UDC 669.017:539.16

COMPARISON OF BLISTERING OF W BULK AND COATINGS UNDER H_2, D_2 AND He PLASMA IRRADIATION

A.V. Nikitin[1], A.S. Kuprin[1], G.D. Tolstolutskaya[1], R.L. Vasilenko[1], V.D. Ovcharenko[1], V.N. Voyevodin[1,2]
[1]National Science Center "Kharkov Institute of Physics and Technology", Kharkov, Ukraine;
[2]V.N. Karazin Kharkiv National University, Kharkov, Ukraine

The surface topography of W bulk prepared by powder sintering (20 μm thickness) and W coatings deposited by cathodic arc evaporation and by argon ion sputtering was studied under the influence of low-energy hydrogen (deuterium) and helium plasma at room temperature. The surface modifications induced by the plasma irradiation were studied by scanning electron microscopy. It was observed formation of blisters and sputtering. After helium and deuterium plasma irradiation, numerous blisters were observed on the surface of W foils samples and coatings deposited by argon ion sputtering. The surface of W coatings deposited by cathodic arc evaporation was undergone only sputtering process under the same irradiation conditions.

INTRODUCTION

Tungsten (W) will be used as a plasma-facing material (PFM) in the divertor region in ITER, and its use in future fusion devices is also very likely, due to its favorable properties including low hydrogen permeability, low sputtering erosion yield, high thermal conductivity and no chemical reaction with hydrogen [1–4]. The major issue associated with the presently available tungsten grades, in the context of structural applications, is their brittleness at low temperatures [5] which is worsened by irradiation [6]. Surface modifications might be problematic, because they can lead to degradation of heat conductivity. These modifications may further enhance erosion, which could be problematic because tungsten cannot be tolerated in the core plasma. An obvious way to solve this problem is to alloy W with other ductile refractory metals which also present low neutron activation and recently refractory W composites were pointed as a promising alternative to pure W [7]. Structural engineering is in recent years the main method for obtaining coating materials with unique structural states and functional properties.

In many cases increasing of various purposes products functional characteristics is achieved by coating of their surfaces. One of the most promising methods of coatings deposition is vacuum arc method that provides the formation of a wide range of coatings with high adhesion, anti-corrosion, wear-resistant and other properties.

In our previous paper [8] the surface topography of W, Ta, and W-Ta coatings and deuterium retention under the influence of particles of low-energy deuterium plasma was studied. The coatings deposited by argon ion sputtering of W and Ta targets using the gas plasma source employed in this work are free from oxygen enrichment. It was observed formation of blisters as dome and burst or delaminated structures. The W-Ta coating shows improved characteristics: smaller sizes and densities of blisters and a significantly lower thickness of the delaminated layer.

In the actual nuclear fusion devices W will simultaneously or sequentially be irradiated by various ions with high flux such as hydrogen isotopes, helium (He), neutron and other trace impurities [9], which must lead to diffusion and retention of deuterium (hydrogen isotopes) and helium in materials and retention-induced blistering at the surface of PFMs, and result in the exfoliation and melting of surface of PFMs to degrading the stability of fusion reactor [10].

Recent studies indicate that the microstructure of tungsten play a significant role in hydrogen isotope and He irradiation effect [11].

The goal of this paper is the study of the surface topography of bulk tungsten and two types of coatings that are deposited by the vacuum arc method or by the argon ion sputtering and a comparison of their surface microstructure changes under the influence of particles of low-energy hydrogen (deuterium) and helium plasma.

1. EXPERIMENTAL PROCEDURE

In this paper, three types of tungsten samples were investigated: bulk tungsten foil (BF) with 20 μm thickness prepared by powder sintering, tungsten coatings deposited by cathodic arc evaporation (CAE) and tungsten coatings deposited by argon ion sputtering (AIS).

A set of tungsten coatings was formed using unfiltered CAE in a "Bulat-6" system equipped with a W (99.9%) cathode of 60 mm diameter. The substrate-cathode distance was about 150 mm. A vacuum-arc plasma source with magnetic stabilization of a cathode spot was used. The arc current was 140 A. The chamber was evacuated to a pressure of $2 \cdot 10^{-3}$ Pa. Coatings were deposited on the substrates (10×20×1.5 mm) of stainless steel 18Cr10NiTi at a negative bias potential of -50 V without rotation. The substrate temperature during deposition did not exceed 500 °C. The coating deposition rate was of ~ 6 μm/h.

The conditions for obtaining tungsten coatings on stainless steel 18Cr10NiTi by AIS are described in detail in [12].

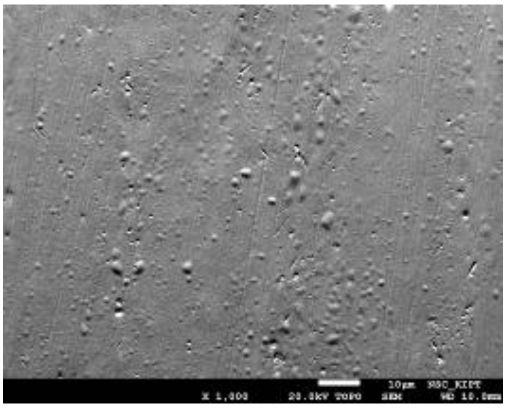
Thickness of all investigated coatings was 5…6 μm.

The disk-shaped specimens (BF, CAE, and AIS) have been irradiated with hydrogen, deuterium, and helium ions using a glow gas-discharge plasma at 1000 V, producing an ion flux of 10^{19} $D^+(H^+)/(m^2 \cdot s)$. The design and principle of operation of the gaseous plasma source used for irradiation of the samples is described in detail in [13]. The specimen temperature was measured by the thermocouple and was (300±2.5) K during irradiation. The central portion of the specimen was irradiated through an aperture, providing an easily-observed boundary between irradiated and unirradiated regions.

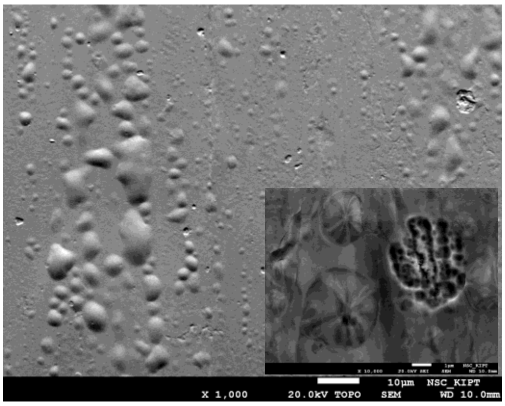
Investigations of surface microstructure before and after irradiation were performed using scanning electron microscope JEOL JSM-7001F. Chemical composition of the tungsten coatings was determined by energy dispersive X-ray spectroscopy – EDS.

2. RESULTS AND DISCUSSION

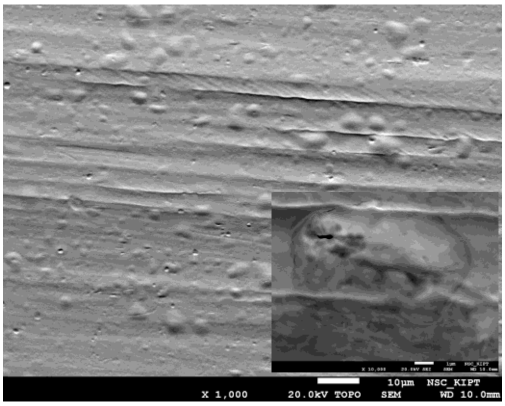
Fig. 1 shows an SEM image of plasma-induced surface changes in tungsten foil (20 µm thickness) bombarded at 300 K with 0.5 keV/H^+, 1 keV He^+ and simultaneously H_2^++He^+ with a dose for each type of particles equal to $1 \cdot 10^{24}$ ion/m^2.



a



b



c

Fig. 1. SEM image of the tungsten foil bombarded with H_2^+(a), He^+ (b) and simultaneously H_2^++He^+ (c) at 300 K. In the insets the structure of individual blisters

Hydrogen exposure leads to development the blisters. The comparison of the shape of blisters shows that blisters at tungsten foil are domes. Blisters size and number in this case are 2 µm and $9 \cdot 10^{10}$ m^{-2}, respectively. The blisters are located mainly along the rolling direction.

Irradiation with helium leads to development the blisters that in average larger and higher than those at H_2 exposure. Blisters have a contrast that characteristic for blisters developing in thin films and the bottom of cracked blister has a porous structure (see Fig. 1,b, inset). Blisters of large irregular shapes are also formed. Likely they are grown due to the coalescence of several dome shaped blisters.

After helium + hydrogen exposure blisters are domes and elongated along the rolling direction (see Fig. 1, c). The density and size of the blisters are in the middle between those for irradiation only by hydrogen or helium plasma. A feature of joint irradiation is the formation of ridges along the rolling direction. In the valleys of these ridges blisters have a contrast which is characteristic for helium blisters. Most of these blisters are ruptured.

In our previous paper we reported about plasma-induced surface changes in W coatings deposited by argon ion sputtering [8]. W coatings (AIS) have a columnar structure (Fig. 2) with a strong axial texture (110) and grain size of 29 nm [12].

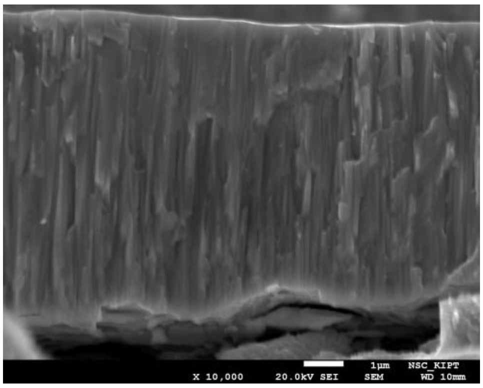


Fig. 2. SEM image of cross-section of W coating deposited by sputtering (AIS)

Fig. 3 shows a SEM image of surface of W coating (AIS) with a columnar structure bombarded at 300 K with 1 keV D_2^+ (0.5 keV/D) to $1 \cdot 10^{24}$ D_2^+/m^2.

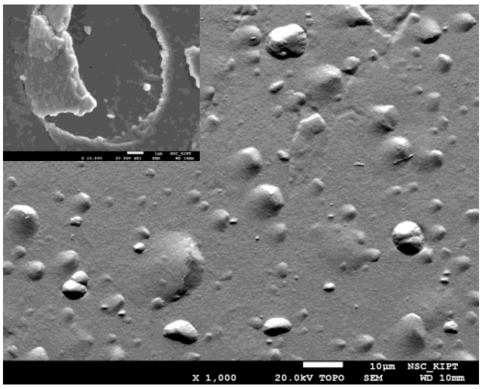
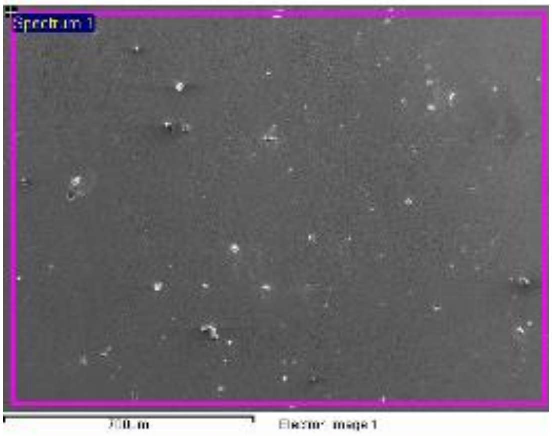


Fig. 3. SEM image of the tungsten coating (AIS) bombarded with 1 keV D_2^+ to $1 \cdot 10^{24}$ D_2^+/m^2 at 300 K. Ruptured blister (inset)

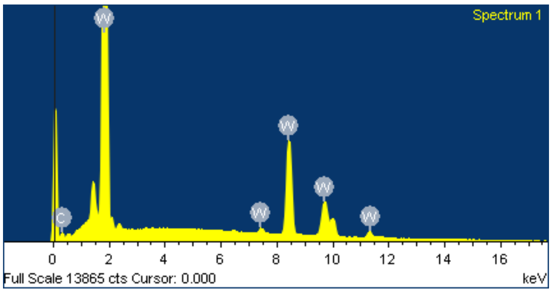
The mean size of the blisters ~ 3 μm and scattered from 0.5 to 10 μm. The blister number is $1.8\cdot10^{10}$ m^{-2}. Almost all blisters at the coating are asymmetric in shape. The average size of blisters is comparable for the tungsten foil and coating, but in the coating the density of blisters is more than four times less.

In addition, the ruptured blisters were found on the surfaces of the W films as seen in Fig. 3 (inset), which implies that during deuterium ions irradiation some big blisters could burst or exfoliate when the internal pressure exceeded a critical limit. On account of some caps of blisters removing after its bursting or exfoliating, the sub-surfaces under the ruptured blisters are clearly visible as shown in Fig. 3 (inset). The surface of the blister caps and the morphology of the sub-surface are characterized by the columnar structure, which retains the morphology of the films before deuterium ions irradiation.

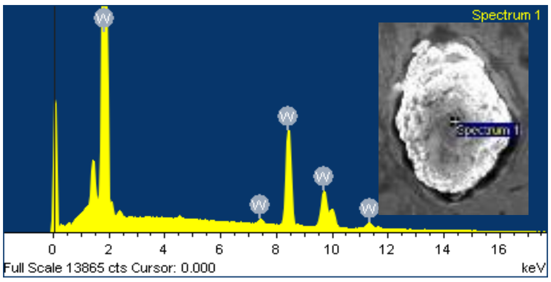
Fig. 4 shows SEM images of surface morphology of initial W coatings deposited by CAE and EDS X-ray spectrums of surface.



a



b



c

Fig. 4. SEM image of initial surface of W coatings (CAE) with droplets (a) and EDS X-ray spectrums of part of surface (b) and droplets (c)

On the tungsten coatings surface macroparticles and craters form (Fig. 4,a). Their presence on the surface is due to the generation of droplets of cathode material in the process of cathodic arc evaporation. The amount of macroparticles on the coating surface is small, which is probably due to a sufficiently low arc discharge current ~ 140 A and a high melting point of tungsten.

The EDS X-ray analysis showed that the coating and droplets consist almost 100% of tungsten. The concentration of oxygen and carbon contaminations in coating is below the detection limit of the EDS method.

Fig. 5 shows a view of fracture of the tungsten coating deposited by CAE. The interface between the coating and substrate is indicated by the dashed horizontal line. The coating thickness is about 5 μm. Within the W coating we can see the grains with dimensions in the μm range and the absence of a pronounced columnar structure.

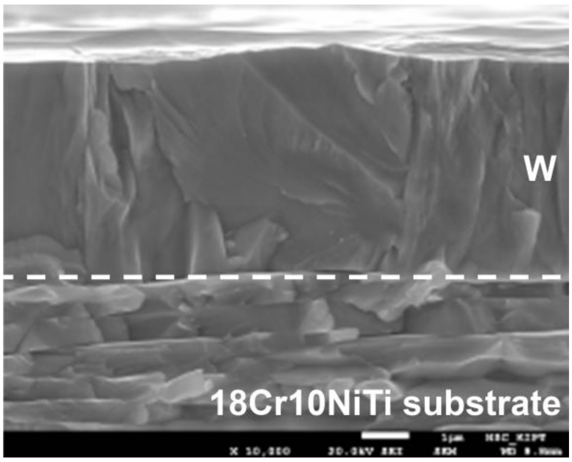


Fig. 5. Cross-section images of W film (CAE) deposited on the substrates of stainless steel 18Cr10NiTi

Fig. 6 shows SEM images of morphology of W coating (CAE) before irradiation. As seen in Fig. 6, the morphology of the W coating shows a similar “nano-ridge” structure, which is the typical morphology of refractory metal films deposited at the relatively low temperatures [14].

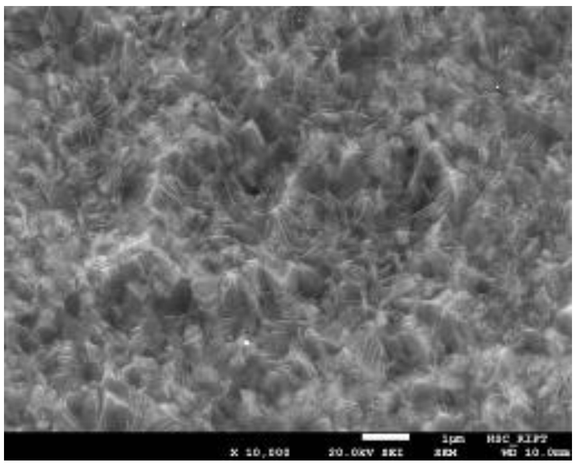
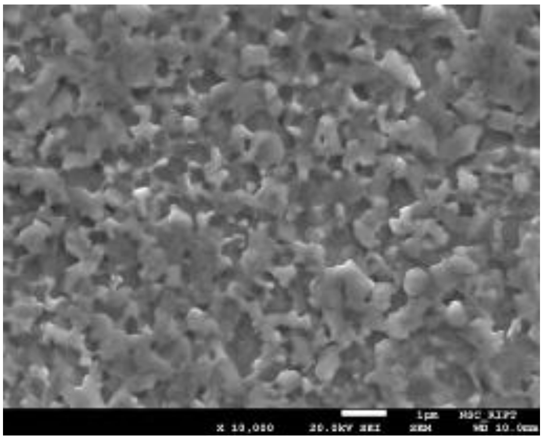
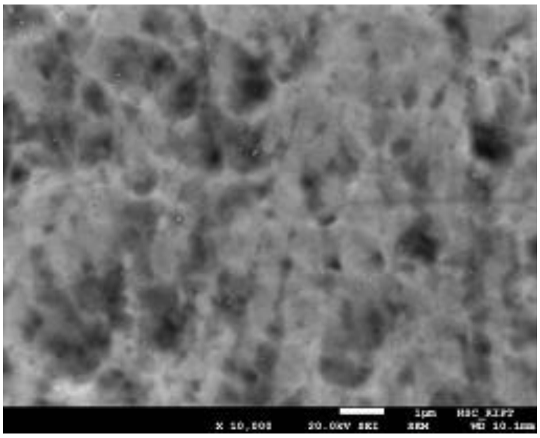


Fig. 6. SEM images of morphology of W coating (CAE) before irradiation

Fig. 7 shows morphology of W coating (CAE) after irradiation at 300 K with 1 keV H_2^+ to $1\cdot10^{24}$ H_2^+/m^2 and with simultaneously D^++He^+ to $1\cdot10^{24}$ ion/m^2.



a



b

Fig. 7. SEM images of morphology of W coating (CAE) after irradiation at 300 K with 1 keV H_2^+ to $1\cdot10^{24}$ H_2^+/m^2 (a) and with simultaneously D^++He^+ to $1\cdot10^{24}$ ion/m^2 (b)

As can be seen from Fig. 7 irradiation of tungsten coatings (CAE) did not lead to the formation of blisters. Only the process of physical sputtering is observed. Sputtering coefficients are $1.14\cdot10^{-2}$ at./ion for hydrogen irradiation. Obtained sputtering coefficients for tungsten coatings (CAE) are lower than for the W coatings (AIS) obtained in the previous work ~ $3.8\cdot10^{-2}$ [15].

In ref. [16] it is noted that there are several reasons to investigate H retention in W films. Firstly, up to now, tungsten coatings were used as the first-wall material in ASDEX Upgrade and JET. Secondly, in future fusion devices W will inevitably be sputtered and re-deposited on nearby surfaces and we can assume that the structure of re-deposited W layers in fusion devices is similar to W films produced by magnetron sputtering. And finally, W films allow the investigation of thin W layers which are thinner than layers that can be produced from bulk material.

Fig. 8 shows a SEM image the structure of re-deposited W layers on W coating which was irradiated at 300 K simultaneously D^++He^+.

As suggested in [17] and shown in present paper the formation of a re-deposited W layers leads to increased erosion of the surface area of the coating, the formation of the strongly ruptured layers.

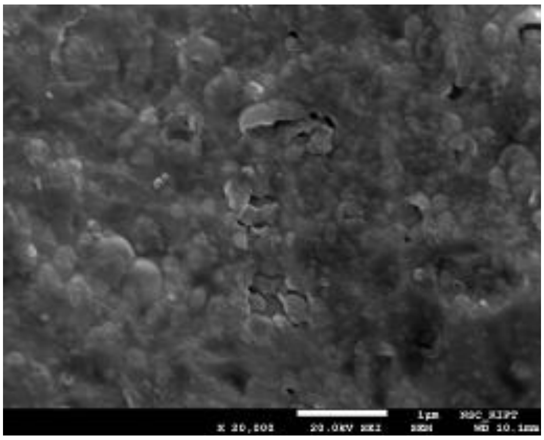


Fig. 8. SEM images of W coating bombarded with simultaneously 1 keV H^++He^+ to $1\cdot10^{24}$ D_2^+/m^2 at 300 K

In ref. [14], the W films with the thickness of 10 µm and grain size below 100 nm by magnetron sputtering and W bulk prepared by powder sintering and warm rolling were exposed to He^+ ions with the energy of 60 keV to fluence of $1.0\cdot10^{22}$ m^{-2} at room temperature. After irradiation, the blisters were observed on both samples, some of which burst in various degrees. The different behavior of blistering on both samples shows clearly by SEM. For instance, the density and the average size of the blisters on the W bulk are larger than on the W film. In addition, the difference in morphologies of sub-surface under ruptured blisters implies that the different behavior of blistering on both samples. It is speculated that GBs in nanostructured material play a dominant role in the blistering after He irradiation.

The reasons for which no blistering is observed in the W coatings deposited by cathodic arc evaporation in the investigated range of doses and at an irradiation temperature of 300 K can be several. Firstly, this is a clear difference in the structure of coatings obtained by CAE and AIS, for CAE coatings columnar structure is absent. Secondly, these coatings can differ greatly in the level of internal stresses, which can also influence on the formation of blisters.

Thus, further investigation is needed to understand the mechanism of suppressing the formation of blisters in tungsten coatings (CAE).

CONCLUSIONS

The surface topography of W bulk foil and W coatings that are deposited by the cathodic arc evaporation and the argon ion sputtering and a comparison of changes of the surface microstructure under the influence of particles of low-energy hydrogen (deuterium) and helium plasma were studied.

It is established formation of blisters on the surface of tungsten foil (20 µm thickness) bombarded at 300 K with 0.5 keV/H^+ or 1 keV He^+ and simultaneously

$H_2^+ + He^+$ with a dose for each type of particles equal to $1 \cdot 10^{24}$ ion/m^2.

It was found plasma-induced blistering on surface of W coatings deposited by argon ion sputtering and having a columnar structure. The average size of blisters is comparable for the tungsten foil and coating, but in the coating the density of blisters is more than four times less.

Irradiation of tungsten coatings produced by the CAE did not lead to the formation of blisters. Only the process of physical sputtering is observed. Sputtering coefficients are $1.14 \cdot 10^{-2}$ at./ion for hydrogen exposure.

REFERENCES

1. M. Rieth, S.L. Dudarev, S.M. Gonzalez de Vicente, J. Aktaa, T. Ahlgren, S. Antusch, D.E.J. Armstrong, M. Balden, N. Baluc, M.F. Barthe, W.W. Basuki, M. Battabyal, C.S. Becquart, D. Blagoeva, H. Boldyryeva, J. Brinkmann, M. Celino, L. Ciupinski, J.B. Correia, A. De Backer, C. Domain, E. Gaganidze, C. García-Rosales, J. Gibson, M.R. Gilbert, S. Giusepponi, B. Gludovatz, H. Greuner, K. Heinola, T. Höschen, A. Hoffmann, N. Holstein, F. Koch, W. Krauss, H. Li, S. Lindig, J. Linke, C. Linsmeier, P. López-Ruiz, H. Maier, J. Matejicek, T.P. Mishra, M. Muhammed, A. Muñoz, M. Muzyk, K. Nordlund, D. Nguyen-Manh, J. Opschoor, N. Ordás, T. Palacio, G. Pintsuk, R. Pippan, J. Reiser, J. Riesch, S.G. Roberts, L. Romaner, M. Rosi´nski, M. Sanchez, W. Schulmeyer, H. Traxler, A. Ureña, J.G. van der Laan, L. Veleva, S. Wahlberg, M. Walter, T. Weber, T. Weitkamp, S. Wurster, M.A. Yar, J.H. You, A. Zivelonghi. Recent progress in research on tungsten materials for nuclear fusion applications in Europe // *J. Nucl. Mater*. 2013, v. 432, p. 482-500.

2. R. Panek, J. Adamek, M. Aftanas, P. Bilkova, P. Boohm, F. Brochard, P. Cahyna, J. Cavalier, R. Dejarnac, M. Dimitrova, O. Grover, J. Harrison, P. Hacek, J. Havlicek, A. Havranek, J. Horacek, M. Hron, M. Imrisek, F. Janky, A. Kirk, M. Komm, K. Kovarik, J. Krbec, L. Kripner, T. Markovic, K. Mitosinkova, J. Mlynar, D. Naydenkova, M. Peterka, J. Seidl, J. Stoockel, E. Stefanikova, M. Tomes, J. Urban, P. Vondracek, M. Varavin, J. Varju, V. Weinzettl, J. Zajac. Status of the COMPASS tokamak and characterization of the first H-Mode // *Plasma Phys. Control. Fusion*. 2016, v. 58, p. 014015.

3. M.J. Simmonds, Y.Q. Wang, J.L. Barton, et al. Reduced deuterium retention in simultaneously damaged and annealed tungsten // *Journal of Nuclear Materials.* 2017, v. 494, p. 67-71.

4. S. Sakurada, K. Yuyama, Y. Uemura, H. Fujita, C. Hu, T. Toyama, N. Yoshida, T. Hinoki, S. Kondo, M. Shimada, D. Buchenauer, T. Chikada, Y. Oya. Annealing effects on deuterium retention behavior in damaged tungsten // *Nucl. Mater. Energy*. 2016, v. 9, p. 141-144.

5. R.E. Nygren, R. Raffray, D. Whyte, M.A. Urickson, M. Baldwin, L.L. Snead. Making tungsten work // *J. Nucl. Mater.* 2011. v. 417, p. 451-456.

6. M.V. Korobova, N.V. Avramenko, A.G. Bogachev, N.V. Rozhkova, E. Osawa. Nanophase of water in nano-diamond gel // *J. Phys. Chem. C*. 2008, v. 111, p. 7330-7334.

7. I. Smid, M. Akiba, G. Vieider, L. Plooch. Development of tungsten armor and bonding cooper for plasma interactive components // *J. Nucl. Mater*. 1998, v. 258-263, p. 160-172.

8. G.D. Tolstolutskaya, A.S. Kuprin, V.N. Voyevodin, A.V. Nikitin, V.D. Ovcharenko, V.A. Belous, R.L. Vasilenko, I.E. Kopanets. Blistering of W, Ta and W-Ta coatings under the influence of particles of low-energy hydrogen plasma // *Problems of Atomic Science and Technology*. 2017, N 5 (111), p. 83-90.

9. V.Kh. Alimov, W.M. Shu, J. Roth, S. Lindig, M. Balden, K. Isobe, T. Yamanishi. Temperature dependence of surface topography and deuterium retention in tungsten exposed to low-energy, high-flux D plasma // *J. Nucl. Mater.* 2011, v. 417, p. 572-575.

10. M.R. Gilbert, S.L. Dudarev, S. Zheng, L.W. Packer, J.Ch. Sublet. An integrated model for materials in a fusion power plant: transmutation, gas production, and helium embrittlement under neutron irradiation // *Nucl. Fusion*. 2012, v. 52, p. 083019.

11. A. Manhard, K. Schmid, M. Balden, W. Jacob. Influence of the microstructure on the deuterium retention in tungsten // *J. Nucl. Mater*. 2011. v. 415, p. S632-S635.

12. V.M. Lunyov, A.S. Kuprin, V.D. Ovcharenko, V.A. Belous, A.N. Morozov, A.V. Ilchenko, G.N. Tolmachova, E.N. Reshetnyak, R.L. Vasilenko. Structure and properties of W, Ta, and W-Ta coatings deposited with the use of a gas-plasma source // *Вопросы атомной науки и техники. Серия «Вакуум, чистые материалы, сверхпроводники».* 2016, №1(101), с. 140-144.

13. A.V. Nikitin, G.D. Tolstolutskaya, V.V. Ruzhytskyi, V.N. Voyevodin, I.E. Kopanets, S.A. Karpov, R.L. Vasilenko, F.A. Garner. Blister formation on 13Cr2MoNbVB ferritic-martensitic steel exposed to hydrogen plasma // *Journal of Nuclear Materials*. 2016, v. 478, p. 26-31.

14. Jiangang Yu, Wenjia Han, Zhe Chen, Kaigui Zhu. Comparison of blistering of W bulk and film deposited by magnetron sputtering under helium irradiation // *Nuclear Materials and Energy*. 2017, v. 12, p. 588-592.

15. V.A. Belous, M.N. Bondarenko, G.P. Glazunov, A.V. Ilchenko, A.S. Kuprin, A.L. Konotopskiy, V.M. Lunyov, V.D. Ovcharenko. Erosion behavior of W-Ta coatings in plasmas of stationary mirror penning discharges // *Problems of Atomic Science and Technology*. *Series "Plasma Physics" (23).* 2017, N 1(107), p. 109-111.

16. P. Wang, W. Jacob, S. Elgeti. Deuterium retention in tungsten films after different heat treatments // *Journal of Nuclear Materials*. 2015, v. 456, p. 192-199.

17. F.T.N. Vüllers, R. Spolenak. Alpha-vs, beta-W nanocrystalline thin films: A comprehensive study of sputter parameters and resulting materials' properties // *Thin Solid Films.* 2015, v. 577, p. 26-34.

Article received 21.03.2018

СРАВНЕНИЕ БЛИСТЕРИНГА ПРИ ОБЛУЧЕНИИ МАССИВНОГО ВОЛЬФРАМА И W-ПОКРЫТИЙ H_2, D_2 И He-ПЛАЗМОЙ

А.В. Никитин, А.С. Куприн, Г.Д. Толстолуцкая, Р.Л. Василенко, В.Д. Овчаренко, В.Н. Воеводин

Изучены изменения топографии поверхности массивного вольфрама, полученного методом порошкового спекания (толщиной 20 мкм), и W-покрытий осажденными вакуумно-дуговым методом и ионным распылением под воздействием низкоэнергетической водородной (дейтериевой) и гелиевой плазмы при комнатной температуре. Поверхностные модификации, индуцированные плазменным облучением, изучались с помощью сканирующей электронной микроскопии. После облучения гелиевой и дейтериевой плазмой на поверхности образцов фольги W и покрытий, нанесенных ионным распылением, наблюдались многочисленные блистеры. Поверхность W-покрытий, осажденных вакуумно-дуговым способом, подвергалась только распылению при тех же условиях облучения.

ПОРІВНЯННЯ БЛІСТЕРІНГА ПРИ ОПРОМІНЕННІ МАСИВНОГО ВОЛЬФРАМУ І W-ПОКРИТТІВ H_2, D_2 ТА He-ПЛАЗМОЮ

А.В. Нікітін, О.С. Купрін, Г.Д. Толстолуцька, Р.Л. Василенко, В.Д. Овчаренко, В.М. Воєводін

Вивчено зміну топографії поверхні масивного вольфраму, отриманого методом порошкового спікання (товщиною 20 мкм), і W-покриттів осадженими вакуумно-дуговим методом та іонним розпиленням під впливом низькоенергетичної водневої (дейтерієвої) і гелієвої плазми при кімнатній температурі. Поверхневі модифікації, індуковані плазмовим опроміненням, вивчалися за допомогою сканувальної електронної мікроскопії. Після опромінення гелієвою і дейтерієвою плазмою на поверхні зразків фольги W і покриттів, нанесених іонним розпиленням, спостерігалися численні блістери. Поверхня W-покриттів, осаджених вакуумно-дуговим способом, піддавалася тільки розпорошенню при тих же умовах опромінення.