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Investigation of plasma exposed W–1% La_2O_3 tungsten in a high ion flux, low ion energy, low carbon impurity plasma environment for the International Thermonuclear Experimental Reactor

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Abstract

Previous investigations of tungsten for the International Thermonuclear Experimental Reactor (ITER) were focusing on using energetic ion beams whose energies were over 1 keV. This study presents experimental results of exposed W–1% La_2O_3 in high ion flux (10^{22} m^{-2}), low ion energies (about 110 eV) steady-state deuterium plasmas at elevated temperatures (873–1250 K). The tungsten samples are floating during plasma exposure. Using a high-pressure gas analyzer, the residual carbon impurities in the plasma are found to be about 0.25%. No carbon film is detected on the surface by the EDX analysis after plasma exposure. An infrared pyrometer is also used as an in situ detector to monitor the surface emissivities of the substrates during plasma exposure. Using the scanning electron microscopy, microscopic pits of sizes ranging from 0.1 to 5 μm are observed on the plasma exposed tungsten surfaces. These pits are believed to be the results of erupted deuterium gas bubbles, which recombine underneath the surface at defect locations and grain boundaries, leading to substrate damage and erosion loss of the substrate material. Low temperature plasma exposure of a tungsten foil indicates that deuterium gas (D_2) is trapped inside the substrate. Macroscopic blisters are observed on the surface. The erosion yield of the W–1% La_2O_3 increases with temperature and seems to saturate at around 1050 K. Scattered networks of bubble sites are found 5 μm below the substrate surface. High temperature plasma exposure appears to reduce the population as well as the size of the pits. The plasma exposed W–1% La_2O_3 substrates, exposed above 850 K, retain about 10^{19} D/m^2, which is two orders of magnitude less than those retained by the tungsten foils exposed at 400 K.

1. Introduction

In the current design of the International Thermonuclear Experimental Reactor (ITER) [1], the lower baffle area will be covered with tungsten, subject to particle flux of 10^{22} m^{-2} s^{-1} and energies between 100 and 500 eV. Studies of the plasma–tungsten interactions are thus vital for the design and operation of the proposed ITER fusion reactor.

Two of the key issues in fusion reactor operation are hydrogen isotopes inventory and permeation in tungsten. Longhurst, in his ITER report [2], indicated that the existence of differences of hydrogen transport parameters in several studies by Franzen et al. [3], Garcia-Rosales et al. [4], Frauenfelder [5] and Anderl et al. [6] were due to different substrate purities and experimental conditions. Orders of magnitude differences in diffusion coefficients and recombination rate coefficients were reported. Ion energies over 1 keV were used to implant the hydrogen into the substrates, most of which were kept at temperatures below 800 K. Their studies focused on gas desorption measurements. Information on substrate conditions after ion beam radiation was not available.

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Gas bubbles formation was reported as early as 25 years ago by Picraux et al. [7] when a helium ion beam was used to profile deuterium implantation in tungsten. The phenomenon was illustrated by Johnson et al. [8], whose TEM pictures showed that bcc metals could form a helium-bubble superlattice. Hydrogen bubbles were not reported in Johnson's paper Kimura et al. [9] reported the damage effect of hydrogen bubbles in type 316 stainless steel. Haasz and Davis, in their recent paper [10], reported that small pits were formed on their surfaces, after high ion energy beams (3 keV D_3^+) irradiation. Their substrates were kept at room temperature.

It is known that energetic ions can induce lattice damage. When the hydrogen atoms are implanted into the substrate, they diffuse along the concentration gradient within the lattice. When they reach a defect site or the grain boundaries, they recombine to form diatomic hydrogen molecules. At the substrate surface, the gas molecules will leave the surface. Within the substrate, the gas molecules are trapped and form bubbles, which is defined here as accumulation of gas molecules in a bounded environment. Once, formed, interstitial diffusion of the diatomic molecules is very difficult, if not totally impossible.

According to Šmid et al. [11], W–1% La_2O_3 tungsten is an attractive candidate for ITER because of lower material and machining costs than other tungsten materials. It has similar thermal conductivity as the W–3Re tungsten, which is expected to be formed after exposing tungsten to neutron radiation. However, no information on plasma exposed W–1% La_2O_3 is available. This study investigates whether deuterium bubbles form without energetic ion bombardment. It reports experiments performed on W–1% La_2O_3 substrates under a high ion flux and carbon contamination free deuterium plasma environment. Deuterium retention in the exposed tungsten substrates is also measured, using thermal desorption spectrometry technique.

2. Experiments

2.1. The PISCES-B facility

The PISCES-B facility is a steady-state plasma facility to study fusion-plasma materials. Maximum heat load can reach as high as 9 MW m^{-2}. Fig. 1 shows a drawing of the vacuum system. It consists of a plasma source region, a main chamber and a loading chamber. The plasma generator consists of a LaB_6 cathode with hot tungsten filaments on its backside. Two turbomolecular pumps with an effective pumping speed of 6500 liters per second are attached to the vacuum chamber. The main chamber is surrounded by three electromagnetic coils, which generate a coaxial magnetic field along the axis of the vacuum system with a magnetic field strength of around 500 Gauss. A 5 cm diameter plasma column is formed along the axis of the vacuum chamber. The sample size is 2.45 cm in diameter. A fast scanning double-Langmuir probe is used to measure the plasma

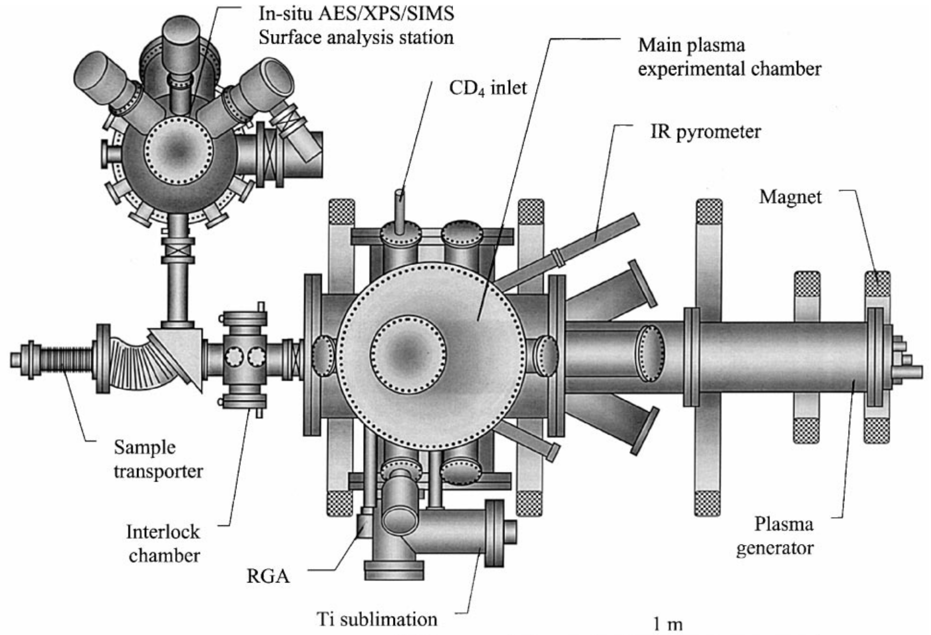

Fig. 1. PISCES-B facility.

temperatures and densities in the radial direction. The facility produces steady plasmas for several hours of cotinuous exposure. The base pressure of the system is 6×10^{-6} Pa. The plasma parameters, T_e (10–60 eV) and $N_e(2 \times 10^{17}$–20×10^{17} m^{-3}), near the target region can be adjusted by varying the gas flow and input power to the heating filaments in the cathode. A water-cooled sample holder controls the sample temperature by its water flow rate. In this study, the electron temperature is about 50 eV and the ion fluxes to the substrates are maintained at about 2×10^{22} m^{-2} s^{-1}. The energies of the ions are about 110 eV. The only variable is the substrate temperature, which varies from 850 to 1250 K. All these parameters are within the ITER's specifications for tritium inventory and permeation study.

The samples, W–1% La_2O_3, used in this investigation are non-polished, as-received tungsten discs from Plansee. Each has a diameter of 2.54 cm and a thickness of 1.5 mm. It is clamped to the water-cooled sample holder with a molybdenum cap. At the center of the sample holder is a K-type TC to measure the substrate temperature. An infrared pyrometer is also attached to the main chamber to remotely monitor the surface composition by observing its surface emissivity during plasma exposure. The samples are heated up by the plasmas and reached their final steady temperatures in about 1 min. They are floating in the plasmas at about negative 110 V and exposed for a period of 1–2. After exposure, the samples remain in the vacuum chamber for about 2 h before they are transferred to the thermal desorption spectrometry (TDS) system for gas retention measurements. The average time to move samples from the PISCES-B to the TDS system is about 10 min. The samples are then pumped down in the TDS system for at least 3 h to reach a base pressure of 4×10^{-6} Pa before taking measurements. Surface analyses are performed using a JEOL T330A SEM, and the energy dispersive X-ray (EDX) analysis system from Kevex.

2.2. In situ monitoring of carbon impurities in plasmas

Knowing that carbon has been deposited on beryllium surface [12] during plasma exposure, a microprobe gas analyzer, MPA-565C, from Ferran Scientific, is used to monitor the partial pressures of the residual carbon species inside the vacuum system. Unlike most RGAs, the gas analyzer has a maximum measurable pressure at 0.66 Pa. Therefore, it can continuously monitor the vacuum conditions throughout the experiments. The species that are monitored include deuterium, D_2, and the CD_x ($x = 1, 2, 3, 4$) radicals, whose masses are 4, 14, 16, 18 and 20 amu respectively. It is easy to distinguish water vapor, whose mass is also 18 amu, from CD_3. Water vapor pressure will drop over time in a vacuum system due to depletion. The partial pressure of CD_3 will maintain a constant ratio with respect to CD_4. In a high vacuum environment such as the PISCES-B facility, the water vapor level is near the detection limit of the high-pressure RGA, which is about 1.3×10^{-6} Pa.

2.3. In situ surface emissivity measurement to monitor surface contamination

Visual inspection through a vacuum window is routinely used to monitor the sample surface during plasma exposure. Nonetheless, the technique is harmful to the human eyes because of the infrared and ultra-violet radiations from the hot sample and the plasma, respectively. The technique is also not reliable when the sample is red hot. A simple and better way to check if a surface is contaminated with carbon during plasma exposure is to use an IR pyrometer, which acts as an in situ detector to monitor the surface emissivity of the substrate. It works perfectly well for carbon and tungsten since carbon has an emissivity close to unity and tungsten has a low emissivity [13]. Knowledge of the emissivity of the W–1% La_2O_3 samples is not necessary because the purpose of the technique is to detect change in surface emissivity, i.e. a qualitative measurement.

The principle is based on Stefan–Boltzmann law [13], in which the total radiation, Q, emitted by a blackbody at temperature T is σT^4, where

$$\sigma = 5.67032 \times 10^{-8}\text{W m}^{-2}\text{ K}^{-4}. \qquad (1)$$

The emissivity, ε, is the ratio of

$$Q/Q_{\text{blackbody}} = (T_b/T_{\text{subtrate}})^4, \qquad (2)$$

where T_b is the equivalent blackbody temperature of the substrate, and $T_{\text{substrate}}$ is the actual substrate temperature. The relation between the surface emissivity and the recorded temperatures during plasma exposure are

$$\varepsilon_{\text{surface}} = \varepsilon_s(T_s/T_{\text{surface}})^4, \qquad (3)$$

where $\varepsilon_{\text{surface}}$ is the emissivity of the substrate surface; ε_s the emissivity setting of the IR pyrometer; T_s the IR pyrometer reading and T_{surface} the actual substrate temperature measured by the thermal-couple wires.

3. Results and discussions

3.1. Impurities in the plasmas

Fig. 2 shows the traces of four gaseous species during one of the plasma experiments. Deuterium gas has a mass of 4 amu. As shown, the pressure jumped to about 4.0×10^{-3} Pa when the gas flow was started. The pressure was further increased when one of the gate valves to the turbomolecular pumps was closed. The D_2 pressure reached a steady value at about 5.7×10^{-2} Pa. The cathode was heated up at the same time. Outgassing of

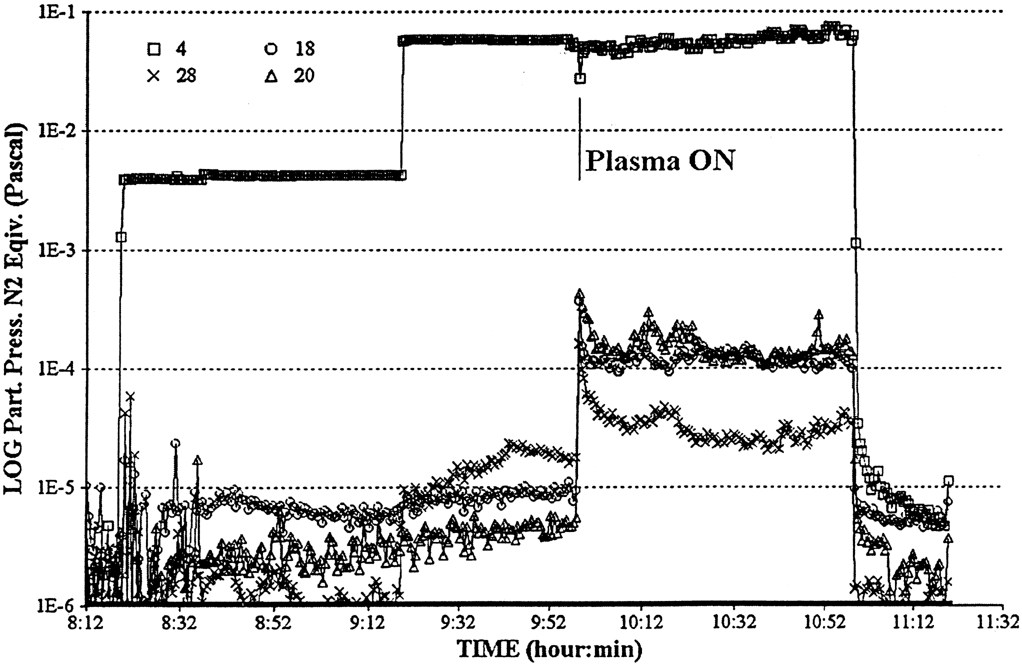

Fig. 2. Traces of gaseous species in PISCES B.

carbon monoxide from the cathode [14] began as shown by the slight increase in mass 28 amu. It should be pointed out that after repeated plasma exposures without venting the main chamber, desorption of carbon monoxide from the cathode gradually ceased. As shown in Fig. 2, the levels of CD_4 (20 amu) and CD_3 (18 amu) jumped more than 10 times when the plasma was started, due to chemical interactions between the atomic deuterium and the residual carbon in the vacuum system. The increase of mass 18, as explained in previous section, represented CD_3 since its magnitude stayed about the same when the plasma was on. The total amount of carbon concentration during plasma exposure is approximately 0.25%, which represents the intrinsic carbon impurity level in PISCES-B. Additional emission spectroscopy measurements during plasma exposure also agree with the RGA technique for determining the carbon concentration [15]. At 0.25% carbon impurity, no change in surface emissivity was observed by the IR pyrometer. Subsequent EDX surface analyses also verified that the tungsten surfaces were free of carbon.

After plasma exposure, the substrate was cooled down to room temperature in about 12 min. When the plasma was turned off, the gas flow was also stopped at the same time. At that moment, deuterium began to be outgassed. This is shown in Fig. 2 by the exponential decay of deuterium (4 amu). A separate test without heating up the cathode and without turning on the plasma showed a sharp fall in deuterium pressure. Desorption of deuterium is therefore coming from the plasma-exposed surfaces, which include the hot cathode, part of vacuum wall, sample and the sample holder. Such outgassing is beneficial because the hydrogen fuel is directly recycled back to the vacuum system. Assuming that the total area of plasma-exposed surface is 20 times of the surface area of the tungsten sample, the amount of this *post-exposure outgassing* is estimated to be 1.6×10^{21} D/m^2 from the exposed tungsten surface.

3.2. Erosion of tungsten

The erosion rate is measured by weight-loss method. It increases with substrate temperature as shown in Fig. 3. The main source of error, which is about 20%, is from the calculation of the ion flux. The error bar is about the size of the symbol used in Fig. 3. At 110 eV energy, deuterium ions hardly sputter the tungsten surface. TRIM calculations [16] show zero sputtering yield at 110 eV. The closest experimental data, compiled by Eckstein et al., showed a sputtering yield of 1.5×10^{-4} at 250 eV ion energy at room temperature [17]. Data at lower ion energy and other temperatures are not available. Because it is impossible to eliminate impurities in the vacuum system, it has been suggested that the sputtering of tungsten is due to impurities sputtering rather than deuterium sputtering.

The ion fluxes to the tungsten substrates were about the same at 2×10^{22} m^{-2} s^{-1} in all experiments. The amount of impurities in the vacuum system stayed about

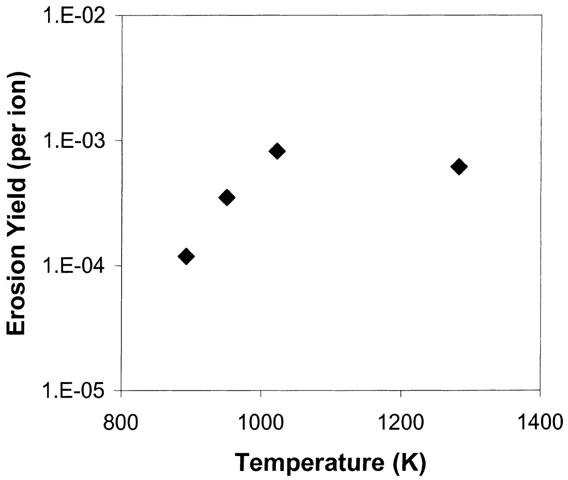

Fig. 3. Measured erosion rate of tungsten.

the same at different substrate temperatures. According to TRIM model, the calculated sputtering rate, assuming a 0.25% carbon impurity and 100% tungsten substrate, should stay the same at 2×10^{-4} atom/ion throughout the temperature range (850–1250 K). The reason is that TRIM code does not include any temperature dependency in the computation of the sputtering yield. The incident ion energies are much higher than the thermal energy of the substrate atoms. Therefore, energies of the incident ions, rather than the thermal energies of the substrate, determine the sputtering yield. However, as shown in Fig. 3, the erosion rate increases with temperature and seems to saturate at around 1050 K. This suggests that substrate temperature is also playing a role *under the plasma conditions* described in this study. Why does TRIM fail in this case? One possible reason is the high ion flux used in these experiments, which leads to a temperature-sensitive process. What process is sensitive to temperature? The suggested answer is bubble formation.

3.3. Surface analyses – bubble formation

Fig. 4(a) and (b) show the W–1% La_2O_3 tungsten surface before and after plasma exposure at 850 K. Pits of several micrometers in size are found on the surface. They are randomly distributed over the surface. The pits are believed to be formed due to the eruption of the hydrogen bubble formed beneath the surface. Fig. 5 shows a cross-sectional view of the bubble sites, showing a network of bubbles 5 μm below the surface. For comparison, the lower left-hand corner of the SEM picture in Fig. 5 shows the undamaged substrate. One network of bubbles was found as deep as 10 μm below the surface. According to the TRIM calculations, ion implantation at 110 eV can only reach an average depth

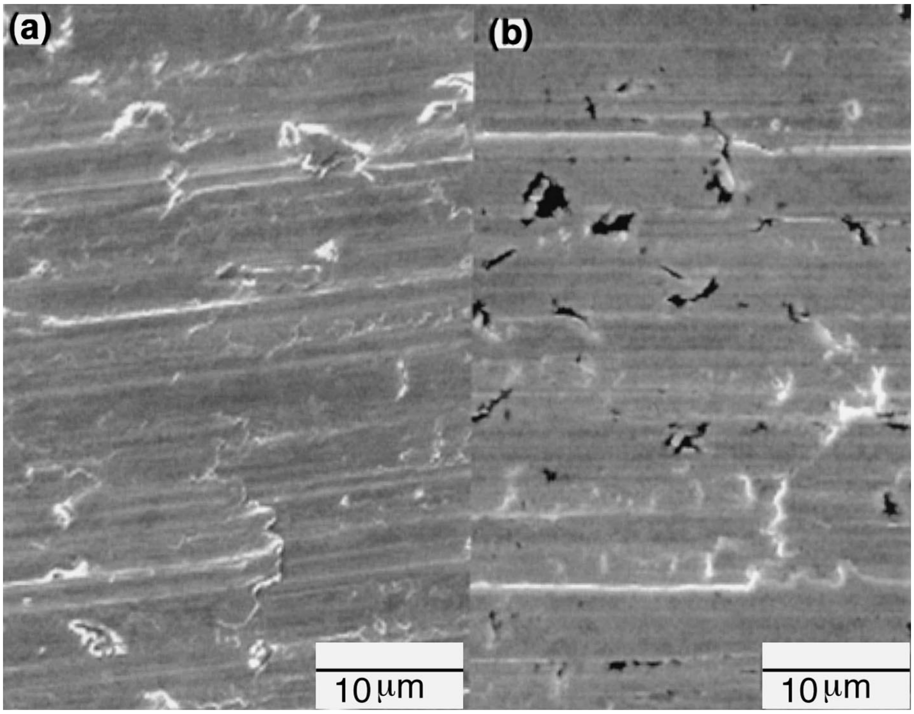

Fig. 4. W–1%La_2O_3 tungsten surface (a) before and (b) after deuterium plasma exposure at 850 K.

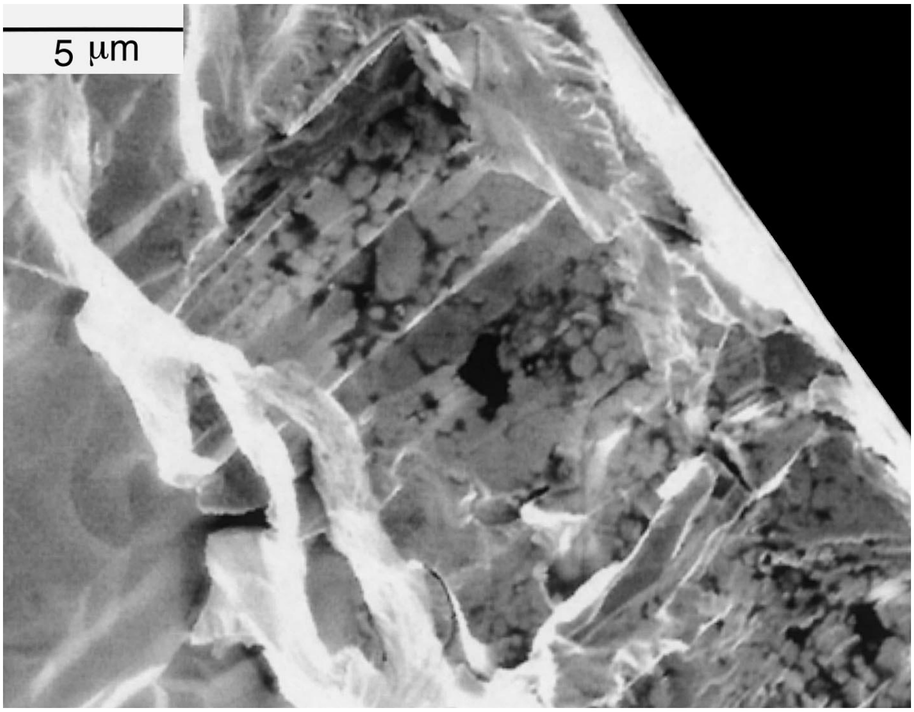

Fig. 5. A network of bubble sites underneath the surface after plasma exposure.

of 1.2 nm. How can the bubbles form four orders of magnitude deeper than the implanted depth?

Once implanted, the deuterium atoms diffuse in all directions. The constant ion flux to the surface acts as a constant source in this diffusion process. An equilibrium is reached when the incident deuterium equals the sum of deuterium leaving the surface and diffusing into the substrate. Bubbles are formed due to recombination of atomic deuterium at defect locations or along grain boundaries. Because of the low ion energies, the defect population is not likely to be increased by the ion bombardment. Intrinsic defect population and the grain boundaries in the W–1% La_2O_3 substrate are thus the controlling factors for the bubble formation. Once formed, the diatomic deuterium molecules cannot diffuse anymore. They are trapped. The pressure grows as more deuterium atoms reach the sites and recombine. The hydrogen bubbles expand and crack the tungsten substrate. When gas bubbles are formed near the surface, they erupt to form pits as shown in Fig. 4. Such eruption process contributes to the loss of tungsten, hereafter referred as bubble erosion.

Using the data compiled by Longhurst [2], the diffusion coefficient of deuterium atoms will approximately double for every 100 K increase in temperature. The recombination rate coefficient varies, depending on which set of data is chosen. It can be 50% reduction or over 1000% increase [6] for every 100 K increment. If bubble erosion is responsible for the part, if not all, of the loss of tungsten, the erosion rate increases as the amount of deuterium atoms reaching the nucleation sites increase. At constant ion flux, the substrate temperature determines the rate of bubble formation. As the substrate temperature increases, the diffusion rate increases. However, loss of deuterium at the surface also increases. After passing 1050 K, as shown in Fig. 3, surface loss of deuterium becomes dominant, which offsets the increase in diffusion rate and the recombination rate. The overall bubble formation rate is reduced, indicated by the slowing down of the erosion rate as well as the reduction of the size and number of the pits on the surface, as shown in Fig. 6.

To show deuterium molecules indeed accumulate inside the plasma-exposed substrate, 100 μm thick tungsten foils have been exposed to deuterium plasma at 400 K. Each foil has a surface flatness of 9.8 nm and 99.95% purity. Fig. 7(a) and (b) are the SEM pictures of the surface before and after deuterium plasma exposure. Macroscopic blisters are observed after exposure. For comparison, exposing the foil at high substrate temperature resulted in a flat surface as shown in Fig. 8. No blister is found.

It is necessary to point out that if different tungsten materials are used, the dynamics of the hydrogen bubble

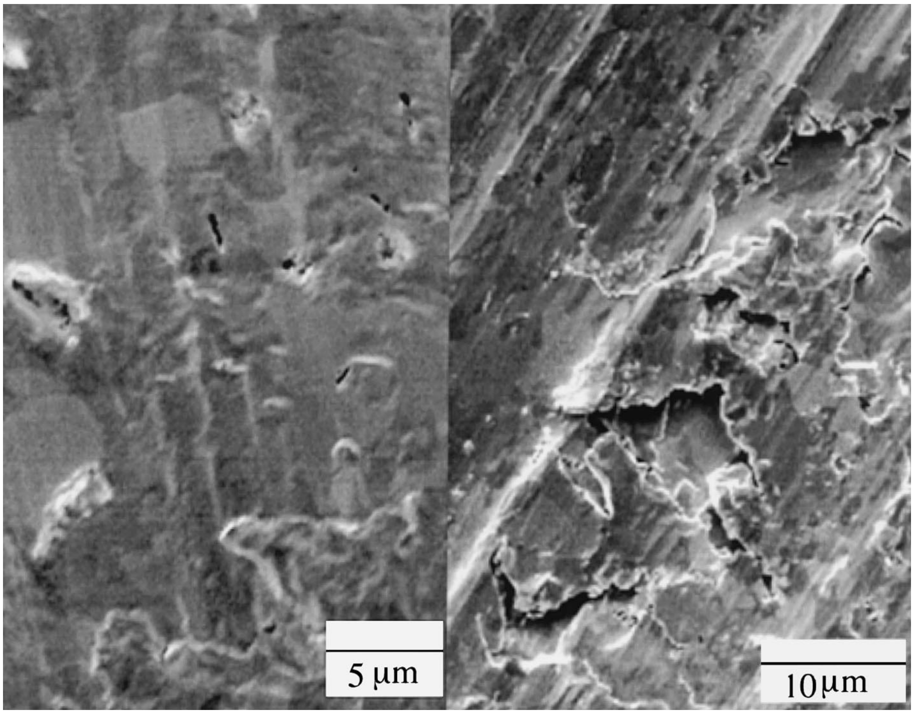

Fig. 6. Pits on tungsten at 1250 K.

formation will be different. This may lead to discrepancies in measuring the values of diffusion and recombination coefficients of deuterium.

3.4. Thermal desorption

One of the major interests in fusion material research is hydrogen isotope retention after plasma exposure. The purpose of TDS measurements of the plasma-exposed tungsten substrates is to determine the amount deuterium retained in the samples even after a prolong period of pumping at low pressure. The measurements were performed using linear temperature ramps (0.52 and 0.32 K/s) to reach a maximum temperature of 1273 K. The results are shown in Fig. 9. The total fluences to the substrates were about 10^{26} D/m^2, which are four orders of magnitude higher than those used by Haasz et al. [10] in their gas retention study. All the W–1% La_2O_3 samples, which were exposed at temperature higher than 850 K, showed an average retention value at about 2×10^{19} D/m^2.

The tungsten foils that were exposed at 400 K have retention values at about 3×10^{21} D/m^2. The major difference is the amount of deuterium molecules outgassed from the substrates. Fig. 10 shows the TDS data for one of the foils. As shown, D_2 is the major deuterium species outgassed from the foil. The species is almost completely desorbed when the temperature reaches around 990 K. The existence of the D_2 species indicates that the implanted hydrogen atoms indeed recombine within the tungsten. At high temperature exposure of the W–1% La_2O_3 substrates, most of the recombined hydrogen molecules find their ways to leave the substrates, leaving behind pits as shown in the SEM pictures.

4. Summary

Bubble formations are observed in the plasma-exposed W–1% La_2O_3 at temperatures from 850 to 1250 K. The exposed samples have no detectable carbon film on their surfaces after exposure to deuterium plasmas, which have less than 0.25% carbon impurities, for a period of 1–2 h. The ion flux to the substrate is 10^{22} m^{-2} s^{-1}. In situ surface emissivity measurements also show no change in surface composition during plasma exposure. Bubble erosion, which is sensitive to temperature, is believed to be the additional process accounting for the loss of tungsten. As the substrate temperature increases, loss of deuterium at the surface becomes significant, thus slowing the bubble erosion. The transition seems to take place at 1050 K when the erosion rate saturates. All the plasma-exposed W–1% La_2O_3 samples

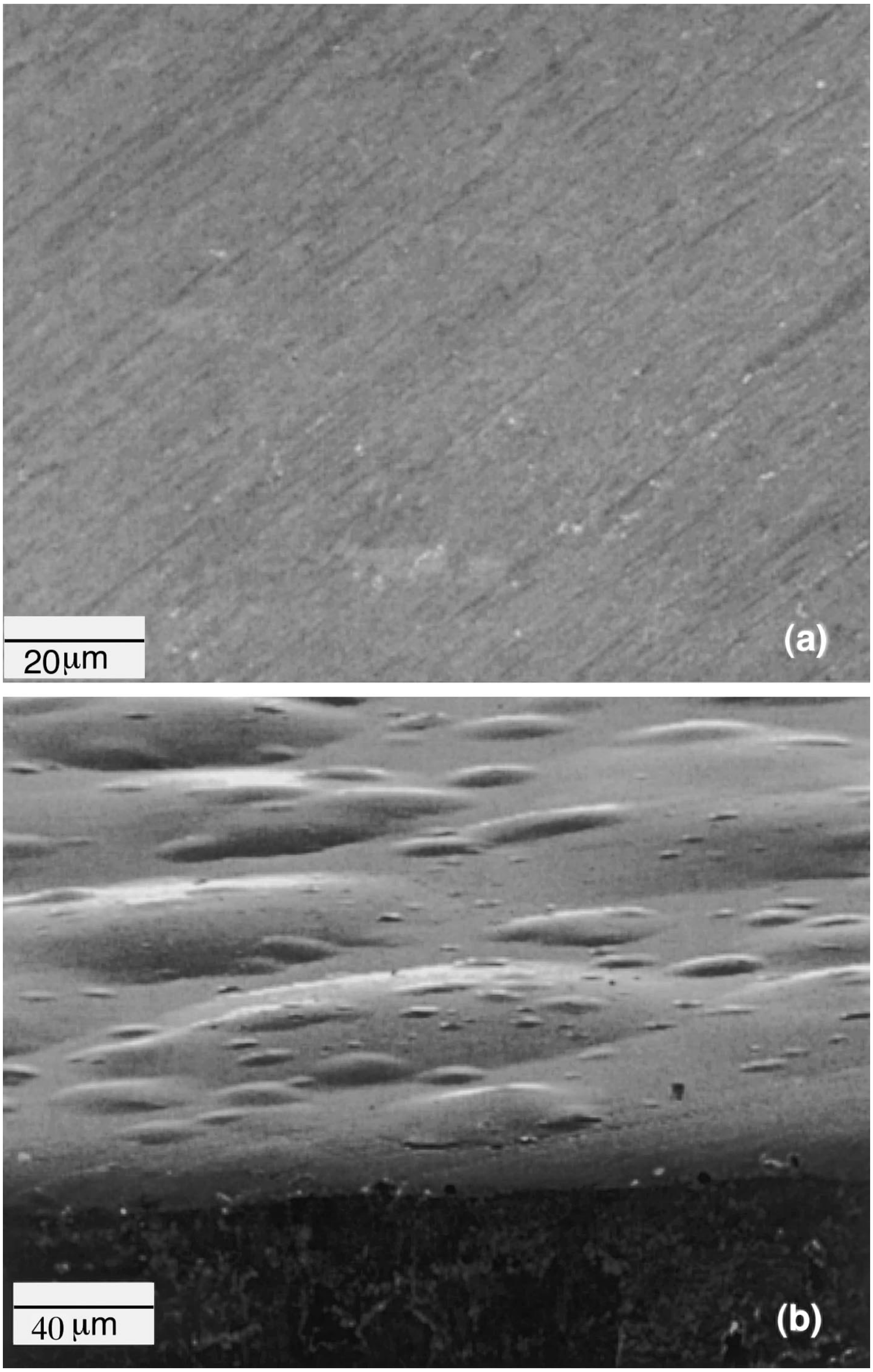

Fig. 7. Tungsten foil (a) before and (b) after deuterium plasma exposure at about 400 K.

retain about 10^{19} D/m^2. Additional TDS measurements of tungsten foils exposed at 400 K show that the implanted deuterium atoms indeed recombine and are trapped inside the substrates to form deuterium molecules, which are almost completely desorbed from the substrates at about 990 K.

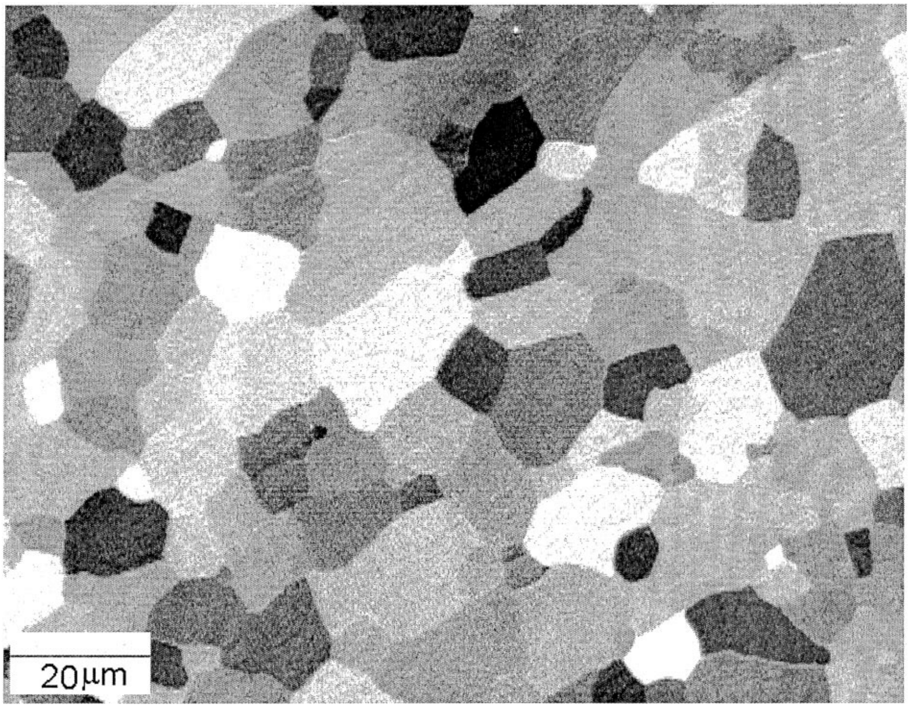

Fig. 8. Plasma exposed tungsten foil at temperature ~1250 K. Grains are visible after digital enhancement of the image.

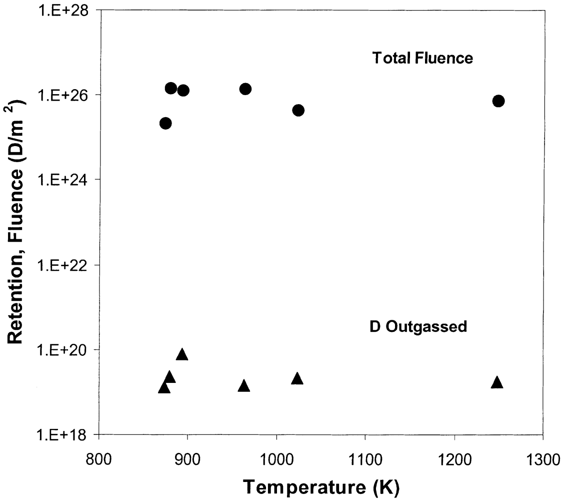

Fig. 9. TDS of plasma exposed W–1% La_2O_3 substrates, showing no significant change in hydrogen retention.

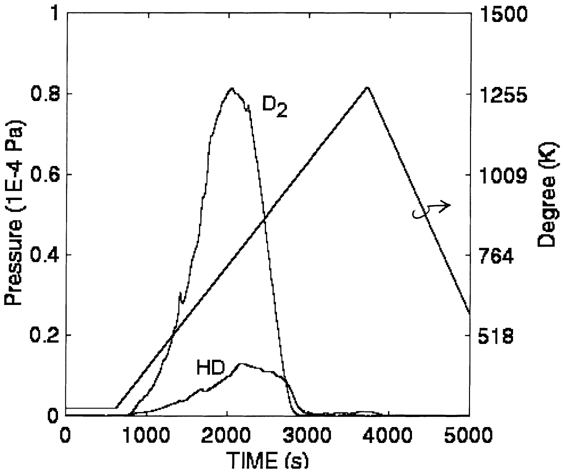

Fig. 10. TDS of plasma exposed tungsten foil at 400 K, indicating a major component of deuterium molecules (D_2), which is insignificant in those W–1% La_2O_3 samples exposed at above 850 K.

Acknowledgements

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