Investigation of tungsten surface carbidization under plasma irradiation

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Abstract. This paper presents the results of studying the formation of a carbide layer under various experimental conditions and the choice of the optimal parameters for carbidization of the tungsten surface under plasma irradiation in methane. Therefore, to assess the effect of the surface temperature of a tungsten sample during experimental work, the surface temperature of the sample was 1300–1700°C, and to assess the effect of the irradiation time, a range within 300–2400 s was selected. From the results of X-ray phase analysis of the surface of tungsten samples, concluded that the temperature of the sample surface and the duration of irradiation have a significant effect on the formation of a carbidized layer on the tungsten surface during plasma irradiation on plasma-beam installation.

1. Introduction
As is known, tungsten (W) and carbon (C) are the most suitable materials as plasma facing materials for a fusion reactor divertor [1]. The presence of structural materials in the installation chamber, as well as their impurities, as a result of erosion, will lead to the formation of mixed layers in the surfaces facing the plasma during redeposition.

To obtain thin carbon films, there are various methods, such as magnetron sputtering, mixing of plasma flows W and C, chemical deposition of C from the gas phase or evaporation of C using an electron beam evaporator [2–7].

Experimental work on the carbidization of the tungsten surface was carried out on plasma-beam installation (PBI) at a sample surface temperature of 1273 K with a residence time of 600 s in methane; however, peaks of low intensity of the crystalline phases WC, W$_2$C are observed and the carbidized layer is not noted [8]. A series of earlier experiments on PBI at a constant surface temperature of 1773 K showed that at this temperature, carbidization occurs with the highest percentages of W$_2$C, WC depending on the irradiation time of 600 s and 3600 s, respectively [9].

In a number of works by the German professor Ch. Linsmeier [4–6] presents studies of the formation of tungsten carbides after deposition of carbon films on a tungsten substrate. Carbon films were deposited at room temperature by the C evaporation method using an electron beam evaporator. The temperature dependence of carbide formation was investigated upon further annealing of the...
tungsten substrate with a carbon film. This method is fundamentally different from the method of carbidization by a beam-plasma discharge. Nevertheless, the method used will make it possible to determine the temperature range of carbide formation in the process of plasma irradiation in PBI.

Results of [10] show that from a temperature of 770 K the formation of semi-carbide \( \text{W}_2\text{C} \) begins. At temperatures above 870 K, this phase and all residual carbon are converted to monocarbide WC. After heating to 1270 K, most of the carbon reacted with tungsten to form WC. Along the course of the curve, it can be expected that at higher temperatures there will be a complete conversion to WC. In all cases, the expected temperature was reached within 10 minutes and maintained for 30 minutes.

In the later work of Professor Ch. Linsmeier [6] investigated the reaction of carbon films on tungsten substrates at annealing temperatures up to 1700 K. Strong diffusion is observed at temperatures above 1000 K and leads to the mutual diffusion of carbon and tungsten and the formation of carbides. The first carbide phase formed is semi-carbide \( \text{W}_2\text{C} \), and at temperatures above 1500 K, the proportion of monocarbide WC increases. This work increases the temperature range of carbide formation.

Despite the different methods of carbide formation, it can be noted that changing the irradiation and exposure time also affects the carbidization of the tungsten surface.

Sum up, based on the theoretical analysis, it was found that diffusion and interaction between W and C begins at 1150 K and leads to the formation of \( \text{W}_2\text{C} \) semi-carbide at the interface. At temperatures above 1200 K, the proportion of monocarbide WC increases. However, in these experiments, the exposure time plays an important role. The study of carbide formation at higher temperatures is of interest.

Therefore, to assess the effect of the surface temperature of a tungsten sample during experimental work, the surface temperature of the sample will vary in the range 1573-1973 K, and to assess the effect of the irradiation time, a range within 300-2400 s was selected.

2. Experimental part

2.1. Experimental installation

In accordance with the goal of the program to ensure the effectiveness of scientific research at the Kazakhstan Materials Science Tokamak (KTM) facility in 2008, an experimental test simulator with a plasma-beam installation (PBI) was created.

A simulation stand with a plasma-beam installation (figure 1) was developed to support the creation and operation of the Kazakhstan materials science tokamak KTM for testing small-sized samples from advanced structural materials and KTM equipment. The installation is focused on versatility and the possibility of quick changeover to solve various specialized tasks.

**Figure 1.** Plasma-beam installation (PBI). Parameters: Electron beam power density \( \leq 500 \text{ kW/cm}^2 \); Electron temperature \( \leq 15 \text{ eV} \); Electron energy \( \leq 20 \text{ keV} \); Diameter of electron beam 1–30 mm; Electron beam current \( \leq 250 \text{ mA} \); Peak gas pressure \( \leq 10^{-3} \text{ Torr} \); Plasma ion energy \( \leq 2000 \text{ eV} \); Ion current \( \leq 1000 \text{ mA} \); Ion flux density \( \leq 10^{22} \text{ m}^{-2} \text{s}^{-1} \); Plasma concentration (\( \text{H}_2 \)) \( \leq 10^{16} \text{ m}^{-3} \).
2.2. Materials and methods

To study the effect of temperature and exposure duration on the formation of a carbidized layer, high purity grade tungsten in the form of a 10 mm rod was chosen.

The production of test specimens of tungsten included the following tasks: cutting the workpiece; preparation of the end surface of cut blanks and obtaining initial data on geometric dimensions.

Identical workpieces in the form of tablets 2.0 ± 0.1 mm thick were cut from a tungsten rod. Recrystallization annealing was used to eliminate the work-hardening caused by plastic deformation that occurs during the manufacture of the rods, as well as changes on the surface layer of the samples resulting from cutting the tungsten rod into blanks. The recrystallization annealing of the samples was carried out on PBI in the electron beam mode. The temperature of the sample was controlled from the back side with a VR-5/20 thermocouple and from the front side with an ISR-6 pyrometer. The temperature of the face side of the sample was 1350°C with a 60-minute exposure.

X-ray phase analysis was carried out under the following conditions: the exposure time (time per step) during shooting was 30.6 s, the scanning step size for diffractograms was 2θ = 0.026°, the investigated angular range was 2θ = 5-153°. The PIXcel1D detector operating mode is a scanning linear detector.

3. Results and discussion

Carbidization experiments were carried out at temperatures of 1300°C and 1700°C with exposure duration from 300 to 2400 s. Table 1 shows the experimental conditions.

| Table 1. Identification of samples and experimental conditions. |
|---------------------------------------------------------------|
| Sample | Electron beam power (W) | Working gas pressure (methane) (Torr) | Ion current (mA) | Temperature (°C) | Exposure duration (s) |
|--------|------------------------|--------------------------------------|-----------------|-----------------|---------------------|
| 1      | 616                    | 1.01·10⁻³                           | 105             | 1300 ± 10       | 300                 |
| 2      | 1093                   | 1.02·10⁻³                           | 153             | 1700 ± 10       | 300                 |
| 3      | 499                    | 1.05·10⁻³                           | 103             | 1300 ± 10       | 1200                |
| 4      | 958                    | 1.03·10⁻³                           | 142             | 1700 ± 10       | 1200                |
| 5      | 530                    | 1.05·10⁻³                           | 106             | 1300 ± 10       | 1800                |
| 6      | 1086                   | 1.01·10⁻³                           | 152             | 1700 ± 10       | 1800                |
| 7      | 460                    | 1.01·10⁻³                           | 94              | 1300 ± 10       | 2400                |
| 8      | 845                    | 1.10·10⁻³                           | 136             | 1700 ± 10       | 2400                |

The study of the carbidization of the tungsten surface was carried out by the method of X-ray phase analysis. The metallic tungsten phase has a cubic system (space group Im-3m). Transition metals with a body-centered cubic (BCC) structure (V, Nb, Ta, Cr, Mo, W) form carbides with a cubic or hexagonal metal sublattice. A change in the crystal structure of metals during the formation of carbides indicates strong metal-carbon interactions, while direct interactions between carbon atoms are negligible. Tungsten semi-carbide (W₂C) and tungsten monocarbide (WC) are isolated. In addition, in the range of compositions between W₂C and WC, there is a cubic phase γ-WCₓ (x ≤ 1); according to modern concepts, it is referred to crystalline modifications of tungsten monocarbide [11].

Figure 2 shows results of X-ray analysis. In sample 1, the main phase is the hexagonal tungsten semi-carbide phase. Low intensity peaks are identified as peaks belonging to the tungsten monocarbide and tungsten metal phase. In the phase composition of sample 2, the content of the semi-carbide phase and the phase of metallic tungsten is practically the same. There is no tungsten monocarbide phase.
Figure 2. Diffraction patterns of the investigated samples (the places of localization of the peaks of the tungsten monocarbide phase are marked in yellow, green - the tungsten semi-carbide phase, blue - the tungsten peaks).

The highest content of the semicarbide phase (more than 95%) was obtained in the phase composition of samples 4, 6 and 8. Peaks of very low intensity, barely distinguishable above the background level, are identified as peaks belonging to the phase of metallic tungsten.

In the composition of sample 3, the main phase is also the phase of tungsten semicarbide of the hexagonal system. Low intensity peaks are identified as peaks belonging to the metallic tungsten phase and the tungsten monocarbide phase, respectively.

In the phase composition of sample 5, the main phase is tungsten semi-carbide; the peaks of tungsten monocarbide have a lower intensity. In sample 7, the main phase is the hexagonal tungsten monocarbide phase. Low intensity peaks are identified as peaks belonging to the metallic tungsten phase and tungsten semi-carbide phase.

The quantitative results of the X-ray phase analysis of the samples are presented in table 2. The data are presented with an accuracy of 0.1% in order to register the appearance of peaks when changing the experimental mode.

Table 2. Results of quantitative phase analysis of samples.

| Sample | W (cubic) | WC (hex., P-6m2) | W2C (hex., P-31m) |
|--------|-----------|------------------|-------------------|
| 1      | 7.9       | 15.2             | 77.0              |
| 2      | 52.8      | -                | 47.2              |
| 3      | -         | 16.5             | 83.5              |
| 4      | 1.4       | -                | 98.6              |
| 5      | -         | 28.2             | 71.8              |
| 6      | 4.5       | -                | 95.5              |
| 7      | -         | 86.1             | 13.9              |
| 8      | 0.4       | -                | 99.6              |
Provided that the sample contains tungsten carbides in the composition range of tungsten monocarbide and semi-carbide, diffractograms carry information about the structural state of the material with a thickness of 1.5-1.4 μm (at an angle of 2θ ~ 30°) to 5.5-4.9 μm (at an angle of 2θ ~ 135°).

4. Conclusion
Carbidization of the tungsten surface using the PBI is a relatively new method that simulates the processes of C deposition and the formation of mixed layers in the tokomak divertor. Nevertheless, this theoretical analysis of the literature shows that a change in the surface temperature of a tungsten sample and exposure time, regardless of the method of deposition of carbon films, will directly affect the surface carbidization of tungsten.

Experimental work was carried out to assess the effect of temperature and exposure duration on the formation of a carbidized layer on the tungsten surface during plasma irradiation on PBI, and an X-ray phase analysis of the surface of tungsten samples was carried out after the experiments.

Based on the results of X-ray phase analysis of coatings of tungsten samples, the following conclusion can be drawn that the formation of semi-carbide at a temperature of 1700°C is completed, regardless of the duration of irradiation. In this case, the formation of tungsten carbide occurs at a temperature of 1300°C and depends on the duration of the exposure.

From the results of X-ray phase analysis of the surface of tungsten samples, it can be concluded that the temperature of the sample surface and the duration of irradiation have a significant effect on the formation of a carbidized layer on the tungsten surface during plasma irradiation on PBI.

Acknowledgments
The work was carried out at the National Nuclear Center of the Republic of Kazakhstan within the framework of a scientific and technical program on the topic "Investigation of the interaction of plasma with a carbidized tungsten surface".

References
[1] Bolt H, Barabash V, Federici G, Linke J, Loarte A, Roth J and Sato K 2002 J. Nucl. Mater. 307–311 43–52
[2] Zellner M B and Chen J G 2004 Surf. Sci. 569 89–98
[3] Romanus H, Cimalla V, Schaefer J A, Spieß L, Ecke G and Pezoldt J 2000 Thin Solid Films 359 146–9
[4] Luthin J and Linsmeier Ch 2000 Surf. Sci. 454–456 78–82
[5] Linsmeier Ch, Luthin J, Klages K U, Wiltner A and Goldstraß P 2004 Phys. Scripta 2004 86–91
[6] Linsmeier Ch, Reinelt M and Schmid K 2011 J. Nucl. Mater. 415 S212–8
[7] Wang P and Jacob W 2014 Nucl. Instrum. Meth. B 329 6–13
[8] Sokолов I A, Skakov M K, Miniyazov A Z, Tulenbergenov T R and Kайрыдь G K 2019 Vestnik KazNAYEN (Bulletin of the Kazakh National Academy of Natural Sciences) 1 44–9 [in Russian]
[9] Zhanbolatova Ġ, Baklanov V, Tulenbergov T, Miniyazov A and Sokolov I 2020 Vestnik NYATS RK (Bulletin of the National Nuclear Center of the Republic of Kazakhstan) 4 77–81 [in Russian]
[10] Massalski T B 1996 Binary Alloy Phase Diagrams (Materials Park: ASM International)
[11] Kurlov A S and Gusev A I 2013 Fizika i khimiya karbidov volframa (Physics and chemistry of tungsten carbides) (Moscow: Fizmatlit) [in Russian]