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TEM study on deuterium-irradiation-induced defects in tungsten and molybdenum

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Abstract

Deuterium-irradiation-induced defects in tungsten (W) and molybdenum (Mo) were examined by transmission electron microscopy (TEM). The observed defects were perfect dislocation loops of interstitial type with the Burgers vector of $a/2\ \langle 1\,1\,1\rangle$ type. The loop plane has non-integer Miller indices nearly parallel to the $\{1\,1\,0\}$ plane. Subsequent growth of some dislocation loops was observed during further irradiation with W by post-irradiation of 1 MeV electrons in a high-voltage electron microscope. This growth is ascribed to the dissociation of SIA-D complexes (SIA: self-interstitial atom, D: deuterium) and subsequent absorption of the released interstitial atoms by nearby dislocation loops. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Tungsten (W) and molybdenum (Mo) have been proposed as candidates for plasma facing materials because of their low sputtering yield, low hydrogen solubility and high-melting temperature [1,2]. These metals have been actually used as test materials of a limiter (TEXTOR [3–11]), a diverter (ASDEX-U [12–14], and alcator [15]) in Tokamaks, all directly facing high-temperature plasmas.

Since the plasma facing materials are exposed to hydrogen isotope irradiation in a nuclear fusion reactor, the production of irradiation defects and accumulation of the hydrogen isotopes occurs in the materials, degrading material properties and influencing hydrogen recycling. These phenomena are closely related to the interaction between the irradiation defects and the implanted hydrogen isotopes. Therefore, an understanding of the interaction between the irradiation defects and the implanted hydrogen isotopes is required.

There have been a lot of fundamental studies on metal–hydrogen interactions. Hydrogen trapping at crystal defects has been intensively studied, and a good review is given by Myers et al. [16]. It is, however, incorrect to say that hydrogen behavior in W and Mo is well understood not only due to hydrogen's poor solubility, but also due to the effects of impurities found in these high-melting points metals. Impurities, dislocation loops, and bubbles have been reported to be the main trapping sites of D atoms in W and Mo [17]. Nagata et al. have measured the depth distribution of self-interstitial atoms (SIAs) and implanted ions in deuteron (D^+)-irradiated Mo and W by means of channeling experiments [18], and found that an appreciable amount of implanted D atoms were released by thermal annealing at moderate temperatures. They attributed the release to partial relaxation of the lattice distortion due to dissociation of extended defects formed by D^+ irradiation. This work provides a clue to describe the hydrogen–defect interaction in W and Mo because the implanted D atoms were considered to be trapped in the extended defects, which were distributed beyond the displacement damage distribution. In this respect, transmission electron microscopy (TEM) is one of the most useful complementary experimental methods because one can directly identify the defect structures and their spatial distributions, especially of extended defects, produced by hydrogen isotope irradiation.

Sakamoto et al. [19,20] have examined hydrogen ion (H^+)-irradiation defects in W and Mo by TEM. They

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noted that the primary defects formed were dislocation loops for an incident energy (E_0) of H^+ larger than ~4 keV, whereas plate-like hydrogen clusters were produced at $E_0 \sim 3$ keV. Bubbles were also observed for the irradiation temperature higher than 873 K. The nature of these various defects, however, was not explicitly described. We believe that it is very important to know the atomic structure and the nucleation process of the defects induced by the hydrogen isotope irradiation, because these must be the first step to consider the interaction between the defects and hydrogen isotopes. This is the motivation for the present work.

2. Experimental

Materials used in the present work were high purity single crystal W and Mo purified by a zone-melting method, with a purity of 99.99% and 99.999%, respectively. These were cut into 3 mm diameter disks after mechanically polishing down to 0.1 mm in thickness, and then electropolished with a 2 wt% NaOH aqueous solution for W and a 12.5 wt% H_2SO_4 methanol solution for Mo, to prepare thin foils for TEM observation. It was confirmed by TEM that the specimens contained no dislocations or other visible defects before ion-irradiation.

The TEM samples were irradiated with 10 keV D^+ instead of H^+ because of its higher defect production rate. The irradiation was performed perpendicular to the surface at room temperature under a vacuum of 8.0×10^{-6} Pa. The ion flux was $6.0 \times 10^{18}/\mathrm{m}^2$ s and the fluence ranged from 5.0×10^{21} to 3.0×10^{22} m^{-2}. TEM observation was conducted with a JEM200CX electron microscope operated at 200 kV and an H-1250ST high-voltage transmission electron microscope (HVTEM) operated at 1 MV.

3. Results

Figs. 1(a) and (b), respectively, show dark-field images of the D^+-irradiated Mo and W with the diffraction vectors shown. The fluences were 2.0×10^{22} and 5.0×10^{21} m^{-2} for (a) and (b), respectively. Dislocation loops with various sizes were observed both in W and Mo. Similar dislocation loops have been observed in the case of H^+ irradiation [19,20]. We thus consider that the defect structure is of the same type for both D^+ and H^+ irradiation.

Fig. 2 shows the widely distributed size distribution of the dislocation loops in W measured from the images. The number of the loops generally decreases with increasing size. At higher fluences the number density of the loops increased, but their maximum size remained unchanged. If most of the dislocation loops nucleated at the very early stage of the irradiation and grew with prolonged irradiation, then their size distribution would show a sharp peak at a certain size and the number of very small loops would not be observed. It is therefore concluded that the nuclei of the loops were produced continuously during irradiation and all the loops visible in the images would have the same mechanistic origin.

In order to identify the nature of the dislocation loops in W, a number of dark-field images were taken with different diffraction vectors, as shown in Figs. 1(b)–(e). Figs. 1(b) and (c) show a set of the dark-field images with the opposing diffraction vectors, $\mathbf{g} = 1\,1\,0$ and $\mathbf{g} = \bar{1}\,\bar{1}\,0$, respectively. The dislocation loop indicated by a thick arrow shows the inside- and outside-contrast in (b) and (c), respectively. The stereo observation showed that the loop was inclined with the upper edge pointing upward out of the page. The above observations lead us to a conclusion that the loop is of interstitial type [21].

The contrast of the same dislocation loop indicated by the thick arrows vanishes in Figs. 1(d) and (e), where $\mathbf{g} = \bar{1}\,0\,\bar{1}$ and $\mathbf{g} = \bar{2}\,1\,\bar{1}$. Since the contrast of a dislocation vanishes when its diffraction vector is perpendicular to the Burgers vector of the dislocation, the Burgers vectors of the observed dislocation loops should be parallel to the $[1\,1\,\bar{1}]$ direction. Furthermore, Fig. 1(e) shows that the $[1\,1\,\bar{1}]$ direction was not on the loop plane. This suggests that the dislocation loops are not formed by a mere glide motion on the loop plane but by the segregation of displaced interstitial atoms. Since no stacking fault fringes were observed in the loops, they should be perfect dislocation loops having Burgers vector of $a/2\,\langle 1\,1\,1\rangle$ type. Similar experiments were also carried out for Mo, which resulted in the same conclusion.

The next step for full identification of the dislocation nature is to determine the Miller indices of the plane on which the dislocation loops were lying. This is usually performed by specifying the direction of the loop plane normal with the loops viewed edge-on. Such an example is shown in Fig. 1(f). Though the loops indicated by thick arrows are considered to be viewed edge-on, their contrasts do not clearly exhibit straight lines, but have notches. The direction perpendicular to the loop plane was close to the $[0\,1\,\bar{1}]$ direction but was actually along the direction with non-integer Miller indices. This is also supported by the fact that circular dislocation loops were observed along the $\langle 1\,1\,0\rangle$ direction. It is thus concluded that the dislocation loops lay on a higher order plane having steps with low order Miller indices, possibly on the $\{1\,1\,0\}$ planes.

It should be mentioned that some of the dislocation loops accidentally grew when observed in an HVTEM operated at 1 MV, an example of which is shown in Fig. 3. The image in (b) was taken at the same imaging condition as (a) at a few seconds after the image (a) was taken. It is seen that the dislocation loop indicated by the arrow slightly grew but the other surrounding loops hardly changed. Such growth occurred suddenly near the center of the observation area where the electron

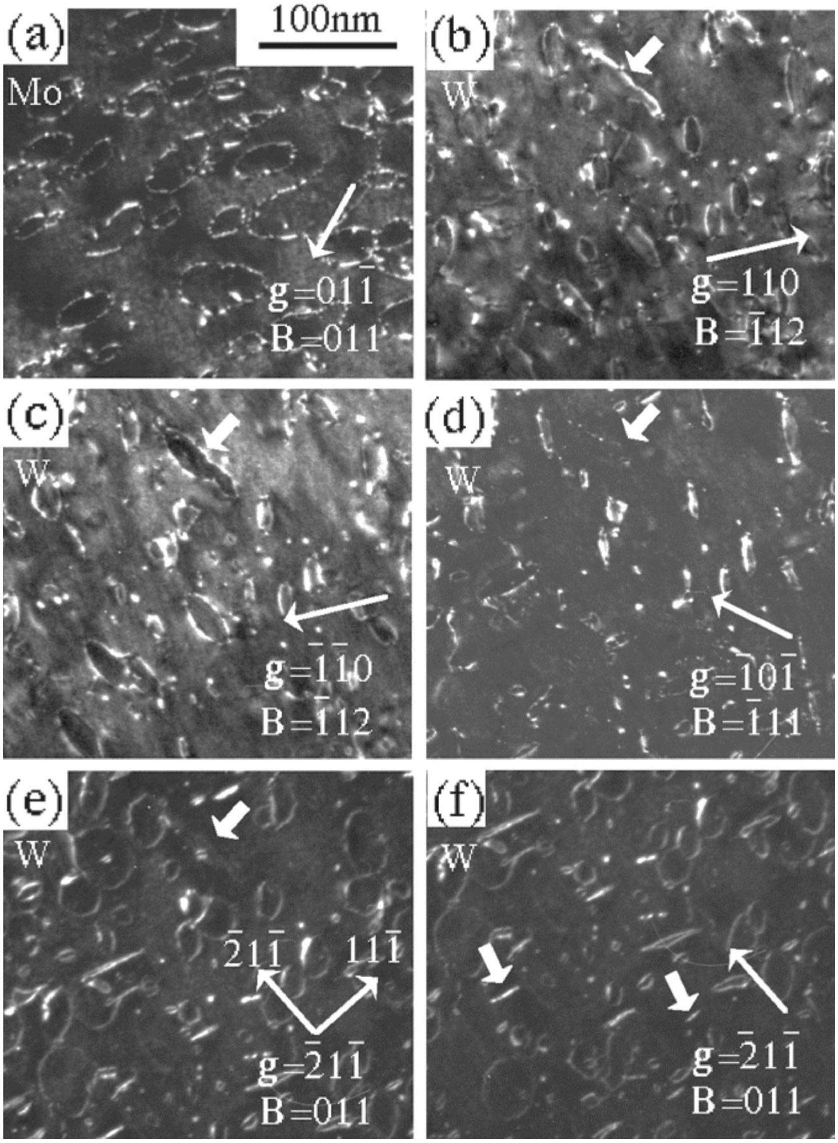

Fig. 1. Dark field images of dislocation loops produced by 10 keV D^+ irradiation (6.0×10^{18} /m^2 s) at room temperature: (a) in Mo (2.0×10^{22} D^+/m^2); (b)–(f) in W (5.0×10^{21} D^+/m^2). Diffraction vector, **g**, and incident beam direction, *B*, with which each image was taken, are indicated in insets.

beam was focused to obtain a good contrast. To the authors' knowledge, such loop growth has not been observed previously during observation in an electron microscope.

4. Discussion

4.1. Structure of dislocation loop

The nature of the dislocation loops in W and Mo produced by D^+ irradiation was identified in the preceding section. Now we consider the characteristic features of the dislocation loops.

The BCC structure consists of a two-layer stacking sequence of the $\{110\}$ plane, ABABAB. If an additional $\{110\}$ plane is inserted, as was considered in the previous section, the resultant stacking sequence is either ABAABAB or ABABBAB. Since this stacking disorder considerably raises the energy associated with the loop, the stacking disorder would be unfaulted by a glide motion of the dislocation on a close-packed plane, possibly on a $\{110\}$ plane. The Burgers vector of the dislocation formed by such an operation is the

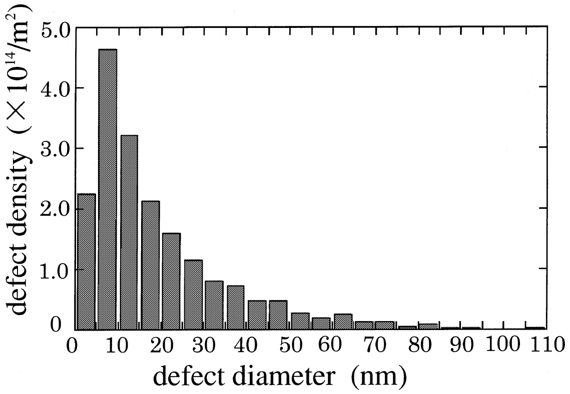

Fig. 2. Size distribution of the dislocation loops in W, irradiated by 10 keV D^+ (5.0×10^{21} m^{-2}) at room temperature.

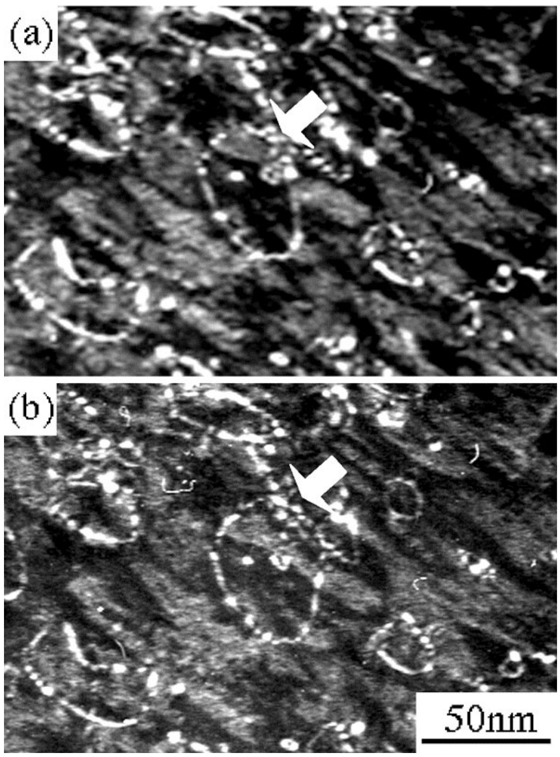

Fig. 3. Growth of dislocation loop in W during HVTEM observation operated at 1 MV.

$a/2\ \langle 1\,1\,1\rangle$ or $a/2\ \langle 1\,1\,\bar{1}\rangle$ [22], which is inclined to the loop plane. This is considered by the authors to be the most likely structure of the observed dislocation loops. The loops will grow by absorption of interstitial atoms and subsequent unfaulting, which can cause the notched loop planes with non-integer Miller indices, as experimentally observed.

4.2. Growth of loop by post-irradiation of 1MeV electron

The growth of the dislocation loops during the HVTEM observation is thought to be caused by the absorption of interstitial atoms because the dislocation loops are the result of the planar segregation of interstitial atoms, as discussed in the previous section. Possible sources of the interstitial atoms are (1) interstitial atoms newly produced by 1 MeV electron irradiation, (2) shrinkage of dislocation loops near the one growing, and (3) invisible interstitial atoms pre-existing in the matrix.

Since the displacement threshold energy of W is 44 eV [23], an electron energy larger than about 3 MeV is necessary to displace W atoms. The possibility (1) is accordingly dismissed. The possibility (2) is also excluded because shrinkage of the surrounding loops was not observed. Therefore, the source of the interstitial atoms is thought to be possibility (3).

In W Nagata et al. [18] have reported that extended defects, or dislocation loops, have spread into regions deeper than the defect distribution predicted by the TRIM code calculation. This phenomenon suggests that the defect formation be brought about not only by displacement damage but also by the presence of D atoms because the implanted D atoms are distributed over the region deeper than the damage distribution. It is thus plausible to consider that SIA-D complexes are first formed and they act as the nuclei of the dislocation loops. These complexes would be formed continuously by prolonged irradiation, and some of these remain in the matrix.

Another experiment showed that H^+ irradiation into Mo formed SIA-H complexes with a binding energy of 2.1 eV [24], and it is considered that similar complexes are formed in H^+- or D^+-irradiated W. This also suggests that the implanted D atoms have a correlation with the defect formation and some of them should exist as SIA-D complexes in the matrix.

From the above facts, we can describe the following scenario for the loop growth during 1 MeV electron irradiation. Some interstitial atoms displaced by D^+ irradiation formed the dislocation loops and others remained in the form of SIA-D complexes in the matrix. These complexes would be dissociated by focused 1 MeV electrons because the maximum transferred energy by a 1 MeV electron to a W atom is approximately 35 eV which is larger than the expected binding energy of the complex. The released interstitial atoms were then absorbed in the dislocation loops nearby, which contributes to the loop growth. 200 keV electrons can impart a maximum energy of 3.3 eV, which is just comparable to the expected binding energy. Hence, the 200 keV electrons cannot easily dissociate the complexes. This explains the fact that the loop growth was never observed in a 200 kV microscope.

5. Summary

The deuterium-induced defects in W and Mo were examined by TEM. Dislocation loops were observed when the incident ion energy was 10 keV at a fluence of 0.5×10^{22}–3.0×10^{22} m^{-2} at room temperature. The loops were determined to be the perfect dislocation loops of interstitial type with the Burgers vector of $a/2 \langle 1\,1\,1 \rangle$ type. The loop plane has non-integer Miller indices nearly parallel to the $\{1\,1\,0\}$ plane. These loops were not all formed at the initial stage of the irradiation, but were continuously nucleated and grew to their final size with continued irradiation.

Growth of the dislocation loops was observed during observation in W by post-irradiation of 1 MeV electrons in a high-voltage electron microscope. This growth is ascribed to the dissociation of interstitial-deuterium complexes and the subsequent absorption of the released interstitial atoms by the dislocation loops nearby.

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