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Isotope effects in thermal release of H and D implanted into WC layers on graphite

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Abstract

Thermal release of H and D implanted into WC layers graphite with 5 keV H_2^+ and 5 keV D_2^+ ions has been measured by means of the elastic recoil detection technique. It has been found that the thermal release on isochronal annealing takes place in three stages: the two stages at the lower temperature take place from the two trapping sites in the WC crystallites, and the last stage at the higher temperature from graphite phase segregated in grain boundaries of the WC layers. The isothermal release from the graphite phase has been measured at different temperatures at 350, 450, and 550°C, for H and 450, 550 and 650°C for D, respectively. The isothermal release data have been analyzed by using the mass balance equations and the rate constants involved have been determined by fitting their solution to the experimental data. The thermal desorption spectrum has been theoretically calculated from the solution of the mass balance equations. It has been also found that the calculated thermal desorption spectrum agrees excellently well with the experimental one obtained by Wang et al. in IPP Garching. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermal release; Hydrogen recycling; Plasma – material interaction

1. Introduction

In future fusion devices, high-Z refractory metal and carbon are planned to be used simultaneously as the divertor plate and the first wall armor, respectively. The mutual redeposition of sputtered substances modifies the surface layers of the materials into the metal carbides under plasma irradiation at high temperature for long-term discharge.

Refractory metal carbides have a desired property of low sputtering yield [1]. There is a concern that the sputtering of high-Z metal induces radiative cooling of the hot core plasma, but TiC and WC layers coated on graphite have shown that the sputtering of metals is suppressed at high temperatures due to self-sustaining coverage of the surface with segregated carbon layers supplied from graphite substrate even under high heat flux plasma irradiation [2–5]. The metal carbide layers grown due to the mutual redeposition is sustained for long-term discharge. Nevertheless, data on hydrogen isotopes in high-Z metal carbides are hardly available [6]. Therefore, it is quite important to investigate hydrogen isotopes behavior in refractory metal–carbon composite materials.

In previous papers [7,8], we have reported the experimental results on retention and thermal re-emission of H and D implanted into WC layers deposited on graphite plates. It has been found that the re-emission of retained H and D due to thermal annealing takes place in three stages: A large amount of H and D is re-emitted from the WC crystallites in the two stages at the lower temperature and a small amount of the remainder is re-emitted from carbons in grain boundaries of the WC layers in the last stage at the higher temperature. The isothermal re-emission profiles at different temperature

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have been analyzed using the mass balance equations with two different traps in the WC crystallites.

In this paper, we report the experimental results on the thermal re-emission of H and D retained in graphite phase segregated in the grain boundaries of the WC layers in the last stage and discuss the isotope difference in the rate constants of the elementary processes leading to the re-emission. Moreover, the thermal desorption spectra of H and D, implanted up to saturation, from the WC layers are theoretically calculated from the isothermal re-emission profiles, namely the solutions of the mass balance equations and are compared with the experimental data obtained by the Garching group [6].

2. Experimental

Isotopic graphite plates (IG-110U) of $0.5 \times 5 \times 35$ mm^3 in size were used as a substrate of the specimen. The surface of the graphite was polished with fine diamond past on which a W-firm of 400 nm in thickness was deposited by electron beam heating. The WC layers were prepared by direct current heating of the graphite substrate at 1400°C for 30 min. The specimen was characterized by means of the Rutherford backscattering spectroscopy (RBS) and the X-ray diffraction (XRD) techniques. It was found that the average atomic composition of WC layers by RBS was $C/W = 0.96 \pm 0.04$ and the lattice constants for hexagonal lattice were also $a_0 = 2.93 \pm 0.01$ Å and $C_0 = 2.85 \pm 0.02$ Å. The XRD analysis showed single phase peaks of WC and graphite peaks, thus a small fraction of graphite phase being expected to exist in grain boundaries, since the WC layers were polycrystalline. The effective volume of the graphite phase was estimated to be several % of WC layers from the retained fraction of hydrogen [8].

In order to remove residual hydrogen, the specimen was heated at 1000°C for 10 min before hydrogen isotopes implantation. The implantation into the WC layers was done with 5 keV H_2^+ or 5 keV D_2^+ ion beam up to saturation at room temperature at a flux of 2.4×10^{13} cm^{-2} s^{-1}. The concentrations of H and D in the WC layers were measured by means of the elastic recoil detection (ERD) technique [9], in which 1.7 MeV He^+ ion beam impinges on the WC surface at an angle of 85° to the surface normal and recoiled ions were also detected at a forward angle of 82° to the surface normal. An irradiation fluence of the probing He^+ ions for the ERD measurement was monitored by means of the RBS technique.

3. Experimental results

First of all, protium and deuterium retentions in the WC layers deposited on graphite irradiated with 5 keV H_2^+ and 5 keV D_2^+ ions were measured as a function of irradiation time. It was found that the retained numbers of H and D increase rapidly at an early stage of irradiation and then saturates at a level ($\sim 1.7 \times 10^{22}$ cm^{-3}) which decreases by a factor of about 15% in several hours of terminating the irradiation due to spontaneous re-emission, as reported in the previous paper [8].

The retained numbers of H and D in the WC layers after isochronal annealings for 10 min are shown as a function of temperature in Fig. 1, where the vertical axis represents the retained numbers of H and D normalized by the initial saturation numbers, respectively. From Fig. 1, the re-emission of both H and D is seen to take place in three stages. The plot indicates that the first stage takes place at retained fractions of 1.0–0.6, the second stage at retained fractions of 0.6–0.2 and the last stage at retained fractions below 0.2. In the previous paper [8], the isothermal annealing re-emission for the two stages at the lower temperature were analyzed in detail. The last stage at the higher temperature is attributed to re-emission from the graphite phase segregated in grain boundaries.

Isothermal re-emission curves for H and D measured at different temperatures, after pre-annealings at 250 for 30 min and at 350 for 30 min, respectively, are shown as a function of time in Figs. 2(a) and (b), where the vertical axis represents the retained numbers normalized by those after the pre-annealings, which are shown in parentheses for each curve. It is clearly seen from Figs. 2(a) and (b) that the retained numbers of H and D decrease rapidly in the beginning of annealing and hereafter decrease gradually with time and there exists a clear isotope effect in the thermal re-emission. These results are very similar to those for graphite [9].

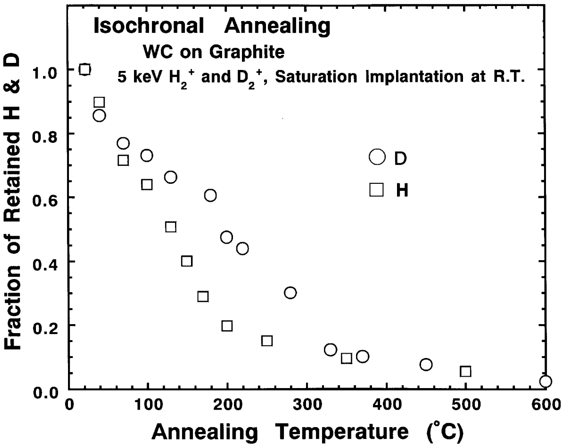

Fig. 1. Retained fration of H (□) and D (○) in a WC layer, implanted up to saturation at room temperature, after isochronal annealings for 10 min.

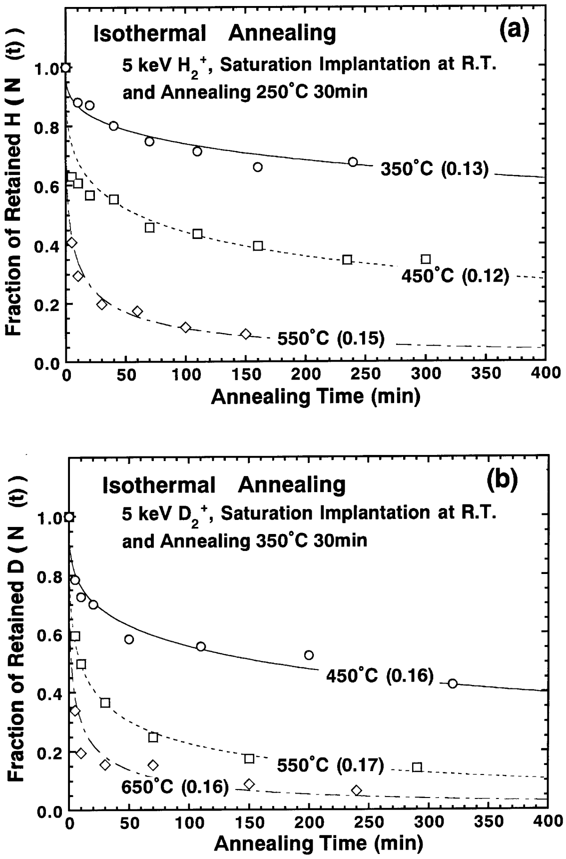

Fig. 2. (a) Retained fration of H in a WC layer, implanted up to saturation at room temperature and heated at 250°C for 30 min, during isothermal annealing at temperatures of 350, 450 and 550°C. The solid lines represent the best fitting curves calculated using the mass balance equations. (b) Retained fration of D in a WC layer, implanted up to saturation at room temperatures of 450, 550 and 650°C. The solid lines represent the best fitting curves calculated using the mass balance equations.

4. Discussion

4.1. Analysis of isothermal re-emission curves

The initial rapid decay observed in Fig. 2(a) and (b) is ascribed to no retrapping of thermally detrapped hydrogen due to no existence of available trapping sites because the pre-annealings at 250°C and 350°C do not re-emit H and D trapped in graphite phase in grain boundaries, but only re-emit H and D trapped in the WC crystallites. The late slow decay is attributed to strong retrapping of thermally detrapped hydrogen into vacant trapping sites produced by the initial decay. Therefore, the decay of the hydrogen concentration in the graphite phase should be also analyzed by solving the mass balance equations governing the time evolution of the concentrations of hydrogen migrating freely and trapped in a single trapping site which take into account the following elementary processes as in graphite: thermal detrapping, retrapping and local molecule recombination between free species leading to the re-emission. According to the same procedure as in graphite described in the previous study [9], the decay kinetics of hydrogen in carbons in grain boundaries of the WC layers is expressed by the following equation.

$$\frac{C_0}{n_0}\left[1-\frac{1}{N(t)}\right] - 2\ln[N(t)] + \frac{n_0}{C_0}[N(t)-1] = -2\frac{K_1}{C_0}\left(\frac{\sum_{d3}}{\sum_T}\right)^2 t, \tag{1}$$

where $N(t)$ is the average concentration of hydrogen trapped in the trapping site of carbon normalized by the initial one n_0, C_0 the trap density, $\sum_{d3}$ the thermal detrapping rate, $\sum_T$ the trapping rate and K_1 is the local molecular recombination rate between free species.

First of all, the thermal detrapping rates were determined from initial slope of the decay curves in Figs. 2(a) and 2(b). The experimental values of $\sum_{d3}^{H}$ and $\sum_{d3}^{D}$ are shown as a function of $1000/T$ (K) in Fig. 3.

Secondly, the value of (K_1/C_0) $(\sum_{d3}/\sum_T)^2$ were determined by ploting the value of left-hand side computed by substitution of the data points in Figs. 2(a) and (b) into $N(t)$ of Eq. (1) with $n_0 = C_0$ as a function of t in log–log scale. The experimental values of the effective recombination rates for protium and deuterium are plotted as a function of $1000/T$ in Fig. 4.

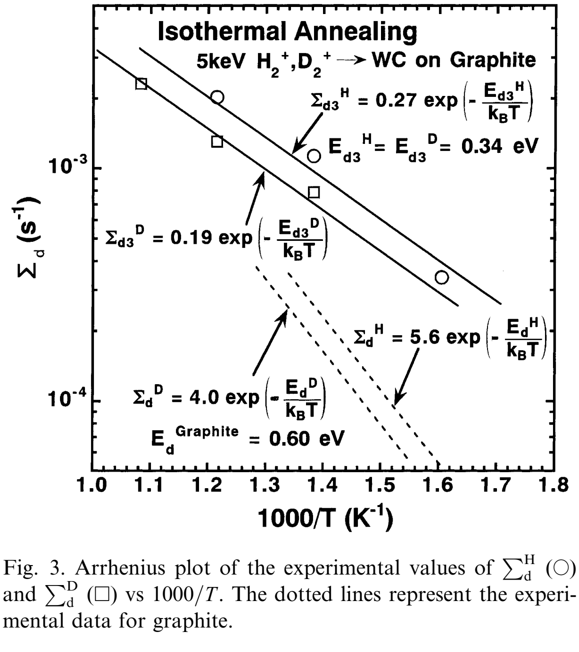

Fig. 3. Arrhenius plot of the experimental values of $\sum_d^H$ (○) and $\sum_d^D$ (□) vs $1000/T$. The dotted lines represent the experimental data for graphite.

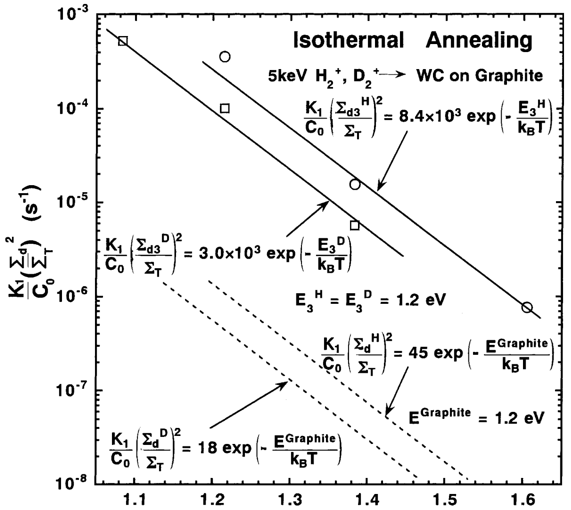

Fig. 4. Arrhenius plot of the experimental recombination rate constants of $(K_1^{HH}/C_0)(\sum_d^H / \sum_T^H)^2$ and $(K_1^{DD}/C_0)(\sum_d^D / \sum_T^D)^2$. The dotted line represent the experimental data for graphite.

From data in Fig. 3, the activation energies of thermal detrapping rates are calculated to be about 0.34 eV for H and D and the pre-exponential factors are also determined to be 0.27 for H and 0.19 for D, respectively, which is an isotope effect in the thermal detrapping rate. The former values are considerably lower than that for graphite [9]. The activation energies of the effective molecular recombination rate are also calculated to be about 0.2 eV for both H and D and the pre-exponential factors to be 8.4×10^3 for H and 3.0×10^3 for D, respectively, from Fig. 4. The activation energies of the molecular recombination rate are eventually the same as those in graphite, but the pre- exponential factors are two orders of magnitude higher than those in graphite. The isotope difference in the pre-exponential factors of the effective molecular recombination rates is estimated to be 2.8, thus the isotope difference in the values of $K_1/\sum_T^2$ being calculated to be 1.4 which is very close to that (1.2) obtained for hydrogen in the WC crystallites.

4.2. Calculation of thermal desorption spectrum from isothermal decay kinetic of hydrogen concentration

As described in the preceding section, we have determined the rate constants of the elementary processes involved in the mass balance equations using the experimental data on the isothermal decay curves. Here, in order to certificate the mass balance equations and the rate constants involved, we calculate the thermal desorption spectrum from Eq. (1) and compare it with the experimental one [6]. When the specimen temperature is expressed as $T_1 = T_0 + \gamma t$, where T_0 is the initial temperature and γ is the speed of temperature rise, the thermal desorption spectrum $F(T_1)$ of the hydrogen molecule is calculated from Eq. (1), as follows:

$$F(T_1) = \mid \mathrm{d}N(T_1)/\mathrm{d}T_1 \mid = \frac{\tau n_0}{\gamma C_0} \frac{N^2(T_0+T)}{\{1-(n_0/C_0)N(T_0+T)\}^2} - \exp\left(-\frac{E_\tau}{k(T_0+T)}\right)\left\{1+\frac{E_\tau T}{k(T_0+T)^2}\right\}, \quad (2)$$

where $T = \gamma t$ and $(K_1/C_0)(\sum_{d3}/\sum_T)^2 = \tau\exp(-E_\tau/kT_1)$. When $N(T_0+T) \ll n_0/C_0$, $N(T_0+T)$ is approximated to be

$$N(T_0+T) = \frac{1}{1+(n_0\tau/C_0\gamma)T \times \exp(-E\tau/k(T_0+T))}. \quad (3)$$

Thus, $F(T_1)$ is finally written is an analytical from:

$$F(T_1) = \frac{n_0\tau}{C_0\gamma} \times \frac{\exp(-(E\tau/k(T_0+T)))(1+(E\tau T/k(T_0+T)^2))}{[(1-(n_0/C_0))+(n_0/C_0)(\tau/\gamma)\exp(-(E\tau/k(T_0+T)))]^2}. \quad (4)$$

It is noted that $F(T_1)$ is the thermal desorption spectrum of hydrogen trapped in carbon segregated in grain boundaries of the WC layers deposited on graphite.

In the previous work [8], we have calculated the decay kinetics of hydrogen trapped in two different trapping sites in the WC crystallites and also have determined the values of the effective molecular recombination rates from the experimental data on the isothermal decay curves of the hydrogen concentration. Therefore, we have calculated the total thermal desorption spectra of H_2 and D_2 from the WC layers, which are shown in Fig. 5. In numerical calculations, the fractions of hydrogen trapped in the three different traps: two traps in the WC crystallite and one trap in the graphite phase were determined to be 0.4, 0.4 and 0.2 so that the isochronal decay curves in Fig. 1 could be well reproduced using three isothermal decay curves of them. The values of their fractions are also described in Figs. 5(a) and (b). It is seem from Fig. 5 that the thermal desorption spectrum of D_2 consists of three peaks situated at 430, 530, and 860 K, which agrees excellently well with the experimental data obtained by Wang et al. in the IPP Garching group [6]. The fact is concluded to indicate that the mass balance equations governing the time evolution of hydrogen in the WC layers deposited on graphite and the rate constants of elementary processes involved there are very effective.

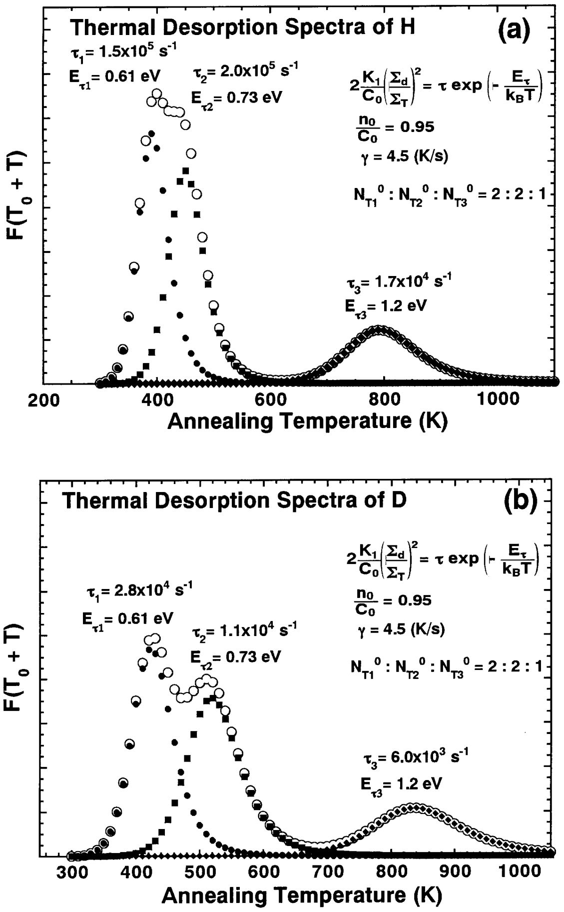

Fig. 5. (a) Thermal desorption spectra of H_2 from a WC layer, calculated from the solution of the mass balance equations for ramp speed of 4.5 K s^{-1} and $n_0/C_0 = 0.95$ using the experimental values of $(K_1/C_0)(\sum_d / \sum_T)^2$ for three kinds of traps. (b) Thermal desorption spectra of D_2 from a WC layer calculated from the solution of the mass balance equations in a similar way to those of H_2.

5. Conclusions

We have measured retention and thermal re-emission of hydrogen isotopes (H and D) implanted into the WC layers deposited on graphite by means of the ERD techniques, analyzed the experimental data on the thermal re-emission using the mass balance equations involving the elementary process; thermal detrapping, retrapping and local molecular recombination leading to be the re-emission, and determined the rate constants of the elementary processes.

We have also calculated the thermal desorption spectrum of deuterium from the solution of the mass balance equations proposed with the experimental rate constants, namely the decay kinetics. It has been found that the calculated thermal desorption spectrum agrees excellently well with the experimental data obtained by Wang et al. [6] in the IPP Garching group. Therefore, it is conclude from the fact that the mass balance equations are applicable to describe the time evolution of hydrogen isotopes implanted into the WC layers deposited on graphite, if the diffusion term is added, and moreover the rate constants of elementary processes for tritium can be extrapolated from the isotope effects in the rate constant for protium and deuterium.

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