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Role of grain boundaries and carbon deposition in deuterium retention behavior of deuterium plasma exposed tungsten

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Abstract

Data on deuterium retention in W single and polycrystals exposed to D plasma at 500 K are presented. The energy of D ions was well below the threshold of damage production. In a W polycrystal the deuterium spreads to a depth of about 4 μm. In contrast, no deuterium was found even at a depth of 2 μm in a W single crystal. This is an indication of significant grain boundary transport of deuterium at relatively low temperature. It has been found that ~10 nm thin carbon layers grown on the plasma facing surface can be a barrier for D penetration into the bulk of tungsten.

Keywords: Carbon; Hydrogen; Hydrides; Tungsten; Grain boundaries

1. Introduction

Deuterium retention in tungsten irradiated with low-energy (<1 keV) deuterium was investigated both in ion beam experiments by Haasz et al. [1] and under plasma exposure by Causey et al. [2] and Sze et al. [3]. For incident fluences above 10^{23} D/m^2, D retention peaks at exposure temperatures around 500–600 K [1–3]. Depth profiling by nuclear reaction analysis (NRA) showed that the deuterium concentration in the first micrometers from the irradiated surface is not in excess of ~0.1 at.% [1,2], with the exemption of the very near ~100 nm surface layer where a concentration of about 1 at.% was measured [2]. It should be emphasized that deuterium amounts calculated from NRA profiles were found to be less than the total retention evaluated from thermal desorption spectroscopy (TDS) measurements. This behavior is a demonstration that under D ion bombardment the deuterium diffuses into the bulk of the specimen. Direct evidence for significant bulk retention was published by Haasz et al. [1]. They found practically equal deuterium concentrations of 0.05 at.% in the near surface layers at front and back sides of 25 μm thin W foil irradiated with 500 eV D ions to a fluence of 10^{24} D/m^2 at 500 K. Moreover, an integration of this concentration through the sample thickness gave the total retention close to the TDS value.

In this work, we attempt to clarify the role of grain boundaries in deuterium retention by exposing a W single crystal and polycrystal to deuterium plasmas. In addition, an influence of carbon deposition during D plasma exposure on the retention was studied. Deuterium ions with energy well below the threshold of damage production were used.

2. Experimental procedures

2.1. Tungsten specimens

A rod of W single crystal prepared by double electron-beam zone melting method was used for sample manufacture. The specimen as a plate of $3 \times 2 \times 0.1$ mm^3 in size, denoted SW, was cut from the rod by spark cutting in a manner that the plasma facing surface was parallel to (1 0 0) plane. The plate was mechanically and electrochemically polished followed by annealing at 800 K for 10 min in a vacuum of 10^{-5} Pa.

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As polycrystalline material, a W foil, product of powder metallurgy, 50 μm thick and 99.94 wt% pure, was used. The specimen as a plate of 4×3 mm^2 in size, denoted PW, was cut from the foil sheet by mechanical clippers. No additional surface treatment was applied in the present work similar to Ref. [1]. Before plasma exposure the specimen was annealed at 800 K for 10 min in a vacuum of 10^{-5} Pa.

2.2. D ion irradiation

In one set of experiments a low-pressure arc-discharge plasma was used. Negative potential was supplied to a hot tungsten filament while the anode grid was grounded. Typical discharge parameters were the following: voltage 25 V, current 500 mA, deuterium pressure 1 Pa. The sample holder was biased at −150 V with respect to the anode to extract deuterium ions from the plasma. Taking into account the relatively low D_2 pressure used, the sheath is believed to be collision-free, suggesting that the main fraction of ions impacts the sample surface with an energy of 150 eV. For all D ions (D^+, D_2^+, D_3^+) present in the plasma this energy is well below the threshold of damage production. The ion current flowing to the specimen holder was 0.5 mA. This leads to an ion flux density of $(3.6–5.4) \times 10^{20}$ D/m^2 s with lower and upper limits corresponding to the bombardment with only D_2^+ or D_3^+ ions, respectively.

The SW specimen was placed in the holder between two 0.1 mm thick nickel plates of 4×3 mm^2 in size spot-welded to each other. The plasma facing plate has a circular diaphragm of 1.5 mm in diameter, allowing the plasma exposure of the specimen. The PW specimen was fixed in the holder by spot-welding. A W–Re thermocouple spot-welded to the back plate was used for measuring the sample temperature. Changing the distance between the sample holder and the arc cathode varied the sample temperature.

2.3. Carbon deposition experiment

In the second set of experiments the PS samples were exposed to the plasma of a magnetron discharge. A principal diagram of the experimental setup is shown in Fig. 1. The discharge is ignited in D_2 gas. The grounded walls of the vacuum chamber are the discharge anode. The graphite cathode is sputtered with ions accelerated in the sheath. The samples are placed at the holder located 7 cm above the cathode center. A negative potential of 150 V with respect to the anode is supplied to the holder providing the ion bombardment of the sample. In this geometry, the samples are bombarded also with reflected deuterium and sputtered carbon.

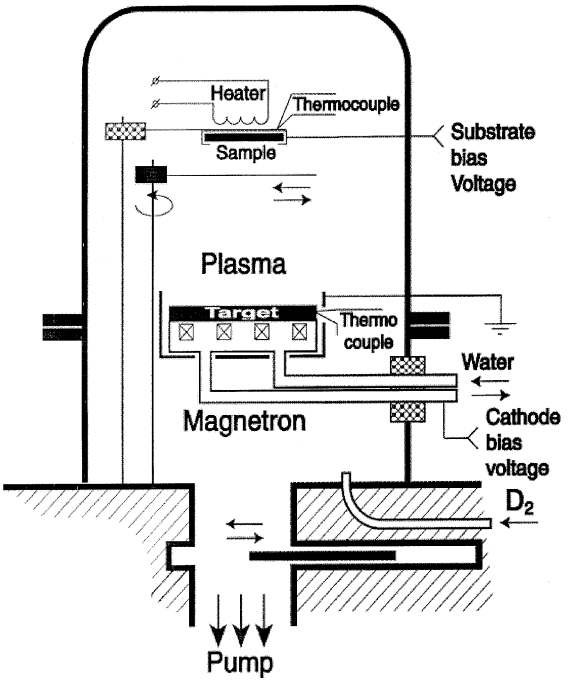

Fig. 1. Principal diagram of W exposure in our magnetron setup.

2.4. Thermal desorption spectroscopy

Thermal desorption measurements were carried out in a UHV chamber with a background pressure of 10^{-6} Pa. The samples were clamped between two nickel strips heated by electric current. The sample temperature was measured by W–Re thermocouple spot-welded to one of the strips. Linear ramping with a rate of no more than 4 K/s was used in the present work. The release of D_2 and HD molecules was monitored by QMS. The QMS was calibrated against tested H_2 and D_2 leaks. The sensitivity to HD was assumed to be the average of the H_2 and D_2 sensitivities.

3. Experimental results and discussion

3.1. D ion irradiation of W single and polycrystal

The same SW specimen was successively exposed to D plasma at 500 K for two hours followed by TDS analysis. Total retained amounts were calculated by integrating the D_2 and HD spectra. The results are 2.3×10^{21} and 1.4×10^{21} D/m^2 for the first and the second run, respectively. After the third exposure, before TDS analysis, the specimen was electropolished removing about 2 μm thick layer. No deuterium desorption was found from this specimen within the detection limit of 5×10^{18} D/m^2.

Notice that post-irradiation inspection by Electron Probe Microanalysis showed that plasma exposure gives no additional carbon contamination of SW specimen as compared to the background level of $\sim 10^{20}$ C/m^2. This is an indication of relatively clean plasma conditions in our experiments. Another explanation might be an effective erosion of deposited carbon with atomic deuterium around 500 K [4]. It is apparent, therefore, that very thin a-C:D films growing on the sample surface might contain only $\sim 10^{20}$ D/m^2, so that the deuterium detected in TDS is governed by gas trapping in the tungsten.

After exposure under the same conditions the PW specimen was cut into four pieces. Two of them were analyzed by TDS in as-exposed state. Two other pieces were electropolished before TDS run: one – with removing about 2 μm thick layer and the second – about 4 μm. Integrating the spectra gave the following results: 0.80×10^{21}, 1.1×10^{21} and 0.4×10^{21}, 0.25×10^{21} D/m^2, respectively. In contrast to the single crystal a significant bulk retention is found for the polycrystalline tungsten.

3.2. Impact of carbon deposition on D retention

In the present experiments the D_2 pressure was set to around 0.1 Pa and the discharge parameters were the following: voltage 380 V, current 1 A. The mean ion current density at the sample was measured to be about 1 mA/cm^2. Assuming that both D_2^+ and D_3^+ ions impinge on the sample surface this leads to D ion flux density in the range $(1–2) \times 10^{20}$ D/m^2 s. Notice that the flux density of reflected deuterium is a few 10^{19} D/m^2 s as can be evaluated from TRIM reflection coefficient and from geometry of the experiment.

With respect to carbon incident flux, the following arguments might be taken into account. As the graphite target-cathode was kept at a temperature of 320 K and an energy of ions incident at the cathode is in the $\sim$100 eV range the sputtered particles are mainly deuterocarbon radicals weakly bonded with the graphite surface [4,5]. When being sputtered these radicals have energy of a few eV and, therefore, would stick efficiently at the 300 K tungsten. At 300 K the carbon deposition rate was found to be $\sim 10^{19}$ C/m^2 s. It should be noticed that carbon carrying ions might be present in the plasma as impurities that would lead to additional carbon deposition at the sample surface. However, separate experiments using a 95% C + 5% W mixed target showed that no tungsten sputtering occurs if the target and the surrounding walls are kept at temperatures below 320 K [6]. This is due to the fact that the energy of the D ions bombarding the magnetron cathode is well below the threshold for physical sputtering of tungsten. From these experiments the level of carbon impurities in the plasma is assessed to be about 1% [6]. This leads to estimated carbon flux at the sample of $\sim 10^{18}$ C/m^2 s. It might be concluded, therefore, that the carbon flux incident at the sample surface in the present experimental conditions is mainly due to the radicals sputtered from the graphite target.

In the present work the PW samples were exposed at 500 K. At this temperature the deposited carbon is effectively re-eroded by thermal D atoms formed in the plasma [4]. Consequently, only a carbon areal density of 5×10^{20} C/m^2 (this corresponds to $\sim$10 nm thin film of 1 g/cm^3 density) was detected at the samples after 60 min exposure. TDS measurements give the deuterium retained amount of 3×10^{20} D/m^2. Similar to Section 3.1 one sample was electropolished after the plasma exposure, removing about 2 μm thick layer. No deuterium release was detected from this specimen.

The origin of deuterium desorbed from the as-exposed sample is not clear from these TDS results. On the assumption that all the deuterium is located in the surface carbon film the D/C ratio is obtained to be 0.6. This is quite a reasonable value for a-C:D films [4]. On the other hand, typical TDS spectra measured from various W samples (Figs. 2(a) and (b)) are not characteristic of the a-C:D films. In Fig. 2(c) the spectrum of a 600 nm thick a-C:D film deposited on PW sample held at a temperature of 320 K is shown for comparison. The main fraction of retained deuterium leaves the film at a high temperature stage above 1000 K. In opposite, the spectra of all W samples exposed to D plasmas at 500 K including that covered with a thin carbon film, show significant D losses at lower temperatures.

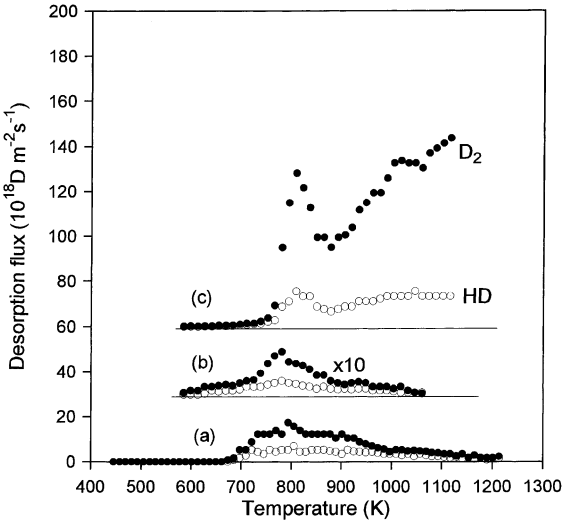

Fig. 2. Thermal desorption spectra of D_2 and HD molecules from: (a) SW sample exposed to D plasma at 500 K; (b) PW sample exposed to a magnetron plasma at 500 K and (c) 600 nm thick a-C:D film deposited by magnetron sputtering of graphite on the 320 K substrate. Heating rates were (a) 4 K/s, (b) and (c) 1.5 K/s.

3.3. Fusion application

In contrast to Alimov and Scherzer results [7] we do not find any remarkable deuterium retention in the bulk of single-crystalline tungsten. For polycrystalline tungsten, in agreement with earlier results [1,2], large deuterium amounts are found to a depth of at least 4 μm. This result indicates that (i) grain boundary transport of deuterium is significant even at 500 K and (ii) there is a type of deuterium trapping in addition to implantation-induced trapping. These traps seem to be located at grain boundaries and be stable even at 500 K. With respect to tritium permeation assessments for fusion devices, such transport might be concerned if the back side of tungsten armor will contact readily with coolant.

For low energies typical of the divertor, the main part of the incident deuterium will be buried in the top ~10 nm thin carbon films grown on the tungsten tiles. The rate of deuterium penetration from hydrogenated carbon to the underlying metal layers seems to depend on interface microstructure. Our experiments show that this reaction might be rather slow as compared to the D penetration rate when low energy deuterium impinges on the clean tungsten surface.

4. Conclusions

The deuterium retention in W single and polycrystals exposed to D plasmas at 500 K was studied. The energy of the D ions was well below the threshold of damage production. In W polycrystal the deuterium spreads to a depth of about 4 μm. In contrast, no deuterium was found even at a depth of 2 μm in a W single crystal. This is an indication of a significant grain boundary transport of deuterium at relatively low temperatures where no permeation can be detected using a mass-spectrometry technique. However, the ~10 nm thin carbon layers grown on the plasma facing surface can be a barrier for D penetration into the bulk of tungsten.

Acknowledgements

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