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Influence of coexisting hydrogen isotopes on diffusion of tritium in niobium

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Abstract

The tracer diffusion coefficient of tritium in Nb has been measured at 523 K under the condition that tritium coexists with protium or deuterium. These data suggest the trend that the tracer diffusion coefficient of tritium in NbH_xT_y is somewhat larger than that in NbD_xT_y, though a definite conclusion has been reserved because their difference is small and comparable to the scattering of the experimental data. The concentration dependence of tracer diffusion coefficient of tritium in NbH_xT_y and NbD_xT_y can be practically considered to be equal to that of NbT_x. On the basis of these experimental data and the data reported by Fukai et al., it has been suggested that the tracer diffusion coefficient of lighter hydrogen isotopes is appreciably influenced by coexisting heavier hydrogen isotopes but that of heavier hydrogen isotopes is scarcely influenced by coexisting lighter hydrogen isotopes. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In D–T fusion reactor engineering, the diffusion coefficient of tritium is crucially important to evaluate the tritium permeation rate through structure materials and tritium inventory in the reactor system. Therefore, accumulation of a database of the diffusion behavior of tritium in various materials is required.

In the present study, we have taken up the diffusion behavior of tritium in the isotope mixture dissolved in metals. The question whether the diffusion of tritium is influenced or not by the coexisting protium and/or deuterium is an important problem for two reasons: one is that the diffusion of tritium is often experimentally studied by using tritium diluted by protium or deuterium. The other is that tritium actually coexists with deuterium in plasma facing materials of D–T fusion reactors.

The correlation of diffusion between different hydrogen isotopes has been studied by Fukai et al. [1] by measuring the tracer diffusion coefficient of protium with a NMR method in an isotope mixture of protium and deuterium dissolved in Nb. According to their study, the tracer diffusion coefficient of protium is appreciably influenced by the coexisting deuterium i.e. it is decreased with increase of the concentration of deuterium. Therefore, it may be interesting and important to examine to what extent the tracer diffusion coefficient of tritium in Nb is influenced by the coexisting protium or deuterium. It has been also reported that the tracer diffusion coefficient of protium and deuterium has large concentration dependence i.e. the mobility of protium and deuterium decreases drastically with increase of their concentration in Nb [2,3]. The diffusion coefficient of tritium in Nb has been measured with Gorsky effect by Qi et al. [4], but its concentration dependence has not been measured. Therefore, it is also interesting and important to examine the concentration dependence of the tracer diffusion coefficient of tritium in Nb.

From these view points, in the present study, the tracer diffusion coefficient of tritium in Nb has been measured under the condition that tritium coexists with protium or deuterium. In this experiment, the technique of the discharge implantation method, which has been developed by the present authors, has been used. This experimental technique is useful to measure the tracer diffusion coefficient of hydrogen isotopes in the isotope mixture dissolved in solid materials [5].

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2. Experimental

The experimental procedure to measure the tracer diffusion coefficient D of tritium is as follows: First, a small amount of tritium is implanted in the region of 30 μm in depth from the end surface of a rod-shaped specimen. Then, this specimen is exposed to air to make a natural oxide layer on the specimen surface. This natural oxide layer plays the role of a barrier which prevents tritium leaking out of the specimen at evaluated temperatures at which diffusion annealing is carried out. This barrier effect of niobium oxide depends on the hydrogen concentration in Nb. In the concentration region in which the present diffusion experiment is carried out, the barrier effect has been confirmed to be valid in the temperature region below 523 K. The concentration dependence of the tracer diffusion coefficient can be measured by making tritium diffuse into the specimen, in which protium or deuterium is uniformly dissolved in advance. The concentration of protium or deuterium in Nb is changed up to 0.75 atomic fraction in the present experiment. The uniformity of the concentration of protium or deuterium in the specimen is important for accurate measurements. After diffusion annealing, the concentration profile of tritium is measured by the sectioning method. The details of this procedure are as follows.

2.1. Specimen preparation

Rod-shaped specimens of niobium (purity: 99.9%, 2 mm in diameter, 40 mm in length) were heated in vacuum (10^{-5} Pa) at 1273 K for 1 h to remove hydrogen as an impurity. Some specimens were loaded with protium or deuterium using the gas absorption method. After hydrogen loading, the specimens were sealed in an evacuated pyrex glass tube, and heated at 523 K for one week to make the hydrogen concentration uniform. Then, tritium was implanted into the end surface of the rod specimens with the discharge implantation method, the details of which were described in our previous paper [5]. The abundance ratio of tritium to protium in the used tritium gas was about 1×10^{-5}. During the implantation of tritium, the specimen was cooled with liquid nitrogen to prevent migration of the implanted tritium.

2.2. Diffusion annealing

After the implantation, the specimen was exposed to air for few minutes to produce a thin oxide layer on the side surface and sealed in an evacuated pyrex glass tube (10^{-1} Pa). Then diffusion annealing was carried out at 423, 473 and 523 K in the case of the specimen in which protium and deuterium were not dissolved in advance. In the case of the specimen in which protium or deuterium was dissolved in advance, diffusion annealing was carried out only at 523 K. An annealing time t was chosen to make the mean penetration depth $(2Dt)^{1/2}$ to be 10 mm. When the diffusion annealing was finished, the specimen was quickly cooled down to the liquid nitrogen temperature and cut into seven pieces.

2.3. Measurement of diffusion profile of tritium

The hydrogen isotope contained in each piece was vacuum extracted from the specimen heated at 1273 K and collected by making use of adsorption on the active carbon chilled at liquid nitrogen temperature. Then, the collected hydrogen gas was liberated into a calibrated volume by warming the active carbon to room temperature, and the pressure of the hydrogen gas was measured with diaphragm gauge. The concentration of protium or deuterium dissolved in each piece was calculated from the pressure rise. After the volumetric determination, the hydrogen gas was oxidized with CuO and the produced water was collected in a vial. The radioactivity of the water was measured with a liquid scintillation counter. The details of the oxidation apparatus is described in the previous paper [6].

2.4. Determination of the tracer diffusion coefficient of tritium

In the present diffusion experiment, the characteristic diffusion depth $(2Dt)^{1/2}$ of about 10 mm was much larger than the thickness of the implantation region. Therefore it can be supposed that tritium was initially on the surface as a plane source. Furthermore, the specimen length of 40 mm was much larger than the diffusion length, so the diffusion medium could be considered to be semi-infinite.

With the initial and boundary conditions, the solution on the one-dimensional diffusion equation gives the concentration profile $C(x,t)$ of tritium isotopes at time t as

$$C(x,t) = \frac{M}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right), \tag{1}$$

where M is the total amount of tritium initially existing as a plane source, x is the distance from the surface. Adjusting Eq. (1) to the experimental profile, the tracer diffusion coefficient D can be determined from the slope of $\ln C(x,t)$ vs. x^2 plots.

3. Results

An example of the plot of $\ln C(x,t)$ vs. x^2 in the case of the measurement under the condition that tritium does not coexist with any other isotope, is given in Fig. 1, which shows a good linearity. This good linearity

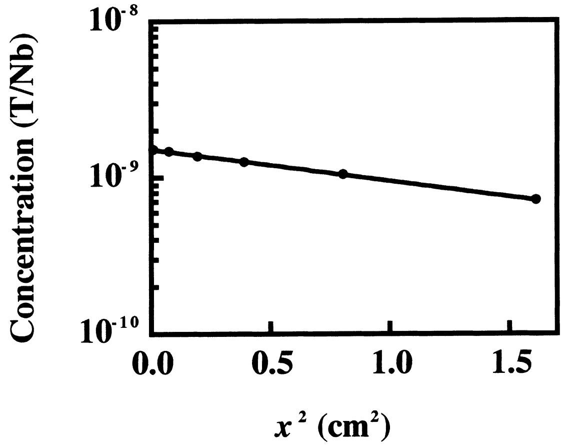

Fig. 1. The experimental concentration profile of tritium after diffusion annealing at 523 K for 6 h. Solid line was determined by the least-squares fitting.

can be considered to be a verification of the validity of the present diffusion model. The temperature dependence of the tritium diffusion coefficient in identical experimental condition is shown in Fig. 2, where the solid line represents the values calculated from the data reported by Qi et al. [4]. As it is seen in this figure, the present data are in agreement with their values. The activation energy of diffusion and the frequency factor are calculated to be 0.14 eV and 5×10^{-4} cm^2/s, respectively, by the least-squares fitting of the present data. These values are in good agreement with the values reported by Qi et al. [4]: their values are 0.133 eV and 5×10^{-4} cm^2/s, respectively. It should be noted that these diffusion coefficients can be compared with the tracer diffusion coefficients, because the concentration of tritium is extremely low in these cases.

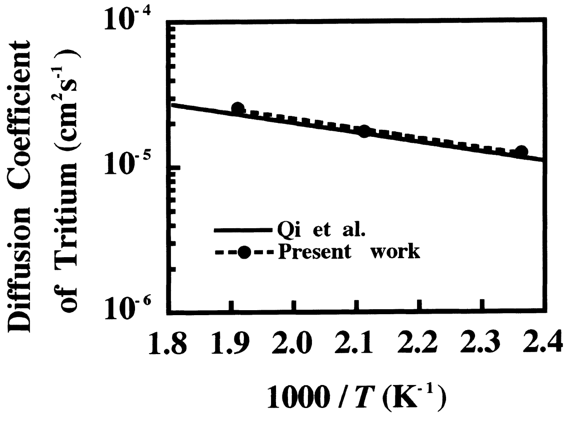

Fig. 2. The Arrhenius plots of the diffusion coefficient of tritium.

The tracer diffusion coefficients of tritium measured in conditions when tritium coexists with protium or deuterium are given in Fig. 3. Solid and dashed lines are to guide the eye. It seems from Fig. 3 that the tracer diffusion coefficients of tritium in NbH_xT_y are somewhat larger than those in NbD_xT_y, though a definite conclusion cannot be made because the difference is small and comparable with scattering of the experimental data.

4. Discussion

4.1. Influence of the coexisting hydrogen isotopes on the mobility of tritium

The present data given in Fig. 3 suggest that the difference of tracer diffusion coefficient of tritium in NbH_xT_y and in NbD_xT_y is small. On the other hand, Fukai et al. [1] reported that the tracer diffusion coefficient of protium is noticeably influenced by coexisting deuterium e.g. in the case of $NbH_xD_y(x+y=0.5)$, the tracer diffusion coefficient of protium at 500 K decreases from 9.5×10^{-6} to 6.9×10^{-6} cm^2/s with change of y from 0 to 0.45. These contradictory experimental results can be reconciled if we suppose that the tracer diffusion coefficient of lighter isotopes is influenced by coexisting heavier isotopes but that of heavier isotopes is scarcely influenced by coexisting lighter isotopes. This supposition can be confirmed by measuring the tracer diffusion coefficients of deuterium and protium as a function of the isotope abundance ratio. Such measurement is now planned by the authors.

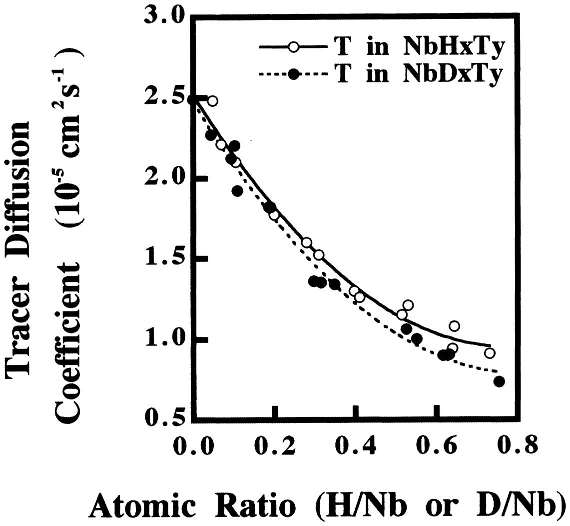

Fig. 3. Concentration dependence of the tracer diffusion coefficient of tritium at 523 K.

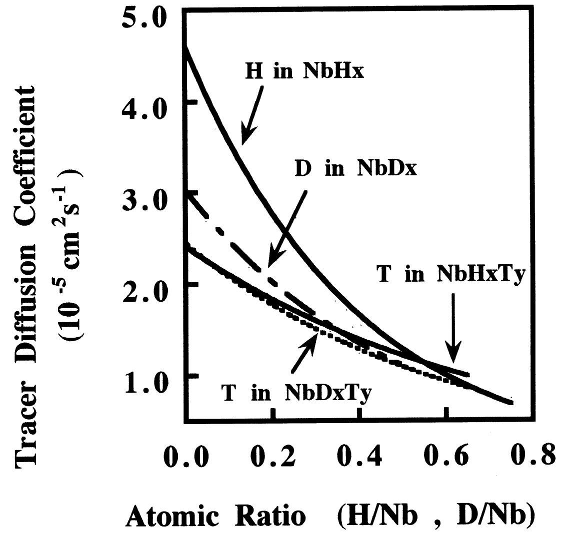

Fig. 4. Comparison of the tracer diffusion coefficients of hydrogen isotopes.

4.2. *Comparison of the tracer diffusion coefficient of tritium with that of deuterium and protium*

In Fig. 4, the present data for tritium at 523 K are compared with the data for protium and deuterium. The curve for deuterium is calculated from the data reported by Qi et al. [4] and Bauer et al. [2]. In the case of protium, the curve was calculated from the data reported by Qi et al. [4] and Bauer et al. [2] at concentrations less than 0.5 atomic fractions and from the data reported by Fukai et al. [1] at concentrations higher than 0.5 atomic fractions. As it is seen in this figure, the tracer diffusion coefficients of hydrogen isotopes approach one another with increase of concentration. Since the present data do not show significant difference between NbH_xT_y and NbD_xT_y, the influence of the coexisting hydrogen isotopes upon the mobility of tritium can be considered to be practically independent of the kind of isotopes. Therefore, it can be concluded that the concentration dependence of the tracer diffusion coefficient of tritium in NbT_x follows the data for NbH_xT_y and NbD_xT_y.

5. Conclusions

1. The tracer diffusion coefficient of tritium in Nb has been measured under the condition that tritium coexists with either protium or deuterium.
2. The tracer diffusion coefficient of tritium in NbH_xT_y was found to be somewhat larger than that in NbD_xT_y, though the definite conclusion has been reserved because their difference is appreciably small and comparable to the extent of scattering of the data.
3. The concentration dependence of the tracer diffusion coefficient of tritium in NbT_x is considered to be very close to that in NbH_xT_y and NbD_xT_y.
4. It has been suggested that the tracer diffusion coefficient of lighter isotopes must be appreciably influenced by heavier isotopes but the tracer diffusion coefficient of heavier isotopes must be scarcely influenced by lighter isotopes.

Acknowledgements

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