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RESEARCH OF THE STRUCTURAL-PHASE STATE OF TUNGSTEN SURFACE LAYER CROSS-SECTION AFTER CARBIDIZATION IN A BEAM-PLASMA DISCHARGE USAGE ELECTRON MICROSCOPY METHODS

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This paper presents research results on the structural-phase state of a tungsten surface layer cross-section after carbidization in a beam-plasma discharge. Tungsten surface carbidization in a beam-plasma discharge was conducted in a plasma-beam installation (PBI). Research on the cross-section structure of the surface layer of tungsten samples after carbidization at temperatures of 1000 °C, 1200 °C, and 1400 °C was conducted using transmission and scanning electron microscopy. Based on the results of SEM studies, a multilayer EMF map and local elemental analysis were obtained, based on which the depth of penetration of carbon atoms into tungsten was evaluated. It is established that the penetration depth is ~20 μm. The surface layer fine structure was researched using TEM. For TEM analysis of the tungsten sample cross-section with a carbidized layer, sections were prepared by ion thinning using an Ion Slicer EM-09100 IS unit. According to the research results, it was revealed that after carbidization, tungsten is available in the surface layer mainly in the composition of carbides WC and W_2C. On bright-field TEM images of the cross-section of the surface layer of tungsten samples after carbidization at a temperature of 1200 °C and 1400 °C, bending extinction contours are revealed, which indicate the elastically stressed state of the sample surface layer, which leads to bending-torsion of the foil.

Keywords: tungsten, tungsten carbide, the interaction between plasma and materials, irradiation.

INTRODUCTION

Since 2013, it has been decided to use W and Be as (PFM) for the International Thermonuclear Experimental Reactor [1]. However, C impurities are always present in tokamaks, as observed in the ASDEX-Upgrade W-wall [2]. At the same time, today there are research thermonuclear reactors where graphite is used as a plasma-facing material [3]. However, erosion and transport of sputtered PFM ions will lead to the formation of co-deposited mixed W–C layers [4–7]. The formation of mixed W–C layers will affect the processes of plasma interaction with PFM surfaces.

The papers [8, 9] present the results of studying the formation of a carbidized layer on the tungsten surface using a beam-plasma discharge (BPD). Methane was used as a working gas during the ignition of the PBD. As a result of interaction with an electron beam, gaseous methane decomposes into fragments such as H^+, H^{2+}, C^+, CH^+, CH^{2+}, CH^{3+} and CH^{4+}, which makes it possible to simulate the conditions of local transfer of carbon atoms along surfaces wetted by plasma due to hydrocarbons.

In order to study the formation of mixed W – C layers after carbidization in a beam-plasma discharge, as well as to evaluate the depth of penetration of carbon atoms into the volume of tungsten, this paper presents the results of research on the tungsten surface layer structural-phase states in a cross-section using transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

1. METHODS AND MATERIALS

The method of tungsten surface carbidization using a beam-plasma discharge is described in [8, 9] and implemented on a plasma-beam installation (PBI). A detailed description of the installation is presented in [10–12]. In paper [9], the temperature dependence of the carbidized layer formation on tungsten surface under plasma irradiation in the temperature range of 700–1700 °C was studied. The tungsten carbide formation in the surface layers was confirmed by X-ray analysis and SEM. To identify the phase composition on the W samples surface, the Crystallography Open Database and the PDF-2 ICDD Release 2004 database were used.

In this research, the fine structure of the tungsten surface layer cross-section after carbidization was studied using an HRTEM JEM-2100F microscope at an accelerating voltage of 200 kV (Joel, Japan) with a Schottky thermal field gun. Thin sections were prepared for TEM analysis by ion thinning using an Ion Slicer EM-09100 IS (Jeol, Japan). Preliminary sample preparation for the Ion Slicer consisted of fabricating a parallelepiped with dimensions of 2.8 mm × 0.5 mm × 0.1 mm, which was closed at a thin wide end with a special protective tape and thinned with an argon ion beam with an accelerating voltage of 6 kV at an angle of 2°. The etching lasted for 20 hours. This procedure allows studying the structure of a material at a strictly defined depth from the surface and to obtain electron diffraction patterns with precise depth control at a pitch of 25 nm. Thinning is

controlled by the image received from the CCD camera and regulated by a personal computer. Microdiffraction with TEM was used for phase analysis.

The microstructure of the carbidized layer on the cross-section of the samples, as well as the assessment of penetration depth of carbon atoms into tungsten, were studied using the SEM JSM-7500FA (Joel, Japan) (Scientific and Educational Innovation Center "Nanomaterials and Nanotechnologies" TPU (Tomsk, Russia)) and the Tescan SEM Vega 3 with X-Act energy-dispersive spectral analysis attachment [13, 14] (Tescan, Czech) (Institute of Atomic Energy Branch RSE NNC RK).

2. Results and Discussion

Earlier in our research [9], based on the results of microstructural analysis, it was established that on the surface of samples irradiated at a temperature of 700–1200 °C, the presence of a carbon coating in the form of a continuous film was observed. The presence of a carbon film on the surface of tungsten samples was confirmed by elemental analysis data [9]. It is known that in fusion reactors using carbon and tungsten as plasma-facing materials, during the reprecipitation between C impurities, mixed layers are formed with clear boundaries between W, the W–C mixed layer, and C deposits in the form of a coating [15, 16]. At the same time, the previous results of [9] indicate a strong dependence of the deposited layers (both carbon and mixed layers) on the surface temperature of tungsten samples.

The research results of the microstructure and elemental composition of the sample surface layer cross-sections obtained using SEM, are shown in Figure 1.

On the multilayer EDS map (Fig*ure* 1c) in the near-surface region, a mixed distribution profile of tungsten and carbon is observed with a pronounced boundary between the mixed layer W – C and the substrate material W. It can be seen from the data that the thickness of the mixed region is ~20 μm.

Figures 2–4 show SEM images and results of local elemental analysis of the sample cross-section irradiated at 1000 °C, 1200 °C, and 1400 °C.

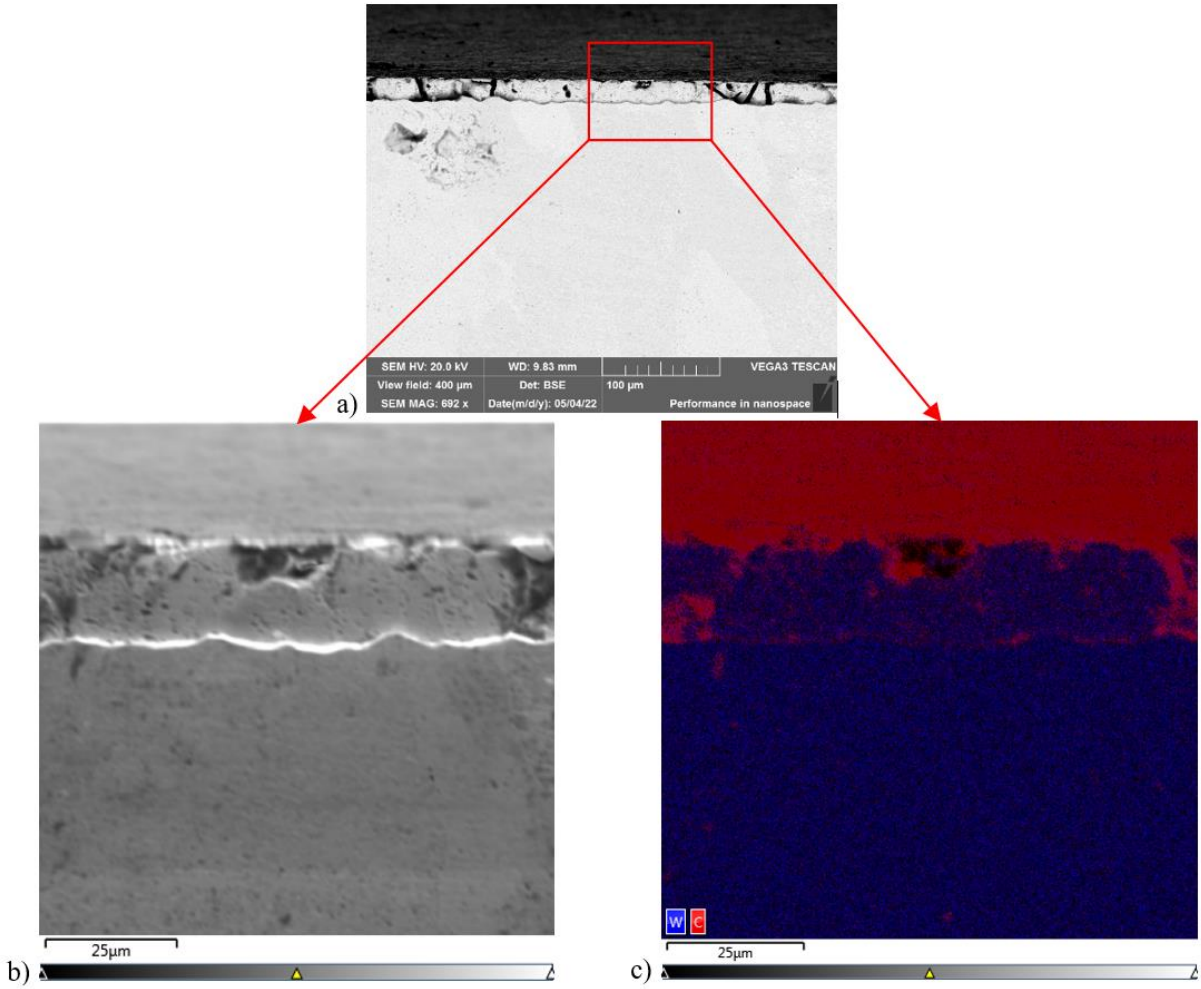
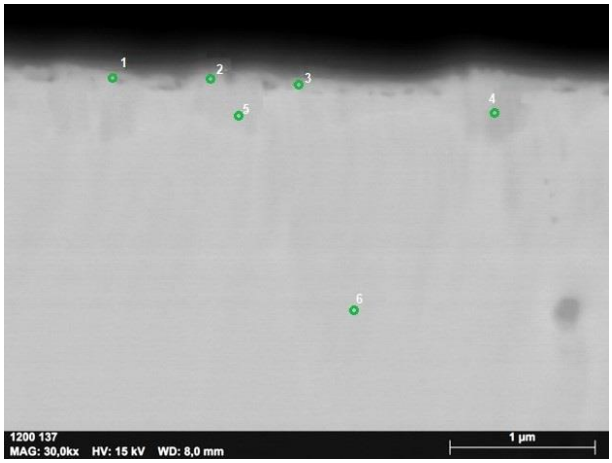
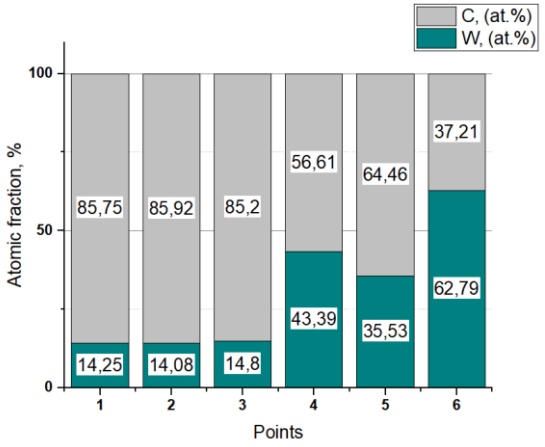


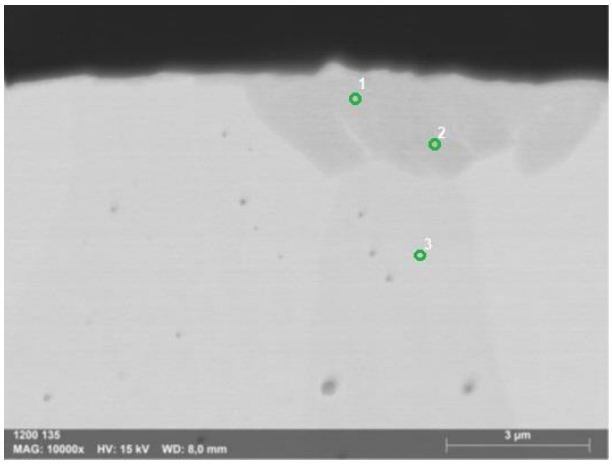
Figure 1. SEM image of a sample cross-section irradiated at a temperature of 1000 °C, with a ruler scale of 100 μm (a) and 25 μm (b) and a multilayer EDS map with separately selected W and C distribution maps (c)

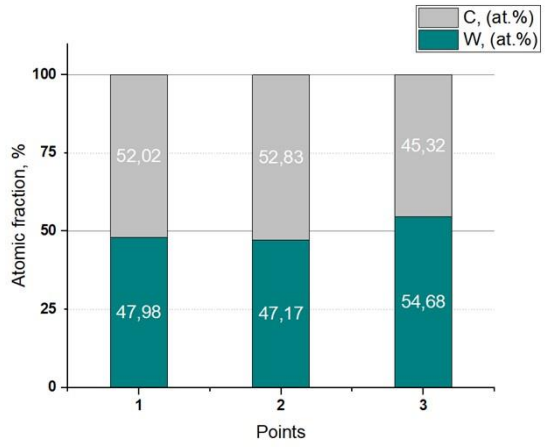




a) b)

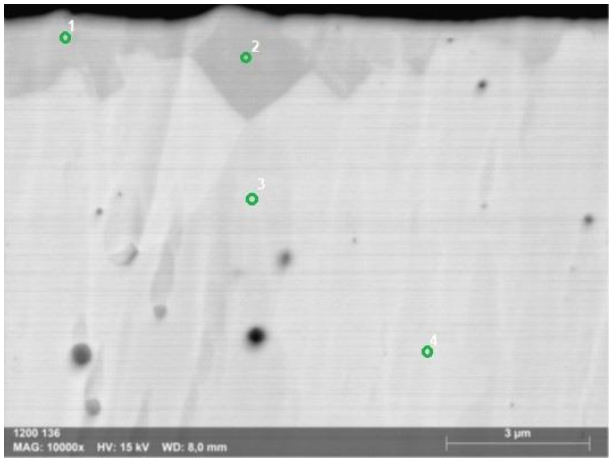
Figure 2. SEM image of a sample cross section irradiated at a temperature of 1000 °C and local elemental analysis corresponding to points 1–6

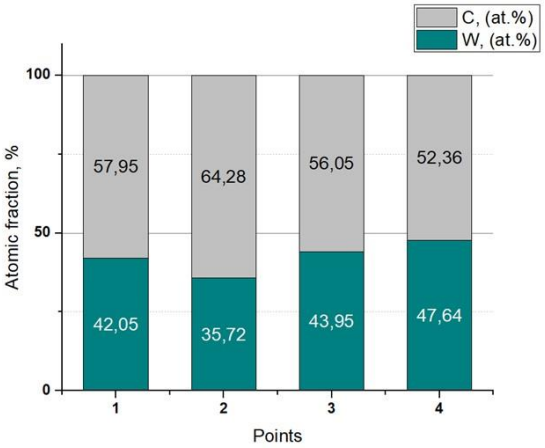




a) b)

Figure 3. SEM image of a sample cross section irradiated at a temperature of 1200 °C and local elemental analysis corresponding to points 1–3





a) b)

Figure 4. SEM image of a sample cross section irradiated at a temperature of 1400 °C and local elemental analysis corresponding to points 1–4

According to the elemental analysis results, the carbon mass fraction in the near-surface layer of the sample irradiated at a temperature of 1000 °C (corresponding points 1–3 in Figure 2) is maximum, which also confirms the presence of a thin carbon film [9]. However, according to the values at points 4–6 (Figure 2b), the carbon content decreases from the surface to the depth of the sample. As Figures 3 and 4 show, after irradiation of the sample surface at a temperature of 1200 °C and 1400 °C, there is a sharp change in the ratios of atomic fractions between tungsten and carbon. In [9], it was found that at high temperatures, the thermally unstable carbon film is destroyed and carbon is already present in a chemically bound form, forming phases of tungsten carbides, as evidenced by the XRD results (Figure 1 in [9]). The obtained data of the elemental analysis of the transverse section confirms the judgment about the high thermal dependence of the carbon film.

The results of TEM studies confirm the presence of carbide phases WC and W_2C in the tungsten surface layer. On the diffraction pattern, the peak of the W_2C phase had a low intensity, which indicated its low content [9]. Figure 5a shows a bright-field TEM image of a thinned near-surface region in the cross-section of a sample irradiated at a temperature of 1000 °C, selected for microdiffraction. The electron diffraction patterns obtained from the areas marked on 5a by circles 1, 2, 3, and 4 are shown in Figures 5b, 5c, 5d, and 5e, respectively.

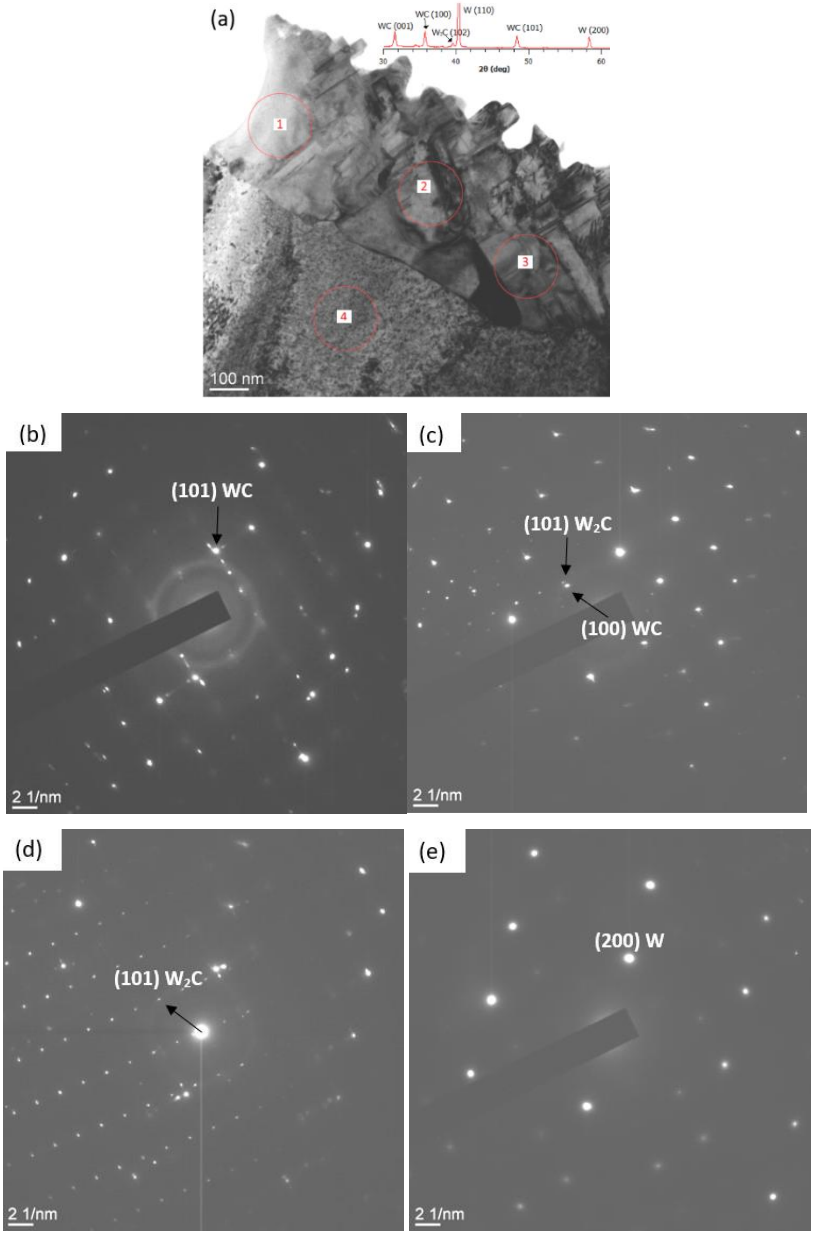


Figure 5. TEM image of the structure of a sample irradiated at a temperature of 1000 °C: a – bright field; b – e micro electron diffraction patterns obtained from the areas highlighted in (a) by circles: 1 – 5b, 2 – 5c, 3 – 5d, 4 – 5e

The electron diffraction pattern in area 1 corresponds to reflections of the WC (101) phase. Microdiffraction in area 2 (Figure 2c) shows the presence of reflections of two phases of W carbide (W_2C (101) and WC (100)). In area 3, a reflection of the W_2C phase (101) was also revealed. The electron diffraction pattern in area 4 corresponds to the phase of metallic tungsten. The results obtained allow concluding that the surface layer is a mixture of three phases: tungsten carbides of the composition WC and W2C, and W. In this case, areas with a high content of tungsten are detected in the sample volume. The indexing was conducted within the WC (P-6m2) and W2C (P-31m) hexagonal structures. At the same time, the presence of an orthorhombic W_2C structure cannot be excluded.

When obtaining tungsten carbides by sintering [17], WC grains are characterized by regular shapes in the form of a triangular prism and plates. However, in this research, more blurred boundaries of the newly formed phases are observed in the samples irradiated at 1000 °C; this may be because carbide formation has resulted from the diffusion of carbon ions into the volume of tungsten.

Figure 6 shows a TEM image of a sample cross-section irradiated at 1200 °C.

In the bright-field image (Figure 6a), the arrows indicate the WC interlayer along the grain boundary, and bending extinction contours are observed. The presence of a large number of bending extinction contours indicates the elastically stressed state of the sample surface layer, which leads to bending-torsion of the foil. Additional internal stresses may be created due to the generation of dislocations and the development of a dislocation structure. Based on the accumulation of dislocations of the same sign, the formation, and growth of new carbide particles at the grain boundaries and slip bands inside the crystal.

The electron diffraction pattern obtained from section (a) in Figure 6a corresponds to the WC and W_2C phases. Figures 6c and 6d show dark-field images in the (100) WC and (101) W_2C reflections, respectively.

Figure 7 shows a TEM image of a sample cross-section irradiated at 1400 °C. On bright-field images, a small number of bending contours of extinction is also observed.

The microelectronic diffraction patterns in areas 1 and 4 (Figures 6c, 6f) contain reflections (101) W_2C phases. Microdiffraction in areas 2 and 3 (Figures 6d, 6e) shows the presence of the WC (101) phase. However, in area 3 on the micro electron diffraction pattern, reflections of carbon with an hcp lattice are observed. Therefore, the surface layer contains carbon and tungsten carbides of composition WC and W_2C.

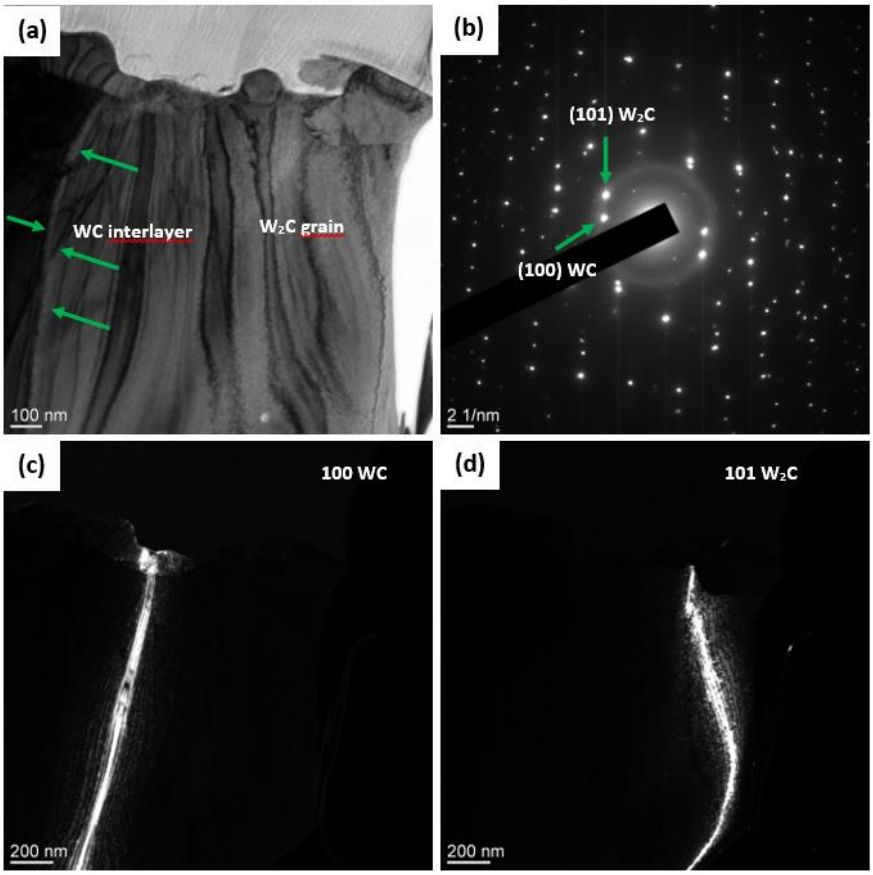


Figure 6. TEM image of the structure of a sample irradiated at a temperature of 1200 °C: a – bright field; b – micro electron diffraction pattern obtained from the area (a); (c, d) dark fields obtained in the [100] WC (c) and [101] W_2C (d) reflections. Arrows in (b) indicate reflections in which dark fields were obtained.

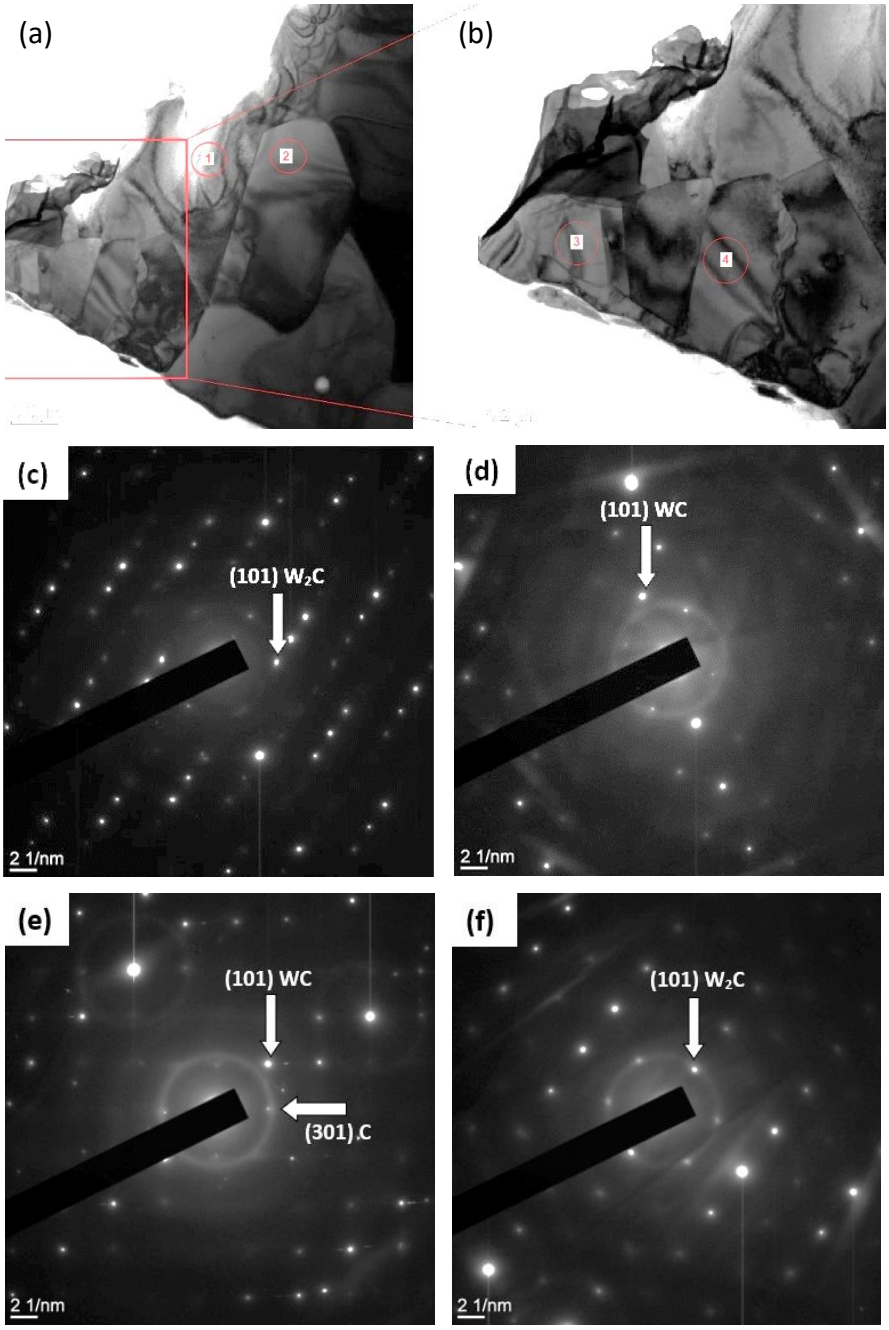


Figure 7. TEM image of a sample structure irradiated at a temperature of 1400 °C; a, b – bright field; c – f micro electron diffraction patterns obtained from the areas highlighted in (a) and (b) by circles: 1 – 6c, 2 – 6d, 3 – 6e, 4 – 6f

Performing microdiffraction on the samples showed that the results are comparable with elemental analysis and XRD measurements given in [9].

CONCLUSION

Previously, the temperature dependence of the carbidized layer formation on the tungsten surface was studied by the beam-plasma discharge method in the temperature range of 700–1700 °C. In this research, electron microscopy (SEM, TEM) is used to analyze the structural-phase state of the tungsten surface layer in the cross-section after carbidization at temperatures of 1000 °C, 1200 °C, and 1400 °C. Based on the results of SEM studies, a multilayer EDS map and local elemental analysis were obtained, based on which the depth of penetration of carbon atoms into tungsten was evaluated. It is established that the penetration depth is ~20 μm. The depth distribution of elements in the near-surface layer of the sample irradiated at a temperature of 1000 °C confirms the presence of a thin carbon film. However, the carbon content decreases from the surface to the depth of the sample, which indicates the presence of carbon in a chemically bound form. Samples irradiated at temperatures of 1200 °C and 1400 °C show a sharp change in the ratios of atomic fractions between tungsten and carbon.

The atomic ratio of tungsten to carbon is closer to 2:1, which indicates the formation of the W_2C phase.

To reveal the internal structure of the surface layer of the samples, TEM images were obtained from their cross-sections. For TEM analysis of the tungsten sample cross-section with a carbidized layer, sections were prepared by ion thinning using an Ion Slicer EM-09100 IS unit. According to the research results, it was revealed that after carbidization, tungsten is present in the surface layer mainly in the composition of carbides WC, and W_2C. On bright-field TEM images of the surface layer cross-section of tungsten samples after carbidization at a temperature of 1200 °C, and 1400 °C, bending extinction contours are revealed, which indicate the elastically stressed state of the sample surface layer.

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СӘУЛЕЛІК-ПЛАЗМАЛЫҚ РАЗРЯДТА КАРБИДТЕНГЕННЕН КЕЙІН ВОЛЬФРАМ БЕТТІК ҚАБАТЫНЫҢ КӨЛДЕНЕҢ ҚИМАСЫНЫҢ ҚҰРЫЛЫМДЫҚ-ФАЗАЛЫҚ КҮЙІН ЭЛЕКТРОНДЫҚ МИКРОСКОПИЯМЕН ЗЕРТТЕУ

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Бұл жұмыста сәулелік-плазмалық разрядта карбидизациядан кейінгі вольфрамның беткі қабатының көлденең қимасының құрылымдық-фазалық күйін зерттеу нәтижелері берілген. Вольфрам бетін сәулелік-плазмалық разрядта карбидизациялау плазмалық-сәулелік қондырғыда жүргізілді. 1000 °С, 1200 °С, 1400 °С температурада карбидизациядан кейін вольфрам үлгілерінің беткі қабатының көлденең қимасының құрылымын зерттеу трансмиссиялық және сканерлеуші электронды микроскоп арқылы жүргізілді. Сканерлеуші электронды микроскоптағы зерттеулердің нәтижелері бойынша энергия-дисперсиялық спектрометрдің көпқабатты картасы және жергілікті элементтік талдау алынды, оның негізінде вольфрамдағы көміртегі атомдарының ену тереңдігінің бағасы жасалды. Енгізу тереңдігі ~20 мкм екені анықталды. Беткі қабаттың жұқа құрылымын зерттеу трансмиссиялық электронды микроскоптың көмегімен жүзеге асырылды. Трансмиссиялық электронды микроскопта карбидтелген қабаты бар вольфрам үлгілерінің көлденең қимасын талдау үшін қималар Ion Slicer EM-09100 IS қондырғысы арқылы ионды жұқарту арқылы дайындалды. Зерттеу нәтижелері бойынша карбидизациядан кейін беткі қабаттағы вольфрам негізінен WC, W_2C карбидтерінің құрамында болатыны анықталды. 1200 °С, 1400 °С температурада карбидизациядан кейін вольфрам үлгілерінің беткі қабатының көлденең қимасының жарқын өрістегі суреттерінде үлгінің беткі қабатының серпімді күйін көрсететін иілу сөну контурлары анықталады, бұл фольганың иілу-бұралуына әкеледі.

Түйін сөздер: *вольфрам, вольфрам карбиді, плазманың материалдармен әрекеттесуі, сәулелену.*

ИССЛЕДОВАНИЕ МЕТОДАМИ ЭЛЕКТРОННОЙ МИКРОСКОПИИ СТРУКТУРНО-ФАЗОВОГО СОСТОЯНИЯ ПОПЕРЕЧНОГО СЕЧЕНИЯ ПОВЕРХНОСТНОГО СЛОЯ ВОЛЬФРАМА ПОСЛЕ КАРБИДИЗАЦИИ В ПУЧКОВО-ПЛАЗМЕННОМ РАЗРЯДЕ

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В настоящей работе представлены результаты исследований структурно-фазового состояния поперечного сечения поверхностного слоя вольфрама после карбидизации в пучково-плазменном разряде. Карбидизация поверхности вольфрама в пучково-плазменном разряде была осуществлена на плазменно-пучковой установке. Исследования структуры поперечного сечения поверхностного слоя образцов вольфрама после карбидизации при температуре 1000 °С, 1200 °С, 1400 °С были проведены методами просвечивающей и сканирующей электронной микроскопии. По результатам исследований на СЭМ были получены многослойная карта ЭДС и локальный элементный анализ, на основе которых сделана оценка глубины проникновения атомов углерода в вольфрам. Установлено, что глубины проникновения составляет ~20 μм. Исследование тонкой структуры поверхностного слоя выполнялось при использовании ПЭМ. Для ПЭМ-анализа поперечного сечения вольфрамовых образцов с карбидизированным слоем были подготовлены шлифы методом ионного утонения на установке Ion Slicer EM-09100 IS. По результатам исследований выявлено, что после карбидизации вольфрам в поверхностном слое присутствует главным образом, в составе карбидов WC, W_2C. На светлопольных ПЭМ-изображениях поперечного сечения поверхностного слоя образцов вольфрама после карбидизации при температуре 1200 °С, 1400 °С выявлены изгибные контуры экстинкции, которые свидетельствует об упруго-напряженном состоянии поверхностного слоя образца, что и приводит к изгибу-кручению фольги.

Ключевые слова: *вольфрам, карбид вольфрама, взаимодействие плазмы с материалами, облучение.*