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DOI:
10.1016/j.jnucmat.2019.05.004

Irradiation hardening induced by blistering in tungsten due to low-energy high flux hydrogen plasma exposure

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Abstract

In this work, the microstructure evolution in the near-surface of tungsten under hydrogen (H) plasma exposure conditions was observed by means of scanning electron microscopy (SEM), plasma focused ion beam (FIB) and transmission electron microscopy (TEM) techniques. Blisters, with existing dislocations distributed around obviously, were observed beneath the tungsten surface when the exposure temperature was 573 K, which was rarely reported in previous studies. However, H bombardment at 1273 K did not lead to the formation of blister-like microstructures. Correspondingly, irradiation hardening occurred after low temperature exposure, but not after high temperature exposure, according to the Berkovich nano-indentation experiments. In order to characterize the indentation size effect and irradiation hardening behavior of plasma-exposed materials, a mechanistic model was proposed for the hardness-depth relationship. A good agreement between the experimental indentation data and theoretical results revealed that plasma-induced dislocations play a dominant role in determining the increase of hardness for H plasma-exposed tungsten.

Keywords: Blistering, Irradiation hardening, TEM, Nano-indentation, Theoretical model

1. Introduction

Tungsten has become one of the most promising candidates for the plasma facing materials (PFMs) in the ITER divertor because of its favorable physical properties such as the high thermal conductivity, high melting temperature and low sputtering yield [1]. As a PFM, tungsten would be subject to the exposure of high flux (10^{22}~10^{24} $m^{-2} \cdot s^{-1}$) and low-energy (from tens of eV to several hundreds of eV) H plasma, which might congregate on the surface of tungsten to form blisters or penetrate through the surface and diffuse deeply into the bulk [2, 3].

Noteworthy, plasma exposure-induced defects are blamed for the degradation of the mechanical properties of tungsten. In terms of H penetration, a few previous studies have reported its effects on the irradiation hardening. For instance, Terentyev et al. [4] found that interstitial H atoms are strongly bound to screw dislocations, and the growth of multiple H_N clusters could result in the punching of a jog as indicated by the density functional theory calculations and TEM observation. In their following study, the mechanical properties of deuterium (D) plasma-exposed tungsten was tested by the Berkovich nano-indentation, and the surface hardening was attributed to the D deposition measured by the corresponding nuclear reaction analysis (NRA) profile [5]. Zayachuk et al. [6] also suggested that the irradiation hardening after high flux D plasma exposure originated from the trapping of diffusing D atoms by dislocations in both deformed and recrystallized tungsten.

In the meanwhile, H blisters, acting as the primary surface modification at the service condition [7] are also expected to be strongly connected with the changes of mechanical properties after H plasma exposure. For example, according to the analysis of elastic plates theory and finite element simulation, Li et al. [8] reported that the bulging deformation and growth of a blister are directly controlled by the yield stress and fracture energy, respectively. The formation of blisters is generally associated with a cavity/crack in the sub-surface, which has already been confirmed by the FIB fabricated cross-section observations [9-11]. It is known that blister formation includes the nucleation of cavity/crack and growth of these nuclei. The nucleation mechanisms of cavities in recrystallized W are suggested as the dislocation loop punching initially from vacancies [12-14], dislocations [4, 15, 16], and H platelet aggregations [17], but not yet experimentally confirmed. While, the growth mechanisms of cavities are generally acknowledged as the plastic deformation [11, 18, 19], dislocation loop punching [20] and agglomeration of H-vacancy complexes [21, 22]. Theoretically, these mechanisms deserve to have significant effects on the irradiation hardening behavior of plasma-exposed materials, owing to the triggered damage defects. For instance, according to the plastic deformation theory, dislocations distribute around the blisters are expected to contribute to the hardening. Unfortunately, so far, there is no direct experimental proof for these theoretical assumptions. Therefore, further attention undoubtedly should be paid in dealing with the explicit hardening mechanism behind blisters.

These considerations inspire the motivation of this work, in which, the blistering and hardening mechanisms of H plasma-exposed tungsten are, respectively, studied by experimental observations and theoretical models. SEM, plasma FIB and TEM techniques are utilized to observe the damage microstructures in tungsten under the H plasma exposure at different temperatures. The analysis of these plasma-induced microstructures is intended to help explain the plastic deformation mechanisms of blisters-induced dislocations. Then, the Berkovich nano-indentation tests are performed to characterize the hardness-depth relationship of tungsten with and without plasma exposure. In order to analyze the fundamental hardening mechanisms, a mechanistic model is proposed by physically taking into account the hardening contribution of exposure-induced defects and geometrically necessary dislocations (GNDs).

2. Experiment

Polycrystalline tungsten of 99.99 w.t.% purity was supplied by Plansee Gruppe, Austria. The bulk tungsten was cut from the as-received materials, then heat treated in a vacuum at 1873 K for 2 h after electro-polishing and before plasma exposure. The average grain size is about 50 μm on the surface which is normal to the exposure direction. High flux H plasma exposures were performed in the Magnum-PSI linear plasma device (DIFFER, Eindhoven, the Netherlands), which allowed for the steady-state exposures of target materials in ITER-relevant conditions [23]. In this experiment, a superconducting magnet of the Magnum-PSI provided a alterable magnetic field strength up to 1.8 T, in order to control the plasma into a beam (FWHM ≈ 20~28 mm) [24]. The H plasma flux arriving at the surface of the specimen was calculated from the electron temperature, and the density was measured by Thomson scattering [25] The ion flux, herein, was about $2\sim3\times10^{23}\ m^{-2}\cdot s^{-1}$, and the total fluence was fixed to be about $1.5\times10^{26}\ m^{-2}$. The ion energy was controlled by negatively biasing the sample, and was fixed to be ~50 eV. The surface temperature of each sample was controlled by the water cooling system from the back side of the samples, and monitored by an IR camera. The temperature conditions across the surface during the exposure were 573 K and 1273 K, respectively.

An Xe^+ plasma FIB system (FEI Helios G4) was used to extract foils from the irradiated tungsten, in order to observe the cross-section parallel to the exposure direction. Previous literatures have shown that the depth of damage introduced by the Xe^+ plasma FIB created 20~40% less damage than that created by a Ga^+ FIB [26, 27]. A final flash electro-polishing procedure [28] was used to remove the beam damaged layer induced by plasma FIB on both sides of the lamellae at 14 V in 0.5 w.t.% NaOH aqueous at 273 K for 4 ms. The TEM microstructural characterization was carried out on an FEI Talos F200 at 200 keV. The detection of irradiated damage defects was developed under two-beam condition in Scanning TEM mode.

Nano-indentation experiments were performed with Agilent Technologies Inc. Model Nano Indenter G200 nano-indentation with the continuous stiffness measurement (CSM). A Berkovich indenter tip was applied to measure the mechanical properties. The oscillation amplitude and frequency were set to be 2 nm and 45 Hz, respectively. At least 20 indents spaced by 70 μm have been measured on each sample, which can eliminate the influence of the plastic zone between each indentation. The maximum penetrating depth was 1 μm. The testing temperature was controlled to be 290 ± 1 K.

3. Hardness-depth relationship for plasma-exposed materials

3.1 Model development

It is recognized immediately that two primary mechanisms result in the hardening behavior of ion-irradiated materials tested by nano-indentation. One is the well-known indentation size effect arising from the generation of GNDs when the indenter pierces into the materials. The other is the incremental increase of hardness due to the presence of irradiation-induced defects [29, 30].

Preliminarily, the Taylor relationship is generally used to estimate the deformation resistance that the critical resolved shear stress can be written as

$$\tau_{\mathrm{CRSS}} \propto \mu b\sqrt{\rho} \tag{1}$$

where μ and b, respectively, refer to the shear modulus and magnitude of the Burgers vector. ρ denotes the total density of dislocation barriers. Following the Mises flow rule and Tabor's factor, the hardness of the indented materials is given as [31]

$$H = 3\sqrt{3}\mu b\alpha\sqrt{\rho} \tag{2}$$

where α is the hardening coefficient of dislocations. Without irradiation effect, two dislocation sources mainly contribute to ρ, which include the GNDs, ρ_{G}, and statistically stored dislocations (SSDs), ρ_{S}. Following the work of Nix and Gao [31], the hardness of unirradiated material H_{uni} can be recast based on Eq. (2) as

$$H_{\mathrm{uni}} = 3\sqrt{3}\mu b\alpha\sqrt{\bar{\rho}_{\mathrm{G}} + \bar{\rho}_{\mathrm{S}}} = H_0\sqrt{1 + \frac{\bar{h}^*}{h}} \tag{3}$$

where $\bar{\rho}_{\mathrm{G}}$ and $\bar{\rho}_{\mathrm{S}}$ refer to, respectively, the average density of GNDs and SSDs within the plastic zone, and can be expressed as

$$\bar{\rho}_{\mathrm{G}} = \frac{3}{2bM^3\tan\theta}\frac{1}{h} \quad \text{and} \quad \bar{\rho}_{\mathrm{S}} = \frac{3}{2b\tan\theta}\frac{1}{h^*} \tag{4}$$

where θ denotes the angle between the surface of the conical indenter and the plane of the sample surface. M is a dimensionless coefficient which is associated with the plastic zone. h is referred as the indentation depth. The derivation process of Eq. (4) is reported in details in reference [31, 32]. Note that, $\bar{h}^* = h^*/M^3$ and h^* is the characteristic length depending on the density of SSDs through H_0, which is the hardness arising from the SSDs alone [31] and is given by

$$H_0 = 3\sqrt{3}\mu b\alpha\sqrt{\bar{\rho}_{\mathrm{S}}} \tag{5}$$

For plasma-exposed materials, there exists an obvious increase of the density of SSDs, which is inhomogeneously distributed in the damage layer. To characterize the additional hardening behavior induced by these plasma-induced dislocations, the hardness with plasma effect can be given in the following form, i.e.

$$H_{\mathrm{irr}} = 3\sqrt{3}\mu b\alpha\sqrt{\bar{\rho}_{\mathrm{S}} + \bar{\rho}_{\mathrm{G}} + \Delta\bar{\rho}_{\mathrm{S}}} = H_0\sqrt{1 + \frac{\bar{h}^*}{h} + \frac{\Delta\bar{\rho}_{\mathrm{S}}}{\bar{\rho}_{\mathrm{S}}}} \tag{6}$$

where $\Delta\bar{\rho}_{\mathrm{S}}$ is the average density of the plasma-induced SSDs within the plastic zone beneath the indenter tip, which is calculated by dividing the total length of plasma-induced SSDs (ΔL_{S}) by the volume of the plastic zone (V), i.e.

$$\Delta\bar{\rho}_{\mathrm{S}} = \frac{\Delta L_{\mathrm{S}}}{V} = \frac{\int_0^R \pi\left(R^2 - x^2\right)\Delta\rho_{\mathrm{S}}(x)dx}{\frac{2}{3}\pi R^3} \tag{7}$$

where R is the radius of the plastic zone, and $\Delta\rho_{\mathrm{S}}(x)$ is the density distribution of plasma-induced SSDs within the irradiated layer. Considering the non-uniform distribution of the plasma-induced SSDs as observed in the experimental results (see Fig. 5 in the following), $\Delta\rho_{\mathrm{S}}(x)$ is assumed to follow as

$$\Delta\rho_{\rm s}(x)=\begin{cases}\Delta\rho_{\rm s}^{\max}\left(1-\frac{x}{L_{\rm d}}\right)^{n},x\le L_{\rm d}\\ 0,x>L_{\rm d}\end{cases}\tag{8}$$

where x and $L_{\rm d}$, respectively, describe the distance from the sample surface and depth of the damage layer. $\Delta\rho_{\rm s}^{\max}$ defines the peak value of the density of plasma-induced SSDs, and $n\ge 0$ is a parameter that refers to the profile of the defect distribution. The similar expression of $\Delta\rho_{\rm s}$ has been used before in the previous study [32]. To compute the average defect density $\Delta\bar{\rho}_{\rm s}(x)$ from the $\Delta\rho_{\rm s}(x)$ above, the volume of the plastic zone induced by the indenter is needed. There is a consensus that the plastic zone is generally noted as a hemisphere zone [32, 33]. The radius of the hemispherical plastic zone could be estimated as $R=M\cdot h$ [32, 34].

With the increase of the indentation depth, the size of the plastic zone under the indenter tip also increases gradually. Here, we define $h_{\rm c}^{\rm sep}$ as the critical indentation depth at which the plastic zone reaches the maximum depth of the damage layer $L_{\rm d}$, and could be written as $h_{\rm c}^{\rm sep}=L_{\rm d}/M$.

When the plastic zone is fully inside the irradiated zone, i.e., $R\le L_{\rm d}$, or $h\le h_{\rm c}^{\rm sep}$, as shown in Fig. 1 (a), $\Delta\bar{\rho}_{\rm s}(x)$ in the plastic zone is established as the following equation,

$$\Delta\bar{\rho}_{\rm s}(x)=\frac{\int_0^R\pi(R^2-x^2)\Delta\rho_{\rm s}^{\max}\left(1-\frac{x}{L_{\rm d}}\right)^{n}{\rm d}x}{\frac{2}{3}\pi R^3}=\Delta\rho_{\rm s}^{\max}\sum_{r=0}^{n}\frac{3{\rm C}_n^r}{(r+1)(r+3)}\left(\frac{h}{h_{\rm c}^{\rm sep}}\right)^{r}\tag{9}$$

When $R>L_{\rm d}$, or $h>h_{\rm c}^{\rm sep}$, as shown in Fig. 1 (b), $\Delta\bar{\rho}_{\rm s}(x)$ can be reduced as

$$\Delta\bar{\rho}_{\rm s}(x)=\frac{\int_0^{L_{\rm d}}\pi(R^2-x^2)\Delta\rho_{\rm s}^{\max}\left(1-\frac{x}{L_{\rm d}}\right)^{n}{\rm d}x}{\frac{2}{3}\pi R^3}$$

$$=\Delta\rho_{\rm s}^{\max}\left[\sum_{r=0}^{n}\frac{3{\rm C}_n^r(-1)^r}{2(r+1)}\frac{h}{h_{\rm c}^{\rm sep}}-\sum_{r=0}^{n}\frac{3{\rm C}_n^r(-1)^r}{2(r+1)}\left(\frac{h}{h_{\rm c}^{\rm sep}}\right)^{3}\right]\tag{10}$$

where ${\rm C}_n^r=\frac{n!}{r!(n-r)!}$.

By substituting Eqs. (4), (9) and (10) into Eq. (6) yields the depth dependent hardness of plasma-exposed materials,

$$H_{\rm irr}=\begin{cases}H_0\sqrt{1+\frac{\bar{h}^*}{h}+\sum_{r=0}^{n}P(r)h^r}\ ,h\le h_{\rm c}^{\rm sep}\\ H_0\sqrt{1+\frac{\bar{h}^*}{h}+\frac{T}{h}-\frac{Z}{h^3}}\ ,h>h_{\rm c}^{\rm sep}\end{cases}\tag{11}$$

where $P(r)=\frac{{\rm C}_n^r(-1)^r}{(r+1)(r+3)\left(h_{\rm c}^{\rm sep}\right)^r}2b\tan\theta h^*\Delta\rho_{\rm s}^{\max}$,

$T(r)=\sum_{r=0}^{n}\frac{{\rm C}_n^r(-1)^r}{(r+1)}b\tan\theta h^*\Delta\rho_{\rm s}^{\max}h_{\rm c}^{\rm sep}$,

and $Z(r)=\sum_{r=0}^{n}\frac{{\rm C}_n^r(-1)^r}{(r+3)}b\tan\theta h^*\Delta\rho_{\rm s}^{\max}\left(h_{\rm c}^{\rm sep}\right)^3$.

3.2 Parameter calibration

Intuitively, a few parameters are generally known prior to the indentation experiments such as θ, μ and b. Others like L_{d}, $\Delta\rho_{\mathrm{s}}^{\max}$, n, $\bar{\rho}_{\mathrm{s}}$ and α are usually not known prior to the indentation test. The hardness model as expressed in Eq. (11) contains a few parameters, thereinto, seven physical parameters appear explicitly, including H_0, $\bar{h}^*$, $h_{\mathrm{c}}^{\mathrm{sep}}$, P, T, Z and n. In the following, the method for the calibration of these parameters is introduced by fitting the experimental data.

Firstly, one should note that H_0 and $\bar{h}^*$ are independent of irradiation effect. The $H_{\mathrm{uni}} - h$ relationship can be transformed into the $(H_{\mathrm{uni}})^2 - 1/h$ curve, which should be a straight line, theoretically, at which its intercept with the vertical axis is H_0^2 and its slope is $H_0^2\bar{h}^*$. Thus, the value of H_0 and $\bar{h}^*$ could be obtained.

Next, with the known values of H_0 and $\bar{h}^*$, the experimental data with irradiation effect can be expressed in the form as $f(h) = (H_{\mathrm{irr}}/H_0)^2 - \bar{h}^*/h - 1$. According to Eq. (11), $f(h)$ can be further expressed as

$$f(h) = \left(\frac{H_{\mathrm{irr}}}{H_0}\right)^2 - \frac{\bar{h}^*}{h} - 1 = \begin{cases} \sum_{r=0}^{n} P(r)h^r, h \le h_{\mathrm{c}}^{\mathrm{sep}} \\ \frac{T}{h} - \frac{Z}{h^3}, h > h_{\mathrm{c}}^{\mathrm{sep}} \end{cases} \tag{12}$$

It is conceivable that $h_{\mathrm{c}}^{\mathrm{sep}}$ is the significant bridge connecting the plastic zone with irradiation properties. Apparently, $h_{\mathrm{c}}^{\mathrm{sep}}$ could be extracted from the experimentally obtained $f(h) - h$ curve, since it is considered as the critical point for two different shapes in the curve. Then, the parameters P, T, Z and n could be formulated with respect to fitting $f(h)$ for the entire range of h by the linear and nonlinear regression method. In this way, the parameterization of the hardness model could be completed.

Finally, the theoretical expression for the hardness-depth relationship with plasma irradiation effect should be established spontaneously, according to Eq. (11) and all the known parameters. In summary, in order to carry out the theoretical hardness profile, the derivation procedure of the theoretical model consists of the following steps.

(1) Define $f(h)$ as $f(h) = (H_{\mathrm{irr}}/H_0)^2 - \bar{h}^*/h - 1$, and substitute Eq. (11) into $f(h)$ to obtain Eq. (12), which plays a key role for the theoretical analysis.

(2) Obtain H_0 and $\bar{h}^*$ from the experimental $(H_{\mathrm{uni}})^2 - 1/h$ curve, which should be a straight line, theoretically, at which its intercept with the vertical axis is H_0^2 and its slope is $H_0^2\bar{h}^*$.

(3) Extract $h_{\mathrm{c}}^{\mathrm{sep}}$ from the experimentally obtained $f(h) - h$ curve, which is taken as the critical point for the two different shapes in the curve.

(4) Obtain parameters P, T, Z and n by using the linear and nonlinear regression method to fit $f(h)$ for the entire range of h.

(5) Obtain the theoretical $H_{\mathrm{irr}} - h$ curve by substituting the parameters H_0, $\bar{h}^*$, $h_{\mathrm{c}}^{\mathrm{sep}}$ P, T, Z and n into Eq.(11), which yields the theoretical expression for the hardness-depth relationship with plasma irradiation effect.

4. Results

4.1 Damage Microstructures

Fig. 2 illustrates the surface morphology of tungsten before and after exposure to H plasma at 573 K and 1273 K. The SEM images are taken on the plane-section that is vertical to the exposure direction. It is evident from these images that the plasma exposure causes blistering on the tungsten surface when the exposure temperature (T_{exp}) is 573 K, however, hardly any when T_{exp}=1273 K. The blister size is determined as the equivalent circle diameter of the surface area covered by the blister, and the average blister size is about 0.8 μm when T_{exp}=573 K.

TEM samples at different exposure temperatures were fabricated by the plasma FIB technology, with its unique advantage of obtaining the cross-section view which is parallel to the plasma exposure direction. The micrographs were all recorded under the two-beam condition in the STEM mode. Fig. 3 reveals the microstructures in tungsten after H plasma exposure at 573 K. The cavities, located at the depth range of 0.1~4 μm away from the surface, are corresponding to the blisters on the exposure surface as shown in Fig. 2(c) and (d). According to the enlarged images as shown in Fig. 3(b) and (c), noticeable dislocations are directly observed within 5 μm depth beneath the exposure surface, which obviously indicates that the occurrence of blistering is accompanied with plastic deformation [35]. Corresponding mechanisms will be discussed later.

Fig. 4 describes a visible distinguishable morphology when T_{exp}=1273 K, which is compared with that as observed in the sample when T_{exp}=573 K (as shown in Fig. 3). No visible cavities/blisters or surface structures are observed when it comes to the high exposure temperature. Coincidentally, only a few dislocations appear in Fig. 4, which clearly substantiates that dislocations are associated with the cavities. Owing to the increasing diffusion ability at high exposure temperature, H atoms tend to migrate out of the surface [20] or less H trapped in W [36] , resulting in no presence of blisters.

In addition, the density distribution of plasma-induced dislocation $\Delta\rho_s(x)$ could be derived from the TEM observations, and the results are shown in Fig. 5. It shows that $\Delta\rho_s(x)$ decreases almost linearly with the increase of depth for the sample exposed at 573 K, however, it is close to be zero when the exposure temperature becomes 1273 K.

4.2 Experimental and Theoretical Indentation Hardness

Nano-indentation tests have been widely used to measure the mechanical property changes of irradiated materials due to its advantages of allowing ultra-small scale materials testing and convenience on fabricating samples [37-40]. In order to investigate the effects of the limited penetration in H plasma-exposed tungsten on mechanical properties, we adopted the Berkovich nano-indentation to obtain the indentation hardness as a function of the penetration depth at different explosion temperatures, as shown in Fig. 6 (a). It reveals that the indentation hardness of the sample exposed at 573 K is higher than that exposed at 1273 K, however, there is no apparent change between the pristine tungsten and the sample exposed at 1273 K. Corresponding to the damage microstructures as mentioned previously, it is not hard to understand that the exposure-induced defects are deserved as the primary reason which contributes to the difference of hardness.

To investigate the relationship between the damage microstructure and indentation hardness, the mechanistic model for the depth dependent hardness as given in Eq. (11) is applied for the plasma-exposed tungsten.

Following the parameter calibration as mentioned in Section 3.2, the values of H_0 and $\bar{h}^*$ can be firstly derived from the pristine tungsten. Under plasma exposure, the additional increase of dislocations is believed to be responsible for the irradiation hardening. According to the distribution of the dislocation density as shown in Fig. 5, $\Delta\rho_\mathrm{s}(x)$, when T_exp=573 K, tends to decrease linearly from the maximum value on the surface to zero when $x = L_\mathrm{d}$. Therefore, n = 1 is taken in Eq. (8), and Eqs. (11) and (12) can be recast as

$$H_\mathrm{irr} = \begin{cases} H_0\sqrt{1+\frac{\bar{h}^*}{h}+P_1-Q_1 h}\,, & h \le h_\mathrm{c}^\mathrm{sep} \\ H_0\sqrt{1+\frac{\bar{h}^*}{h}+\frac{T_1}{h}-\frac{Z_1}{h^3}}\,, & h \ge h_\mathrm{c}^\mathrm{sep} \end{cases} \quad (13)$$

and

$$f(h) = \left(\frac{H_\mathrm{irr}}{H_0}\right)^2 - \frac{\bar{h}^*}{h} - 1 = \begin{cases} P_1 - Q_1 h\,, & h \le h_\mathrm{c}^\mathrm{sep} \\ \frac{T_1}{h}-\frac{Z_1}{h^3}\,, & h \ge h_\mathrm{c}^\mathrm{sep} \end{cases} \quad (14)$$

with $P_1 = \frac{2b\tan\theta h^*\Delta\rho_\mathrm{s}^\mathrm{max}}{3}$, $Q_1 = \frac{b\tan\theta h^*\Delta\rho_\mathrm{s}^\mathrm{max}}{4h_\mathrm{c}^\mathrm{sep}}$, $T_1 = \frac{b\tan\theta h^* h_\mathrm{c}^\mathrm{sep}\Delta\rho_\mathrm{s}^\mathrm{max}}{3}$ and $Z_1 = \frac{b\tan\theta h^*\left(h_\mathrm{c}^\mathrm{sep}\right)^3\Delta\rho_\mathrm{s}^\mathrm{max}}{12}$.

Note that there exist five irradiation-related parameters as expressed in Eq. (13), namely, P_1, Q_1, T_1, Z_1 and $h_\mathrm{c}^\mathrm{sep}$. When taking P_1 and $h_\mathrm{c}^\mathrm{sep}$ as the independent variables, the rest three can be expressed as $Q_1 = 3P_1/(8h_\mathrm{c}^\mathrm{sep})$, $T_1 = 3P_1 h_\mathrm{c}^\mathrm{sep}/4$ and $Z_1 = P_1(h_\mathrm{c}^\mathrm{sep})^3/8$. Therefore, there are only two parameters, i.e. P_1 and $h_\mathrm{c}^\mathrm{sep}$, that need to be fitted by comparing the $f(h) - h$ relationship with experimental data. Taking the sample exposed at 573 K for instance, the theoretical results with fitted parameters are compared with the experimental data as illustrated in Fig. 6. One can see a good agreement is achieved for both the $f(h) - h$ and $H_\mathrm{irr} - h$ relationship. The fitted parameters are listed in Table 1.

While, when T_exp=1273 K, $H = H_0\sqrt{1+\bar{h}^*/h}$ is adopted due to the limited increase of the dislocation density in the irradiation region (as illustrated in Fig. 5). The fitted results of the sample exposed at 1273 K are virtually the same with those of the pristine tungsten, which are coincident with the experimental features, as shown in Fig. 6 (a). It turns out that a desirable agreement is observed between the theoretical predictions and experimental data.

In order to further validate the rationality of the fitted parameters, the distribution of the $\Delta\rho_\mathrm{s} - h$ relationship when T_exp=573 K is compared between the experimental data and theoretical results deduced from Eq. (8) with fitted parameters. The specific procedures are as follows. According to the experimental data as shown in Fig. 5, L_d could be extracted as 4 μm for the sample exposed at 573 K. With $M = L_\mathrm{d}/h_\mathrm{c}^\mathrm{sep}$ and

$h^* = \bar{h}^* \cdot M^3$, both M and h^* can be obtained. Since b and $\tan\theta$ are known for tungsten which, respectively, equals 0.275 nm and 0.358 [31], $\Delta\rho_s^{\max}$ is calculated by $\Delta\rho_s^{\max} = 3P_1/(2b\tan\theta h^*)$. Therefore, the theoretical expression of $\Delta\rho_s - h$ is obtained and compared with experimental data, as shown in Fig. 7. As expected, a reasonable agreement is achieved that can verify the validity of the fitting procedure.

5. Discussion

Substantially, irradiation hardening in plasma-exposed materials has been generally ascribed to dislocations (loops) [6], bubbles or cavities [5, 41] and D penetration [42], etc. However, the specific roles played by distinct damage defects on irradiation hardening are rarely reported in previous literatures. The main concern in this study is to quantify the effect of irradiation-induced defects on the hardening of H plasma-exposed tungsten. Therefore, in this section, the hardening mechanisms for H plasma-exposed tungsten at different exposure temperatures are formulated with respect to the damage microstructures and indentation results.

When T_{exp}=573 K, blisters on the surface and corresponding cross-sectional structures were observed by SEM and TEM images. More specially, dislocations dramatically appeared around the blisters. It is conceivable that the growth of blisters is facilitated by the movement of dislocations and their multiplication, which has been reported as the plastic deformation mechanism [35]. However, it is well known that the exposure temperature has a significant impact on blistering in tungsten [11]. Owing to the enhanced diffusion ability and less amount of trapped H in W at high temperature, the formation and growth of the H platelet will be suppressed. Therefore, when T_{exp}=1273 K, no blister-structures and rare dislocations were observed as shown in Figs. 2 (b) and 4.

It is notable that the fundamental mechanisms resulting in irradiation hardening can be categorized into the source hardening and friction hardening. For friction hardening, the increase of external force originates from the stress-activated cutting of dislocation network and obstacles by sliding dislocations, which belongs to a long-range interaction that is determined by the virtue of their stress fields [43]. In this study, an obvious increase of dislocation density was observed when T_{exp}=573 K, which strengthens the dislocation-dislocation interaction by virtue of their stress fields. Therefore, it is believed that friction hardening is the fundamental mechanism that results in irradiation hardening when T_{exp}=573 K. Moreover, it has been proved by our theoretical model that the hardness-depth relationship with plasma exposure effect can be effectively characterized when the effect of exposure-induced dislocations is considered. When T_{exp}=1273 K, no remarkable change of the hardness is noticed when compared with that of the pristine tungsten. It can be ascribed to the rare existing dislocations. Thus, the hardness model without irradiation effect, i.e. the Nix-Gao model [31], is applied to fit the hardness-depth data of the sample exposed at 1273 K, and a satisfied agreement is obtained when compared with the experimental data.

6. Conclusions

In this paper, we attributed the irradiation hardening mechanism to the damage microstructures of H plasma-exposed tungsten at different exposure temperatures. Experimental measurements such as SEM, TEM and Berkovich nano-indentation techniques, as well as the establishment of a mechanistic model were combined to explore the intrinsic mechanism. The main results can be summarized as follows:

(1) When T_{exp}=573 K, the cavities located at the depth range of 0.1~4 μm beneath the exposure surface are corresponding to the blisters on the exposed surface. Dislocations dramatically appeared around the cavities.

(2) When T_{exp}=1273 K, no visible blisters and rare dislocations were observed, owing to the enhanced diffusion ability and less amount of trapped H in W at high temperature.

(3) The irradiation hardening appeared in the sample exposed at 573 K, however, no remarkable change of the hardness was observed between the sample exposed at 1273 K and pristine tungsten.

(4) In order to characterize the indentation size effect and irradiation hardening behavior of plasma-exposed materials,, a mechanistic model was carried out to characterize the indentation hardness as a function of the indentation depth. A good agreement between the experimental indentation data and theoretical results revealed that plasma-induced dislocations play a dominant role in determining the increase of hardness for H plasma-exposed materials.

In conclusion, this study established the relationship between the mechanical properties and microstructure evolutions of plasma-exposed tungsten, with the collaboration of both experimental and theoretical efforts.

Acknowledgments

This work was supported by National Magnetic Confinement Fusion Science Program of China under Grant 2014GB117000 and the National Nature Science Foundation of China under Contract No. 51471092, No. 11802344 and No.11405150, the Tsinghua Scholarship for Overseas Graduate Studies, and the initial funding supported by Central South University. Furthermore, the technical supports from DIFFER, Netherlands, and the Center for Electron Microscopy of the University of Birmingham, UK, are acknowledged. W.Q. Chen is grateful for valuable supports on TEM and plasma FIB techniques from Dr. Jing Wu, Dr. Jinsen Tian and Dr. Minshi Wang from the University of Birmingham, and flash polishing from Dr. Robin Schaeublin of ETHZ Switzerland. The help of Mr. Wangguo Guo from Beihang University on this work is gratefully acknowledged.

Reference

[1] T. Hirai, F. Escourbiac, S. Carpentier-Chouchana, *et al.*, ITER full tungsten divertor qualification program and progress, Phys. Scr. T159 (2014) 014006

[2] Y.Z. Jia, W. Liu, B. Xu, *et al.*, Subsurface deuterium bubble formation in W due to low-energy high flux deuterium plasma exposure, Nucl. Fusion 57 (2017) 5

[3] X.-S. Kong, S. Wang, X. Wu, *et al.*, First-principles calculations of hydrogen solution and diffusion in tungsten: Temperature and defect-trapping effects, Acta

Mater. 84 (2015) 426-435
[4] D. Terentyev, V. Dubinko, A. Bakaev, *et al.*, Dislocations mediate hydrogen retention in tungsten, Nucl. Fusion 54 (2014) 5
[5] D. Terentyev, A. Bakaeva, T. Pardoen, *et al.*, Surface hardening induced by high flux plasma in tungsten revealed by nano-indentation, J. Nucl. Mater. 476 (2016) 1-4
[6] Y. Zayachuk, D.E.J. Armstrong, K. Bystrov, *et al.*, Nanoindentation study of the combined effects of crystallography, heat treatment and exposure to high-flux deuterium plasma in tungsten, J. Nucl. Mater. 486 (2017) 183-190
[7] R.A. Pitts, S. Carpentier, F. Escourbiac, *et al.*, A full tungsten divertor for ITER: Physics issues and design status, J. Nucl. Mater. 438 (2013) S48-S56
[8] M.Y. Li and J.H. You, Mechanics of tungsten blistering II: Analytical treatment and fracture mechanical assessment, J. Nucl. Mater. 465 (2015) 702-709
[9] M. Balden, S. Lindig, A. Manhard, *et al.*, D2 gas-filled blisters on deuterium-bombarded tungsten, J. Nucl. Mater. 414 (2011) 69-72
[10] W.M. Shu, High-dome blisters formed by deuterium-induced local superplasticity, Appl. Phys. Lett. 92 (2008)
[11] Y.Z. Jia, G. De Temmerman, G.N. Luo, *et al.*, Surface morphology and deuterium retention in tungsten exposed to high flux D plasma at high temperatures, J. Nucl. Mater. 457 (2015) 213-219
[12] J. Roth and K. Schmid, Hydrogen in tungsten as plasma-facing material, Phys. Scr. T145 (2011) 9
[13] Y. Ueda, K. Schmid, M. Balden, *et al.*, Baseline high heat flux and plasma facing materials for fusion, Nucl. Fusion 57 (2017)
[14] A. Manhard, U. von Toussaint, M. Balden, *et al.*, Microstructure and defect analysis in the vicinity of blisters in polycrystalline tungsten, Nucl. Mater. Energy 12 (2017) 714-719
[15] D. Terentyev, G. De Temmerman, T.W. Morgan, *et al.*, Effect of plastic deformation on deuterium retention and release in tungsten, J. Appl. Phys. 117 (2015)
[16] P. Grigorev, L. Buzi, A. Bakaeva, *et al.*, Numerical analysis of TDS spectra under high and low flux plasma exposure conditions, Phys. Scr. T167 (2016)
[17] J. Hou, X.-S. Kong, J. Sun, *et al.*, Hydrogen bubble nucleation by self-clustering: density functional theory and statistical model studies using tungsten as a model system, Nucl. Fusion 58 (2018)
[18] V.K. Alimov, W.M. Shu, J. Roth, *et al.*, Temperature dependence of surface topography and deuterium retention in tungsten exposed to low-energy, high-flux D plasma, J. Nucl. Mater. 417 (2011) 572-575
[19] J. Bauer, T. Schwarz-Selinger, K. Schmid, *et al.*, Influence of near-surface blisters on deuterium transport in tungsten, Nucl. Fusion 57 (2017)
[20] W. Hu, F. Luo, Z. Shen, *et al.*, Hydrogen bubble formation and evolution in tungsten under different hydrogen irradiation conditions, Fusion Eng. Des. 90 (2015) 23-28
[21] W.M. Shu, E. Wakai and T. Yamanishi, Blister bursting and deuterium bursting release from tungsten exposed to high fluences of high flux and low energy deuterium plasma, Nucl. Fusion 47 (2007) 201-209

[22] Y.-N. Liu, T. Ahlgren, L. Bukonte, *et al.*, Mechanism of vacancy formation induced by hydrogen in tungsten, AIP Adv. 3 (2013)
[23] A.S. Kukushkin, H.D. Pacher, A. Loarte, *et al.*, Analysis of performance of the optimized divertor in ITER, Nucl. Fusion 49 (2009)
[24] G.G. van Eden, M.L. Reinke, S. Brons, *et al.*, Plasma radiation studies in Magnum-PSI using resistive bolometry, Nucl. Fusion 58 (2018)
[25] H.J. van der Meiden, R.S. Al, C.J. Barth, *et al.*, High sensitivity imaging Thomson scattering for low temperature plasma, Rev. Sci. Instrum. 79 (2008) 013505
[26] R.D. Kelley, K. Song, B. Van Leer, *et al.*, Xe+ FIB Milling and Measurement of Amorphous Silicon Damage, Microsc. microanal. 19 (2013) 862-863
[27] T.L. Burnett, R. Kelley, B. Winiarski, *et al.*, Large volume serial section tomography by Xe Plasma FIB dual beam microscopy, Ultramicroscopy 161 (2016) 119-129
[28] Y. Huang, H. Zhang, M.A. Auger, *et al.*, Microstructural comparison of effects of hafnium and titanium additions in spark-plasma-sintered Fe-based oxide-dispersion strengthened alloys, J. Nucl. Mater. 487 (2017) 433-442
[29] H. Iwakiri, H. Wakimoto, H. Watanabe, *et al.*, Hardening behavior of molybdenum by low energy He and D ion irradiation, J. Nucl. Mater. 258-263 (1998) 873-878
[30] D.E.J. Armstrong, P.D. Edmondson and S.G. Roberts, Effects of sequential tungsten and helium ion implantation on nano-indentation hardness of tungsten, Appl. Phys. Lett. 102 (2013) 251901
[31] W.D. Nix and H.J. Gao, Indentation size effects in crystalline materials: A law for strain gradient plasticity, J. Mech. Phys. Solids 46 (1998) 411-425
[32] X.Z. Xiao, Q.Y. Chen, H. Yang, *et al.*, A mechanistic model for depth-dependent hardness of ion irradiated metals, J. Nucl. Mater. 485 (2017) 80-89
[33] X. Xiao and L. Yu, Comparison of linear and square superposition hardening models for the surface nanoindentation of ion-irradiated materials, J. Nucl. Mater. 503 (2018) 110-115
[34] H.F. Huang, J.J. Li, D.H. Li, *et al.*, TEM, XRD and nanoindentation characterization of Xenon ion irradiation damage in austenitic stainless steels, J. Nucl. Mater. 454 (2014) 168-172
[35] J.B. Condon and T. Schober, Hydrogen bubbles in metals, J. Nucl. Mater. 207 (1993) 1-24
[36] W. Guo, L. Ge, Y. Yuan, *et al.*, （001）edge dislocation nucleation mechanism of surface blistering in tungsten exposed to deuterium plasma, Nucl. Fusion 59 (2019)
[37] W.C. Oliver and G.M. Pharr, Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology, J. Mater. Res. 19 (2004) 3-20
[38] P. Hosemann, C. Vieh, R.R. Greco, *et al.*, Nanoindentation on ion irradiated steels, J. Nucl. Mater. 389 (2009) 239-247
[39] P. Hosemann, Small-scale mechanical testing on nuclear materials: bridging the experimental length-scale gap, Scr. Mater. 143 (2018) 161-168
[40] W.Q. Chen, X.Y. Wang, X.Z. Xiao, *et al.*, Characterization of dose dependent

mechanical properties in helium implanted tungsten, J. Nucl. Mater. 509 (2018) 260-266
[41] J. Zhao, X. Meng, X. Guan, *et al.*, Investigation of hydrogen bubbles behavior in tungsten by high-flux hydrogen implantation, J. Nucl. Mater. 503 (2018) 198-204
[42] A. Dubinko, D. Terentyev, A. Bakaeva, *et al.*, Effect of high flux plasma exposure on the micro-structural and -mechanical properties of ITER specification tungsten, Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms 393 (2017) 155-159
[43] G.S. Was, Fundamental of radiation materials science, (2017) New York