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Mechanisms of retention and blistering in near-surface region of tungsten exposed to high flux deuterium plasmas of tens of eV

W.M. Shu *, G.-N. Luo, T. Yamanishi

Tritium Technology Group, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

Abstract

The mechanisms of hydrogen retention and blistering in tungsten exposed to high flux deuterium plasmas of tens of eV were studied with a variety of techniques, such as TEM/SEM and TDS. Cross-sectional TEM observations showed that small blisters with diameters around 30 nm and microcracks formed in the near-surface region before the formation of larger blisters with diameters up to a few microns (comparable to grain sizes). The TDS results indicated that deuterium mainly existed in the molecular form in tungsten after the plasma exposure. These results suggest that crystal defects like vacancies could be generated by the intrusion of a large number of hydrogen isotope atoms in the near-surface region of tungsten.

1. Introduction

Blistering can occur at the tungsten surface, even if the ion energy is too low to create displacement damage such as vacancies [1–8]. Sze and co-workers observed blisters with diameters of a few to a few hundreds of microns on the surfaces of tungsten foils exposed to high ion flux (10^{22} $D^+/m^2/s$) and low ion energy (about 110 eV) deuterium plasmas at 400–500 K [1,2]. Haasz et al. found blisters with diameters of a few to a few tens of microns on the surfaces of tungsten pre-annealed at 1473 K after exposure to deuterium ion beam with an ion flux of about 10^{20} $D^+/m^2/s$ and energy of 500 eV at 500 K [3]. Venhaus et al. reported that un-annealed samples and samples annealed at 1473 K showed extensive blistering with many blister caps removed and no blistering, respectively, after exposure to the mixed deuterium and tritium plasmas with a high ion flux of 1.7×10^{22} ions/m^2/s and low ion energy of 100 eV at 423 K [4]. Wang et al. [5] reported that the blister size increased and the number decreased with deuterium fluence from 10^{19} to 10^{21} D^+/cm^2 at the energy of 1 keV and room temperature and no blisters were found at elevated temperatures between 600 and 800 °C. Tokunaga et al. [6] found that blisters were formed on powder metallurgy tungsten by deuterium irradiation with ion fluxes ranging from 4.8×10^{21} to 1.2×10^{22} $D^+/m^2/s$ and a low ion energy of 100 eV at temperatures of 708–843 K, and the amount of blisters and their average size increased with increasing fluence from

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* Corresponding author. Tel.: +81 29 282 6452; fax: +81 29 282 5917.

E-mail address: shu.wataru@jaea.go.jp (W.M. Shu).

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7.5×10^{25} to 3.0×10^{26} D^+/m^2. Ye et al. [7] observed blister formation on a tungsten surface under a low energy (about 90 eV) and high flux (2×10^{21} $H^+/m^2/s$) hydrogen plasma exposure at the surface temperature less than 950 K and the fluence higher than 3×10^{24} m^{-2}. Ueda et al. [8] investigated the impact of carbon impurities in hydrogen ion beams on tungsten blistering at a hydrogen ion flux of about 4×10^{21} $H^+/m^2/s$ and energies of 100–1000 eV.

The above research has clearly demonstrated that hydrogen isotope exposure with energy as low as 100 eV can definitely produce blistering at the tungsten surface. However, the mechanism of blistering is not well understood yet and requires further investigation. In this work, tungsten plates annealed at 1473 K were exposed to deuterium plasmas with incident energies ranging from 7 to 98 eV and a fixed flux of 10^{22} $D^+/m^2/s$, and the blistering and hydrogen retention in the near-surface region were investigated with a variety of techniques, such as scanning and transmission and scanning electron microscopy (SEM and TEM), and thermal desorption spectroscopy (TDS).

2. Experimental

Tungsten plates with 99.7% of theoretical density and an averaged grain size of about 2 μm were prepared by powder metallurgy and hot-rolled reduction, and then annealed at 1473 K for 30 min. The plates were subsequently cut and double-sided polished into samples of 10 × 10 × 2 mm. The tungsten material has a purity of 99.99 wt% with principal impurities (in weight ppm) of Mo and Fe ∼ 10, C and O < 30. The polished samples were cleaned in an acetone ultrasonic bath prior to placing into the deuterium exposure chamber. The apparatus for plasma exposure is a linear plasma source, which consists of sections of vacuum chamber and pumping, cooling water, gas admittance, power supply, plasma generation, plasma delivery, sample holder and plasma diagnosis [9]. The ion energy was determined from the bias voltage and the plasma potential of −4 V measured by a Langmuir probe, taking into account the predominant ion species of D_2^+. A fixed flux of 1×10^{22} $D^+/m^2/s$ and varying incident energies from 7 to 98 eV were used in the exposure. The main impurity in the plasma was oxygen with a concentration less than 1 ppm. A comparison between this work and the previous research [1–8] is made in Fig. 1, in which the ion flux is plotted against ion energy, and the coverage of both flux and energy for ITER divertor dome, baffle and liner [10] is also shown.

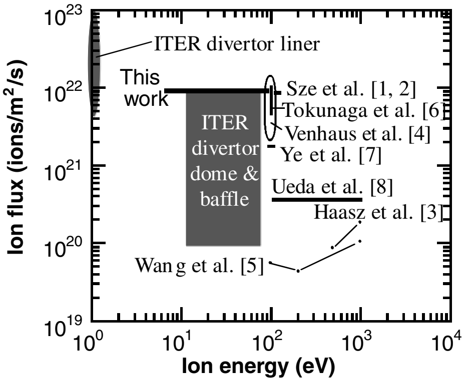

Fig. 1. A summary of flux and energy used in recent research on W blistering. For comparison, the design values of the ITER divertor are also shown.

Blister formation on the surface of tungsten exposed to the deuterium plasmas was observed by a scanning electron microscopy (Real Surface View Microscope, KEYENCE VE-7800) at a tilt angle of 45°. Thin foils for transmission electron microscopy (TEM) were prepared with a focused ion beam (FIB) microsampling system (HITACHI FB-2000A). Procedures to prepare the thin foils are: (a) W deposition (to reduce damage during the specimen fabrication in the region for observation), (b) removal of material with a fine Ga^+ (20 keV) beam to obtain a foil, (c) welding of a W needle to the foil by W deposition, (d) cutting to separate the foil from the irradiated disk, (e) welding the foil to a mesh by W deposition and (f) removal of the damaged layer near the foil surface formed during FIB processing by an Ion Miller (GENTILE MILL, TECHNOLOGY LINDA). Then, the plasma exposure-induced microstructural defects were examined with a TEM (JEOL JEM-2000FX).

Thermal desorption spectroscopy (TDS) was used to evaluate deuterium retention in the tungsten samples after the deuterium plasma exposures via integrating the deuterium release rate with respect to time. A standard deuterium leak with an inaccuracy lower than 10% was employed to calibrate the quadrupole mass spectrometer (QMS) prior to each TDS analysis so that the calibrated release rate during TDS could be obtained. During TDS, an infrared heater was used to heat the irradiated samples at a ramp rate of 5 K/s.

3. Results and discussion

3.1. Blistering

A typical SEM image is shown in Fig. 2, where blisters with diameters of about 0.1–2 μm are shown on the surface of tungsten exposed to 98 eV deuterium plasma with a fluence of 10^{25} D/m^2, along with a cross-section view of a large blister with a diameter of about 2 μm that was exposed by the FIB technique. Before removing the material with Ga$^+$ ions, a protective thin layer of tungsten was deposited on the blister. From the cross-sectional SEM image of this blister, the thickness of the blister cap was determined to be about 0.4 μm, two orders of magnitude greater than the implanted range. In addition, the maximum blister size observed in this study is 1–2 orders of magnitude smaller than that of blisters formed on tungsten exposed to 100–1000 eV hydrogen isotope plasmas reported before [1–8]. For instance, Sze and co-workers observed much larger blisters with the diameters up to a few hundreds of microns on tungsten foils exposed to a high ion flux (10^{22} m^{-2} s^{-1}) and low ion energy (about 110 eV) deuterium plasma at 400–500 K [1,2], and Ye et al. observed blisters with the size of a few tens to a few hundreds of microns formed on a tungsten surface under a low energy (about 90 eV) and high flux (2×10^{21} H$^+$/m^2/s) hydrogen plasma exposure at the surface temperature less than 950 K [7]. Since the microstructures of tungsten used in this study are almost isotropic with an averaged grain size of about 2 μm, it seems that the maximum size of blisters is independent of the incident energy and the exposure temperature, but instead it could be strongly influenced by microstructure features like grain size.

Thus, the behavior of blistering on tungsten exposed to high flux and low-energy plasma was further investigated by FIB/TEM. The cross-sectional TEM images are shown in Figs. 3–5 for a sample exposed to 7 eV deuterium plasma with a fluence of 10^{25} D/m^2. At the exposure conditions, visible blisters could not be observed by the SEM

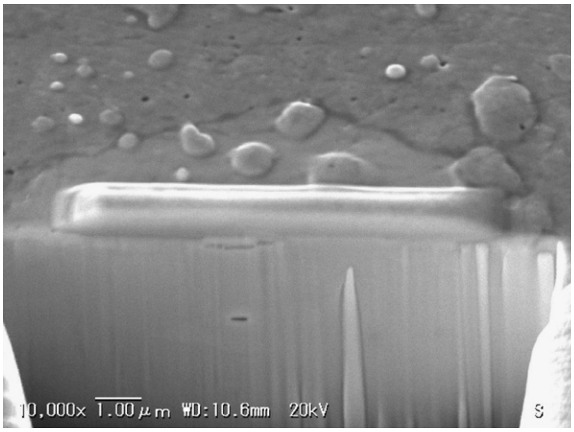

Fig. 2. Blisters formed on W surface and cross-sectional SEM image of a blister viewed at a tilt angle of 45°.

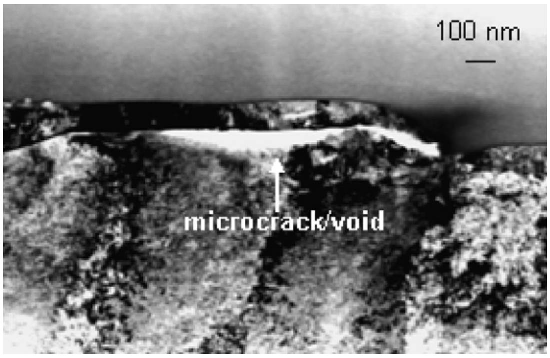

Fig. 3. XTEM image of microcrack/void along grain boundary.

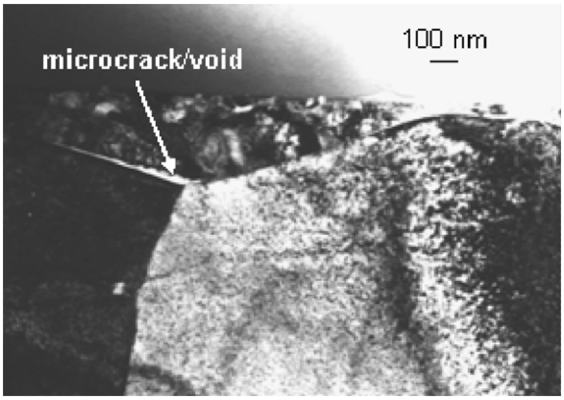

Fig. 4. XTEM image of microcrack/void at grain corner.

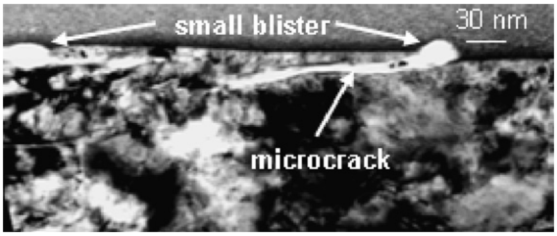

Fig. 5. XTEM image of small blisters with a diameter of around 30 nm and microcracks.

with a resolution of about 0.1 μm. A microcrack/void was generated at the depth of about 100 nm along the grain boundary almost parallel to the surface (Fig. 3), and a void was generated at the grain corner at the depth of about 300 nm and microcrack extended along the grain boundary (Fig. 4). In addition, small blisters with a diameter of around 30 nm and microcracks formed in the near-surface region before the formation of larger blisters with diameters of up to a few microns (Fig. 5). The observations indicate that the maximum size of blisters (about 2 μm) is limited by the microstructure, especially by grain sizes. Much larger blisters observed by the previous researchers like Sze et al. [1,2] could be caused by the crystal texture of the tungsten foils used in their study.

3.2. Retention

The deuterium retention in the exposed samples was measured using a thermal desorption spectrometer (TDS). The TDS spectrum of deuterium shows a peak around 770–970 K at a heating rate of 5 K/s, implying a predominant release in its molecular form from the blisters. The relationship between the amount of retained deuterium and the fluence shows a sudden drop at a certain fluence, indicating that deuterium retention is limited by rupture of blisters. The maximum retention in samples exposed to the plasma at room temperature is around 10^{20} D/m^2. In addition, the relationship between the amount of retained deuterium and the plasma exposure temperature shows the maximum retention at around 400–500 K. Above 700 K, the retention decreased to a quite low level, and blisters disappeared at the exposure of 900 K [11].

Ogorodnikova et al. [12] introduced two kinds of traps to describe the deuterium retention in tungsten exposed to low-energy ion beams. One is low-temperature traps: intrinsic defects (dislocations, grain boundaries, some impurities, presence of bulk oxide) with a trapping energy of 0.85 eV distributed over the whole sample thickness; and another is high-temperature traps: ‘ion-induced’ traps associated with deuterium agglomeration in molecules and bubbles near the implanted surface and deuterium trapping in vacancies with a trapping energy of 1.45 eV. These latter form and grow during implantation, are distributed near the surface and correlated with the implantation range. Many of the other studies such as those by Van Veen et al. [13] and Sakamoto et al. [14] have shown that hydrogen decorates pre-existing voids and can create new ones if they do not already exist. Causey [15] argued that using tungsten in a plasma-facing application may eventually result in moderate inventories of hydrogen isotopes in the bubbles and blisters (unless the tungsten is maintained at very high temperatures). Such blister formation may also eventually result in tungsten being released into the plasma. Tungsten can be released into the plasma either through grain ejection [1] or by evaporation due to the creation of open blister caps that lose their thermal contact with the material below.

How are the ‘ion-induced’ traps generated, and why could blistering occur in annealed tungsten exposed to deuterium plasmas with energies much smaller than that required for generating displacements? In Doppler broadening measurements with slow positron beams, we found that the vacancy concentration in the near-surface region of tungsten is increased by deuterium plasmas with energy of 38 eV [16]. This new evidence, together with TEM and TDS results suggests that vacancies could be generated by the intrusion of a large number of hydrogen isotope atoms in the near-surface region in tungsten due to lowering of the formation energy of vacancies.

4. Conclusions

(1) Blisters with the maximum diameter of about 2 μm (comparable to grain size) were formed on the tungsten surfaces after plasma exposure, and small blisters with a diameter of around 30 nm and microcracks were generated in the near-surface region before the formation of larger blisters. The maximum size of blisters is limited by the microstructure, especially by the grain size.

(2) After deuterium plasma exposure, deuterium was retained predominantly in the molecular form. This suggests that crystal defects like vacancies could be generated by the intrusion of a large number of hydrogen isotope atoms in the near-surface region of tungsten.

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