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Diffusion and trapping of tritium in vanadium alloys

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Abstract

Tritium diffusion in a vanadium alloy (V–4Cr–4Ti) has been investigated at temperatures ranging from 230 K to 573 K. Tritium was loaded into the surface layers of the alloy specimen with an ac-glow discharge. Before and after diffusion annealing of the specimen, tritium diffusion profiles were measured by means of an imaging plate (IP) technique. Tritium diffusion coefficients (D_T), which were evaluated by fitting a numerical solution of the diffusion geometry employed here to the obtained diffusion profiles, were a little smaller than those for pure V with the activation energy of 0.13 ± 0.01 eV. Below 320 K, in addition, the Arrhenius plot of D_T bent downwards showing a larger activation energy of 0.19 ± 0.01 eV, probably owing to the trapping effect of both of Cr and Ti. The effect of alloying elements on tritium diffusion and the influence of tritium release from the surface were discussed.
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1. Introduction

Low activation vanadium alloys are one of candidate structural materials of a nuclear fusion reactor, in particular, equipped with a liquid lithium blanket [1]. Tritium retention and permeation out of the reactor system are concerns from a standpoint of tritium inventory and safety issue, although the details of such blanket systems are not clear at the present stage. Since vanadium alloys are known as a hydrogen absorbing material and hydrogen diffusion in them is very fast [2–5], tritium behavior is one of the critical issues of tritium safety. Therefore, we have started to examine tritium diffusion in V–4Cr–4Ti (NIFS-HEAT-II) [6].

In a previous study [7], we have successfully applied an imaging plate (IP) technique to observe tritium concentration profiles in rod-shaped V–4Cr–4Ti alloys and determined tritium diffusion coefficients, D_T, at temperatures ranging from 373 to 573 K. The obtained D_T was comparable to that for V–4Ti alloy [2], but the trapping effects of alloying elements and other impurities on tritium diffusion was not still clarified.

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In the present study, we have determined tritium diffusion coefficients in V–4Cr–4Ti using the IP technique in a more wider temperature range from 230 K to 573 K. V–4Cr–4Ti coupons were used instead of the rod-shaped one used in the previous work, in order to get clearer tritium diffusion profiles in the specimen. Tritium (T) diluted in hydrogen gas (H_2) was loaded onto the surface of the coupon with an ac-glow discharge method [8]. The tritium profiles before and after diffusion annealing were examined with IP. In this experiment, high tritium containing surface layers were clearly separated from the tritium diffusion profiles. The existence of such layers would be a safety issue for handling vanadium alloys faced a D-T plasma. Based on the tritium profiles obtained, we have focused on characteristics of the tritium release from the surface layers, tritium diffusion and trapping effects of alloying elements in V–4Cr–4Ti during the diffusion annealing.

2. Experimental

In the present study, V–4Cr–4Ti alloy (NIFS-HEAT II) coupons (25 mm long, 4 mm wide and 0.2 mm thick) heated in a vacuum (10^{-5} Pa) at 1273 K for 2 h were used as specimens. The surface of the specimens was mechanically polished with abrasive papers and finished with 0.3 μm Al_2O_3 powder.

By means of an ac-glow discharge method, an apparatus of which is shown in Fig. 1, tritium was loaded onto the top end side surface of the specimens which were held in an electrode. The discharge was made by applying an altering electric potential of 3 kV between two electrodes in hydrogen gas containing tritium ($T/H = 10^{-6}$) of 30 Pa for 40 min. As shown in Fig. 1, the lower part of the discharge tube was immersed into liquid N_2 filled in a Dewar flask in order to prevent temperature rise of the specimen during the loading.

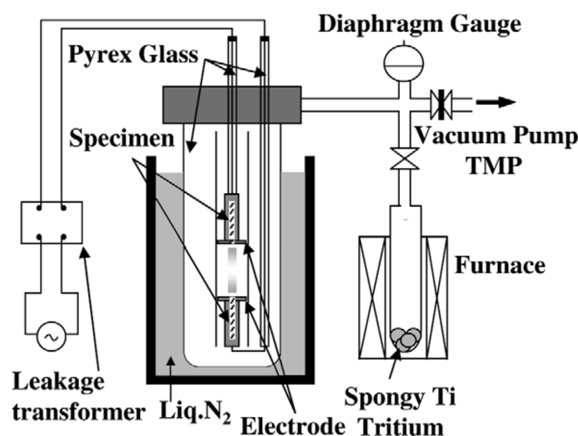

Fig. 1. Schematic drawing for apparatus used for tritium ac-glow discharge loading.

Immediately after the loading, the side surface of the specimen was exposed to an imaging plate (IP: FUJIFILM BAS-TRI2025) in a vacuum container (10^{-1} Pa) cooled in liquid N_2 for 24 h. Then, IP was processed by IP reader (FILMFILM BAS2500) to get areal intensity profiles of photo-stimulated luminescence (PSL) which correspond to areal tritium retention profiles.

After the tritium loading, specimens were diffusion-annealed at a temperature ranging from 230 K to 573 K in vacuum (10^{-1} Pa below 303 K and 10^{-5} Pa above 323 K) for a given time t, which was determined so that the diffusion depth $(2D_T t)^{1/2}$ was adjusted to be around 6 mm. Then, the tritium distribution from the top end to the bottom end, corresponding to a tritium diffusion profile, was measured by IP as mentioned above. It should be pointed out that tritium release from the major surface area, i.e. perpendicular to the diffusion direction, was prohibited by the surface oxide layers. The barrier effect of the surface oxide layers was limited below 573 K, above which the oxide disappeared because oxygen was dissolved into the bulk. Accordingly, tritium release became appreciable above 573 K, and the release rate increased rapidly above 623 K. Hence the measurements were limited below 573 K.

Although the surface oxide layers are required as the barrier for tritium release, an excess oxygen uptake from the environment should be suppressed during the diffusion annealing. The excess oxygen uptake could result in thicker oxide layers, which prohibit the escaping of β^- rays from the surface to be detected by IP (the escaping depth of tritium β^- ray from vanadium is less than 2 μm). Therefore, the diffusion annealing above 303 K was carried out in vacuum of 10^{-5} Pa. During the lower temperature annealing, a specimen container was evacuated up to 10^{-1} Pa to prevent humidity condensation on the specimen surface. At 303 K, the diffusion experiments were performed at both pressures (10^{-1} and 10^{-5} Pa) and no appreciable differences in the tritium diffusion coefficients were observed. In any case, even the thin oxide layers, which formed during the diffusion annealing, could somewhat prevent

the β^- rays to escape from specimen surface. Therefore, the surface layers were removed with the abrasive paper to obtain a clear PSL profile, before the specimen was exposed to IP. The removal of the surface layers did not influence the tritium diffusion profiles.

3. Results and discussion

Fig. 2 shows the initial PSL profile (tritium image) and averaged PSL intensities along diffusion depth (diffusion profile) at the wide surface of the specimen just after the tritium loading. Tritium penetration into the depth was appreciable even before the diffusion annealing. In addition, the enlarged image in Fig. 2 shows the brighter area extending to the left side from the top end of the specimen (0 depth). This is due to the exposure of IP with β^- rays traveling in the air from tritium on the top end surface of the specimen: i.e. hence the PSL intensity of this bright area corresponds to the tritium retained in the front end surface layers. In an additional experiment, the surface PSL intensity of the present specimen was compared with that of V–4Cr–4Ti bulk one with uniform tritium concentration. Based on the PSL intensity and the isotope abundance ratio ($H/T = 10^6$), the hydrogen concentration (C_H) in the surface layers was estimated to be 5–20 at.%. Even after the diffusion annealing, this bright region remained especially at low temperature annealing. Fig. 3(b) shows the change of the surface tritium retention which was determined by integrating PSL intensities in the dotted square in the Fig. 3(a). As seen in the Fig. 3(b), a heat treatment higher than 500 K is required to remove the high tritium concentration layers and hence this high tritium containing surface layer very likely corresponds to hydride. Therefore hydrogen released from the surface by the decomposition of the hydride seems to be separated from the diffusing hydrogen in the bulk. In the tritium release experiment out of specimen as mentioned above, the amount of tritium was not measurable at 500 K

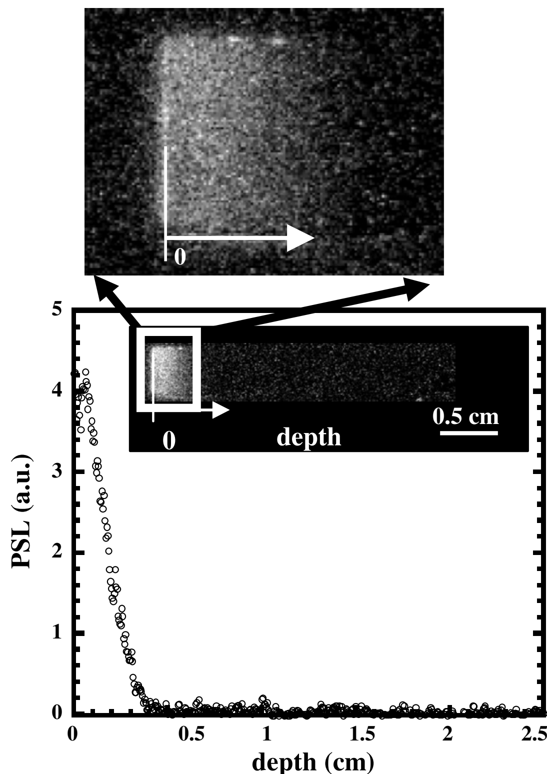

Fig. 2. Tritium image and diffusion profile just after the tritium loading obtained by the IP technique.

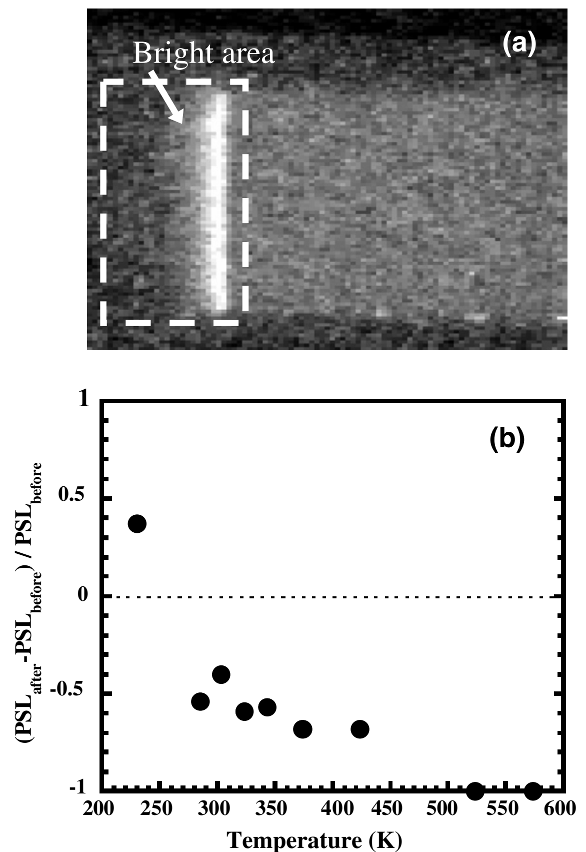

Fig. 3. (a) Tritium image for high tritium containing surface layers and (b) changes of the tritium retention in the surface layers with diffusion annealing.

because of low isotope abundance ratio. In any case, the appearance of the surface hydride under tritium plasma exposure might become a critical issue for tritium handling and safety in fusion reactors.

As seen in Fig. 2, the tritium diffusion was already occurred during the tritium loading, though the specimen was cooled down to prevent the tritium diffusion. In the present experiment, the surface temperature during the loading was not measured but it could be much higher than liquid N_2 temperature owing to the heat generated by glow discharge. Immediately after stopping the discharge, however, the specimen was cooled down to liquid N_2 temperature and this initial tritium distribution was retained during the storage in the vacuum vessel cooled in liq. N_2. Hence the diffusion annealing started with this initial tritium distribution.

Because of the initial tritium distribution, a simple theoretical model such as diffusion with thin film source in a semi-finite media could not be applied to determine the tritium diffusion coefficient (D_T). Therefore, a one-dimensional diffusion equation of tritium concentration C_T,

$$\frac{\partial C_T}{\partial t} = D_T \frac{\partial^2 C_T}{\partial x^2}$$

with the initial distribution such as shown in Fig. 2 was numerically solved. Changing a diffusion coefficient as a parameter, the diffusion equation was solved until the solution fit to the tritium profile to get D_T. In Fig. 4, the diffusion profile of tritium

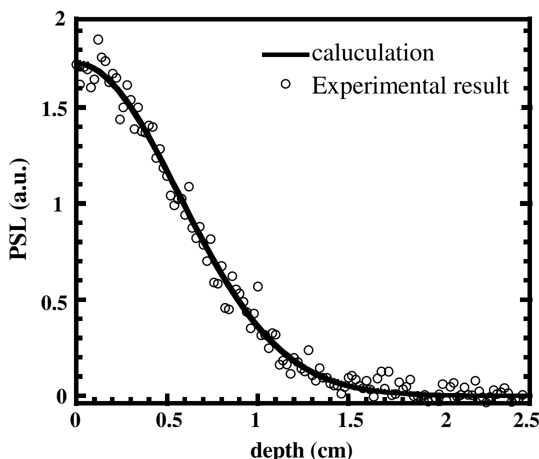

Fig. 4. Tritium diffusion profile in a specimen diffusion-annealed at 373 K compared with the best fitted numerical solution of the diffusion equation.

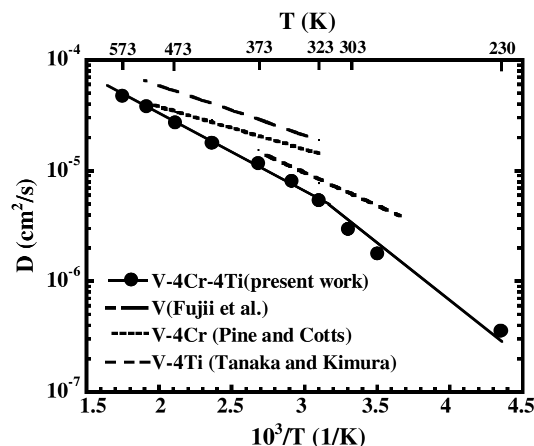

Fig. 5. Arrheinus relation of tritium diffusion coefficients in V–4Cr–4Ti together with literature data for pure V, V–4Ti and V–4Cr. The last two literature data for hydrogen were divided by $\sqrt{3}$.

in a specimen diffusion-annealed at 373 K for 3 h was compared with the best fit solution. Obtained values of D_T were plotted in Fig. 5 against inverse temperatures (Arrhenius plot) together with literature values [2–4]. The data obtained at pressures of 10^{-1} and 10^{-5} Pa at 303 K are not distinguishable in Fig. 5, because their values are almost same. It is noted that the Arrhenius plot of the obtained D_T bent downward below 320 K to give two different activation energies of 0.13 ± 0.01 eV and 0.19 ± 0.01 eV, above and below 320 K, respectively. At higher temperatures the present D_T are quite similar to those obtained in the previous study [7].

There are no data on tritium diffusion in V–4Cr and V–4Ti to be directly compared. Here, assuming an isotope mass effect on diffusion coefficients of hydrogen and tritium to be proportional to the square root of the mass ratio, $\sqrt{3}$, the results on hydrogen diffusion coefficients in V–4Cr and V–4Ti reported respectively by Pine and Cotts [4] and Tanaka and Kimura [2] are compared in Fig. 5. Above 320 K, the present data are quite similar to that for V–4Ti, and little less than pure V and V–4Cr without significant difference in the activation energies among all. Since the heat of solution of H in Ti is higher than that in V, Ti in V is highly likely to work as a trapping site in hydrogen diffusion.

In comparison with the pure vanadium data, the lower diffusion coefficient of tritium in the present study could be mainly owing to the trapping by

Ti. Still the effect of Cr is possible as appeared in a little smaller diffusion coefficient for V–4Cr in this temperature range. In literature data for both cases of V–4Ti and V–4Cr, no bending in the Arrhenius plot was observed, then we can safely conclude that the downward bending below 320 K in the present data is due to trapping by both alloying elements of Ti and Cr.

4. Conclusions

1. Characteristics of the surface layers highly containing tritium and diffusion behavior of tritium in V–4Cr–4Ti were successfully examined with the imaging plate technique in a temperature range from 230 K to 573 K.
2. Hydrogen content of the top surface after ac-glow discharge is estimated to be 5–20 at.%, probably owing to hydride formation. A heat treatment higher than 500 K was required to remove the high hydrogen containing surface layers, which supports the hydride formation.
3. The tritium diffusion coefficients (D_T) in V–4Cr–4Ti were successfully determined. Above 320 K, the values of D_T were very near to those for pure V and V–4Ti alloy with the activation energy of 0.13 ± 0.01 eV. Below 320 K, the Arrhenius relation bent downward to give a larger activation energy of 0.19 ± 0.01 eV, probably owing to a trapping effect of both of Cr and Ti.

Acknowledgements

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