Influence of temperature on tungsten carbide formation in a beam plasma discharge

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Abstract. This paper presents a method of tungsten surface carbidization using a plasma-beam setup to assess the effect of temperature on the formation of tungsten carbides. Methane was used as a plasma-forming gas. The working gas pressure in the chamber was (1.3-1.4)×10⁻¹ Pa. Experiments on the formation of carbides were carried out at different temperatures (700-1000°C). It was recorded that at a temperature of 700°C, crystallization centers of a carbon film appear on the sample surface. With an increase in the irradiation temperature to 800°C and 900°C, the surface of the samples is covered with a continuous carbon film. As a result of the experimental work carried out, it was found that the formation of tungsten semicarbide occurs at 900°C. A further increase in temperature leads to the formation of tungsten monocarbide.

1. Introduction
Tungsten and graphite were supposed to be used as candidate materials for the divertor of the ITER [1-3]. However, it was found that the use of graphite will lead to a significant accumulation of tritium in it [4]. Nevertheless, today there are research fusion reactors using both elements, tungsten and carbon [5-7]. The presence of various materials, as well as impurities in the installation chamber will lead to the formation of mixed layers on surfaces plasma facing components, which can affect the material characteristics. Consequently, the study of the formation of tungsten carbides is still of great importance.

The processes of co-deposition of tungsten and carbon in the tokomak divertor are simulated by various methods of applying surface coatings to study mixed layers, in particular, a carbidized surface.

There are various methods for producing thin carbon films, such as magnetron sputtering, mixing of plasma streams of tungsten and carbon, chemical vapor deposition of carbon from the gas phase, or evaporation of carbon using an electron beam evaporator [8-12].

In this paper, we consider the method of tungsten surface carbidization using a beam-plasma discharge (BPD), which was carried out on a plasma-beam installation (PBI) [13, 14].

2. Experimental part
2.1. Experimental installation
The PBI is intended for testing methods for measuring plasma parameters when studying the interaction of the plasma of the Kazakhstan material testing tokamak (KTM) [7] with candidate materials, for testing diagnostic equipment and materials for KTM, as well as for the development of existing and development of new methods modeling loads on structural materials.

PBI includes an electron gun chamber, a BPD gas-discharge chamber surrounded by magnetic field coils, and a chamber for interaction of BPD with the material. All three chambers are separated by removable diaphragms of differential pumping, equipped with systems for connecting gas supply and gas pressure control. The interaction chamber has side flanges that allow the installation of vacuum units, a loading target device, diagnostic devices, as well as visual observation, photographing and spectrometry of processes in the working volume through quartz windows and a system of mirrors. The general scheme of the installation is shown in figure 1.

![Figure 1. Schematic diagram of PBI.](image)

Plasma is generated in a constant magnetic field of 0.1 T using a beam-plasma discharge, which is carried out when the electron beam interacts with the working gas in the discharge zone. An electron gun with an indirectly heated tungsten cathode makes it possible to generate an electron beam with a current of 1 A at an accelerating voltage of up to 30 kV. The electron beam scanning system allows you to adjust the beam diameter from 0.1 to 3 cm per target.

The plasma flow generated in the discharge zone flows freely along the lines of force of the magnetic field into the interaction zone, in which samples of the materials under study are installed on the water-cooled collector. The plasma in the chamber has a density \((\geq 10^{18} \text{ m}^{-3})\) with an electron temperature of 3-15 eV.

2.2. Materials and experiments
Samples from a tungsten rod \(\varnothing 10 \text{ mm}\), grade HP (high pure tungsten without additives) were prepared in the form of disks with a thickness of 2±0.1 mm to study the effect of temperature on the formation of tungsten carbide in a beam-plasma discharge. The end face (one) of all the blanks was mechanically ground and polished to a roughness \(\text{Ra} = 0.02 \mu\text{m}\). Tungsten samples were annealed on PBI in the electron beam mode before carrying out experiments on carbidization [14]. The temperature of the samples during annealing was 1350±20°C, the duration was 1 hour. Plasma gas in the form of methane (CH4) is used to carbidize the tungsten surface on PBI. The working gas pressure was \((1.3-1.4) \cdot 10^{-1} \text{ Pa}\).

Experiments on the formation of tungsten carbides were carried out in the temperature range from 700°C to 1000°C with a step of 100°C with an irradiation duration of 1 hour. The registration and
control of the temperature on the front and back sides of the surface of the samples was carried out using pyrometers of the METIS M318 and IMPAC ISR 6 Advanced brands and a tungsten-rhenium thermocouple of the VR-5/20 type, respectively. The use of two pyrometers is explained by the fact that they have a different temperature measurement range. The METIS M318 pyrometer has a spectral range of 1.65-2.1 μm, a temperature range of 150-1200°C. Pyrometer IMPAC ISR 6 Advanced two-channel with spectral ranges of 0.90 and 1.05 μm, temperature range 800-2500°C.

The samples were cooled to room temperature and removed from the vacuum interaction chamber after irradiation. Further, the samples were sent to carry out work on the study of the surface of tungsten samples.

The study of the structure and elemental composition of the surface of tungsten samples after irradiation on PBI were investigated in the topographic contrast mode using a JEOL-6390 scanning electron microscope with a JED-2300 energy dispersive spectral analysis attachment. The X-ray diffraction patterns of the samples were recorded on an Empyrean diffractometer in Cu Kα-radiation, with a scanning linear detector PIXcel1D. To identify the phase composition on the surface of the samples, we used the Crystallography Open Database [15] and the PDF-2 ICDD Release 2004 database.

3. Results and discussion

The metallic tungsten phase has a body-centered cubic structure (BCC) (space group Im-3m). Numerous studies of the tungsten - carbon system have led to the conclusion that there are two carbides in the system: semi-carbide (W₂C) with a hexagonal close-packed lattice, and monocarbide (WC) with a simple hexagonal lattice [16].

During the analysis of the phase composition of the samples, it was noticed that when the diffractometric data cards corresponding to the tungsten phase were superimposed on the diffractogram, the experimental peak intensities did not completely coincide with the bar diagram of the card used, despite the complete correspondence of the angular positions. In this regard, diffractometric data cards of metallic tungsten No. 00-004-0806, tungsten semi-carbide No. 03-065-3896 and tungsten monocarbide WC No. 00-051-0939 were used to identify the phase composition [15]. On the obtained diffraction patterns of the samples, as can be seen from figure 2, diffraction lines of tungsten monocarbide and tungsten semi-carbide are observed. The areas of peaks of tungsten monocarbide are highlighted in orange on the diffractograms, areas of peaks of tungsten semi-carbide are marked in green, and areas of tungsten peaks are blue.

Figure 2. Diffraction patterns of the initial sample and samples T-700, T-800, T-900, T-1000 (the locations of the WC phase peaks are marked in orange, the W₂C phases are green, and the tungsten peaks are blue).
The basis of the phase composition of the samples surface in the initial state and at temperatures of 700°C and 800°C is metallic tungsten of the cubic syngony. The semi-carbide phase of the orthorhombic syngony appears in the phase composition with an increase in the surface temperature to 900°C with a content of less than 5% according to the data of an automatic estimate of the content. The base of the phase composition is metallic tungsten. The tungsten monocarbide phase of the hexagonal system, the quantitative content of which about 15%, appears in the composition in addition to the phase of orthorhombic carbide semi-carbide (< 5%) at a temperature of 1000°C. The cubic phase of metallic tungsten also remains the basis of the phase composition.

The results of determining the chemical composition of the surface of the samples before plasma irradiation are shown in table 1.

| Name            | C  | W  |
|-----------------|----|----|
|                 | Wt.% | At.% | Wt.% | At.% |
| Original        | 2.29 | 26.42 | 97.71 | 73.58 |
| After annealing | 3.24 | 33.92 | 96.76 | 66.08 |

The surfaces of tungsten samples were thermally etched during recrystallization annealing (figure 3). The structure of the sample is characterized as fine-grained. Small grains, the size of which varies in the range of 2-3 μm, are prone to accumulation and are distributed around relatively large grains less than 10 μm in size, outlining them along the perimeter.

![Figure 3. Microstructure of the thermally etched surface of a tungsten sample before plasma irradiation.](image)

Upon visual inspection, the surface of the samples after plasma irradiation on PUF at temperatures from 700°C to 1000°C is characterized by the presence of a continuous coating of a dark shade. SEM images and the elemental composition of the sample surface are shown in figure 4 and table 2, respectively.
Figure 4. Structure of the investigated surface of tungsten samples after plasma irradiation.

Table 2. Elemental analysis of the surface of tungsten samples after plasma irradiation.

| Name  | C Wt.% | C At.% | W Wt.% | W At.% |
|-------|--------|--------|--------|--------|
| T-700 | 61.40  | 96.05  | 38.60  | 3.95   |
| T-800 | 72.71  | 97.61  | 27.29  | 2.39   |
| T-900 | 80.34  | 98.43  | 19.66  | 1.57   |
| T-1000| 67.76  | 96.99  | 38.24  | 3.01   |

Most likely, at a low irradiation temperature (at 700°C), crystallization centers appear on the tungsten surface, as a result of which growth with increasing temperature forms a continuous carbon film. According to the literature, depending on the negative bias voltage and temperature applied to the sample, various carbon structures are formed on the sample surface, this can be a diamond-like film, graphite, amorphous carbon, etc [17, 18]. As can be seen from table 2, the mass fraction of carbon increases with an increase in temperature to 900°C, while the content of tungsten decreases. This indirectly indicates an increase in the thickness of the carbon coating.
A subsequent increase in temperature to 1000°C led to delamination and partial destruction of the formed film, which indicates their relatively low temperature stability. At the same time, by the nature of destruction, the carbon film is fragile and has low adhesion to the tungsten surface.

4. Conclusion
The study of the structure of the tungsten surface showed that at a temperature of 700°C, crystallization centers of the carbon film begin to appear on the surface of the sample. With an increase in the irradiation temperature to 800°C and 900°C, the surface of the samples is covered with a continuous carbon film. According to the results of X-ray phase analysis, it was found that at 900°C, the interaction between tungsten and carbon begins and leads to the formation of tungsten semicarbide. After heating to 1000°C in the phase composition, in addition to the tungsten semicarbide phase, the tungsten monocarbide phase is fixed. The results obtained are in good agreement with the literature data.

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