Evolution of the surface structure the proton-irradiated tungsten during isochronal annealing in the temperature range 600-1000 °C

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Abstract. This paper presents the research results the surface structure evolution of high-purity tungsten after irradiation with 350 keV protons and subsequent annealing in the temperature range 600 – 1000 °C. Irradiation to a fluence of $5 \times 10^{17}$ cm$^{-2}$ leads to blisters formation on the irradiated surface. Successive two-hour annealing results in the evolution of the distribution of blisters - the total number of blisters decreases while the fraction of larger blisters increases. At an annealing temperature of 1000°C, the blisters dissolve. Do not observed the blisters disclosure and surface flaking both after proton irradiation and subsequent annealing in temperature range 600 – 1000 °C.

1. Introduction

Tungsten has found wide application in industry and is currently considered one of the most promising structural materials for new generation nuclear reactors and controlled fusion installations (FR), since tungsten is refractory, highly hard and chemically resistant material. In particular, in the prototype of a fusion power reactor - the ITER tokamak, a full-size divertor will be made of tungsten [1-2].

Using tungsten as FR structural material raises questions about its radiation resistance, because in FR materials are exposed to neutrons, alpha-particles, protons and high temperatures. One of the effects of materials irradiation with light charged particles are blistering and flaking. Blistering and flaking are induced by irradiation with ions of gases, i.e. helium and hydrogen ions [3-4], which are components of thermonuclear fuel. These effects result in surface erosion and, according to the authors [5], should be considered as the most dangerous mechanisms of material destruction. Blistering and flaking, along with sputtering, lead both to a change in the mechanical properties of the material and to the entrance of erosion products into the thermonuclear plasma, which, in turn, leads to disruption of the fusion reaction. Factors affecting the change in the surface structure, involving the formation of gas-filled bubbles, include both the characteristics of the irradiated material and the irradiation conditions: elemental composition, method of manufacturing and preparing the material for irradiation, crystal grain size, elastic modulus, shear modulus, internal stresses, crystallite orientation, surface roughness, temperature and fluence of irradiation, type of irradiated ions, etc.

Studies the tungsten tendency to blistering and flaking have been carried out earlier and the main feature are known [6-8]. But as mentioned above, blisters formation strongly depends on the tungsten grade, preparation methods, strength characteristics, etc., and can vary greatly. To study changes in the surface structure under proton irradiation, we have chosen tungsten produced by traditional technology.
- sintering of powders at a temperature of ~ 2500°C in a hydrogen flow. The selected material meets the requirements for purity, density and strength properties (microhardness). A specific feature of the investigated tungsten is weak expressed texture. The proton energy was chosen equal to 350 keV for the following reason - a relatively large number of studies are devoted to the study of the blistering effect in the energy range of 10-200 keV, there are single studies at irradiation with high-energy protons (1.75 MeV and above), and for the range 200-1000 keV there are no data in the literature.

2. Samples, irradiation procedure and research methods

High-purity tungsten was selected for research, meeting the requirements to tungsten for the ITER divertor[9]. The content of impurities in the investigated tungsten is below the threshold of determination by the method of energy dispersive analysis. According to the data of X-ray diffraction analysis, the diffractogram of the studied material corresponds to the BCC lattice of tungsten with a weakly manifest texture, Figure 1.a. The diffractogram contains reflections from the planes (110), (200), (211), and (220). The ratio of the intensities of the peaks for these planes is \( \Phi(110) / \Phi(200) / \Phi(211) / \Phi(220) = 1.0 / 0.4 / 0.3 / 0.7 \), while the ratio of the intensities of the same planes with a random crystallite orientation is \( \Phi̍(110) / \Phi̍(200) / \Phi̍(211) / \Phi̍(220) = 1.0 / 0.3 / 0.5 / 0.1 \) [10]. A weakly manifests texture is a distinctive feature of the chosen for study tungsten, since using the work hardened tungsten with evident expressed texture is proposed as a material for the FR divertor. The measured hydrostatic density is \( \rho = 19.1 \, \text{g/cm}^3 \), the Vickers microhardness \( Hμ = 646 \, \text{MPa} \). Samples for irradiation and subsequent studies were cut from a massive piece and were plates with dimensions of \( 12 \times 12 \times 5 \, \text{mm} \). The surface was subjected to mechanical grinding and polishing. Made by atomic force microscopy picture of the prepared surface is shown in Figure 1.b. It can be seen that the surface is rather smooth, roughness \( \sim 8-10 \, \text{nm} \). On the control sample, using electrolytic etching, the grain structure was revealed, see Figure 1c. It can be seen that the grain size does not exceed 120 \( \mu \text{m} \).

![Figure 1. Structure of the studied tungsten, a – diffractogram; b – roughness of the specimens prepared surface; c – grains structure](image)

Investigations the surface structure of irradiated tungsten were carried out by two technique. First is scanning electron microscopy (SEM) using HITACHI TM 4000 electron microscope (Japan). Second technique was atomic force microscopy (AFM) performed on the scanning nanohardness tester "NanoscanCompact" (Russia), which makes it possible to study the surface relief.

Irradiation with protons was performed at the UKP-2-1 accelerator of the Institute of Nuclear Physics in Almaty. Irradiation was carried out at room temperature (27 °C) with 350 keV protons up to a fluence of \( 5 \times 10^{17} \, \text{cm}^2 \). It is note, that in [4-6] it was reported that the threshold for the formation of blisters in tungsten is \( 2.4 \times 10^{18} \, \text{cm}^2 \), hence the proton irradiation fluence in present work less then threshold fluence according [4-6]. The duration of irradiation to achieve the required fluence was 9 hours at a current of 2.5 \( \mu \text{A} \). According to calculations using the SRIM program, the projectile range of 350 keV protons in tungsten is 1.38 \( \mu \text{m} \), straggling is 0.35 \( \mu \text{m} \). The maximum concentration of hydrogen and vacancies generated by 350 keV proton irradiation is reached in the range 0.8 - 1.2
μm from the surface. In this region created conditions for the nucleation and growth of gas filled bubbles and for their manifestation on the surface under certain conditions - that is for blistering formation.

To reveal the role of temperature in the evolution of the structure after proton irradiation, successive two-hour vacuum annealing were carried out at temperatures of 600, 800, and 1000 °C. The preset temperature reached within an hour, cooling down was together with the furnace.

3. Research results and discussion
The structure of surface irradiated with protons is shown in Figures 2 a, b. The figures show that the irradiation led to appearance of numerous rounded shape hillocks with a diameter of 10-20 μm.

![Figure 2. SEM (a, c, e, g) and AFM (b, d, f, h) images of the tungsten surface; a,b – after proton irradiation, c,d - after proton irradiation and 600 °C annealing, e,f - after proton irradiation and 800 °C annealing, g,h - after proton irradiation and 1000 °C annealing](image-url)
Hillocs represents blisters filled with hydrogen (Figure 2 a), protruding above the surface by 100–500 nm (Figure 2 b). The distribution of blisters is dominated by bubbles with sizes of 10-20 microns - 90% of the total, bubbles with sizes <10 microns make up 9% and sizes up to 20 microns - 1%. Bubbles larger than 25 µm in diameter, were not found.

Process of the surface structure forming shown in Figure 3, a is as follows. When irradiated in the straggling area, i.e. zone with an increased concentration of hydrogen atoms and vacancies, favorable conditions for nucleation of gas-filled bubbles are created. Bubbles grow due to absorption of vacancies, implanted hydrogen atoms and bubbles coalescence, which leads to an increase in bubble size. Gas in the bubbles creates pressure, which initiates their drift to the surface and the formation of dome-shaped bubbles on the surface, i.e. - blisters. As can be seen from Figure 2, blisters do not open to the surface, i.e. no flaking of the surface is not observed. This means that the gas pressure in the bubbles is less than the ultimate strength of the material and not enough to break the dome cover. This, in turn, means that the proton fluence, equal in our experiment to $\Phi = 5 \times 10^{17} \text{cm}^{-2}$, is less than the critical one, which is estimated according [6] as $\Phi_{cr} = n \times 10^{18} \text{cm}^{-2}$ (n=2-4).

Post-radiation annealing at 600°C results in change the surface structure, see Figures 2 c, e. The density of bubbles on the surface decreased, while their average size and the height above the surface increase. In the absence of proton irradiation, the growth of blisters sizes occur by the coalescence of bubbles and, as a result, the average size of the bubbles increases. As before, there are no blisters with a destroyed dome, hence, hence, the gas pressure in the bubbles is insufficient to destroy the blisters.

Changes in the surface structure after the next annealing at 800°C are shown in Figures 2 e, f. The density of blisters on the surface decreased even more in comparison with blisters density after annealing at 600°C; at the same time, the height of the blister dome above the surface decreased also. The explanation of observed changes is penetration of hydrogen through the dome and perimeter of the blister and its output by micro cracks and grain boundaries. No opening of the blisters to surface and no flaking of the surface layer is observed.

And, finally, after annealing at 1000°C, blisters almost completely disappear from the surface, see Figure 2 g, h. Only small hillocks with ≤10 nm diameter and ~50 nm height are observed, as well as pits of the same sizes in the place of the dissolved blisters. There is no significant erosion of the surface associated with flaking, but the surface roughness has increased significantly due to the dissolution of the blisters.

Changes in surface morphology can be explained as follows. The amount of hydrogen implanted in tungsten under irradiation with protons with energy 350 keV up to fluence of $5 \times 10^{17} \text{cm}^{-2}$ was sufficient for blisters formation on the surface. The gas pressure in the bubbles, which determined by the amount of implanted hydrogen, was insufficient to open bubbles on the surface. Successive annealing in the temperature range 600-800°C changed the size distribution - the fraction of large blisters increased. But annealing did not lead to an increase in the gas pressure in blisters and blisters was not destroyed. Annealing at a temperature of 1000 °C led to the disappearance of blisters due to the evaporation of hydrogen atoms from the bubbles and their desorption from the surface due to migration along grain boundaries and cracks.

4. Conclusion

Study the evolution of tungsten surface structure irradiated with 350 keV protons allows us to make following conclusions:

- Tungsten irradiation with 350 keV protons tofluence $\Phi = 5 \times 10^{17} \text{cm}^{-2}$ at room temperature leads to blistering formation, although, as follows from the literature data, the threshold fluence of blistering in tungsten under proton irradiation is $4-6 \times 10^{18} \text{cm}^{-2}$.
- Blisters are not opened to the surface, that is, there is no surface erosion. This is due to the gas pressure in the bubbles less than the ultimate strength and not enough to break the dome cover. Dominate size in blister size distribution is 10-15μm.
- Successive post-radiation vacuum annealing in the temperature range 600 –800 °C results in evolution of the size distribution - the total number of blisters decreases, but the fraction of large
blisters with diameter of 20-25 µm grows and appear blisters with sizes> 25 µm. Opened to the surface blisters is not observes also.

- After annealing at 1000 ºC, the blisters dissolve, and the surface layers do not flakes off. There is no significant erosion of the surface.

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