperature played a major role in removing surface oxide layers and made hydrogen easy to release by normal diffusion.

References

[1] H. Nakamura *et al.,* Fusion Eng. Design **81**, 1339 (2006).

[2] Y. Kimura *et al.,* J. Nucl. Mater. **417** 896-899 (2011)

[3] H. Nakamura *et al.,* Fusion Eng. Design **70** 163 (2004)

[4] D. Mueller *et al.,* J. Nucl. Mater. **241-243** 897 (1997)

[5] M. Higaki *et al.,* Proceedings of TRITUM 2013 (2013)

[6] T. Otsuka *et al.,* J. Nucl. Mater. **417** 1135 (2011)

[7] T. Otsuka *et al.,* Psys. Scri. T145 014035 (2011)

[8] E. Serra *et al.,* J. Nucl. Mater. **245** 108 (1997)

[9] F. Schliefer *et al.,* J. Nucl. Mater. **283-287** 540 (2000)

[10] T. Tanabe *et al.,* Fusion Eng. Design **25** 1 (1984)

[11] T. Tanabe *et al.,* Trans. Jpn. Inst. Metals **25** 1 (1985)

[12] T. Otsuka *et al.,* J. Alloys and Compounds **580** S44-S46 (2013)