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Tritium retention study of tungsten using various hydrogen isotope irradiation sources

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Abstract

Tritium retention behavior of wrought tungsten samples was investigated by exposure to various hydrogen isotope irradiation sources under controlled sample characterization and temperature. It is shown that the thermal desorption behavior of deuterium implanted in the bulk was strongly correlated to the change in the microstructure of tungsten. Especially, dislocations produced during fabrication play a significant role in increasing hydrogen retention. From thermal desorption experiments using 100 eV deuterium/tritium and 3 keV deuterium ion beams, annealing wrought tungsten at 1773 K reduced tritium retention to about one fifth of that of the unannealed case. However, even without annealing, the ratio of retained atoms/incident ions of hydrogen isotope for wrought tungsten was 5×10^{-6} at an incident ion fluence of 7×10^{25} ions/m^2 and a temperature of 523 K, which was lower than the values reported. Results of CVD and single crystal tungsten are also presented.

1. Introduction

Tungsten is one of the candidate materials to be used for the divertor of the international thermonuclear Experimental Reactor (ITER), because of its high heat flux resistance [1]. However, the database necessary for estimation of the tritium inventory in the ITER divertor is very limited and have large discrepancies [2–9]. This may have a large influence on the safety analysis and decontamination process of used divertor cassettes.

Several methods are being considered for tungsten armor tiles in the ITER divertor, such as powder-sintered and hot-rolled, chemical vapor deposition (CVD), etc. Anderl et al. [3] pointed out the existence of extensive trapping in wrought tungsten samples and a reduction in the trapped fraction by annealing, which resulted in the elimination of the high density of dislocations introduced during sample fabrication. The change in the microstructure of wrought tungsten has been investigated by measurements of the electric conductivity, internal friction, X-ray diffraction, etc. [10–12]. It is known that the migration of interstitial atoms, vacancies and dislocations take place as temperature is increased. Finally, recrystalization starts at a temperature over 1070 K. However, little information on the relationship between such change of microstructure and hydrogen retention is known.

There is another issue which has not been revealed yet, i.e. the contributions of low energy neutral particles to tritium inventory. The flux arriving at the ITER divertor is estimated to be comparable to that of charged particles. In our previous report of tritium retention in graphite [13,14], it was shown that interactions with atomized hydrogen isotope particles result in large hydrogen isotope retention. However, currently little information is available on the interaction between neutral hydrogen isotope particles of low energy (eV or sub-eV level) and tungsten.

In this paper, we report on the retention hydrogen isotopes by thermal desorption of tritium and deuterium for wrought tungsten samples exposed to various irradiation sources under controlled sample characterization. These results are discussed in comparison to those

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obtained with CVD and single crystal tungsten irradiated with a deuterium ion beam.

2. Experimental

2.1. Tritium plasma experiment

The tritium plasma experiment (TPE) [15] at the Tritium Systems Test Assembly at Los Alamos National Laboratory was used for measurements of the amount of tritium retained in some wrought tungsten samples. Fig. 1 shows the sample holder used for the present study, which was designed and manufactured in JAERI. This was mounted to the 8 in. flange of the end port of the TPE main chamber for D–T ion beam irradiation. The ion beam through the aperture bombarded and heated the sample on the copper sample holder base with a cooling tube. The sample temperature was controlled by thermal conductivity of the backing plate inserted between the sample and the copper heat sink, and was monitored by a thermocouple attached to the back side of the sample. A 100 eV D–T (D:T ration = 29:1) ion beam with a current of 1.0 A (irradiated area 2.0 cm ϕ, ion flux 2×10^{22} ions/m^2 s) on the sample were irradiated for 1 h (total fluence 7×10^{25} ions/m^2). The other experimental conditions for ion irradiation was similar to those of the experiment carried out for beryllium by Causey et al. [16].

After the irradiation process was completed, the tungsten sample was transferred to an outgassing system. The sample was heated at a ramp rate of 20 K/min from room temperature up to 1473 K. A gas mixture flow of 99% He and 1% H_2 was swept over the

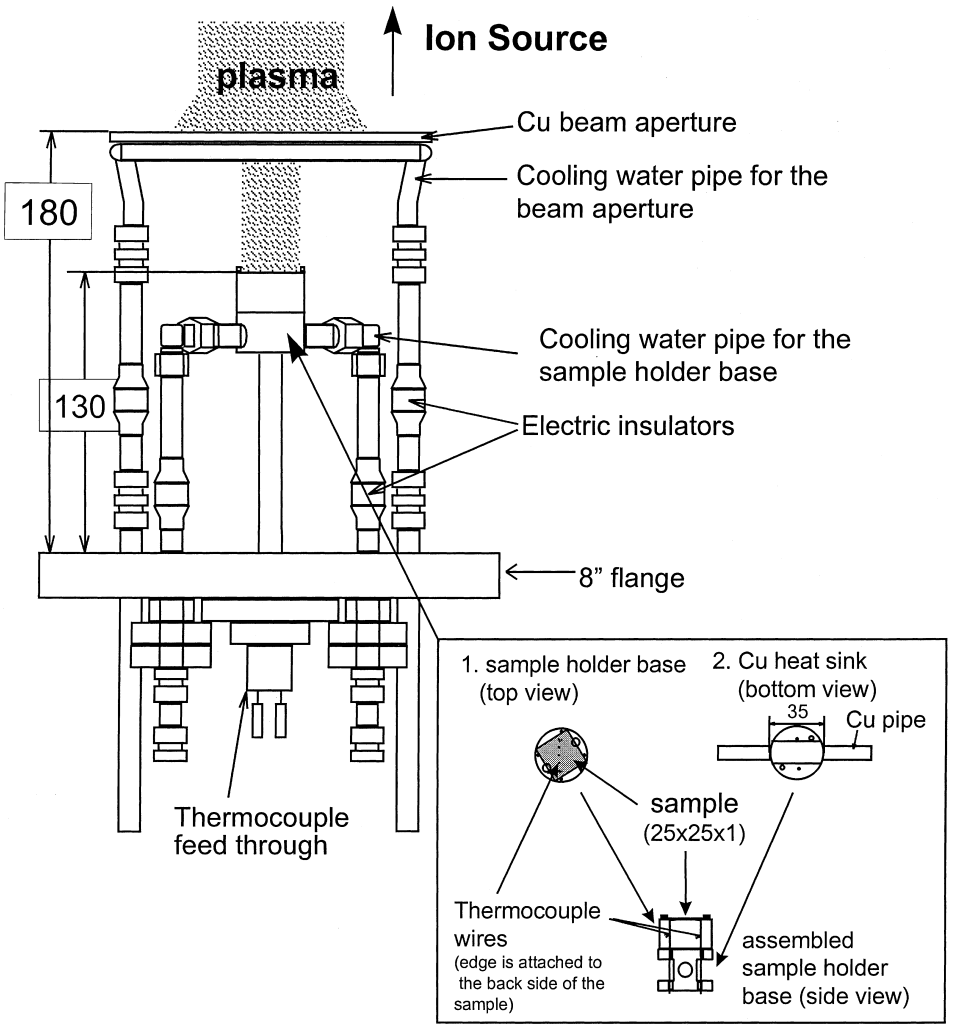

Fig. 1. The JAERI sample holer used for TPE (numbers are in mm).

sample. Tritium concentration in the gas flow was continuously monitored by an ion chamber, and the total amount of hydrogen retained in the tungsten sample was determined by correcting the ratio of gases in the gas flow.

Tungsten specimens used for TPE were 25 mm × 25 mm × 1 mm^t sheets cut form a high purity sheet (supplied from Rare Metallic > 99.95 wt%, wrought). Chemical impurities in the received sample, on an atomic ppm basis, were C-30, Ca-30, Cr-10, Fe-50, K-10, Mo-300, Na-20, Ni-20, P-50, S-5 and Ti-20. Two types of samples were prepared, and they were made from the same lot material. One was irradiated with D–T ion beam "as received", the other was annealed at a temperature of 1773 K for 1 h, which could eliminate most of the dislocations in the sample [3]. Annealing was performed under vacuum below 6×10^{-5} Pa before loading the sample to the sample holder. Impurities, such as carbon and oxygen covering the sample surface could be removed during irradiation of pure deuterium (ion flux: 2×10^{22} ions/m^2 s) at the idling time of the ion source, until the sample temperature reached its designated value. Little deposition of other impurities, such as copper, was observed by an XPS surface analysis after ion beam irradiation.

2.2. Thermal desorption experiments with 3 keV deuterium ion beam irradiation

Thermal desorption spectra (TDS) of deuterium were observed from unannealed wrought, annealed wrought, CVD and single crystal tungsten samples irradiated with a deuterium ion beam of 3 keV. The tungsten sample was set in a quartz tube, which was a part of the main vacuum chamber of the vacuum system and centred in an infrared furnace. The sample was pre-heated at about 1270 K for 30 min, which resulted in the vaporization of tungsten oxides. Samples were then sputtered with a 5 keV, 3 μA argon ion beam for 1 h to remove a residual oxide layer on the sample surface before deuterium ion beam irradiation. Ion beam irradiation with an ion current of 1 μA at 2×2 mm^2 area (flux: 1.6×10^{18} ions/m^2 s) for 8 h (total fluence: 4.5×10^{22} ions/m^2) at temperatures of 300, 373, 473 and 673 K were followed by observations of a deuterium ($m/e = 4$) TDS carried out with a Q-mass connected to the same vacuum chamber. A high ramp rate of 80 K/min was taken for the present experiments. This procedure results in having the desorption rate peaks distinguished in the TDS by preventing a large part of deuterium from being released before the desorption rate reached its maximum at high temperature.

All types of tungsten samples (thickness: 2 mm, cut to fit the 15 mm ϕ Mo sample holder) were provided from Tokyo Tungsten. The major chemical impurities in the samples when received, on an atomic ppb basis, were C-430, N-500, Na-240, A1-2600, Si-1000, Ca-1800, Ti-120, Cr-0520, Mn-110, Fe-4600, Ni-440, Cu-54, Mo-160 and Sn-190, in the wrought sample (purity: 99.9988 wt%) and C-130, N-25, F-310, CI-34, Ca-<40 in CVD sample (purity: 99.99998 wt%), respectively. The single crystal tungsten sample was manufactured by recrystalization of a very pure tungsten sample at high temperature.

2.3. Thermal desorption experiments of samples irradiated with deuterium RF plasma

To distinguish the characteristics of hydrogen isotope retention in the bulk of the wrought sample from those of the near surface area, exposure of unannealed and annealed wrought tungsten samples to low energy atomized deuterium particles produced by RF discharge was carried out [12,13]. The sample was electrically floated to the RF plasma and kept at over 10 cm from the RF plasma arc, so we assumed that the dominant particles hitting the sample are neutral particles of low energy in the eV–sub eV range. The samples were exposed to RF plasma at room temperature for 3 h with an atomized deuterium particle flux of 8×10^{21} atoms/m^2 s on the sample. Each sample was pre-heated at about 1170 K for 30 min to remove the oxide layer on the sample surface before deuterium RF plasma irradiation, but no additional cleaning, like sputtering by argon plasma, was carried out. The unannealed and annealed wrought samples were the same ones used for the experiments stated in Section 2.2. TDS were taken using a Q-mass attached to the vacuum system of this apparatus and the different type furnace used to heat the sample up to 1770 K with a ramp rate of 20 K/min.

3. Results and discussion

Fig. 2 shows the thermal desorption spectra of tritium released from the unannealed and annealed wrought tungsten samples irradiated with the D/T ion beam. It is obvious that annealing at 1773 K significantly reduced hydrogen isotope retention in wrought tungsten. In the TDS of the unannealed sample, two major maximum peaks of hydrogen isotope release rate were observed, one at around 780 K and the other at around 1300 K. In the annealed sample, a small peak at around 900 K was observed, and the tritium concentration still increased at the higher temperature region above 1000 K. However, the temperature of another desorption peak was out of the outgassing system range (<1473 K). The total amount of retained tritium and hydrogen isotopes derived were 184.4 μCi and 3.6×10^{20} atom/m^2 for the unannealed sample, and 34.3 μCi and 6.7×10^{19} atom/m^2 for the annealed one against the total amount of irradiated tritium and hydrogen isotope, 36 Ci and 7×10^{25} ions/m^2. To identify the states of hydrogen

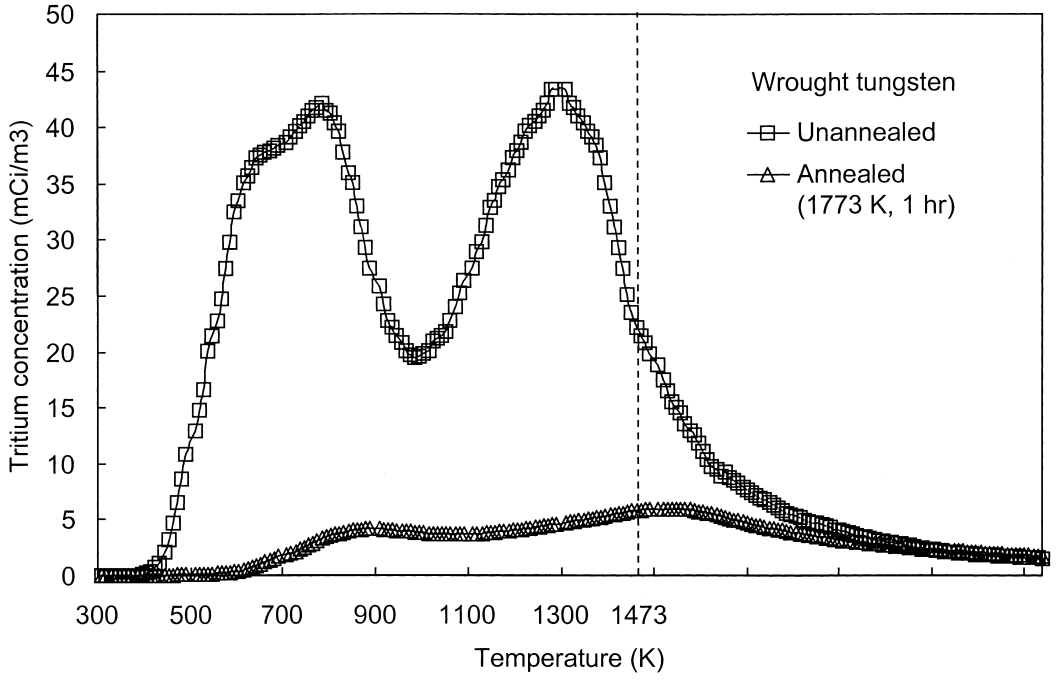

Fig. 2. TDS of tritium from the wrought tungsten samples irradiated with 100 eV D/T ion beam in the TPE (temperature was raised to 1473 K and held).

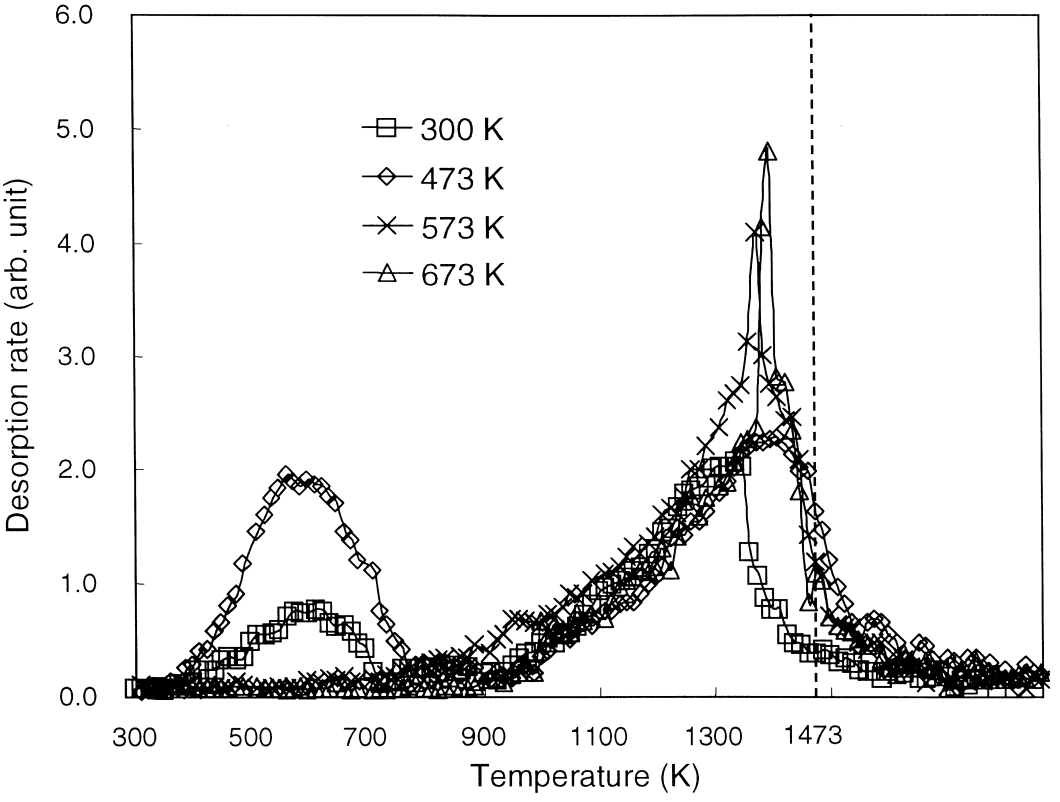

Fig. 3. TDS of deuterium from the unannealed wrought tungsten irradiated with 3 keV deuterium ion beam (temperature was raised to 1473 K and held).

isotopes which contributed to those peaks of deuterium release rate from unannealed and annealed wrought tungsten, exposure of a 3 keV deuterium ion beam and neutral particles produced by RF discharge to another wrought tungsten samples of higher purity was carried out, and TDS of deuterium were observed.

Fig. 3 shows TDS of deuterium (D_2, $m/e=4$) from the unannealed samples irradiated with 3 keV deuterium ion beam at temperatures of 300, 373, 473 and 673 K. There were two peaks of deuterium release rate maximum at around 600 and 1400 K in the TDS of samples irradiated at 300 and 373 K. However the former peak became smaller for samples irradiated at 473 and 673 K. This can be attributed to the temperature dependence of the trap density.

The effects of annealing at 1773 K on TDS of wrought tungsten samples are shown in Figs. 4 and 5 with TDS of the CVD and single crystal tungsten samples. In both TDS taken with annealed wrought samples irradiated at 300 and 473 K, there was no peak observed in the high temperature region over 1000 K, while a small peak was observed in the case of irradiation at 300 K, and two peaks at 780 and 850 K for irradiation at 473 K. In the TDS of the CVD and single crystal tungsten samples, there was no peak observed in the high temperature region over 1000 K either. In the TDS of CVD sample, there was a peak at around 820 K in both cases of irradiation at 300 and 473 K. In the TDS of the single crystal tungsten sample, there was almost no peak observed for irradiation at 300 K and a small peak at 860 K for that at 473 K. Similar results of TDS peaks of wrought and CVD tungsten samples were presented in the report by Garcia-Rosales et al. [9]. The discrepancy of the peak temperatures in this report and our work can be attributed to differences in ramp rates.

Fig. 6 shows the TDS of deuterium from the unannealed and annealed wrought tungsten samples which were exposed to deuterium RF plasma at room temperature. At around 750 K, the TDS of the unannealed sample had a larger peak than the annealed one did. However no peak was observed in the high temperature region over 1000 K for either case.

According to the results obtained above, it is clear that trapping sites, which existed specially in a "as received" wrought tungsten sample, capture the implanted hydrogen isotopes and could be eliminated by annealing at a temperature of 1773 K. The ratios of the retained

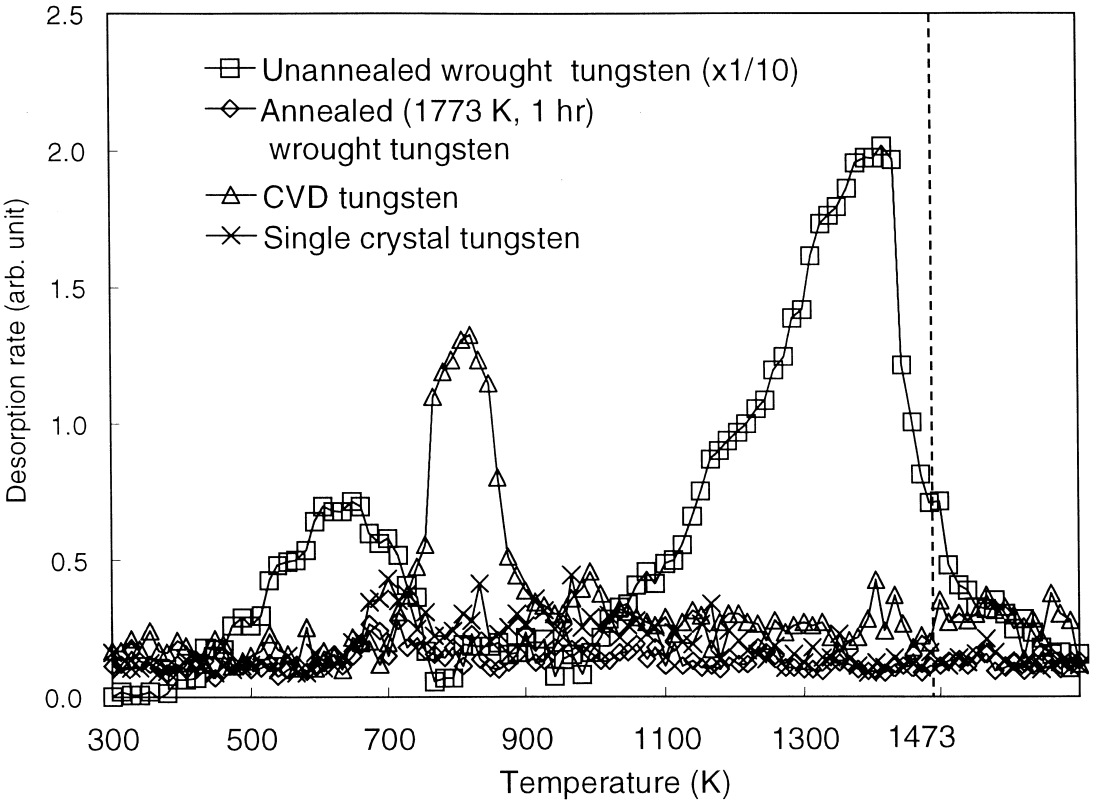

Fig. 4. TDS of deuterium from the various tungsten samples irradiated with 3 keV deuterium ion beam at 300 K (temperature was raised to 1473 K and held).

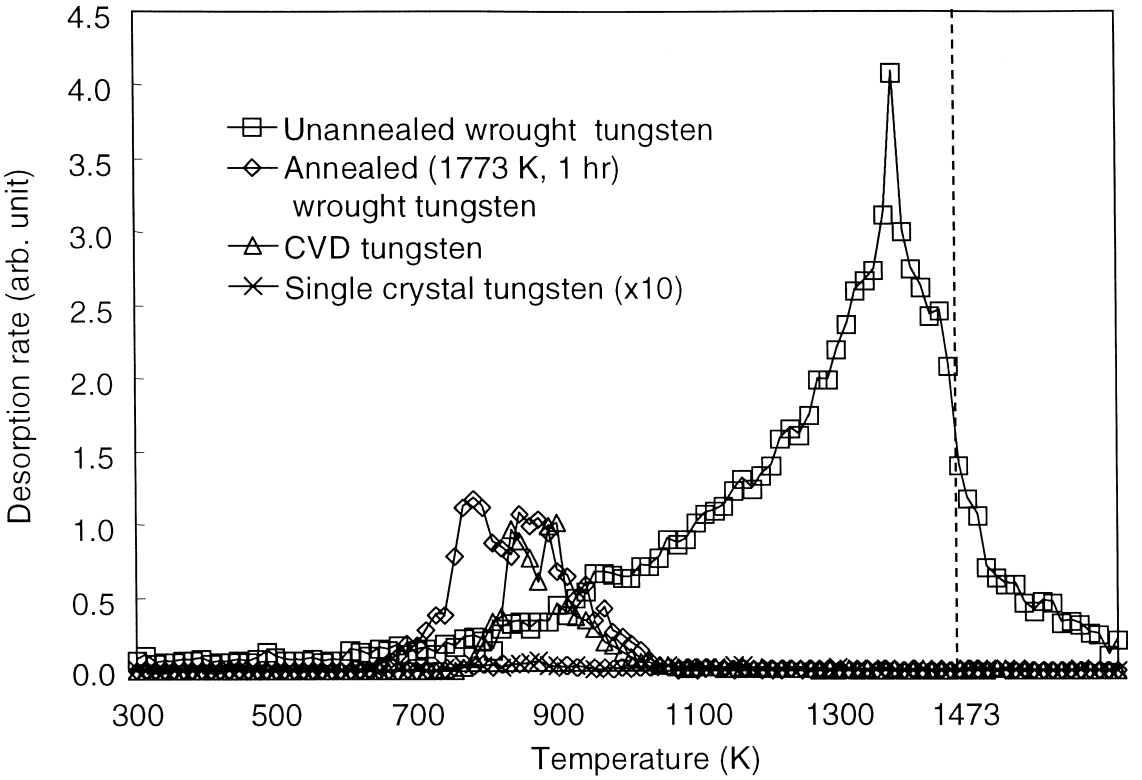

Fig. 5. TDS of deuterium from the various tungsten samples irradiated with 3 keV deuterium ion beam at 473 K (temperature was raised to 1473 K and held).

hydrogen isotope amounts in the unannealed wrought sample to that in the annealed one were 5.4 for TPE and 4.8 for 3 keV ion irradiation at 473 K. These values are very close to one of the trap densities for unannealed and annealed wrought tungsten estimated by Anderl et al. [3]. It was reported that vacancies in tungsten start moving in the temperature range above 473 K, dislocations in wrought tungsten start moving above 673 K [10,11]. Therefore, the peak of deuterium desorption rate maximum at 600 K in the TDS of the unannealed tungsten sample can be attributed to vacancy motion, which transfer hydrogen isotope to the surface, and the other peak at 1400 K can be attributed to dislocation motion which might be associated with channelling of deuterium release. In fact, a "burst" like peak was observed in the TDS of the sample irradiated at 473 and 673 K as in Fig. 3. Production and motion of vacancies in an unannealed wrought tungsten may be strongly correlated with dislocations, because the TDS was quite reproducible even when a sample which has been re-used after a TDS measurement associated with heating up to a temperature 1473 K, which was high enough to eliminate vacancies. This implies that vacancies may be reproduced as far as the dislocations exist in wrought tungsten.

The peak of TDS after ion beam irradiation at 473 K was consistently larger than that after ion beam irradiation at 300 K, for annealed, CVD and single crystal tungsten. This can be attributed to increase of vacancy concentration in higher temperature. The same explanation would be applied to the increase of the peak intensity of the TDS of the unannealed sample irradiated at 373 K comparing to the one irradiated at 300 K. However, at a temperature above 473 K, capture of vacancies at the interface of dislocation might take place, which results in significant reduction of thermal desorption at around 600 K in the TDS. In the case of wrought tungsten exposed to deuterium RF plasma, it can be said that atomized particles did not have enough energy to enter deeply into the lattice of tungsten bulk, and were trapped in only vacancies within the layers close to the surface and never reached to the dislocations. This implies that vacancies may play a role in transferring hydrogen to the dislocation.

4. Conclusions

Results of hydrogen isotope retention in tungsten are summarized as follows:

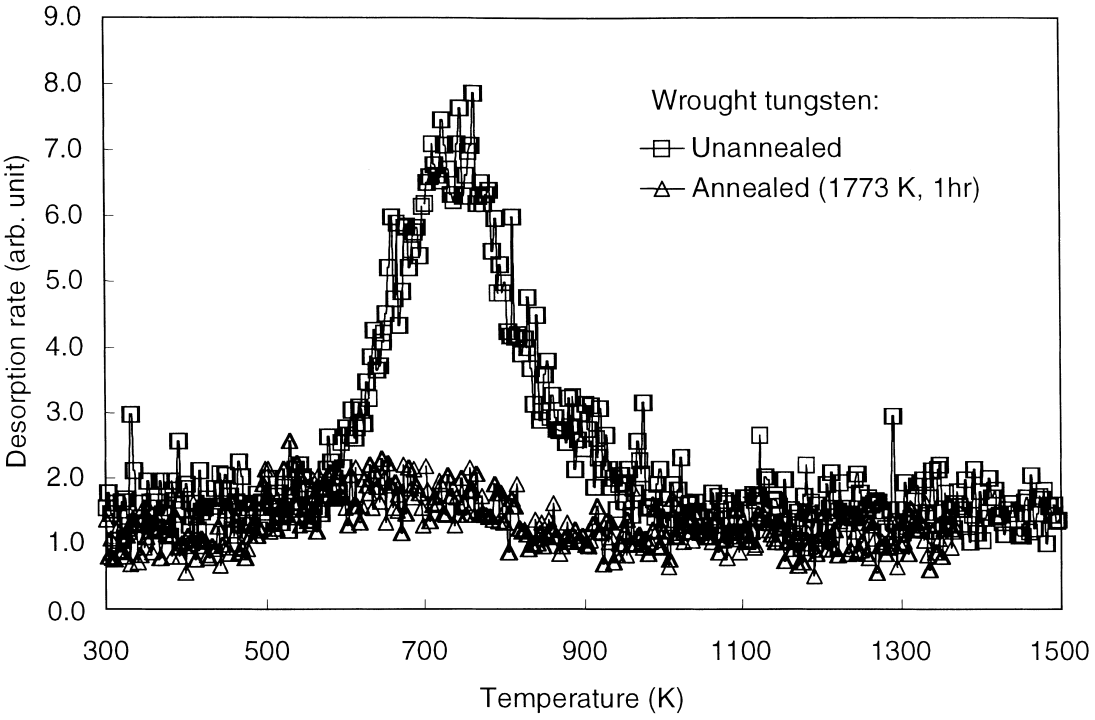

Fig. 6. TDS of deuterium from the wrought tungsten samples exposed to deuterium RF plasma at room temperature.

(1) From the thermal desorption experiments using TPE and 3 keV deuterium ion beam, annealing wrought tungsten at 1773 K reduced tritium retention to about one fifth of that in unannealed tungsten. However, even without annealing at 1773 K, the ration of retained atoms/incident ions of hydrogen isotope for wrought tungsten was 5×10^{-6} at an incident ion fluence of 7×10^{25} ions/m^2 and a temperature of 523 K, was lower than the value reported in the past.
(2) It is shown that the thermal desorption of deuterium implanted in the bulk was strongly correlated to change in microstructure of tungsten. Especially, dislocations produced during sample fabrication process play a significant role to increase hydrogen retention.
(3) The contribution of neutral particles to tritium retention in the tungsten armor tile is negligible at room temperature. However, further investigation at higher temperature and with cleaner surface conditions are necessary.

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