

Influence of Thermal and Radiation Effects on the Phase Composition, Structure and Stress-Strain State of Ti-W-B System Coatings Deposited from Ion-Atomic Fluxes

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The regularities of the formation of ion-plasma coatings of Ti-W-B system and the impact of postcondensation treatment on their phase composition, structure, substructure and stress state are studied. It is shown that at a low content of Ti-component (up to 2 at.%) two-phase state from β -WB- and (Ti, W)B₂-phases is formed. Annealing at 1270 K leads to the grain growth of the β -WB-phase mainly. When the content of Ti is more than 5 at.%, a single-phase (Ti, W)B₂ state of the coating is formed. Structure and substructural characteristics of these coatings are stable at annealing and proton irradiation with the energy of 200 keV up to the dose of $6.5 \cdot 10^{17}$ cm⁻². Influence of thermal-radiation exposure affects the change of the stress-strain state (relaxation of compressive strain). The observed changes are explained on the basis of minimizing the free energy of the system.

Keywords: Ion-plasma coatings, Irradiation, X-ray diffraction studies, Annealing, Separation of complex profiles.

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1. INTRODUCTION

Borides belong to the class of inorganic compounds which are characterized by infusibility, high chemical and radiation stability and metal-similarity that is expressed in their high electrical and thermal conduction, magnetic properties, specific electron structure [1].

According to their structure, borides occupy an intermediate position between penetration phases and intermetallic compounds [1]. Presence of a strong Me-B-bond allows to reach high functional properties in materials on their basis [1-10]. A unique complex of properties, which is appropriate for diborides of transition metals, determines the prospects of their application as high-temperature stable and radiation stable materials [10]. In this case, the highest physical-mechanical properties can be obtained when producing materials based on the most complex boron compounds, for example, materials which have composition of quasi-binary concentration cross-sections of ternary systems: Ti-Ta-B, Ta-Hf-B, Ti-W-B, and Ti-Zr-B [2-17].

Ceramic quasi-binary TiB₂-WB₂ system has shown high strength in combination with high hardness in a bulk macrocrystalline state. Strength in bending tests of about 1000 MPa was achieved for this quasi-binary system in a bulk state at hardness of 28 GPa, although strength and hardness of TiB₂ and WB₂ separate components do not exceed 400 MPa and 26-27 MPa, respectively [2]. Here, plasticity index which is defined by the hardness H -to-modulus of elasticity E ratio takes sufficiently small values: $H/E \leq 0.06$.

From this it follows that with the increase in the system complexity by the transition to the quasi-binary state, a qualitative change of the properties takes place that provides for structural changes connected with their phase state. To understand the latter, it is necessary to plot a ternary (composed of three components of quasi-binary system – Ti, W, and B) equilibrium diagram. This

plotting gains a special importance in the case of the formation of a high level of the stress-strain state, since such state induces strain non-equilibrium additionally to the concentration and structural ones [18, 19].

In Fig. 1 we represent the concentration triangular Ti-W-B with three constituent binary systems. It is seen that for binary Ti-W-component at low temperatures the region of solid solutions based on α -Ti or β -Ti with bundle of β_1 - and β_2 -phases is formed. Formation of the boride phases is typical for Me-B binary diagrams. In Ti-W system in a liquid state, components are indefinitely soluble in each other. Complex system with three intermediate phases from B side (TiB, Ti₃B₄, TiB₂) is formed during crystallization. Mutual solubility of the components in a solid state is almost absent [20].

Four compounds are formed in W-B system, namely, W₂B, WB, W₂B₅ (or according to the equilibrium composition WB₂ [11]), WB₄ (or WB₁₂). WB compound has two polymorphous forms (α , β). Solubility of B in W is equal to 0.15 at.% at the temperature of 2920 K and 0.025 at.% at the temperature of 2270 K [21].

Crystal structure of Ti-B and W-B system phases is given in Table 1.

In Fig. 1b we show the equilibrium state diagram for quasi-binary TiB₂-WB₂ cross-section [11, 17, 18]. As seen, a single-phase (Ti, W)B₂ state based on the TiB₂ lattice (structural type of AlB₂) is stable at high temperature 2500 K up to a large content of WB₂-component (about 60 mol.%). With decreasing temperature, solubility considerably decreases and at 1270 K it reaches some percentage. Mixture of two phases: (Ti, W)B₂ based on the TiB₂ lattice and (W, Ti)B₂ based on the W₂B₅ lattice, is a stable state in the low-temperature region under the equilibrium conditions.

Further development prospects of diboride materials are significantly connected with their nanostructural state [22]. A priori formation of such type of state takes place for the ion-plasma methods of production of the

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coatings based on the penetration phases of transition metals [19, 23-26].

The aim of the present work consists in the study of the influence of thermal and radiation effects on the phase composition, structure, stress-strain state and sub-structural characteristics for a wide range of the compositions of ion-plasma (magnetron sputtering) coatings of the quasi-binary TiB₂-WB₂ system.

Table 1 – Crystal structure of Ti-B and W-B system phases

Phase	Prototype	Lattice parameters, nm		
		<i>a</i>	<i>b</i>	<i>c</i>
TiB ₂	AlB ₂	0.3030	–	0.3228
TiB	FeB	0.7103	0.3048	0.4551
W ₂ B	CuAl ₂	0.5566	–	0.4748
β-WB	CrB	0.3124	0.8415	0.306
α-WB	α-MoB	0.3097	–	1.602
W ₂ B ₅ (WB ₂)	W ₂ B ₅	0.2977	–	1.387
WB ₄ (WB ₁₂)	WB ₄	0.2993	–	0.3161

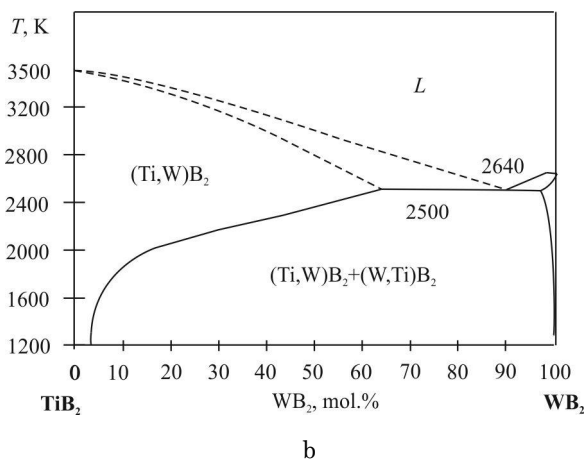
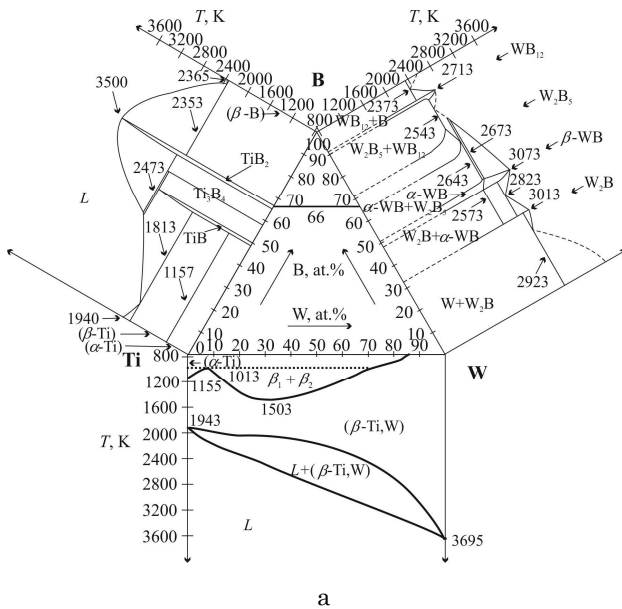


Fig. 1 – Concentration triangle Ti-W-B with three constituent binary systems (a) and quasi-binary TiB₂-WB₂ cross-section (b)

2. OBJECTS AND METHODS OF INVESTIGATION

Targets for sputtering of the diameter of 50 mm and thickness of 4 mm were manufactured by hot pressing of the mixture of TiB₂ and W₂B₅ powders which provided the preparation of the equilibrium state of TiB₂ + W₂B₅ two-phase system of different compositions [2]. On the obtained X-ray diffraction spectra from targets in two-phase state one reveals peaks from TiB₂ crystal lattice (P6/mmm space group, hexagonal lattice with the ratio of lattice periods $c/a \approx 1.07$ [10]) and W₂B₅ crystal lattice (W₂B₅ structural type, D⁴_{6h}-P6₃/mmc space group [11]).

As an example, in Fig. 2 we illustrate the X-ray diffraction spectrum obtained for targets of quasi-binary system of the following composition: 54 mol.% of TiB₂ – 46 mol.% of WB₂.

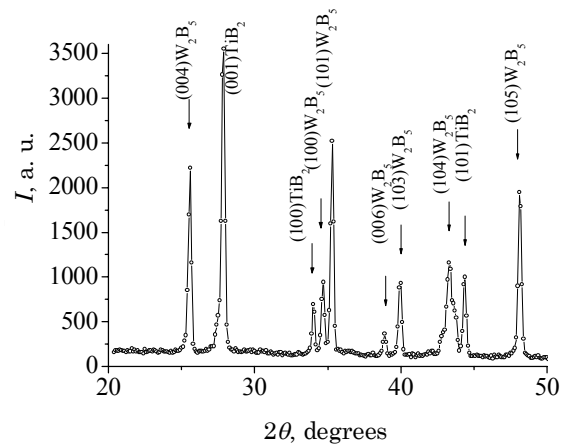


Fig. 2 – Region of the diffraction pattern from the target of quasi-binary system of the following composition: 54 mol.% of TiB₂ – 46 mol.% of WB₂ (Cu-K_α radiation)

The coatings are obtained by the direct current (DC) magnetron sputtering method in the Ar atmosphere of the targets of W₂B₅ and TiB₂ compositions and targets of TiB₂-W₂B₅ quasi-binary system with TiB₂ content from 1 mol.% to 90 mol.%.

Argon pressure (P_{Ar}) in the vacuum chamber during target sputtering was equal to 0.1-0.2 Pa. Deposition rate was $V \approx 0.08$ nm/s at the magnetron power of $W = 42$ W (voltage 420 V, current 100 mA) and distance from the target to the substrate of 60 mm. Before coating deposition, substrates were previously degassed during 1 hour at the temperature of 970 K in the vacuum of $2 \cdot 10^{-6}$ Pa. Low sputtering power provided with rather small and uniform heating of the substrate to 370 K by deposited atoms. Additional heating of the substrates in the temperature range of 570-1220 K was performed by the resistance heating unit. Key investigations in the work were carried out on the condensates deposited at the substrate temperatures of $T_s = 870-970$ K.

Coatings were deposited on the substrates of monocrystalline silicon of the thickness of 340-420 μm, aluminum foil of 15 μm, beryllium foil of 35 μm, and also on the plates of glass ceramic, tantalum and niobium. In addition, the detailed structural investigations were performed on the coatings deposited on silicon polished plates, and structural data obtained on other substrates was used for a qualitative comparison.

Concentration of elements was determined by the secondary ion mass spectrometry (SIMS) method on the plant MS-7201 and also by the secondary (fluorescent) emission spectra (X-ray fluorescence analysis – XFA) on the device SPRUT-2.

Information about the structure, substructure and stress state was obtained by the analysis of the position, intensity and width of diffraction reflexes. X-ray diffraction investigation of the samples was carried out on the diffractometer DRON-3 in Cu- K_{α} radiation. Detection of scattering was performed in the discrete shooting mode with the scanning step varying in the range of $\Delta(2\theta) = 0.01-0.05^{\circ}$ depending on the width and intensity of diffraction lines [27]. Phase composition of the samples was determined by the comparison of the obtained diffraction patterns with the ASTM data [28, 29].

Investigations of the substructural characteristics (crystallite size and microstrain) were carried out by the approximation method of some orders of images by the standard plotting technique of the Hall plots [27].

Degree of texture perfection ($\Delta\omega$) was determined by the half-height width of the diffraction reflex taken in ω -scanning. The value of $\Delta\omega$ characterizes the degree of disorder of crystallites.

For nanodispersed films, as well as for amorphous-like structure, the stress-strain state was studied by the deflection of the coated substrate. The Stoney equation was used for the calculation of the stress value [30].

In some cases we have determined the stress-strain state in polycrystalline coatings using X-ray “ $d\text{-sin}^2\psi$ ”-method [27].

Annealing of the coatings was performed during one hour in the vacuum chamber under the pressure of $9 \cdot 10^{-7}$ Torr at the temperatures of 1070 and 1270 K.

Irradiation was carried out on the simulator [31] by a proton and electron beam which was unwrapped over the area of 100 cm^2 at the total current of protons and electrons of $5-20 \mu\text{m}$. Accelerating voltage was equal to 200 kV.

Working volume of the vacuum chamber, where the tests are realized, was pumped out by a turbo-molecular pump also equipped by nitrogen traps and screens. Exposure time was equal to 14.5 hours that corresponds to the radiation dose of $6.5 \cdot 10^{17} \text{ cm}^{-2}$, temperature of the coating surface did not exceed 370 K.

3. RESULTS AND DISCUSSION

Analysis of the obtained X-ray diffraction spectra has shown that formation of the nanostructured (crystallite size from 3 to 100 nm) state occurs for a whole range of compositions at the deposition temperature lower than 1270 K.

Two-phase state is typical for the coatings with the content of titanium atoms less than 10%. $2\theta = 25-60^{\circ}$ angular range in Cu- K_{α} radiation is the most convenient diffraction region for the extraction of phases and estimation of their volume composition.

In Fig.3a, b, c we present the regions of the diffraction spectra of the coatings with different content of titanium atoms.

Volume content of phases in the coating, as well as the determination of crystallite sizes and dynamics of their change during annealing, was performed by pro-

gramming methods of separation of complex profiles of the diffraction reflexes which are overlapped [32].

The obtained results are generalized in Table 2.

Analysis of the obtained results shows that with increasing content of titanium, transition from (β -WB and (Ti, W) B_2) two-phase state to (Ti, W) B_2 single-phase state occurs in the coating.

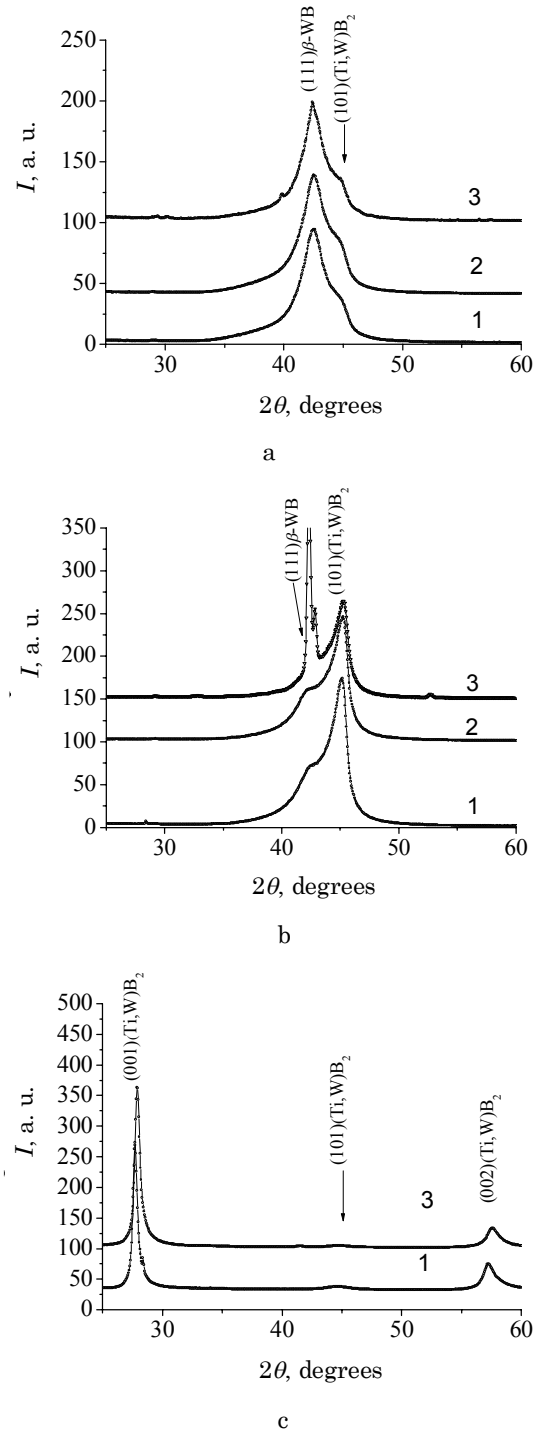


Fig. 3 – Regions of the diffraction spectra of the Ti-W-B system coatings with different atomic content:

(a) 0.57 at. % of Ti, 35.94 at. % of W, 63.41 at. % of B;

(b) 1.89 at. % of Ti, 33.1 at. % of W, 65.01 at. % of B;

(c) 21.12 at. % of Ti, 12.36 at. % of W, 67.43 at. % of B.

Curve 1 – coating spectrum after deposition; curve 2 – after annealing at 1070 K, curve 3 – after annealing at 1270 K

Table 2 – Volume content of the phases and crystallite size of the coatings of different composition in the initial state and after 1 hour annealing at the temperatures of 1070 and 1270 K

Series number		1	2	3	
Composition, at. %	Ti	0.57	1.89	20.21	
	W	36.02	33.1	12.36	
	B	63.41	65.01	67.43	
β -WB	Volume content, %	Initial state	95	58	–
		Annealing, 1070 K	95	50	–
		Annealing, 1270 K	89	35	–
	Crystallite size, nm	Initial state	5.4	4.5	–
		Annealing, 1070 K	5.4	5.0	–
		Annealing, 1270 K	5.9	48.5	–
(Ti, W)B ₂	Volume content, %	Initial state	5	42	100
		Annealing, 1070 K	5	50	–
		Annealing, 1270 K	11	65	100
	Crystallite size, nm	Initial state	11.1	11.5	31.0
		Annealing, 1070 K	11.4	11.5	–
		Annealing, 1270 K	11.7	12.0	31.3

Annealing of the coatings with a low content of Ti-component leads to the growth of grain-crystallites of the β -WB-phase almost without changing crystallite sizes of the (Ti, W)B₂-component. We should note that in the coating, which contains 1.89 at. % of Ti, at the initial phase relation of 58 vol. % β -WB – 42 vol. % (Ti, W)B₂ annealing at 1270 K leads to the appearance of foliation with significant change in the phase relation and strong increase in the average size of grain-crystallites during annealing of the β -WB-phase (Fig. 3b, Table 2).

In the coating with a large content of titanium (3-d series) annealing does not lead to the change in the single-phase state and area of preferred growth orientation of crystallites (001), and is accompanied by the shift of diffraction maxima toward the region of large angles. The latter is typical for ion-plasma coatings with initial stress-strain state of compression. In this case, shift of the maxima toward the region of large angles indicates relaxation of the initial stress-strain state occurring in the annealing.

In general, we have to note that in nanocrystalline materials with non-equilibrium phase state the macrostress-strain state gains a particular importance in the prediction of the structural-phase stability and efficiency (see [33, 34]).

High level of macrostresses in ion-plasma coatings deposited at $T_s = 970$ -1220 K leads to the bending of the “coating/substrate” system. In the condensates obtained on glass ceramic substrates such bending is observed at the lower temperature $T_s = 970$ K than in the “coating-substrate” system of monocrystalline silicon $T_s = 1020$ -1120 K. Dome-like form (with a dome from the side of the film) of the bending of the “coating/substrate” system during target sputtering of Ti-W-B system implies the development of compressive macrostresses in the coatings.

During sputtering of the tungsten diboride target one can observe bending of the system in the opposite direction that is inherent to the development in the coatings of tension stresses. Estimation of the compressive macrostresses (σ_{com}) by the bending value of the coating of 50 mol. % TiB₂ – 50 mol. % WB₂ composition ($T_s = 1220$ K, substrate of monocrystalline silicon of the thickness of 385 μ m) using the Stoney formula (see [30]) is equal to $\sigma_{com} \approx -6.5$ GPa.

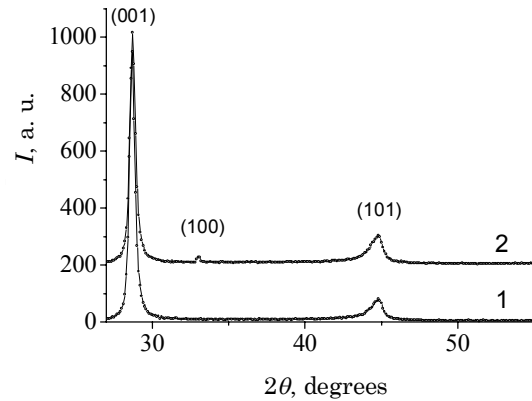
At the lower temperature T_s , when significant bending of the substrate does not occur under the action of macrostresses, the stress-strain state was studied using the X-ray “ d - $\sin^2\psi$ ”-method.

The performed analysis has shown that in the coatings deposited at $T_s = 870$ K (ratio Ti/W ≈ 1) one can observe a huge compressive strain (ε) which achieves the value of -2.8 %. This strain is induced by the compressive stress $\sigma_{com} \approx -8.9$ GPa.

In the coatings with less Ti/W ratio (i.e. with larger specific content of the WB₂-component) the value of the maximum elastostrained state decreases. Thus, at the ratio Ti/W = 0.33 compressive strain decreases and becomes equal to -0.6 %, and at Ti/W ≈ 0.2 compressive strain is equal to -0.4 % (all investigations concern the coatings deposited at $T_s = 870$ K).

Study of the influence of the open space factors on the investigated materials by simulation of radiation exposure [35] was carried out by the irradiation by a proton and electron beam with the energy of 200 keV of the samples of TiB₂-WB₂ coatings of equiatomic composition by metal atoms.

Irradiation of the coatings did not lead to the noticeable change in the phase composition (Fig. 4). Samples both before and after irradiation were single-phase ones, (Ti, W)B₂ solid solution with crystallites which have the hexagonal crystal lattice. Crystallite size also has not undergone significant changes. However, small increase in the width of diffraction reflexes in terms of the Selyakov-Scherrer formula indicates the decrease in the average crystallite size from 22 nm before to 19-20 nm after irradiation. Ion bombardment of the samples led to a slight deterioration of the degree of perfection of the initial texture of the coating with plane (001) which is parallel to the growth surface (Fig. 4, spectra 1, 2).

**Fig. 4** – Regions of the diffraction spectra of the coatings of the composition 50 mol. % TiB₂ – 50 mol. % WB₂ obtained at $T_s = 970$ K: 1 – initial spectrum, 2 – after radiation

Such decrease is revealed in the change of the ratio of the integral intensity to the crystallite texture plane (001) and, for example, (101). Thus, ratio of the texture maximum (001) to (101) before irradiation was equal to 9, and after irradiation – it decreased to 7.2.

The most substantial irradiation up to the dose of $6.5 \cdot 10^{17}$ cm⁻² affected the change (relaxation) of the initial stress-strain compressive state of the crystal lattice formed under the action of the “atomic peening” effect during deposition. In the initial state (after deposition)

compressive strain of $\varepsilon = -1.0\%$ was developed in the coatings. As the result of irradiation, the strain value decreased to -0.76% . Thus, after irradiation thermodynamic state of the coating transferred to more equilibrium state, since it is known that strain leads to the increase in the system energy by the value of $1/2 E\varepsilon^2$, where E is the Young's modulus.

4. CONCLUSIONS

1. Conditions of appearance of the two-phase state from the β -WB- and (Ti, W)B₂-phases are determined for the ion-plasma coatings of the Ti-W-B system.

2. Using the programming methods of separation of complex diffraction profiles, it is established that high-temperature vacuum annealing leads to the growth of crystallites in the β -WB-phase mainly.

3. We have analyzed the influence of the deposition conditions on the formation of the stress-strain state of the coatings. It is established that Ti-W-B system coatings are in the compressive stress state after deposition.

4. Investigations of the influence of irradiation by protons with the energy of 200 keV up to the dose of $6.5 \cdot 10^{17} \text{ cm}^{-2}$ on the structural-stress state of the coatings have shown the considerable relaxation of the initial compressive macrostrain at almost constant structure and substructural characteristics.

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