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Characteristics of traps for hydrogen in helium-irradiated copper

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Abstract

Characteristics of traps for hydrogen in helium-irradiated copper were experimentally studied by use of nuclear reaction analysis (NRA). Samples were continuously charged with deuterium from RF plasma during the experiment. The results showed that two types of traps associated with radiation damage were produced, called traps 1 and 2 here. From the temperature dependence of the deuterium concentration observed by NRA and the deuterium permeation flux, the trapping energies were estimated to be 0.65 eV for trap 1 and 0.57 eV for trap 2. The production ratio of trap 1 per atomic displacement was 0.0021. The density of trap 2 reached a constant value of 6×10^{25} m^{-3} at high irradiation doses. Traps 1 and 2 are assumed to be vacancy clusters and interstitial loops, respectively.

1. Introduction

Copper and copper alloys are candidates for high thermal conductivity layers such as coolant pipes in plasma-facing components of fusion reactors [1,2], and the evaluation of tritium inventory in these materials is one of the important issues. It is generally considered that the tritium inventory in copper is not so significant because copper is an endothermic metal with positive heat of solution for hydrogen isotopes. When the components are irradiated by energetic particles, however, radiation-induced defects will trap hydrogen to increase the inventory [3,4].

In our previous work [5], depth profiles of deuterium in helium-irradiated copper have been observed by nuclear reaction analysis (NRA) and the following results were obtained: (1) a large amount of deuterium is trapped in the helium-irradiated region, (2) the traps are not associated with the injected helium atoms but rather to the displacement damage, (3) there exist two types of traps, for convenience called trap 1 and trap 2 here, and (4) the profile of trap 2 is flat while that of trap 1 is similar to a distribution of atomic displacements.

In the present work, complementary experiments are conducted and the data are analyzed together with the previous data to derive some characteristics of the traps.

2. Experimental

Two experiments were conducted in the present work; one was deuterium depth profiling by the NRA, denoted as Experiment B, to observe the

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deuterium concentration in the traps and the other was a permeation experiment to estimate the deuterium concentration in the solution site, that is, the concentration of dissolved deuterium.

Since the NRA experiment performed in the previous work [5], denoted as Experiment A, is referred to later, it will be briefly explained here. The sample consisting of a copper membrane with a thickness of 0.1 mm and a purity of 99.999% (Johnson Matthey Plc.) was annealed in a vacuum of 10 μPa at 973 K for 3600 s. One side of the sample, set between two vacuum chambers, was exposed to deuterium RF-plasma and the deuterium permeation flux through the sample was monitored by a quadrupole mass analyzer. A deuterium depth profile on the plasma-exposure side was observed by NRA with the reaction $D(^3He, p)^4He$ [6]. The analyzing beam was 1.7-MeV ^{3}He, from a 4 MV van de Graaff accelerator of Kyoto University. Next, 0.8-MeV ^{3}He ions from the accelerator irradiated the same side to a dose of 1.5×10^{21} m^{-2}. After that NRA was again conducted. The total analyzing dose for NRA was 1.0×10^{20} m^{-2} to minimize irradiation effects [5]. During the experiment, the sample was continuously exposed to the plasma and the depth profiles were observed under conditions of steady state deuterium permeation.

In Experiment B, the sample material, heat treatment, helium irradiation and NRA conditions were the same as in Experiment A, but the plasma conditions were changed to vary the incident flux of deuterium to the sample. NRA was repeated under different permeation fluxes at three different constant temperatures.

Since the deuterium concentration in the solution sites is far below the NRA detection limit, it was estimated from the permeation flux through the sample. For this purpose, the transient behavior of deuterium permeation was monitored after the incident flux of deuterium from the plasma was suddenly changed. The experimental setup and the procedures have been reported elsewhere [7]. The conditions of the sample material, the RF system and the chambers were the same in the above two experiments.

3. Results and discussion

Typical evolution curves in the permeation experiment are shown in Fig. 1. These data were analyzed with the time-lag method [8] where the diffusion coefficient D was directly derived from the time-integral of the permeation flux. Since the calculated curves are in excellent agreement with the experimental measurements, as shown in Fig. 1, it was confirmed that diffusion was the rate-determining process for deuterium permeation under the present experimental conditions. The value of D in the temperature range of 393–630 K obtained from the experimental data can be expressed as,

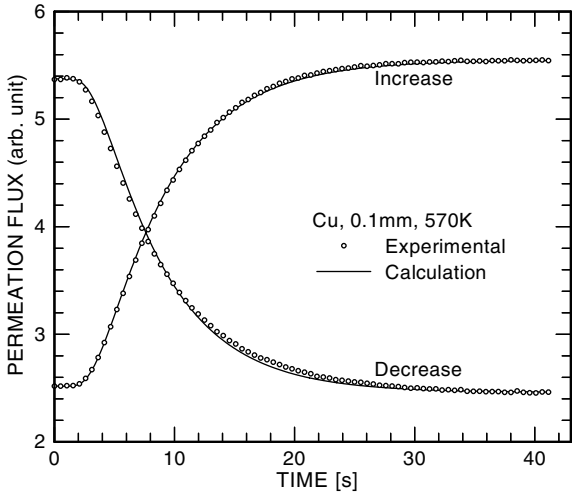

Fig. 1. Typical evolution curves of the deuterium permeation flux after prompt increase or decrease in the deuterium incident flux from the plasma. Also shown are calculated results using an analytical formula for the time-lag method.

$$D = 2.94 \times 10^{-7} \exp(-0.365\ [\mathrm{eV}]/kT)\ [\mathrm{m^2\ s^{-1}}], \quad (1)$$

where k and T are the Boltzmann constant and the sample temperature, respectively. This value agrees with those determined by other researchers [9,10].

In diffusion-limited permeation, the permeation flux J at steady state is proportional to the deuterium concentration in the solution sites, C_s;

$$J = DC_s/L, \quad (2)$$

where L is the sample thickness.

Deuterium depth profiles in the copper sample after irradiation with 0.8-MeV ^{3}He in Experiment B are shown in Fig. 2. The analyzing dose for each run was limited to 1×10^{19} m^{-2} so the data are rather scattered due to statistical errors. Clearer profiles have been seen elsewhere [5]. The peak at 0-depth is attributed to deuterium absorbed on the surface [11] and will not be taken into account in the analysis hereafter. Expansion of the peak to negative depth is attributed to a finite resolution of the NRA system. The profile in the bulk region consists of deuterium in the solution site and in traps. The

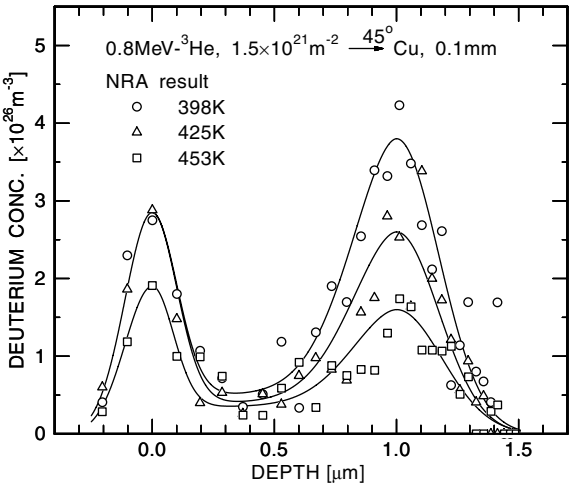

Fig. 2. Deuterium depth profiles in 0.8 MeV-^{3}He irradiated copper in Experiment B.

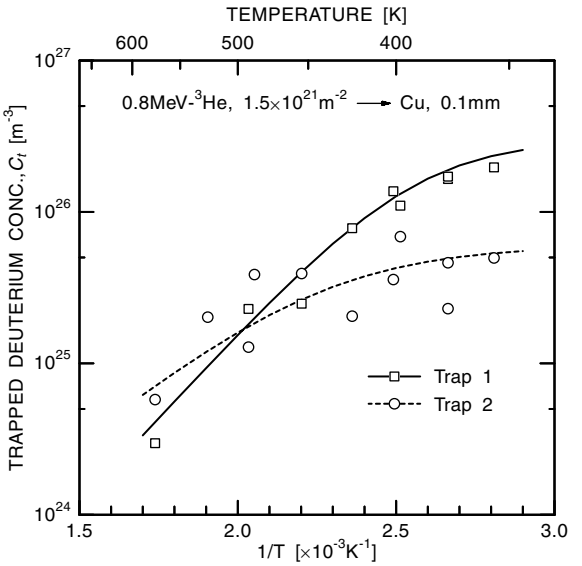

Fig. 3. Temperature dependence of the averaged deuterium concentrations in traps 1 and 2 from Experiment A.

permeation flux J was $2.0 \times 10^{15}\ \mathrm{m^{-2}\,s^{-1}}$ at 398 K so C_s was estimated to be $2.8 \times 10^{22}\ \mathrm{m^{-3}}$ with Eqs. (1) and (2). This concentration is far below the ordinate scale of $10^{26}\ \mathrm{m^{-3}}$ in Fig. 2. The maximum deuterium concentration at 398 K was around $4 \times 10^{26}\ \mathrm{m^{-3}}$ from Fig. 2, which was about 10^4 times as large as C_s. It was therefore found that many traps were produced by irradiation and the profile substantially consisted of trapped deuterium.

The peak deuterium concentration at a depth of around 1-μm decreased by 60% when the temperature increased from 398 to 453 K, while the concentration at 0.4-μm depth decreased by only 30%. This suggests that there are two types of traps, here called trap 1 and trap 2. The concentration profile would be the superposition of the effects of traps 2, uniformly distributed in the radiation-damaged region, and of traps 1, distributed like atomic displacements [5]. The deuterium concentration in traps 1 and 2 were obtained in which the depth region concerned was 0.2–1.3 μm and the displacement distribution was estimated by the TRIM code [12]. The average deuterium concentrations in Experiment A are shown in Fig. 3. The steady-state permeation flux J during NRA observation, and C_s estimated from J using Eq. (2) are shown in Fig. 4.

Since deuterium was continuously fed to the sample, it was assumed there was quasi-equilibrium between the solution site and the trap [13], that is,

$$C_t = C_s C_o/(C_s + hNf), \tag{3}$$

where C_t and C_o are the deuterium concentrations in the trap and the density of the trap, respectively,

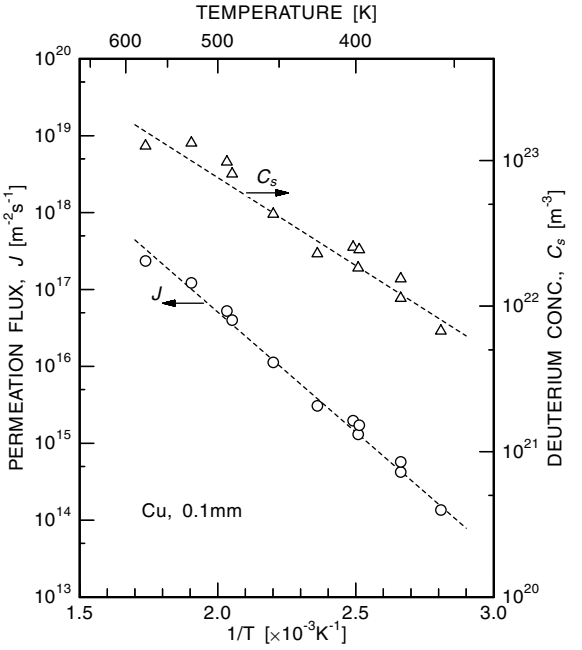

Fig. 4. The steady-state deuterium permeation flux through the sample and the deuterium concentration in solution site in Experiment A. Lines are guides for the eyes.

hN is the density of the solution sites and f is an equilibrium constant. As the traps are not annihilated in the temperature range [5], C_o is taken as a constant. In Eq. (3), hN being much larger than C_s is taken into account. The constant f is expressed as

$$f = \mu \exp(-E_t/kT). \quad (4)$$

In this form E_t is the trapping energy defined as an enthalpy difference between the solution site and the trap and μ is the pre-exponential factor, which represents an entropy difference and becomes unity with no differences. In Fig. 3, C_t for trap 2 increased with decreasing temperature until it became saturated around 6×10^{25} m^{-3}. This value could be regarded as the trap density C_o and f was directly obtained with Eq. (3) as shown in Fig. 5.

In Fig. 3, C_t for trap 1 was not saturated at lower temperatures so C_o was estimated from the data in Experiment B. As in the case of Experiment A, the values of C_t and C_s were estimated from the experimental data. Fig. 6 shows the dependence of C_t for trap 1 on C_s at 398, 425 and 453 K under different incident fluxes in Experiment B. Parameters of f and C_o were successfully fitted to the data with Eq. (3) as shown by broken lines in Fig. 6 and C_o was found to be 3.0×10^{26} m^{-3}. As the irradiation conditions such as particle element, energy and dose were the same, this value of C_o could be applied to Experiment A. From the above results, f in Experiments A and B were obtained as shown in Fig. 5.

From Fig. 5, the pre-exponential factor μ and the trapping energy E_t are found to be 60 and 0.65 eV

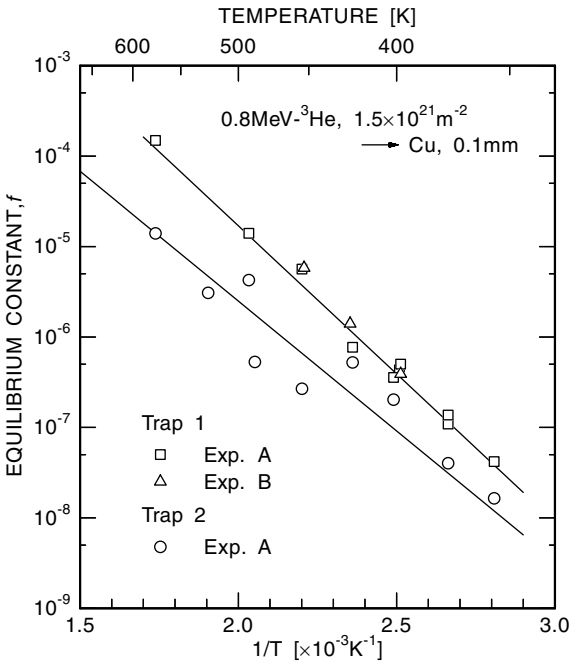

Fig. 5. Temperature dependence of the equilibrium constants for traps 1 and 2.

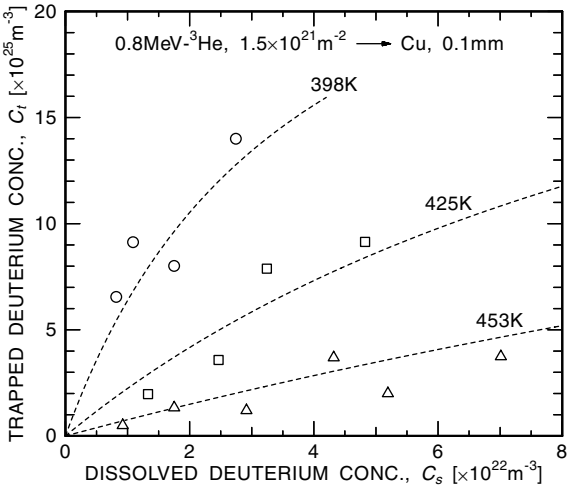

Fig. 6. Evolution in the deuterium concentration in trap 1 with that in solution site in Experiment B.

for trap 1 and 1.4 and 0.57 eV for trap 2, respectively. As E_t for trap 1 is not so different from trap 2 and μ for trap 1 is much larger, f for trap 1 is larger in the temperature range examined. This leads to the conclusion that C_t for trap 1 decreases more rapidly than for trap 2 with increasing temperature as shown in Fig. 3.

In our previous work [5], traps 1 and 2 were assumed to be vacancy clusters and interstitial loops, respectively, on the basis of other researchers' results of the dissociation temperature of vacancy–hydrogen complexes [14], TEM observation of helium-implanted copper [15] and measurement of deuterium retention during linear-ramp annealing [4]. The fact that the value of μ is 1.4 for trap 2 indicates that the entropy difference is close to zero and the configuration of the trap is similar to the solution site. As the solution site for hydrogen is an interstitial one, trap 2 could also be an interstitial site that has a deep potential due to lattice distortion near the loops. The large value of μ for trap 1 indicates, on the other hand, that the configuration of these traps is much different from the interstitial site. A vacancy cluster may fulfill the requirements for such a different configuration.

The density of trap 2 increased with the irradiation dose until it became saturated at higher doses, while that of trap 1 increased almost linearly [5]. Assuming that the number of trap 1 sites is proportional to the number of displacements, the production ratio of trap 1 per displacement is estimated to be 0.0021. Here the displacement energy is taken as 20 eV. The ratio is much smaller than unity

probably because most displaced atoms are annihilated in a very short time just after the displacement process.

The averaged value of the displacement in the present work was 1.7 dpa. In a fusion reactor, more displacements would occur in copper materials, leading to an increase in the tritium inventory. At lower temperatures, the traps are fully occupied by hydrogen and the tritium inventory can be estimated from the trap densities mentioned above. For evaluation at higher temperatures, such as the operating temperatures, the inventory can be estimated with Eq. (3) where C_s should be given by the reactor design. A rough estimation [5] shows that the concentration in traps would be much higher than in the solution site even at elevated temperatures. At still higher temperatures, the traps might be annihilated due to recovery of the irradiation defects, for which little information is presently available.

4. Summary

The characteristics of two types of the traps produced by helium irradiation in copper were successfully determined using the combined technique of NRA with permeation measurement. The trapping energy E_t and the pre-exponential factor μ in the equilibrium constant for trap 1 were 0.65 eV and 60, respectively. The density of trap 1 can be related to the production ratio of 0.0021. The values of E_t and μ for trap 2 were 0.57 eV and 1.4, respectively. The density of trap 2 reached a constant value of $6 \times 10^{25}\ m^{-3}$ at higher irradiation doses. Traps 1 and 2 are assumed to be vacancy clusters and interstitial loops, respectively. As these defects might recover at elevated irradiation temperatures, further investigation of the annihilation behavior of the traps is needed to evaluate the tritium inventory over a wide temperature range.

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