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Hydrogen and deuterium uptake in helium implanted layer of Mo and W

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Abstract

The accumulation of hydrogen isotopes in the helium (He) implanted layer of Mo and W single crystals was studied, focusing on the effects of the high dose irradiation of He ions and on uptake behavior of hydrogen (H) and deuterium (D) in various H_2 and D_2 pressure. A remarkable H uptake occurs in the He saturated layer of the crystals irradiated by 10 keV ^{4}He ions to a dose about 2×10^{22} He/m^2, after the heat treatment up to 850 K. The integrated amount of retained H reaches the same values before the thermal release procedure, though H-uptake rates depend on the gas pressure. The H is preferentially uptaken in the He saturated layer, when D_2 and/or D_2O gas is introduced in the vacuum chamber. The large difference between the H- and D-uptake rates suggest the oxide formation at the crystal surface where the microstructure is significantly changed due to the He irradiation.

Keywords: Tungsten; Molybdenum; Hydrogen isotopes; Helium irradiation; Hydrogen uptake

1. Introduction

Knowledge about the transport mechanism of hydrogen isotopes in the first wall materials in fusion devices is important for control of burning and fueling of plasma. In addition, tritium build-up in the wall surface can be a serious problem concerning the safety. The accumulation and the release of hydrogen isotopes will be strongly influenced by the surface of the plasma facing materials, which can be modified by deposition of low energy particles and by bombardment of the energetic ions. It is well known that the He ion irradiation degrades mechanical properties of the metal surface, and can also provide strong hydrogen trapping sites [1,2]. Although many works have been done concerning the hydrogen retention and release in high-Z metal candidates such as W [3], the He irradiation effects on the hydrogen behavior are not clearly understood.

Previously, we reported that the He pre-irradiation, even with a small dose, into W single crystals strongly affect the retention of post-implanted D ions [4]. Without hydrogen ion implantation, the He irradiation at higher doses caused hydrogen enrichment in the He saturated layer of W crystals [5,6]. In the present work, we examined the uptake of hydrogen and deuterium in the He saturated layer of W and Mo single crystals in different residual gas atmosphere, to provide data relevant to an understanding of the uptake mechanism.

2. Experimental procedure

Specimens used were W and Mo single crystalline disks of 8 mm diameter and 0.5 mm thickness, cut from single crystal rods made by the floating zone melting method. Details of the preparation procedure were described elsewhere [6]. The He ion implantation and the

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ion beam analysis were performed in a vacuum system with a base pressure of 2×10^{-6} Pa, by an ion gun equipped with a velocity filter. The He ion implantation was carried out with incident energies of 10 keV at a temperature of 295 and 820 K up to a dose of about 2×10^{22} He/m^2, with a typical current density of about 1×10^{18} He/m^2 s. During the He ion implantation, the residual gas pressure was kept about 2×10^{-5} Pa.

Because prompt accumulation of the hydrogen occurred just after the He irradiation to a high dose [5], prior to the hydrogen uptake measurements, the specimen was heated up at 850 K for 600 s to remove the accumulated hydrogen. To prevent the effects of atomic hydrogen, the equipments such as ionization gauge, which can create atomic hydrogen, were switched off during the uptake experiments. Concentration depth profiles of hydrogen isotopes and He retained in the surface layer of the specimen were measured at room temperature by elastic recoil detection analysis (ERDA) using 2.8 MeV He^{2+} and 4.0 MeV O^{3+} beams. The experimental set up for the ERD measurements was the same as described previously [5]. Rutherford backscattering spectroscopy (RBS) measurements combined with channeling technique were performed to examine the lattice disorder along the major axis of the specimen, using ^{4}He ions with an incident energy varied from 0.5 to 4.0 MeV. The surface morphology of the He irradiated surface was investigated by atomic force microscopy (AFM) observation in contact mode.

3. Results and discussion

Typical depth profiles of retained hydrogen obtained by the ERD measurements are shown in Fig. 1, for a W crystal irradiated by ^{4}He to a dose of 1.5×10^{22} He/m^2 at 820 K. Just after the He irradiation, the specimen immediately retained considerable amount of H atoms, which had depth profile corresponding to the implanted ^{4}He atoms. During the heat treatment at 850 K for 600 s, 90% of the uptaken H was released from the surface layer. After the heat treatment and cooling down to the room temperature, the H concentration increased again for the specimen kept in the vacuum chamber for 6 h with a residual pressure of about 2×10^{-6} Pa. It should be noted that the observed depth profiles by the ERD measurements for He irradiated surface can be broader than the actual distribution due to deterioration of the depth resolution caused by morphological changes such as blister formation. The H uptake similarly occurred for the specimen irradiated at room temperature.

The areal density of the H uptaken in He saturated layer of the W and Mo crystal in the high vacuum at room temperature is shown in Fig. 2, plotted as a function of the time after the heat treatment. For the Mo crystal, within the 20 h, the retention of H was recovered

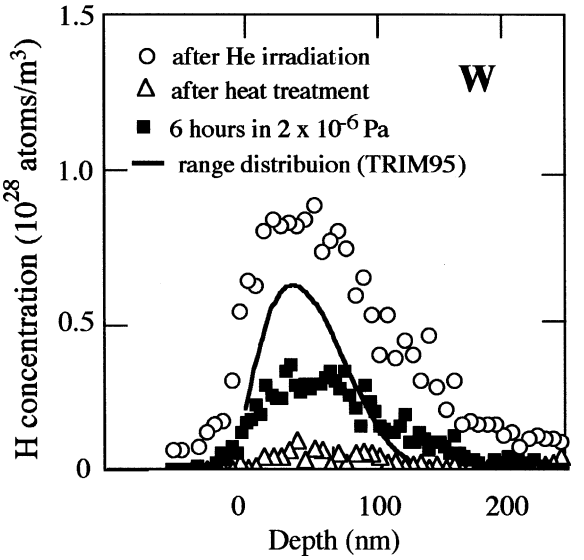

Fig. 1. Concentration depth profiles of H uptaken in the He saturated layer of W and Mo single crystals kept in the vacuum of 2×10^{-6} Pa at the room temperature. The profiles were measured after the He irradiation to a dose of 1.5×10^{22} He/m^2 at the temperature of 820 K (○), and after the subsequent heat treatment at 850 K for 600 s (△), and after 6 h (■). Calculated range distribution (TRIM95) was also inserted as solid line.

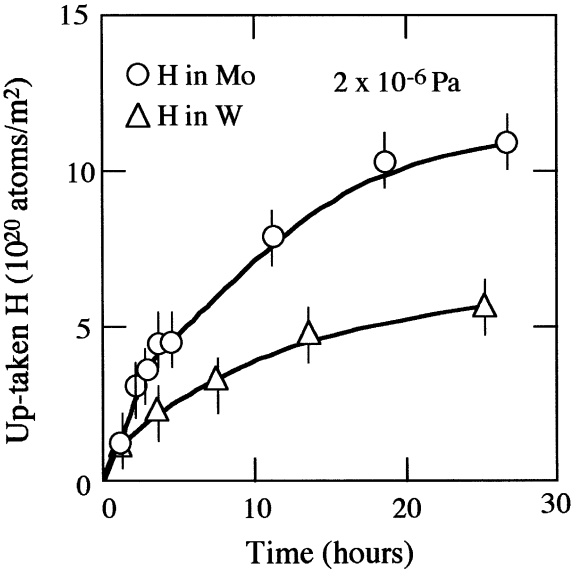

Fig. 2. Total amount of H uptaken in the He irradiated layer of Mo (○) and W(△) crystals, plotted against the time after the heat treatment. The specimens were irradiated by 10 keV He to a dose of 1.5×10^{22} He/m^2 at 820 K, then subsequently heated for 600 s at 850 K.

to nearly the same level as the retained amount before the heat treatment (1.2×10^{21} H/m^2). The initial uptake

rate for the W crystal was similar to that for the Mo crystal at the beginning of the experiment, but with time, the uptake rate for the W crystal became smaller than that for the Mo. It took more than 50 h to reach the original retained level (0.8×10^{21} H/m^2) for W in the same vacuum. The saturation level of the H has not been systematically confirmed yet. It varied between 0.5 and 1.5×10^{21} H/m^2 for He irradiation dose of $1–2 \times 10^{22}$ He/m^2 and temperature of 295 and 820 K. For W crystals, higher retention of H was usually observed in the specimen irradiated at higher temperature. On the contrary, we often found lower retention of H in Mo crystals for higher irradiation temperature.

Fig. 3 shows the H and D uptake rate for the He irradiated W and Mo specimens, when various pressure of D_2 gas was introduced in the vacuum chamber. The D-uptake rates were an order of magnitude less than H-uptake rates for wide range of the residual gas pressure. Below a residual pressure of 10^{-3} Pa, the D retention was too small to determine the uptake rate. According to the quadrupole mass analysis for the pressure better than 10^{-2} Pa, the D containing gas such as D_2O and D_2 were dominant components, though H containing molecules such as H_2, H_2O, HDO still existed. The H atoms were preferentially taken up, while the partial pressure of D_2 and/or D_2O was higher than the hydrogen containing gas. The RBS measurements [7], shows that the large depletion of the scattering yield from the He irradiated W crystal surface could not be explained by the He and H, indicating significant amount of oxygen or carbon in the He implanted layer. There might be formed trioxide hydrate of W and Mo (WO_3 $2H_2O$ [8], MoO_3 $2H_2O$ [9]), which are known to be proton conductive materials. In turn, some of the proton conductive oxides show isotope effects in H and D exchange [10]. The difference of the H and D uptake behavior may be attributed to the oxides formed at the He irradiated surface. Further characterization for these irradiated layers of the specimens are needed to determine the elemental composition and to confirm formation of the compounds. It would also help to understand the mechanisms of hydrogen uptake, trapping and its isotopic difference.

Lattice disorder can be examined qualitatively by detecting dechanneling yield of channeled ion in a single crystal for various analyzing beam energy [11]. Fig. 4 shows dechanneling parameter obtained for ⟨1 1 1⟩ axial direction of W crystals irradiated by ^{4}He ions at temperatures of 295 and 820 K, to doses of 1.0×10^{21} He/m^2 and 1.5×10^{22} He/m^2. The dechanneling parameter was estimated for the depth of about 300 nm including the He implanted zone, in the way as described elsewhere [6]; it corresponds to scattering by the lattice disorder integrated from the surface to 300 nm depth. The larger dechanneling fractions present the more heavily damaged layer for higher dose irradiation. Relatively flat energy dependence of the parameter is shown for the specimens irradiated at higher temperature, indicating the bubble and/or void formation in the He saturated layer. Especially for the specimen irradiated with lower

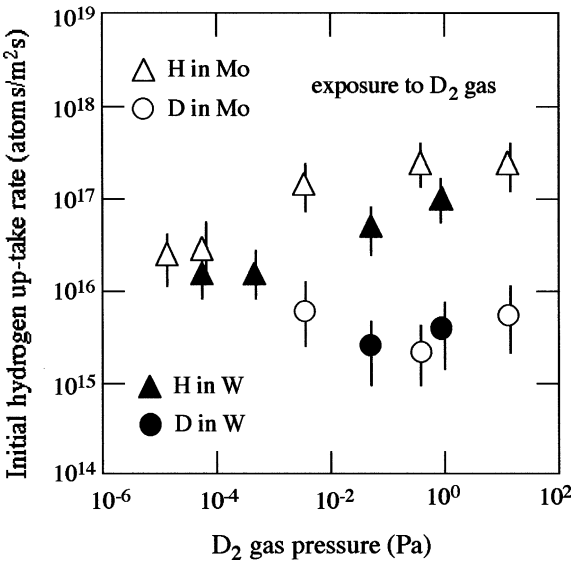

Fig. 3. Initial uptake rate for H and D in He irradiated layer of Mo and W crystals exposed to D_2 gas, plotted against the residual gas pressure, for Mo and W crystals irradiated by 10 keV He at 820 K.

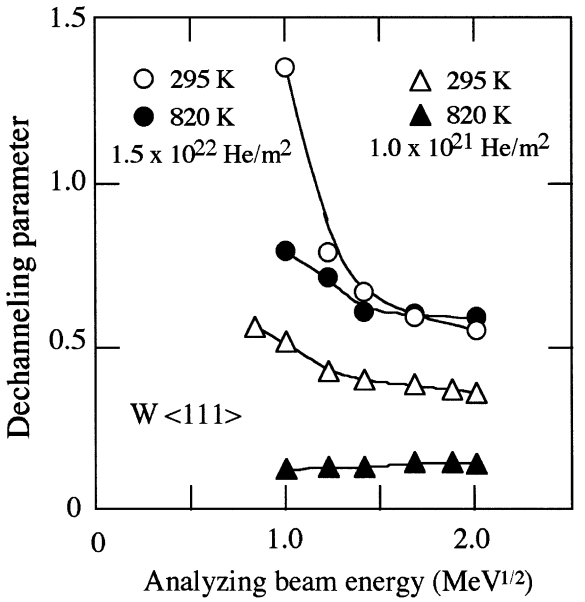

Fig. 4. Dechanneling parameter obtained for ⟨1 1 1⟩ axial direction of W and Mo crystals irradiated by 10 keV He at temperatures of 295 and 820 K to doses of 1.5×10^{21} and 1.5×10^{22} He/m^2, plotted as a function of the square root of the incident analyzing ^{4}He^{++} energy.

dose at higher temperature, small values of the dechanneling parameter may also be related with the ordered bubble formation seen in some BCC metals [12]. The dechanneling parameter decreased with an increase of the analyzing beam energy for the specimen irradiated at room temperature, corresponding to a large number of isolated displaced W atoms. It can be stated that the dechanneling was mainly caused by direct scattering from the displaced W atoms for room temperature irradiation, while the missing lattice atoms from bubbles and voids contributed to the dechanneling process in the surface layer at 820 K irradiation.

AFM images of the W crystal surface were shown in Fig. 5(a) and (b), for the He irradiation of about 1.5×10^{22} He/m^2 at 295 and 820 K, respectively. For 820 K irradiation, blisters were apparently formed of about 1 μm diameter and the height of about 0.1 μm, though the rest of the part appeared as smooth as the un-irradiated surface. Etch-pits with the same sizes of the blister were created probably due to the bursts of the He containing blisters. He irradiation at room temperature resulted a rough surface covered with small bumps and etch-pits, which were not able to detect by the SEM observation [5]. Because the amount of the retained He in W crystals was nearly the same for both irradiation temperature [5], those small bumps were thought to contain He bubbles with high pressure. Because the H uptake was found for both irradiation temperatures, the size of the blisters and etch-pits were not essential for the H uptake behavior, and dissociation of the hydrogen can take place at the surface of these etch-pits. For the lower irradiation doses below 1×10^{21} He/m^2, the H uptake did not occur in the He irradiated layer, where no etch-pits were detected by AFM. Ion implanted hydrogen was retained in this layer, but H atoms were not uptaken from the gas atmosphere. Furthermore, the H uptake was not observed at the oxide surface of the un-irradiated Mo and W single crystal [13]. It is conjectured that the enhancement of the dissociation of hydrogen is attributed to the He irradiation induced etch-pits, whose surface was probably covered with oxide.

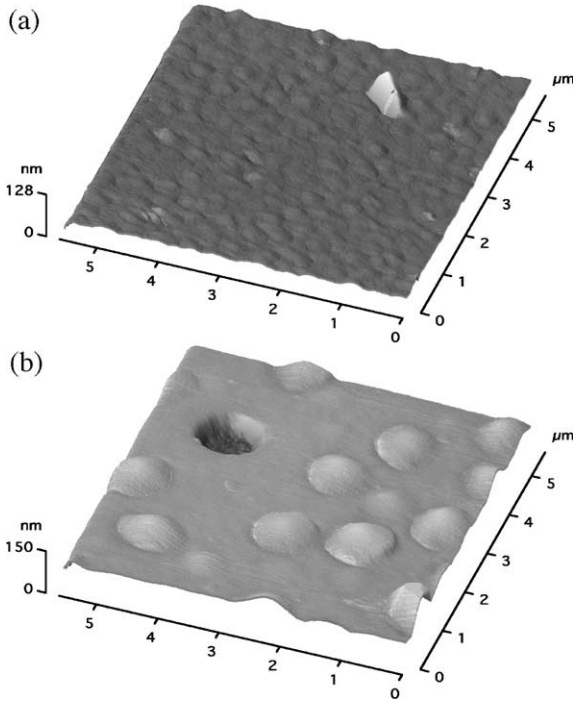

Fig. 5. AFM images of surface of the W crystal irradiated by 10 keV He to a dose of 1.5×10^{22} He/m^2 at 295K (a) and 820 K (b).

4. Summary

The He irradiated surface of the Mo and W crystals shows remarkable capability of the H uptake and significant difference between H- and D-uptake rates. At room temperature, the uptaken H concentration reaches 10–20 at.% within the He saturated layer of the specimen, irradiated by 10 keV He at 295 and 820 K to doses above 1×10^{22} He/m^2. Although the H retention was recovered to the same original level after the long time, the initial uptake rates strongly depended on the residual gas pressure. When the specimen was exposed to the atmosphere mainly containing D_2 and D_2O gas, H atoms were preferentially uptaken in the He saturated layer; the uptake rate for D was an order of magnitude lower than that for H. The observed isotope effects on the uptake behavior might be similar to that in the proton conductive oxide materials. The results suggest that the oxide at the He saturated surface with the exfoliation and etch-pits play an important role for dissociation of hydrogen. Further characterization of the He irradiated layer and systematic studies on hydrogen behavior are necessary to clarify the mechanism of the uptake in the He irradiated layer.

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