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Influence of the Thermal Factor on the Structural and Substructural States of the Quasi-binary TiC-WC System Ion-plasma Coatings

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The influence of the deposition temperature of TiC-WC quasi-binary system ion-plasma coatings (magnetron scheme) of different composition is investigated. The substantial expansion of the probable structural and substructural states under nonequilibrium conditions of receiving a material from ion-plasma fluxes is demonstrated. The composition changes from monophase (Ti, W)C to two-phase (Ti, W)C and α-W_2C, the structure – from the nontextured one to the texture with the axes [111], [100] or [110]. The type of the texture depends on the deposition temperature and composition. When the state on the substructural level is monophase the increase of the substrate temperature leads to the increase in the size of crystallites and microstrain reduction. Creating the second phase determines opposite effects – reduce the size of the crystallites coverage and increase microstrain.

Keywords: Ion-plasma coatings, Quasi-binary TiC-WC system, X-ray diffraction, Phase composition, Texture, Substructure, Thermal factor, Heat of the formation.

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1. INTRODUCTION

The nonequilibrium state of the material when it is deposited from ion-plasma fluxes makes its structure extremely sensitive to the thermal factor [1–7]. This thermal sensitivity is especially vivid when the condensates of solid solution are formed [5–12].

The aim of the paper consists in establishing the regularities of the thermal factor influence on the phase composition formation, structure and substructural characteristics of ion-plasma condensates quasi-binary system WC-TiC are received by the magnetron sputtering.

2. EXPERIMENTAL

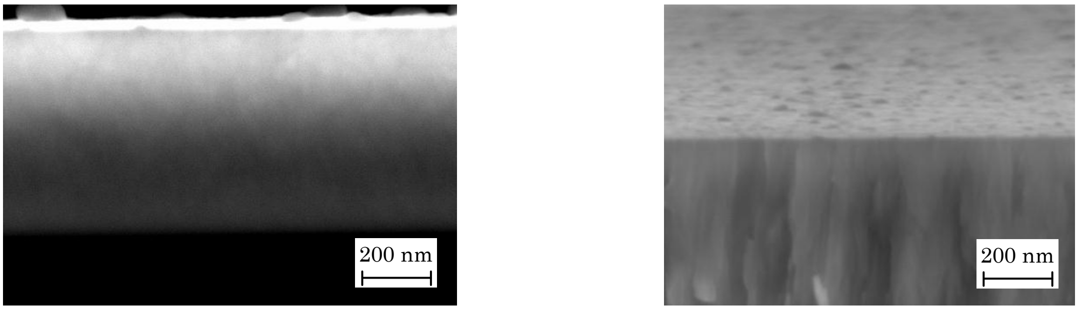
The coatings have been received by the ion sputtering (magnetron scheme) of hot pressed targets with different volumel contents of their constituent WC and TiC components (from 5 mol.% to 100 mol.% TiC). The planar magnetron scheme has been used for sputtering. The sputtering has been carried out in the medium of the inert gas Ar under the pressure (2–3) mTorr. Monocrystallic silicon, 370 μm thick, served as a substrate.

The phase composition, structure and substructure of condensates have been researched by the methods of X-ray diffractometry on the apparatus DRON-3M in Cu – K_α radiation. Substructural properties have been defined by the method of approximating the diffraction line profile form [13].

Surface morphology has been investigated on the scanning electron microscope JEOL JSM-840, and the composition has been defined on fluorescent data by the method of energy-dispersive spectroscopy (EDX).

3. RESULTS AND DISCUSSION

The coatings received at low deposition temperatures have had a nanocrystalline non-oriented structural state (Fig. 1a). When the temperature rises the oriented structure with the fibrous morphology is being formed. In the Fig. 1b the fracture of the coating is shown, on its side surface the longitudinal fibers that have the size 10–15 nm in the plane of a parallel substrate are seen. The height of columns is 100–200 nm.



a
b

Fig. 1 – Photos of the coating side section with the composition 5 mol.% TiC – 95 mol.% WC received at $T_s = 570^oK$ (a), $T_s = 970^oK$ (b)

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The phase state analysis on the basis of X-ray diffractory data concerning the spectra of coatings received at $T_s = 570$ K with different content of the constituents (Fig. 2) has shown that a monophase structural state of the solid solution carbide (Ti, W)C is being formed (structural type NaCl, the overview of the lattice is displayed as an insertion in the Fig. 2). When the content of TiC component increases the transition from a non-textured state to a preferred orientation (200) (with the composition 10 mol.% TiC – 90mol% WC) takes place. When the content of TiC component is more a preferred orientation (111) of crystalites is being formed.

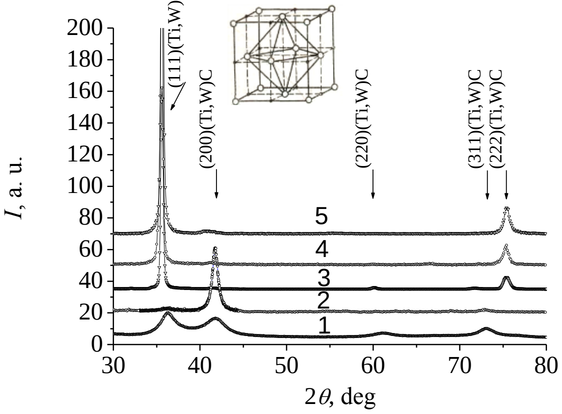


Fig. 2 – Plots of diffraction pattern from TiC-WC quasi-binary system coatings (T_s = 570 K) for the sputtering target compositions:
1 – 5 mol.% TiC – 95 mol.% WC,
2 – 10 mol.% TiC – 90 mol.% WC,
3 – 50 mol.% TiC – 50 mol.% WC,
4 – 75 mol.% TiC – 25mol.% WC,
5 – 90 mol.% TiC – 10 mol.% WC

The deposition temperature increase to 770 K under the small content of titanium gives rise to the axes of texture [100] and [111] (spectra 1 and 2 in the Fig. 3), and a great titanium content (and more than 50 mol.% TiC component correspondingly) – to the preferred orientation with the axis [111] (Fig. 3).

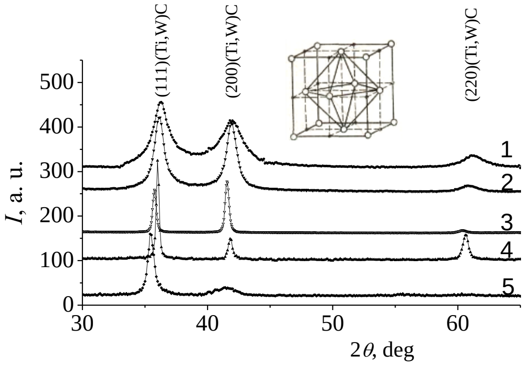
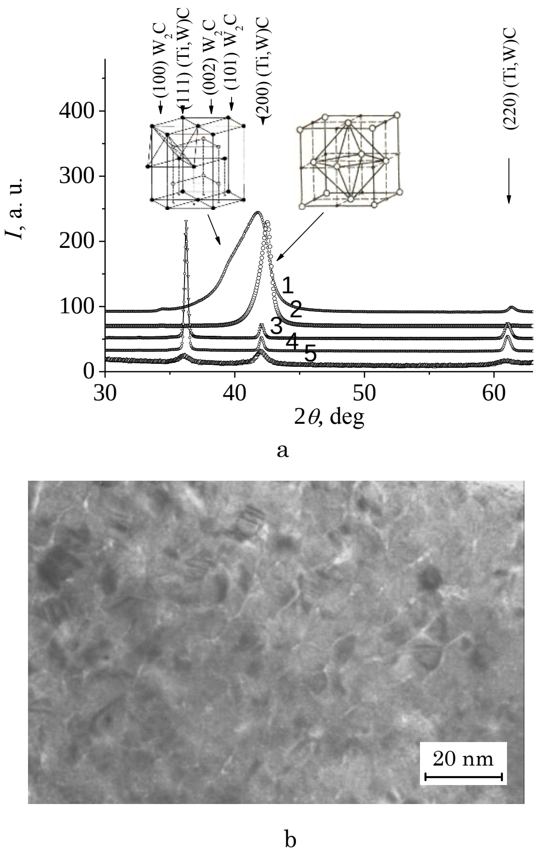


Fig. 3 – Plots of diffraction pattern from TiC-WC quasi-binary system coatings, (T_s = 770 K) for the sputtering target compositions:
1 – 10 mol.% TiC – 90 mol.% WC,
2 – 20 mol.% TiC – 80 mol.% WC,
3 – 50 mol.% TiC – 50 mol.% WC,
4 – 75 mol.% TiC – 25 mol.% WC,
5 – 90 mol.% TiC – 10 mol.% WC

The higher deposition temperature $T_s = 970$ K and a small content of TiC component form a diphase state: apart from the (Ti, W)C phase crystallites with the (200) preferred orientation the formation of tungsten carbide with lower carbon content (W_2C) takes place. According to HRTEM (high resolution transmission electron microscopy) the phase separation leads to the formation of the cellular ordered structure with the average size of the cells 5 nm.

When the target has a composition of 10 mol.% TiC – 90 mol.%WC we can witness the formation of the monophase (Ti, W)C state with the preferred orientation of the plane (200) parallel to the surface (see Spectrum 2 in the Fig. 4). The greater TiC content forms a texture (111).



a

b

Fig. 4 – Plots of diffraction pattern from TiC-WC quasi-binary system coatings (T_s = 970 K) for the sputtering target compositions:
1 – 5 mol.% TiC – 95 mol.% WC,
2 –10 mol.% TiC – 90 mol.% WC,
3 – 50 mol.% TiC – 50 mol.% WC,
4 – 90 mol.% TiC – 10 mol.% WC,
5 – 100 mol.% TiC (a);
electron microscopic photo of the coating with the composition 5 mol.%TiC – 95 mol.% WC (b)

The elemental analysis carried out by energy dispersive X-ray spectroscopy (Table 1) has shown that received coatings are depleted by light atoms. It can be connected with the secondary sputtering during the growth of coatings [14]. The increase in titanium content contributes to the relative growing content of carbon in the coating. It should be mentioned that TiC has high heat of formation (–183.8 kJ/mol). The heat of formation of WC is considerably lower (–37.7 kJ/mol) and a compound is less stable.

Table 1 – The composition of coatings received at $T_s = 970$ K with different correlation of the target constituents (corresponds to Fig. 4)

№ of the spectrum in Fig. 4	The composition of the coating, at.%		
	Ti	W	C
1	2.6	63.3	34.1
2	6.1	56.1	37.8
3	30.9	27.8	41.3
4	48.1	10.3	41.6
5	51.2		48.8

At the deposition temperature T_s = 1070 K and the lowest content of titanium carbide (5 mol.% TiC) the structural state is determined by the lowest carbide W_2C (spectrum 1 in Fig. 5). The growth of TiC component content up to 50 mol% forms two texture axes [100] and [111]. Thus, the higher temperature makes the texture [100] remain till there is a higher TiC component content.

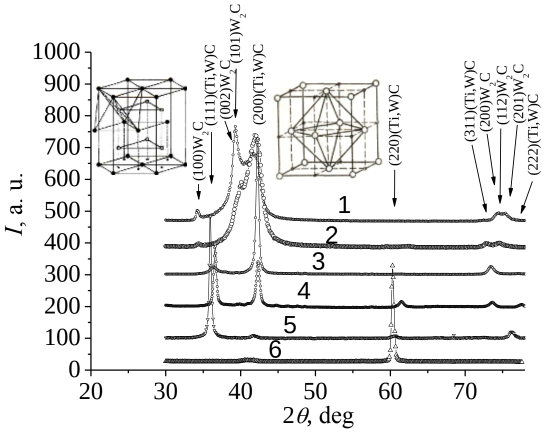


Fig. 5 – Plots of diffraction pattern from TiC-WC quasi-binary system coatings (T_s = 1070 K) for the sputtering target compositions:
1 – 5 mol.%TiC – 95 mol.% WC,
2 – 10 mol.% TiC – 90 mol.% WC,
3 – 20 mol.% TiC – 80 mol.% WC,
4 – 50 mol.% TiC – 50 mol.% WC,
5 – 75 mol.% TiC – 25 mol.% WC,
6 – 90 mol.% TiC – 10 mol.% WC

The method of approximating the profiles of diffraction lines studied the substructure (the size of crystallites, microstrain). In a monophase state the growing temperature makes the size of crystallites increase (Fig. 6). When the two-phase appears there takes place a reverse course of correlation with the inflection of about 970 K (for the composition 5 mol.% TiC – 95 mol.% WC) and more than 1170 K (for the composition 27 mol.% TiC – 73 mol.% WC).

The analogous change in the trend of curve when the two-phase appears is observed in the correlation of microstrain with the substrate temperature during deposition (Fig. 7). In this case in a monophase state the microstrain is reduced while the temperature increases, and two-phases facilitates growing microstrain.

4. CONCLUSION

1. At a low deposition temperature (less than 770 K) in ion-plasma TiC-WC quasi-binary system condensates the single phase – carbide (Ti, W)C – forms in the whole concentration range.

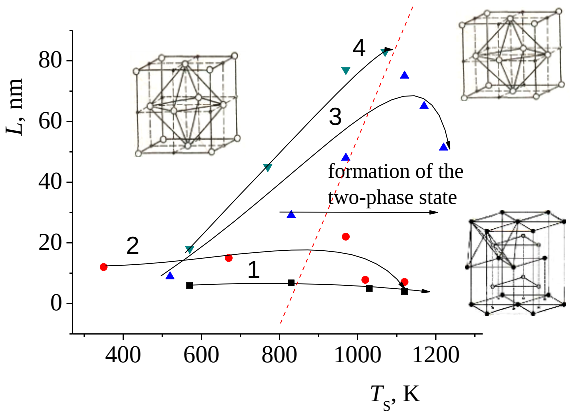


Fig. 6 – The dependence of the size of crystallites (Ti, W) C of substrate temperature. Composition:
1 – 5 mol.% TiC –95 mol.% WC,
2 – 10 mol.% TiC – 90 mol.% WC,
3 – 23 mol.% TiC – 77 mol.% WC,
4 – 34 mol.% TiC – 66 mol.% WC

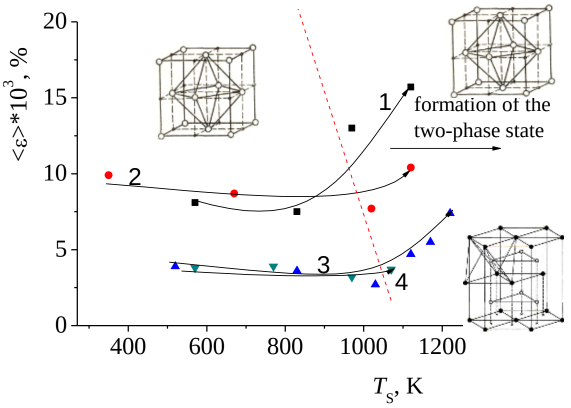


Fig. 7 – Change of microstrain (Ti, W)C crystallites because of the substrate temperature during deposition. Composition:
1 – 5 mol.% TiC – 95 mol.% WC,
2 – 10 mol.% TiC – 90 mol.% WC,
3 – 23 mol.% TiC – 77 mol.% WC,
4 – 34 mol.% TiC – 66 mol.% WC

2. In a monophase state the growing substrate temperature on the substructural level increases the size of crystallites and reduces the microstrain.

3. The highest perfection structure is formed at the temperature 570–770 K in case of equiatomic composition of metallic atoms.

4. The low content (about 10 at.%) of the second element atoms (Ti in the basis of W or W in the basis of Ti atoms) leads to low perfection of the substructure (great microstrain and a small size of crystallites).

5. The formation of α-W_2C phase at the temperature more than 970 K and high tungsten content is determined by the reduced carbon content as a result of the low heat of formation in the system W-C.

6. Increasing deposition temperature stimulates the fact that the axis of preferential growth of crystallites appears. Depending on the deposition temperature and the composition the axes of preferential growth are represented by [111], [100] or [110].

7. The preferred orientation [100] is arisen by the lack of carbon, and the transition to the texture [111] is observed when the relative carbon content in the coating increases.

Влияние термического фактора на фазово-структурные и субструктурные состояния ионно-плазменных покрытий квазибинарной системы TiC-WC

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Проведены исследования влияния температуры осаждения ионно-плазменных покрытий (магнетронная схема) квазибинарной системы TiC-WC разного состава. Показано существенное расширение возможных структурных и субструктурных состояний при неравновесных условиях получения материала из ионно-плазменных потоков. Состав изменяется от однофазного (Ti, W)C к двухфазному (Ti, W)C и α-W$_2$C. Структура – от нетекстурированной к текстуре с осями [111], [100] или [110]. Тип текстуры зависит от температуры осаждения и состава. При однофазном состоянии на субструктурном уровне повышение температуры подложки приводит к увеличению размеров кристаллитов и уменьшению микродеформации. Образование второй фазы приводит к обратным эффектам – повышению дисперсности покрытия и увеличению микродеформации.

Ключевые слова: Ионно-плазменные покрытия, Квазибинарная система TiC-WC, Рентгеноструктурные исследования, Фазовый состав, Текстура, Субструктура, Термический фактор, Теплота образования.

Вплив термічного фактора на фазово-структурні й субструктурні стани іонно-плазмових покриттів квазібінарної системи TiC-WC

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Проведені дослідження впливу температури осадження іонно-плазмових покриттів (магнетронна схема) квазібінарної системи TiC-WC різного складу. Показано суттєве розширення можливих структурних і субструктурних станів при нерівноважних умовах отримання матеріалу з іонно-плазмових потоків. Склад змінюється від однофазного (Ti, W)C до двофазного (Ti, W)C й α-W$_2$C. Структура – від нетекстурованої до текстури з осями [111], [100] або [110]. Тип текстури залежить від температури осадження й складу. При однофазному стані на субструктурному рівні підвищення температури підкладки приводить до збільшення розмірів кристалітів і зменшення мікродеформації. Утворення другої фази приводить до зворотних ефектів – підвищенню дисперсності покриття і збільшенню мікродеформації.

Ключові слова: Іонно-плазмові покриття, Квазібінарна система TiC-WC, Рентгеноструктурні дослідження, Фазовий склад, Текстура, Субструктура, Термічний фактор, Теплота утворення.

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