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Influence of Thermal Factor and Radiation Processing on the Structure and Stress State of TiC-WC System Ion-plasma Coatings

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The deposition temperature and proton radiation influence on the structure and stress-strain state of Ti-W-C system ion-plasma coatings was studied by the methods of wide-angle X-ray diffractometry combined with tensometry. It is found out that during sputtering MeC targets (where Me is a solid solution in the lattice of Ti and W atoms) when the ratio Ti / W reduces the transition from the one-phase state from (Ti, W)C carbide to the two-phase state takes place where the second one is represented by the lower in carbon α-W_2C-phase. Formation of lower phases correlates with depleting the composition by the interstitial element (C) while the content of W in the coating increases that has a relatively small heat of the carbide formation value. Essential changes under irradiation with protons of 200 keV to dose of $6.5 \cdot 10^{17}$ cm^{-2} occur only in a stress-strain state.

Keywords: Ion-plasma coatings, Nanostructure, Ti-W-C System, Phase composition, X-ray diffraction investigation, Stress-strain state, Thermal factor, Heat of the formation, Proton irradiation.

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64.60.My, 61.50.Ks

1. INTRODUCTION

The solid solution ion-plasma coatings on the basis of quasi-binary systems of interstitial phases are those ones that have been most intensively studied recently that is determined first and foremost by high mechanical properties which can be received only in the systems of such a type as a result of separation and ordering [1–9].

The great difference as to the chemical activity to the atoms of interstitial elements (B, C, N) and different types of lattices in an equilibrium state conditioned by it in combination with the considerable divergence as to masses and diffraction capacity correspondingly make the atoms of Ti and W perspective components for the coatings of quasi-binary systems.

The aim of the paper consists in establishing the regularities of the thermal factor and radiation processing influence on the structure and stress state of ion-plasma-coatings received by magnetron sputtering of quasi-binary WC-TiC system.

2. EXPERIMENTAL DETAILS

The coatings have been received by the ion sputtering (magnetron scheme) of hot pressed targets with different volume contents of their constituent WC- and TiC-components (from 5 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. The deposition speed is approximately 0.3 nm/s. Monocrystalline silicon, 370 μm thick, served as a substrate.

Irradiation has been performed by the beam of protons and electrons that has been spread on the area of 100 cm^2 with the general proton and electron flux of 5–20 μA.

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. The volumel percent of phases in the film has been calculated by the standard methods regarding the integral intensity and reflective capacity of several lines of each phase. The analysis of phase composition of coatings has been carried out resorting to the card file ASTM. Substructural properties have been defined by the method of approximating the diffraction line profile form [10].

The composition has been defined on fluorescent data by the method of energy-dispersive spectroscopy, EDX.

The electron microscopy researches have been held on the transmission electron microscope TEM-U ("Selmi", Sumy) at the accelerating voltage 100 kV and electron microscope photos enlargement of 108 000−270 000. The microscope resolution on atomic planes has made 0.2 nm. Ion thinning of film samples, a micron thick, has been made by Xe ions with the energy 5 keV both on the side turned to the substrate and on the condensation surface side. The angle between the ion beam and the sample surface has been equal to 12° while thinning.

3. RESULTS AND DISCUSSION

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. 1) has shown that a one-phase 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. 1). When the content of TiC-component increases the transition

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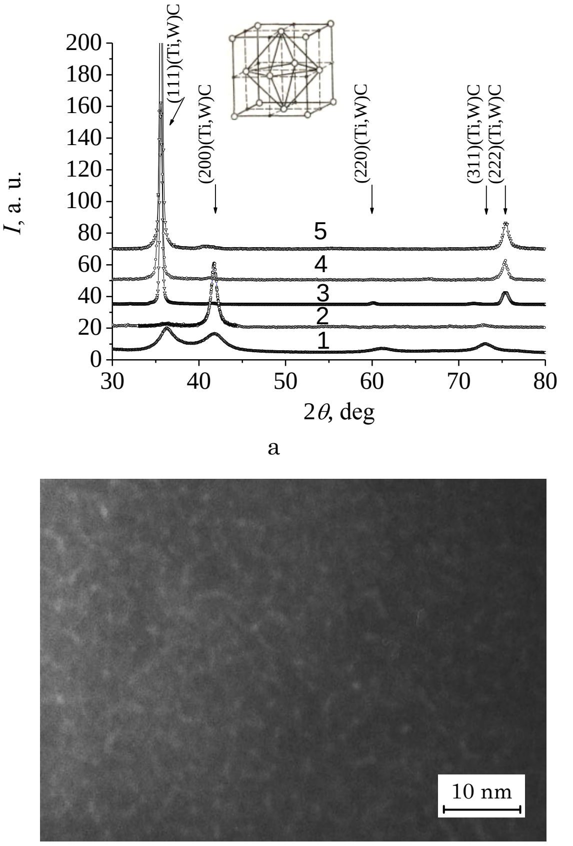
from a non-textured state to a preferred orientation (200) (with the composition 10 mol.% TiC – 90 mol.% WC) takes place. When the content of TiC-component is more a preferred orientation (111) of crystalites is being formed.



a

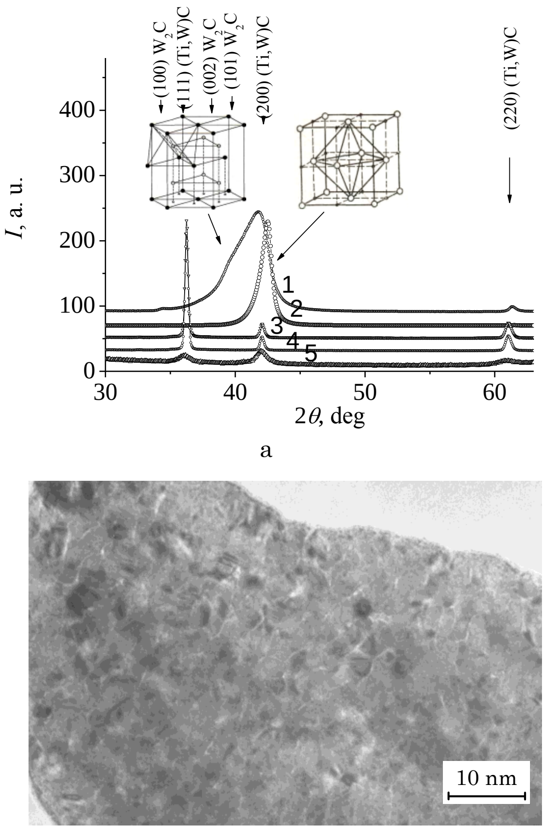
b

Fig. 1 – 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 (a);
electron microscope photo of the coating with the composition 5 mol.% TiC – 95 mol.% WC (b)

The higher deposition temperature T_s = 970 K and a small content of TiC-component form a two-phase 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 (Fig. 2b).

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

The elemental analysis carried out by energy dispersive X-ray spectroscopy has shown that received coatings are depleted by light atoms. It can be connected with the secondary sputtering during the growth of coatings. 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 [11].



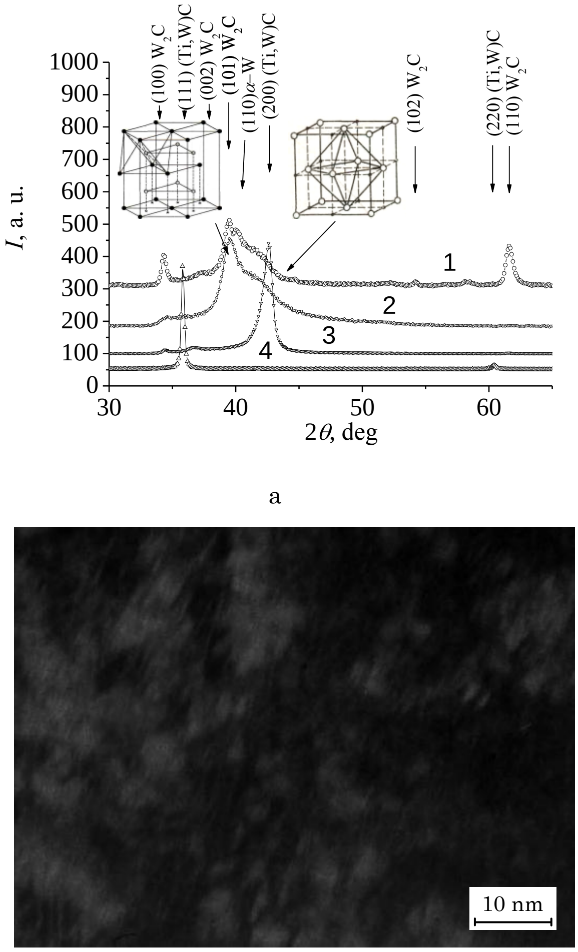
a

b

Fig. 2 – 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 microscope photo of the coating with the composition 5 mol.% TiC – 95 mol.% WC (b)

At the highest deposition temperature T_s = 1120 K (Fig. 3) and the lowest content of titanium carbide component in the target the three-phase state is formed where alongside with the carbide of solid solution (Ti, W)C and lower tungsten carbide W_2C there appears a component much more depleted in carbon – α-W (Spectrum 1 in Fig. 3a). In this case the following characteristic chain of states: W_2C and (Ti, W)C with the preferred orientation (200) → (Ti, W)C with the preferred orientation (200) → (Ti, W)C with the preferred orientation (111) – shifts in the direction of a higher titanium carbide content. For example, the second stage (Ti, W)C with the preferred orientation (200) – in the direction of the composition 20 mol.% TiC – 80 mol.% WC, in contrast to T_s = 570–770 K when such a texture is revealed only when the content makes 10 mol.% TiC and less.

As seen from the photos of high-resolution transmission electron microscopy (Fig. 3b) three-phase condition manifests itself as an area of 10–20 nm strongly depleted in the central portion of the carbon (α-W, black formations in the figure), which are surrounded by lighter formations with the size 30–100 nm (presumably W_2C-phase) and detached from the lightest areas (Ti, W)C with the size 10–30 nm.



a

b

Fig. 3 – Plots of diffraction patterns from TiC-WC quasi-binary system coatings received at T_s = 1120–1170 K:
1 – 5 mol.% TiC – 95 mol.% WC,
2 – 10 mol.% TiC – 90 mol.% WC,
3 – 20 mol.% TiC – 80 mol.% WC,
4 – 75 mol.% TiC – 25mol.% WC (a);
electron microscope photo of the coating with the composition 5 mol.% TiC – 95 mol.% WC (b)

Proton beam irradiation has not changed the types of diffraction patterns principally. Thus, the phase composition and structure (on the texture level) of carbide quasi-binary system coatings can be considered stable to the irradiation simulating the factors of the open space.

The analysis of substructural characteristics concerning the widening diffraction reflexes of coatings before and after irradiation has shown that the size of crystallites does not change, if anything, remaining on the level 28–31 nm in the case of strong texture [111] when the content of TiC-component is large. When the content of WC-component is large the size of crystallites is much smaller: at the deposition temperature 570 K it makes 8–9 nm, and at the temperature 770 K the average size of crystallites increases up to 10–12 nm.

"a-$\sin^2\psi$"-method has been used in the work to investigate stress-strain states. The coatings under investigation have been exposed to compression stresses leading to the compression strain (ε) in the coating growth plane. It was being disclosed in reduction of the lattice spacing when the angle of inclination ψ from the normal to the surface plane increased. The value of the lattice compression strain in coatings with the low content of TiC-component (10–30 mol.%) in the postcondensational state was from –0.5 to –1.4%. The maximum value of the compression strain in the coating was higher and reached from –2.4 to –2.5% when the content of TiC-component was high.

Table 1 presents the results of researching into the macrostrain state of unirradiated and irradiated coating parts (to reduce a mistake in comparing a half of the coating was covered tightly with metal foil that allowed the film to be under the foil in the initial (unirradiated) state).

Table 1 – Results of investigating a macrostrain state of coatings by "a-$\sin^2\psi$"-method

Coating composition	T_s, K	ε, %		$\Delta\varepsilon/\varepsilon$, %	a_0, nm
		initial	irradiated		
90 mol.% TiC – 10 mol.% WC	570	–2.4	–1.8	25.0	0.4332
80 mol.% TiC – 20 mol.% WC	570	–2.2	–1.55	29.5	0.4327
30 mol.% TiC – 70 mol.%WC	570	–1.27	–0.65	49.0	0.4293
20 mol.% TiC – 80 mol.% WC	770	–0.95	–0.4	58.0	0.4287

As one can see in Table 1 there is a general tendency for all the investigated samples: irradiation contributes to the partial relaxation of the initial compression strain. Therefore, on the exposure to irradiation there takes place relaxation of the growth compression strain that becomes most apparent in coatings enriched with WC component reaching the relative change by 29.5% at the proton irradiation dose of $6.5 \cdot 10^{17}$ cm^{-2}.

Summing up the achieved results we can make a schematic phase-texture diagram (Fig. 4). It is clear that a one-phase state of carbide (Ti, W)C with the cubic lattice of NaCl structural type in the case of the relatively low deposition temperature (to 870 K) spreads to the whole concentrational range. It should be mentioned that unlike simple heating when the growing temperature increases the degree of disorder due to more vacancies the increasing substrate temperature during deposition forms a more equilibrium state in comparison with deposition at low temperatures. It is conditioned by the fact that deposited particles have a relatively high energy and the temperature equivalent to it, that is why the higher the deposition temperature is, the less the supercooling is while thermalizing such particles.

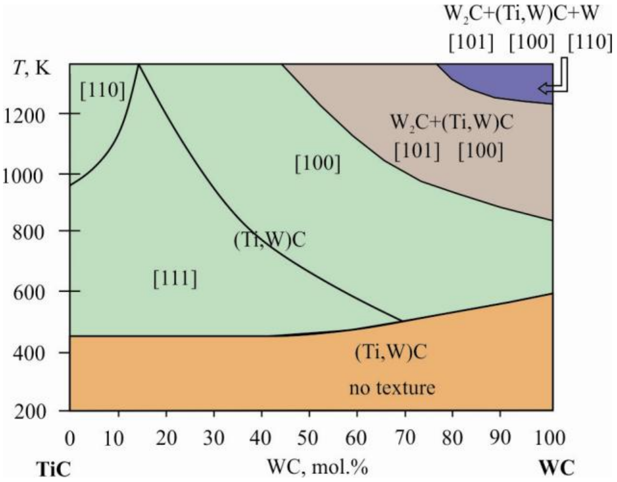


Fig. 4 – Schematic representation of the phase-texture diagram of quasi-binary TiC-WC system ion-plasma coatings

Then formation of (Ti, W)C phase with a relatively simple lattice in the whole concentrational range (see the bottom of Fig. 4) can be explained by relatively low diffusion mobility during great supercooling that stabilizes high-temperature phases with cubic lattices. In particular, it concerns a part of TiC-WC system for the high content of WC-component that forms the phase with the hexagonal lattice at these temperatures in an equilibrium state.

The quasi-binary TiC-WC system coatings have displayed the resistance to irradiation both on the phase composition level and the structural-substructural one.

ACKNOWLEDGMENTS

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