Study of Properties of Tungsten Irradiated in Hydrogen Atmosphere

I. Tazhibaeva[1], M. Skakov[1], V. Baklanov[1], E. Koyanbaev[1], A. Miniyazov[1], T. Kulsartov[1], Yu. Ponkratov[1], Yu. Gordienko[1], Zh. Zaurbekova[1], I. Kukushkin[1], E. Nesterov[2]

[1] National Nuclear Center, branch Institute of Atomic Energy, Kurchatov, Kazakhstan

[2] Tomsk Polytechnic University, Tomsk, Russia

E-mail contact of main author: tazhibayeva@ntsc.kz

Abstract. The research goal is irradiation of the tungsten samples in hydrogen, and post irradiation studies of the samples for microstructure changes after irradiation and their comparison with non-irradiated samples. During the experiments we obtained the comparative characteristics of the microstructure and microhardness of tungsten samples, which were exposed to reactor irradiation in hydrogen and helium atmosphere; we determined the hydrogen diffusion parameters in double forged pure tungsten, and W sorption characteristics towards hydrogen during reactor irradiation. The mechanism was proposed to describe the hydrogen interaction with tungsten during irradiation. Simulation experiments to study the effects of reactor irradiation on the characteristics of the hydrogen isotopes interaction with structural materials of fusion facilities will allow to establish correlation and synergistic effects between influence of fission and fusion reactors on the structural materials of fusion reactors.

1. Introduction

Replenishment of the calculation and experimental database on the properties of structural materials under plasma impacts and gamma-neutron radiation is important to predict the behavior of the materials, in particular, the materials of ITER reactor before its commissioning. Tungsten as a material of low co-deposition rate and high energy threshold of co-deposition (~50 eV) will be used in the components (baffle and plasma-facing elements of divertor), which are exposed to high heat loads under normal operation of reactor, as well as to plasma disruptions, that may lead to surface erosion of plasma-facing structural components. Analysis of the published data showed that currently known grades of industrially manufactured tungsten have caused serious concerns as for its stability and resistance to heat loads in a tokamak-reactor, especially, in the presence of hydrogen, and neutron and other radiations [1]. Taking into account the synergistic nature of cracking in tungsten, as in any other structural materials, due to simultaneous exposure to heat plasma flows, hydrogen isotopes, and neutron and gamma radiation, it is necessary to conduct the experiments to study the effects of reactor irradiation on the parameters of the hydrogen isotopes interaction with tungsten and investigation of properties of tungsten after irradiation.

2. Experimental

2.1. Description of Tungsten Samples

The study object were the samples of polycrystalline tungsten with a purity of 99,99%, double forged pure, less anisotropic than single forged W (tungsten forged in two orthogonal directions aiming to obtain a dense and nearly isotropic grain structure); the samples were manufactured in Julich, Germany. Conditional name of this grade is DF (double forged) tungsten in which anisotropy of grain structure is minimum. The sample size was 12×12×5 mm.

2.2.Irradiation Conditions at Reactor WWR-K

Irradiation of tungsten samples was carried out in a side channel (10-2) of WWR-K reactor of Institute of Nuclear Physics, Almaty, Kazakhstan. Irradiation device included the external case (ampoule), where two capsules with tungsten samples were located (see FIG.1). Ampoule was filled with air of atmosphere pressure. Ampoule with capsules was not sealed and communicated with atmosphere through the tube (diameter of 6 mm, thickness of 1 mm, length of 5000 mm). Capsules were sealed and filled with various gases: hydrogen and helium (pressure of 30 KPa and temperature of 20 $^{\circ}$C). Top capsule was filled with hydrogen, bottom capsule was filled with helium. The ampoule device with two capsules was placed in the case of peripheral water channel of WWR-K reactor. Ampoule was cooling with water of 40 $^{\circ}$C during irradiation. All the ampoule and capsule materials were made from stainless steel Cr18Ni10Ti. There were carried out nine campaigns at the reactor WWR-K, irradiation time was 3255 hours or 135.6 days. Flux density was $7.3 \cdot 10^{13}$ n/cm^{2}s for thermal neutrons, $6.8 \cdot 10^{12}$ n/cm^{2}s for fast neutrons. Gained fluence was $8{,}59 \cdot 10^{20}$ n/cm^2 for thermal neutrons and $7{,}96 \cdot 10^{19}$ n/cm^2 for fast neutrons. Average temperature in ampoule device was 720 $^{\circ}$C.

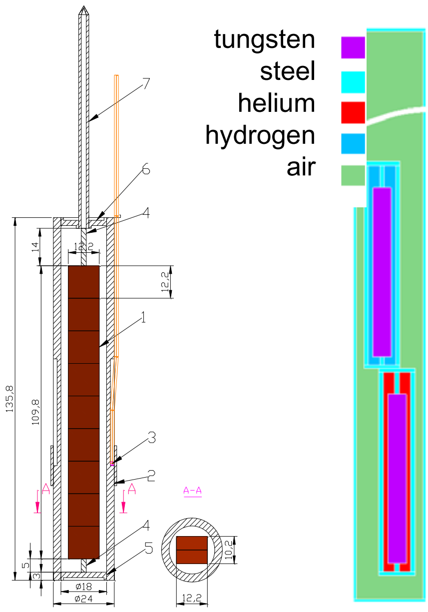

FIG. 1. Layout of ampoule devices with samples: 1 - samples of tungsten, 2 - body of the ampoule, 3 – thermocouple, 4 - the stops, 5 - the bottom, 6 - a cover, 7 – rod.

In total we irradiated 9 tungsten samples in hydrogen and 9 samples in helium. The samples were studies with both polished and untreated surfaces.

2.3.Analytical Equipment and Methods

Examination of the tungsten samples was performed to obtain the data on the changes in the structure and physics-mechanical properties of the material as a result of reactor irradiation. Gamma spectrometric measurements to determine the isotopic composition and activity of the radioactive emitters in the tungsten samples were carried out using a spectrometric complex "InSpector" with a scintillation detector, Canberra. The activity of the irradiated samples was calculated by isotope W^{185}. Micro-structural studies of tungsten samples irradiated in hydrogen and helium were carried out using the optical microscopes and scanning electron microscope. The experiments to study the parameters of hydrogen interaction with tungsten were carried out by thermo-desorption spectroscopy under linear heating with mass-spectrometer registration of the gases released during heating.

3. Results and Discussion

According to the manufacturing technology, the DF-grade tungsten is double-forged with the smallest anisotropy of the grain structure. The activity of the samples after one year of irradiation corresponded to the relatively high values ranging from $2.20 \cdot 10^5$ Bq to $3.30 \cdot 10^5$ Bq. Density of the samples irradiated in hydrogen was averagely lesser than the ones irradiated in helium. The surface microhardness of the samples irradiated in hydrogen was averagely more than 5.43 GPa ($HV_{0.1}$ 553 kgf/mm^2) than the samples irradiated in helium 5.12 GPa ($HV_{0.1}$ 522 kgf/mm^2). At that, micro-hardness of non-irradiated DF-grade tungsten samples was 5.12 GPa ($HV_{0.1}$ 522 kgf/mm^2). (*Reference value of micro-hardness by Vickers for conventional polycrystalline tungsten is equal to 3.43 GPa*).

3.1.Study of Microstructure

The results of micro-structural studies showed that the tungsten surface eroded during long-term irradiation. At that, the surface suffered the changes in its relief and a noticeable difference of microstructure by the individual grains. The grains are structurally differed with both smooth surface and relief structure. A number of studies has shown the similar results; this effect was attributed to the fact that the different crystal planes have different resistance to erosion [2, 3]. The tungsten samples with pre-polished surface, which was irradiated in hydrogen, showed the erosion of surface structure in the form of etched grains. The structure of sample surface revealed the micropores. For example, U5 DF sample had the large pores of 1-3 microns (FIG. 2).

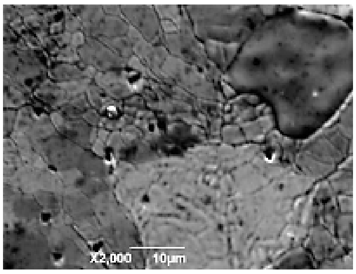

FIG. 2. The typical microstructure of the surface of the tungsten samples irradiated in hydrogen: sample U5 DF – pores of 1-3 μm.

The microstructure of the surface of some samples irradiated in hydrogen showed the small inclusions, the sizes of a few microns. The distribution of inclusions was uniform on a surface, while there was an increased concentration in the microstructure of the grains with a relief structure (FIG. 3(a)).

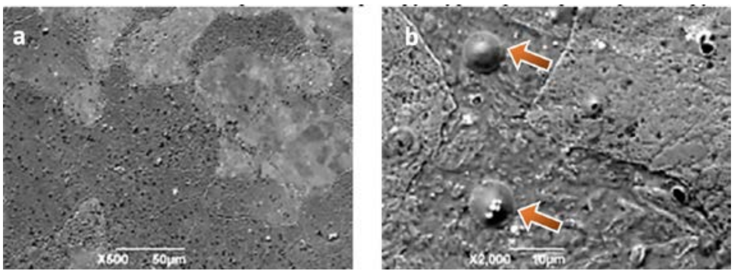

FIG. 3. The microstructure of the surface of the tungsten samples irradiated in hydrogen: formation of pores (a - S8 DF) and blisters (b- R5 DF)

The surface microstructure of R5 DF sample after irradiation in hydrogen showed the bubbles (blisters), with a diameter less than 10 microns (FIG. 3b). This agglomeration of hydrogen in the cavities under the surface was caused by the high pressure, which removed a part of tungsten (in general, only one grain or portion thereof), and which looked like as the bubbles from above. Under high magnifications we could see the signs of the surface melting in the form of tear drops. This is a characteristic phenomenon for tungsten exposed by hydrogen ions [4, 5] usually in the temperature range of 200÷650°C, but it has not been previously observed for reactor irradiation.

Study of the surface microstructure of tungsten samples irradiated in a helium showed little erosion. S4 DF sample had micro-pores, which were unevenly distributed over the surface (FIG. 4a).

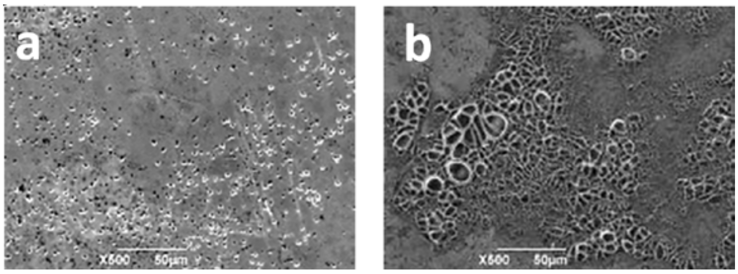

FIG. 4. Features of the surface microstructure of the tungsten samples irradiated in He: formation of micropores (a – S4 DF) and thin films (b – V6 DF).

The surface of V6 DF sample irradiated in helium showed the formations of thin films that were peeling at the edges (FIG. 4b). The study of the structure of T2 DF unpolished sample irradiated in hydrogen atmosphere showed the presence of surface erosion and cracks along the grain boundaries (FIG. 5a). The melting signs were observed in the near-surface layer. Since during preparation of the samples the surface before and after irradiation was not subjected to grinding and polishing, so this may be the result of electroerosion cutting. The same pattern was observed in R8 DF sample with unpolished surface irradiated in helium (FIG. 5b).

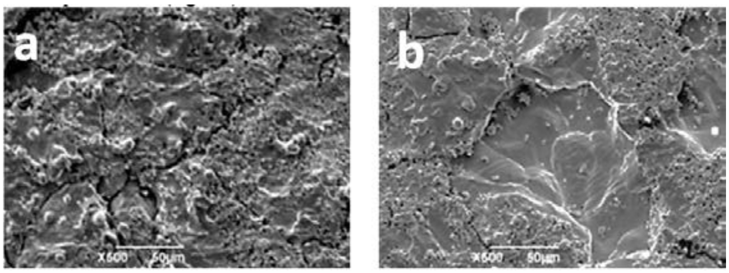

FIG. 5. Comparison of the surface microstructure of the tungsten samples with unpolished surfaces irradiated in hydrogen and helium: T5 DF (H) and R8 DF (He)

Texture index of the samples irradiated in helium was lower than the ones irradiated in hydrogen. Reduction of texture index may indicate a partial disorientation of the crystallites during irradiation. Taking into account that the changes were detected in the surface microstructure of the irradiated polycrystalline tungsten (particularly, the dependence of nature of individual grains erosion from crystallographic planes), it was necessary to determine the crystallographic texture of the material.

As known, the crystallographic texture is the preferred orientation of certain crystallographic planes and directions in the different grains of the polycrystalline in relation to the outer planes and directions. The presence of preferred orientation increases the anisotropy of the material properties and can significantly alter the performance characteristics of a product [6]. Texture of the studied polycrystalline tungsten was set during manufacture of the material, whereby a material was obtained with low anisotropy grains.

In order to determine the degree of orientation of the crystallographic planes in the grains on the surface of the studied polycrystalline tungsten we calculated the texture index of the samples. At that, the study of the texture required the clear knowledge of the direction and nature of mechanical impact, which caused the preferred orientation of the crystallites. Under otherwise equal conditions, a decrease in texture index may indicate partial disorientation of the crystallites during irradiation.

A study of the crystallographic structure of the initial state of polycrystalline tungsten showed the presence of texture, likely deformation texture. The analysis results also showed that there was a number of crystal defects due to the micro- and macrostresses, and the presence of dislocations. After irradiation the defects partially eliminated, which was confirmed by narrowing of the half-width of the diffraction peaks and increase of the their integrated intensity in the samples after irradiation.

Texture indicator *Π* was calculated by the method of standard deviation of reduced pole densities from similar characteristics of the sample without a texture in which planes arrangement had equal probability, n = 6

$$\varPi = \frac{\sum_i (\varPhi_{h_i k_i l_i} - 1)^2}{n-1} \qquad (1)$$

The reduced pole density represented the degree of deviation of the crystallite orientation from uniform distribution, which is in the absence of texture. For a no-texture sample, the reduced pole densities (RPD) of all lines are equal to one. The increase in the RPD values for any line indicated an increase in the number of grains, orientation of which respective planes was parallel to an investigated surface. The reduced pole density $\Phi_{110}/\Phi_{100}/\ \Phi_{111}$ is expressed as follows:

$$\Phi_{hkl} = P_{hkl} / P^0_{hkl} \qquad (2)$$

Changes in the texture parameters may occur under certain thermo-mechanical impacts on the material. In the case of irradiated tungsten, a significant change in the texture should not be expected, because significant change in the arrangement of the crystal lattice grains required a re-crystallization processes, which occurs under temperatures $T_{re\text{-}c} \cong 0.4T_{pl}$. Taking into account the duration and irradiation temperature (t=3255 hours, T_{av}=720°C), it is likely the changes in the lattice imperfection were caused by long-term reactor irradiation and temperature.

The values of reduced pole density and texture index of the samples irradiated in hydrogen and helium are given in Table 1. During the X-ray diffraction analysis the depth of material analysis was not greater than 3 microns (linear absorption coefficient for copper radiation of 330 mm^{-1}) and thus it reflected the characteristics of only a thin near-surface layer. For this approach, the character of processing and, for example, surface microrelief, became significant.

The results showed that most of the samples are characterized by the predominant orientation of grains with crystallographic planes (110) and (111) parallel to the surface under study. Texture indicator that characterizes the deviation of the distribution of the pole densities from equilibrium varied from 1.1 to 1.5 for the majority of the samples, without apparent dependence on the type of samples. However, there was a second group of samples, in which the texture component was in the range from 0.4 to 0.8. At the same time, it is important to note that the observed differences in the distribution of RPD and the texture index values will be different for samples cut out of the same material in different directions.

TABLE 1. VALUES OF REDUCED POLE DENSITY AND TEXTURE INDEX OF DF GRADE TUNGSTEN SAMPLES IRRADIATED IN HYDROGEN AND HELIUM.

#	Main marking	Additional marking	Period of crystallography lattice a_0, Å	RPD $\Phi_{110}/\Phi_{100}/\Phi_{111}$	Texture index, Π
Samples irradiated in hydrogen					
1	3H	U5 DF 117	3.1659	0.02/2.88/2.46	1.30
2	4H	S8 DF 115	3.1659	0.06/2.57/2.33	1.13
3	5H	R5 DF 113	3.1666	0.03/4.17/1.12	1.6
4	6H	Q7 DF 111	3.1660	0.09/2.38/0.74	0.8
5	7H	R6 DF 103	3.1657	0.03/3.25/1.49	1.21
6	9H	W6 DF 109	3.1659	0.04/2.83/1.90	1.11
7	11H	T6 DF 105	3.1661	0.02/3.21/2.01	1.31
8	12H	Q5 DF 101	3.1661	0.02/3.91/1.39	1.51
Samples irradiated in helium					
9	1He	T5 DF 116	3.1660	0.11/2.10/1.20	0.67
10	2He	S4 DF 104	3.1658	0.02/2.88/2.46	1.30
11	6He	S6 DF 114	3.1661	0.03/3.20/2.09	1.33
12	8He	S5 DF 106	3.1660	0.01/3.29/2.20	1.40
13	9He	V5 DF 118	3.1660	0.01/3.37/2.11	1.41
14	10He	V6 DF 108	3.1661	0.02/3.30/2.12	1.38
15	11He	Q6 DF 102	3.1660	0.10/2.36/1.26	0.77
16	12He	R8 DF 122	3.1656	0.31/2.03/1.99	0.79
17	14He	Q8 DF 112	3.1662	0.55/1.69/0.87	0.38

3.2.Experiments on Thermal Desorption of Tungsten Samples

TDS experiments were conducted with the samples cut from the original tungsten samples irradiated in helium (sample size 5.8×5×0.6 mm) and hydrogen (sample size 6.1×5×0.4 mm). Experiments were conducted at a heating rate of 15 K/min in the temperature range (293–1783 K) and showed that the major release peaks of hydrogen gases (methane and hydrogen) are observed at high temperatures. (See. FIG. 6 and 7).

There is a peak at ~ 1700 K at hydrogen release graph for both samples. The methane release graph for both samples shows increase in pressure at ~ 1640-1780 K; at That methane release for the sample irradiated in helium is much larger than for the sample irradiated in hydrogen. The methane release graph for the sample irradiated in hydrogen shows a small but noticeable peak at temperature about 975 K (FIG. 6). The data obtained allowed us to build overall temperature dependence of hydrogen release from the samples (FIG. 7), and amounts were calculated of released hydrogen normalized to the sample weight.

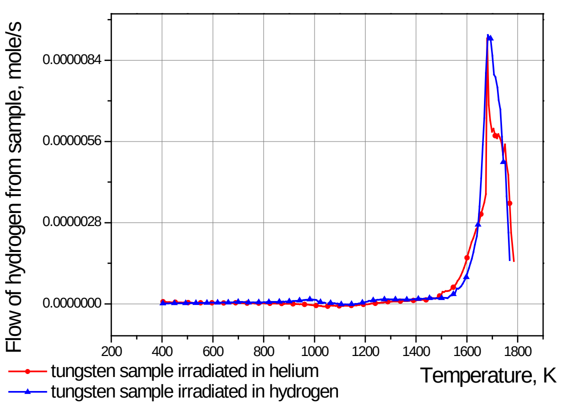

FIG. 6. Dependence of change in hydrogen partial pressure from sample temperature in working chamber of experimental facility

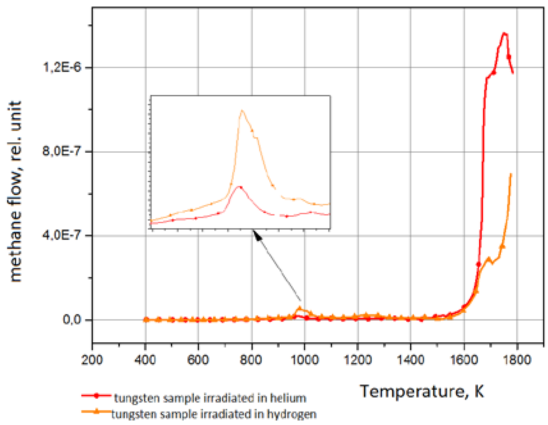

FIG. 7. Dependence of change in methane partial pressure from sample temperature in working chamber of experimental facility

FIG. 8 and Table 2 shows that hydrogen concentration in the tungsten sample irradiated in hydrogen was higher than the hydrogen concentration of the tungsten sample irradiated in a helium atmosphere.

TABLE 2. AMOUNT OF RELEASED HYDROGEN (NORMALIZED TO SAMPLE WEIGHT).

	sample irradiated in helium	**sample irradiated in hydrogen**
Amounts of released hydrogen in H_2, mole/g	1.30E-06	1.88E-06
Amounts of released hydrogen in CH_4, mole/g	4.27E-07	1.41E-07
Total amount of released hydrogen, mole/g	1.72E-06	2.02E-06

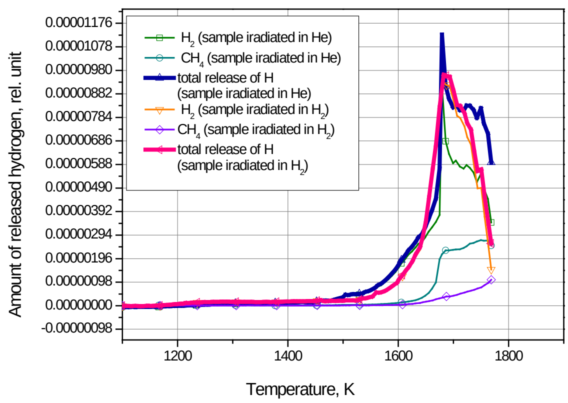

FIG 8. TDS dependencies of hydrogen gases release from tungsten samples.

Release of hydrogen from tungsten sample irradiated in hydrogen atmosphere was mainly in the form of molecules H_2 (93%) and a slightly in a form of molecules CH_4 (7%). Release of hydrogen from tungsten sample irradiated in a helium atmosphere occurred in the form of molecules H_2 (75%), as well as molecules of CH_4 (25%).

4. Conclusion

4.1. Changes in Microstructure of Irradiated Samples

The characterization of DF-grade tungsten samples allowed us to obtain comparative data on the microstructure of the material surface after irradiation in hydrogen and helium environments. It is shown that the microstructure of the polished samples irradiated in hydrogen is characterized by presence of erosion; there were detected micropores, inclusions, and blisters in the form of bubbles, which had not been observed previously under reactor irradiation in a hydrogen atmosphere. Investigation of the surface microstructure of tungsten samples irradiated in a helium environment showed a slight erosion.

The study of structure of the samples with unpolished surfaces before and after irradiation showed the presence of surface erosion and micro-cracks along the grain boundaries. There was the melting signs in the near-surface layer. The surface microhardness of the samples irradiated in hydrogen was averagely more than 5.43 GPa ($HV_{0.1}$ 553 kgf/mm^2) than the samples irradiated in helium 5.12 GPa ($HV_{0.1}$ 522 kgf/mm^2).

The values of reduced pole density and texture index were defined for DF-grade tungsten samples irradiated in hydrogen and helium.

4.2. Absorption and release of hydrogen from the irradiated samples

The hydrogen concentration in the tungsten sample irradiated in hydrogen was higher than in the tungsten sample irradiated in helium atmosphere.

Release of hydrogen from tungsten samples irradiated in hydrogen and helium occurred primarily in the form of molecules H_2 and CH_4. The observed difference in TDS dependencies of release of hydrogen gases from tungsten samples can be explained by decarbonization of the surface layer of tungsten samples irradiated in hydrogen. As a result of high-temperature hydrogen corrosion during irradiation, a part of carbides apparently interacted with hydrogen by reaction $WC+2H_2>CH_4+W$.

During the methane release from the tungsten samples irradiated in hydrogen, we could observe the prominent peak at about 975 K. CH_4 release for these samples exceeded the release from tungsten samples irradiated in helium by more than 100%, which is probably indicative on some special state of hydrogen into tungsten, which occurred under the combined impact of hydrogen and neutron irradiation.

5. Acknowledgements

This research has been performed in the framework and support of the research project “Investigation of Changes in Structure and Properties of Tungsten Irradiated by Neutrons, Alpha-Particles and Heavy Ions within the Temperature Range up to 600'-to Predict its Behavior in Thermonuclear Fusion Reactors.”, CRP No. 17398, IAEA.

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