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Regularities in Forming the Phase Composition, Structure, Substructure and Growth Morphology of Nanostructured Ion-plasma Coatings of Quasi-binary Section Ti-W-B System

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Using the method of X-ray analysis with the diffraction vectors in the plane and perpendicularly to the plane of growth of nanocrystalline W-Ti-B system condensates, regularities of forming the phase composition, structure and substructural characteristics were revealed. The designer's software package «ScecDec» was employed to process the diffraction profiles. The deposition temperature and the ratio of Ti/W atoms in the coatings were used as influential parameters. The models to describe the obtained regularities are suggested.

Keywords: Ion-plasma Coatings, Nanostructured, Ti-W-B System, Phase Composition, Diffraction Vectors

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1. INTRODUCTION

According to its structural state, nanocrystalline materials are intermediate between amorphous and microcrystalline ones, that's why the structure and properties of nanomaterials often differ from the inherent amorphous-like and from the inherent microcrystalline states.

Thus nanocrystalline materials at the stage of transformation from the «amorphous» to the «microcrystalline» may have transient crystal structures metastable at the equilibrium state [1]. However, as it is well known, the transition from an amorphous to a crystalline state is accompanied by decrease of the specific volume and the formation of tensile macrostrain in hard material which is connected with the massive substrate. At the same time, for example, structural compressive stresses, which develop in the deposition material while obtaining it as a result of the near-surface implant of the fractions forming the coating, often appear in nanocrystalline ion-plasma condensates which define the deformed state [2]. The presence of such features characteristic of nanocrystalline materials that have mostly quite unique character specific to a particular technology, makes it difficult to model the properties of these materials without a thorough study of the regularities of their structural and stress-strain states' formation.

In this work, for such a comprehensive study, the material of quasi-binary TiB_2-W_2B_5 system has been selected, which is one of the most perspective ones as to industrial application in mechanical engineering and microelectronics.

2. EXPERIMENTAL DETAILS

Samples of 1...2.5 mm thick were produced by magnetron sputtering of hot-pressed targets TiB_2, TiB_2-W_2B_5 with content of W_2B_5, varying from 23 to 80 molar %, and the W_2B_5 target of a stoichiometric composition with a sector of TiB_2 applied to the surface. In the latter case, as the component TiB_2 was being produced, the composition of the coating was changed. For obtaining condensates there was applied a planar magnetron -type system. The substrate was arranged at the distance of 55 mm above the anode and the distance between the anode targets was 4-5 mm. In the process of obtaining ceramic films the argon pressure in the vacuum chamber (P) was 0.5 Pa. The targets had the following average sizes: the diameter $d = 50$ mm, the thickness $t = 4$ mm.

The samples were obtained from polish silicon wafers and glass ceramics of 380 micrometers and 450 micrometers thick, respectively.

Wide Angle ($2\theta > 10$ degrees) X-ray research of the samples was conducted using the diffractometer DRON-3 in the emission of Cu–K_α, while recording the scattering spectrum in a discrete mode with a scanning step, changing depending on the half-width and the intensity of diffraction lines in the interval $\Delta(2\theta) = 0.01$–0.05 degrees, with an exposure time 20-100 s. The diffraction studies were carried out using «reflection» and «transmission» scheme [3]. In the latter case the investigated samples were separated from bulk substrates beforehand. Processing of the spectral data was carried out using the author's software package «SpecDec» adapted to the challenges solved in the work of [4]. Fig. 1 shows a general view of the program window with processed X-ray diffraction spectrum of condensate obtained at $T_s = 700^\circ$C and the atomic ratio of Ti/W = 0.15.

The analysis of the substructure characteristics (crystallite size and microstrain) was conducted by the approximation method. Calculation was based on the analysis of the width of two orders of reflections from the planes according to the standard method of constructing Hall graphs [5].

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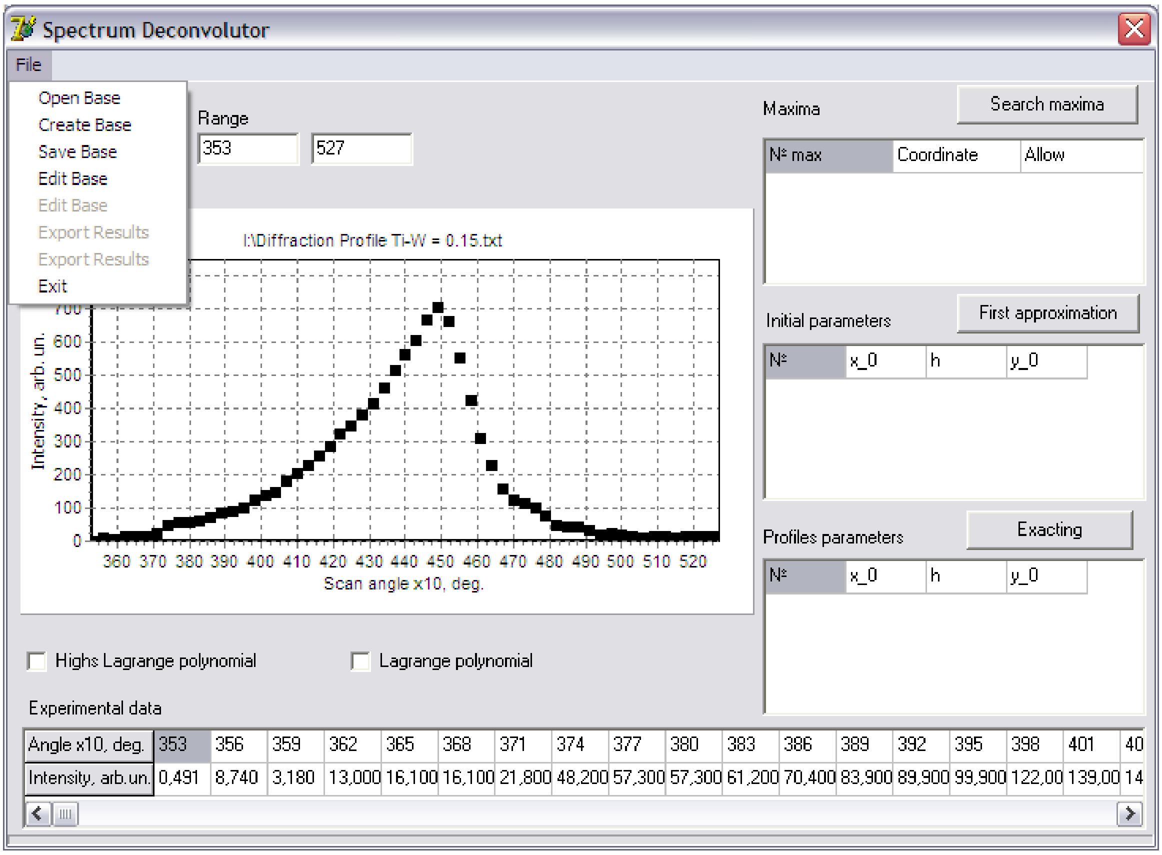


Range 353 527

☐ Highs Lagrange polynomial ☐ Lagrange polynomial

Experimental data

Angle x10, deg.	353	356	359	362	365	368	371	374	377	380	383	386	389	392	395	398	401	40
Intensity, arb.un.	0,491	8,740	3,180	13,000	16,100	16,100	21,800	48,200	57,300	57,300	61,200	70,400	83,900	89,900	99,900	122,00	139,00	14

Fig. 1 – A general view of the program window

3. RESULTS AND DISCUSSION

Fig. 2 shows parts of the diffraction spectra of the coatings obtained at T_s = 700°C. It is seen that when the ratio, in atomic percent, Ti/W changes from 0.61 to 0.33, a second texture of the solid solution crystallites (10.1) appears. At Ti/W < 0.4 a formation of two-phase state: a solid solution (Ti,W)B_2 with hexagonal crystal lattice and the second nanocrystalline phase β-WB with orthorhombohedral crystal lattice.

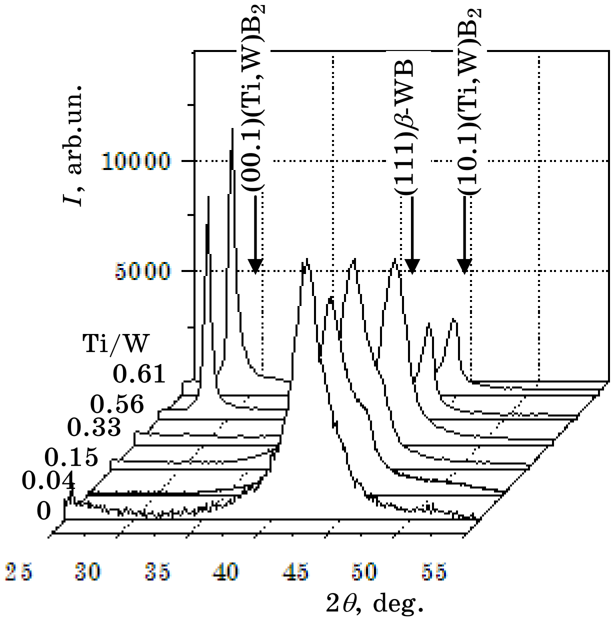


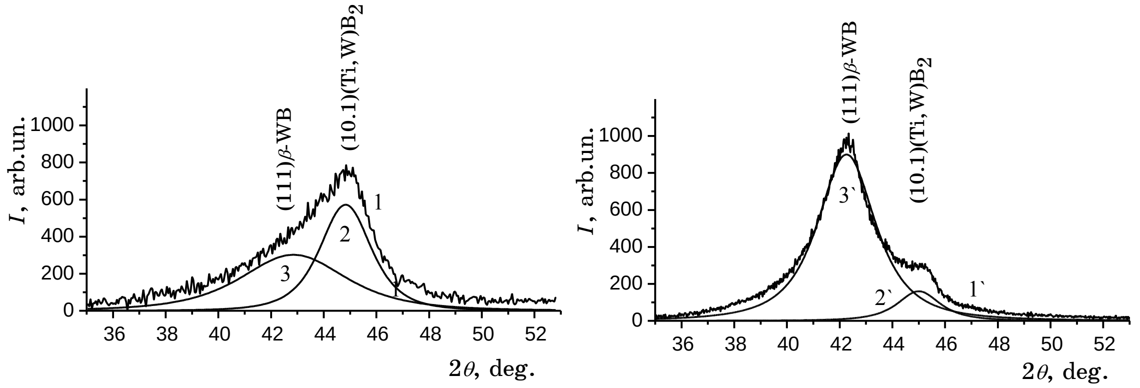
Fig. 2 – X-ray diffraction spectra of condensates obtained at T_s = 700°C with different atomic ratio of Ti/W (shown on the left-hand scale) (the emission of Cu-K_α)

After the diffraction spectra are separated by the program «SpecDec», it can be observed that (Fig. 3) when the ratio Ti/W changes from 0.15 (Fig. 3a) to 0.04 (Fig. 3b) the ratio of the volume content of (Ti,W)B$_2$ and β-WB phases in the coatings obtained at $T = 700$°C varies from 45/55 to 12/88.

The calculation of substructural characteristics, held for the smallest percentage of Ti/W = 0.04 , showed that the crystallite size of (Ti,W)B$_2$ with the dominant orientation (10.1) remained sufficiently large (22 nm), even when volume concentration was small and microstrain was 0,4%. The crystallites β-WB were significantly smaller (4 nm), and the microstrain value in them was less than 0.01%, i.e. close to zero.

Thus, the characteristic feature observed during Ti/W ratio decreasing is reducing the size of the crystalline condensate components to the value of a few nanometres.

The high-temperature annealing when $T_{ann} = 1020$ °C does not result in a noticeable change in the size of crystallites (Ti,W)B$_2$ of solid solution, however, it stimulates recrystallization processes in the original smaller crystallites of β-WB phase. As for the ratio Ti/W = 0.15 the size of crystallites (Ti,W)B$_2$ during an hour annealing when $T_{ann} = 1020$°C (Fig. 4) hardly changes, remaining equal to 7 nm, at the time when β-WB crystallites are increasing in size at that temperature of annealing, on average, from 2.5 nm to 3.2 nm. The relative increase in β-WB phase diffraction lines intensity during annealing shows the increase in its specific volume content that appears to be related to the previously established effect of reducing the content of boron atoms in the coating during high-temperature annealing [6].



a b

Fig. 3 – X-ray diffraction spectra of condensates obtained at $T_s = 700$ °C and the atomic ratio of Ti/W = 0.15 (a) and 0.04 (b): 1, 1'- initial diffraction profiles; 2, 3 and 2', 3'- dedicated to diffraction profile lines

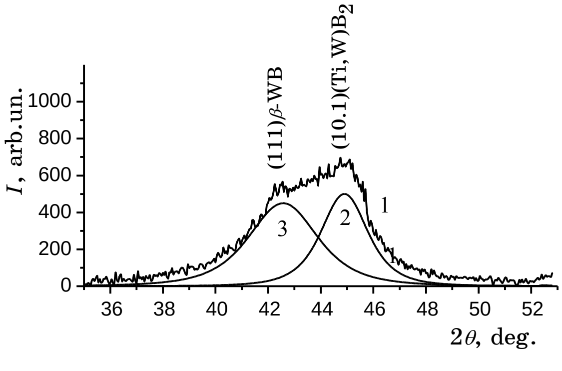


Fig. 4 – X-ray diffraction spectrum of condensate, obtained at $T_s = 700$°C and the atoms ratio Ti/W = 0.15 after an hour high-temperature annealing when $T_{ann} = 1020$°C: 1 – initial diffraction profile; 2.3 – dedicated to diffraction profile lines

REFERENCES

1. A.P. Shpak, O.V. Sobol', Yu.A. Kunitsk'ii, P.G. Cheremskoj, *Samoorganizacija v nizkorazmernyh sistemah* (K.: IMF NANU: 2005) (in Russian).
2. O.V. Sobol', E.A. Sobol', A.A. Podtelezhnikov, *Functional Materials* **6** No5, 868 (1999).
3. O.V. Sobol', O.A. Shovkoplyas, *Tech. Phys. Lett.* **39** No6, 536 (2013).
4. O.Yu. Reshetov, O.A. Shovkoplyas, Yu.M. Lopatkin, *Informatyka, matematyka, mehanika (IMM)*, 219 (Sumy: SumDU: 2007). (in Ukrainian).
5. L.S. Palatnik, M.Ja. Fuks, V.M. Kosevich, *Mehanizm obrazovanija i substruktura kondensirovannyh plenok* (M.: Nauka: 1972) (in Russian).
6. O.V. Sobol, *Functional Materials* **13** No3, 486 (2006).