STRUCTURE AND PROPERTIES OF W, Ta AND W-Ta COATINGS DEPOSITED WITH THE USE OF A GAS-PLASMA SOURCE

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W, Ta and W-Ta coatings were deposited by argon ion sputtering of targets made from appropriate metals using the gas plasma source. Mechanical properties of the obtained coatings were investigated by the methods of X-ray fluorescence analysis, scanning electron microscopy, X-ray diffraction analysis and nanoindentation. It has been shown that the coatings have a *bcc* structure with crystallite size from 16 to 30 nm. Single-component coatings have a columnar structure. Introduction of Ta (5…38%) in the W coating leads to the columnar growth suppression and formation of a condensate with more equiaxial elements. Coatings with such a structure possess the best mechanical properties (H/E-0.7…0.77).

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INTRODUCTION

Tungsten (W), combining in itself such properties as a high melting temperature, high density and wear resistance, as well as, low sputtering ratio and low hydrogen permeability, is one of the main candidates for material of the first wall of fusion reactors [1]. An approach to the improvement of tungsten mechanical properties is its alloying with tantalum [2]. Tantalum (Ta) is a transition metal having a high melting temperature, high strength and low electric resistance, as well as, high chemical inertness at temperature to 150 °C.

W-Ta alloys possess a higher corrosion resistance and better mechanical properties as compared to the pure tantalum. However, the obtaining of these alloys is complicated because of their high melting temperature [3]. Tungsten alloyed with tantalum (5%) has a decreased fragility and lowered deuterium retention in comparison with pure tungsten [4].

Ta-W coatings are widely used in microelectronics as diffusion barriers and metalized layers and as wear-resistant coatings [5, 6]. To obtain nanostructure coatings from refractory metal one uses the ion-plasma deposition methods [5–10]. Nanostructured metallic coatings, unlike the microcrystalline analogs, can have a higher hardness, strength and wear resistance [11, 12]. For example, magnetron nanocrystalline tantalum coatings have the hardness of ~ 11.6 GPa [8], and nanocrystalline and amorphous Ta-W coatings with tungsten concentration of 7.9…9.2 at.% have the hardness of 14.9 and 17.11 GPa, respectively [13]. Nanocrystalline coatings based on two metals have significantly higher radiation resistance, than that of fine-crystalline coatings, and are promising for use under ion-irradiation conditions [14].

So, of a particular interest is to obtain composite nanostructure coatings possessing a high hardness and strength based on refractory metals by varying their concentrations in the wide range.

A goal of the present study was deposition of W, Ta and W-Ta coatings and investigation of their structure and mechanical properties depending on the concentration of elements.

1. EXPERIMENTAL TECHNIQUE

The design and principle of operation of the gas-plasma source (GPS) used for production of multicomponent coatings is described in detail in [15]. In the present paper a vacuum chamber comprises a GPS in the form of a tubular anode of 200 mm in diameter and 380 mm long with a tungsten hot cathode. Outside the anode there is a focusing coil, which generates a magnetic field of about 50 Oe. Experiments were carried using a filament current of a tungsten spiral of 100 A at a positive anode potential in the range of +40…+50 V and under argon pressure of ~ 0.5…0.8 Pa. The discharge current was 30…50 A. Sputtering targets were polycrystalline W and Ta plates onto which a negative potential of -200…-500 V has been applied. The concentration of elements in the coatings was given by the ratio between the areas of tungsten and tantalum targets. The discharge-generated plasma was directed onto the target of the plasma-optical system. The anode-target distance was 50 mm. The ion-current density on the target was 10…20 mA/cm^2. Coatings were deposited on the substrates (10×20×1.5 mm) of stainless steel 18Cr10NiTi and silicon wafers (10×20×0.3 mm) at a negative potential of -50 V. The substrate temperature during deposition did not exceed 500 °C. The reached coating deposition rate was of ~ 6 μm/hour. The deposition rate has been measured by the "shadow knifes" method using the microinterferometer MII-4.

The element concentration in the coating was measured by the X-ray fluorescence method with the spectrometer "Sprut". The phase composition and structure of coatings of the system were studied by the X-ray diffraction analysis using the diffractometer DRON-3 in the Cu-Kα radiation and the scanning electron microscope JSM-7001F.

The nanohardness was measured with a device Nanoindenter G200 by the CSM method [16] to the ~ 200 nm depth of penetration of the Berkovich indenter that was less than 0.1 of the coating thickness. The data for the nanohardness and Young modulus obtained at a penetration depth from 150 to 200 nm were averaged by 10 measurements.

2. RESULTS AND DISCUSSION

The composition of the coatings being formed, controlled by the ratio between the areas of sputtering targets, depends on the sputtering yield of target materials under the given experimental conditions, as well as, on the relative position of targets and samples relatively to the plasma stream. The coating composition measured by the X-ray fluorescence method and the ratio of W and Ta target areas is given in Table.

Dependence of the element concentration in the coating on the sputtering target areas

S_W, %	S_{Ta}, %	W, weight %	Ta, weight %
100	0	100	0
86	14	95	5
67	33	76	24
56	44	62	38
0	100	0	100

X-ray diffraction pattern of the coatings obtained are shown in Fig. 1. It is seen that in all the coatings a bcc crystalline lattice is revealed. The crystalline lattice period and the crystalline grain size, calculated by the position and width of diffraction lines, are presented in Fig. 2. For single-component coatings the period of W and Ta crystalline lattice slightly exceeds the table values for these materials of 0.3165 and 0.3305 respectively that can be related with formation of residual compressive stresses.

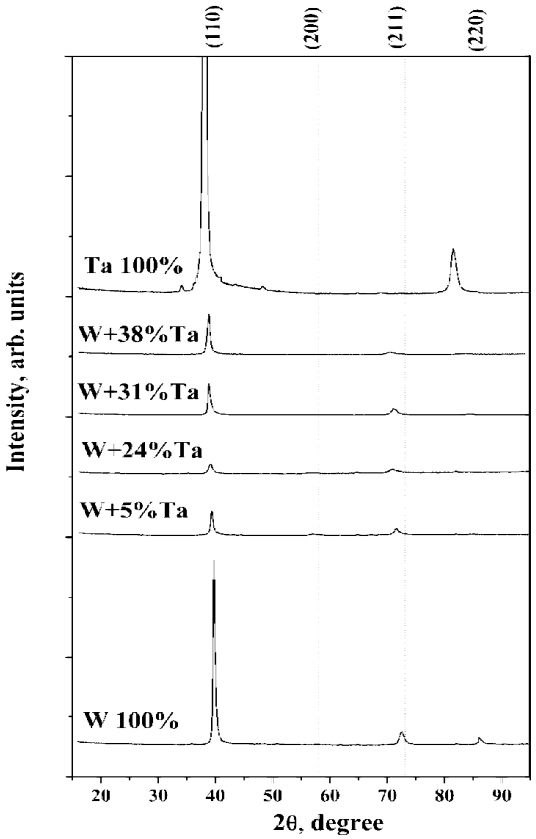
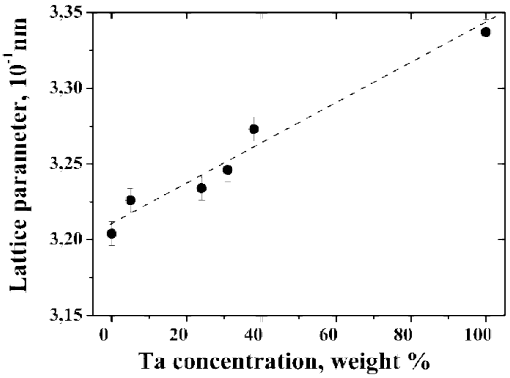
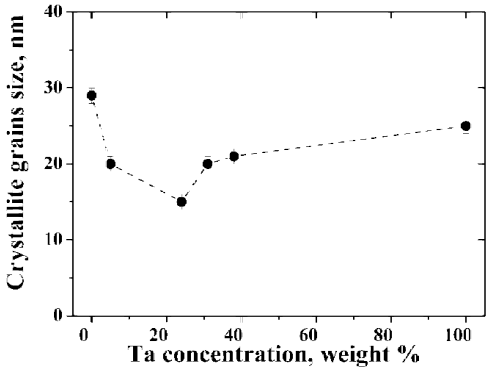


Fig. 1. X-ray diffraction patterns of W and Ta coatings having different compositions (dashed lines show the position of the lines for tungsten)

The ratio of the line strengths in the diffraction patterns evidences on the formation of an axial-type structure with axis [110] in the normal-to-surface direction. This texture is very distinct in the Ta coating. In the diffraction pattern of the coating the lines (110) and (220) are the most intense and the width of the rocking curve of the reflection (110) does not exceed 10 degrees. For tungsten the rocking curve is slightly broader (13 degrees).



a



b

Fig. 2. Lattice period (a) and grain size (b) of W-Ta coatings as a function of the tantalum concentration

One of the conditions for obtaining the Ta coating with bcc structure (110) is a high degree of plasma ionization and ion energy otherwise predominantly a β-Ta phase is formed [7]. Parameters of the magnetron deposition process (argon pressure and ion energy) also have a strong influence on the formation of one or another possible phases (α or β) in the tungsten coatings [5] which differ from each other by mechanical and electric properties. In our case the ion energy of the material being deposited was ~ 50 eV that, apparently, leads to the formation of a bcc structure in the coatings independently on the element concentration.

The crystallite grain size calculated by the Selyakov-Sherrer formula is 29 nm for tungsten and 25 nm for tantalum.

In Fig. 3,a,b shown are the electron-microscope images of cross fractures in W and Ta coatings where a columnar-fiber structure is clearly apparent. So, the strong texture is formed due to the columnar grain growth when the preferred orientation of close-packed planes (110) is observed in the substrate plane. This is a typical columnar structure of grain growth with a slow mobility of atoms being deposited [17]. A similar struc-

ture is characteristic for the tantalum coatings obtained by the magnetron deposition method on the silicon substrates [8, 18]. In our case the average column width is near ~ 100…200 nm.

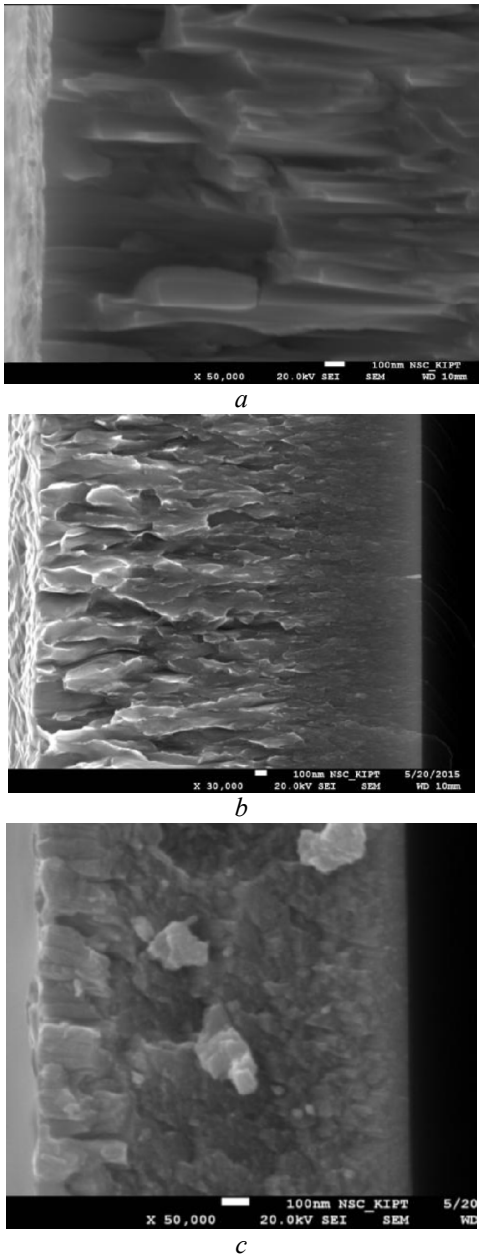


Fig. 3. Microphotographs of the fracture in the 2.5 μm thick W coating (a); 3.5 μm thick Ta coating (b) and 1.5 μm thick W-Ta coating (c)

In all the two-component coatings the formation of a substitutional solid solution having a similar bcc structure was observed. Other phases were not discovered by the X-ray diffraction method. The solid solution lattice period increases linearly with tantalum concentration increasing. The texture in these coating is less distinct, and the grain size is significantly smaller than in the single-component coatings.

These data correlate with the electron microscopy data. It is seen in the electron-microscope image of the W-5Ta coating (see Fig. 3,c) that the columnar growth is suppressed and the structure element size decreases.

For the W-5Ta alloyed coatings the columnar structure is visible only at the external coating surface, and the structure itself is composed of granules of < 50 nm.

Introduction of the second element into the composition of a coating to be deposited prevents columnar structure formation and promotes new grain formation. It can be supposed that in the coatings without columnar structure porous and voids are absent. In the both cases the silicon substrate-coating interface is sharp and even without any visible element-to-element interdiffusion zone.

The nanohardness of the coatings and its Young's module as a function of the element concentration are shown in Fig. 4. The nanohardness of pure tungsten coatings is (17±1) GPa, that is slightly higher than the data for magnetron α-W coatings (H = (12.79±0.94) GPa), obtained in [5]. This difference can be explained by the difference in the value of residual compression stresses which are formed under conditions of ion bombardment of a deposited film surface. The Young modulus for tungsten films is at a level of (420±20) GPa that coincides with literature data on the nanoindentation of monocrystalline samples [19]. The pure tantalum coatings have a nanohardness H = (8±1) GPa and Young modulus H = (8±1) GPa which is higher than that of the monocrystalline tantalum (E = 189 GPa) [19, 20]. In this case the nanohardness of the coating formed is lower as compared with that of magnetron coating (H = 11.6 GPa) [9].

The elastic recovery for all the coatings, independently on their composition, is of ~ 50%, that significantly exceeds the values for metals with a monocrystalline structure (< 5%) [20].

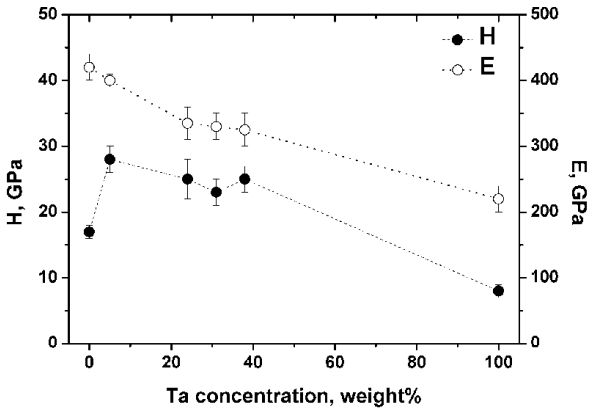


Fig. 4. Nanohardness and Young modulus of W-Ta coatings as a function of the tantalum concentration

The alloying of the coatings with tantalum (5%) sharply increases the nanohardness to (28±2) GPa and slightly decreases the Young modulus to (400±10) GPa. Further increase of the tantalum concentration (24…38%) in coatings leads to the insignificant nanohardness decrease to 23…25 GPa and to the Young modulus decrease to 325…335 GPa. Such a behavior of alloyed coatings may be related with the decrease of crystallite sizes (see Fig. 3,c), as well as, with the common structure changing from the columnar to the granular nanocrystalline one. In this structure the grain boundaries can play a significant role by hampering the dislocation propagation. The grain boundary nature – in

particular, chemical one, can also promote a high hardness, since the *bcc* metals are subjected to impurity segregation [12]. According to [13] the structure factor makes the main contribution into the hardness increase for the W-Ta system, but not the solid-solution hardening.

Fig. 5 presents the nanohardness (H)-to-Young modulus (E) ratio for W-Ta coatings as a function of the tantalum concentration. The H/E ratio is related with the elastic fracture strain [21]. The coatings being resistant to the plastic strain demonstrate higher values of this ratio.

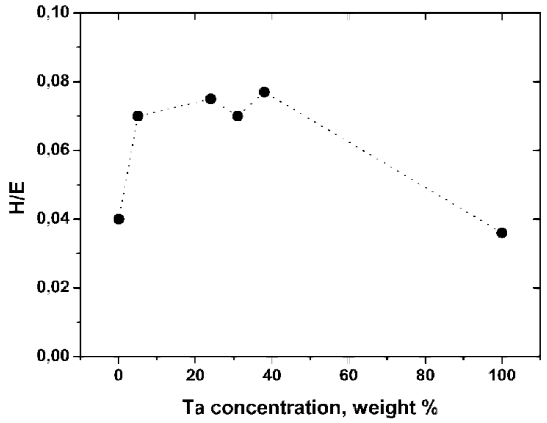


Fig. 5. Nanohardness (H)-to-Young modulus (E) ratio for W-Ta coating as a function of the tantalum concentration

When the Young modulus decreases with simultaneous hardness increasing, the fragility of coatings, as a rule, decreases, and the energy, necessary for fracture is higher in the coatings compared to the plastic material. The W and Ta coatings not alloyed are characterized by the H/E value of ~ 0.04, for W-Ta coatings this ratio increases to ~ 0.07…0.077 that evidences about their higher wear resistance.

CONCLUSIONS

The method of argon ion-plasma sputtering of tungsten and tantalum targets using the gas-plasma source was applied to obtain W, Ta and W-Ta coating with tantalum content from 5 to 38%.

In all this coatings the formation of a *bcc* structure characteristic for tungsten and tantalum is observed. Introduction of the second component in the coating composition leads to the formation of a substitutional solid solution, in which the lattice parameter increases linearly with tantalum content increasing. Single-component W and Ta coatings have a columnar structure with a strong axial structure and grain size of 29 and 25 nm. When tantalum is added in the tungsten coating a more equilibrium granular structure with a less degree of perfection and grain size (15…20 nm) is formed. Coatings with such a structure have higher mechanical properties as compared to the single-component coatings (H = 23…28 GPa, H/E = 0.7…0.77).

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СТРУКТУРА И СВОЙСТВА ПОКРЫТИЙ W, Ta И W-Ta, СИНТЕЗИРОВАННЫХ С ПОМОЩЬЮ ИСТОЧНИКА ГАЗОВОЙ ПЛАЗМЫ

В.М. Лунёв, А.С. Куприн, В.Д. Овчаренко, В.А. Белоус, А.Н. Морозов, А.В. Ильченко, Г.Н. Толмачёва, Е.Н. Решетняк, Р.Л. Василенко

С помощью источника газовой плазмы, путем распыления ионами аргона мишеней из соответствующих металлов получены W, Ta и W-Ta-покрытия. Методами рентгенофлюоресцентого анализа, сканирующей электронной микроскопии, рентгеноструктурного анализа и наноиндентирования изучены: состав, структура, а также механические свойства полученных покрытий. Показано, что покрытия обладают ОЦК-структурой с размером ОКР от 16 до 30 нм. Однокомпонентные покрытия обладают столбчатой структурой. Введение в состав W-покрытия Ta (5...38 мас.%) приводит к подавлению столбчатого роста и формированию конденсата с более равноосными структурными элементами. Покрытия с такой структурой обладают наилучшими механическими свойствами (H/E – 0,7...0,77).

СТРУКТУРА ТА ВЛАСТИВОСТІ ПОКРИТТІВ W, Ta І W-Ta, ЩО СИНТЕЗОВАНІ ЗА ДОПОМОГОЮ ДЖЕРЕЛА ГАЗОВОЇ ПЛАЗМИ

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За допомогою джерела газової плазми, шляхом розпилення іонами аргону мішеней з відповідних металів отримані W, Ta і W-Ta-покриття. Методами рентгенофлюоресцентного аналізу, скануючої електронної мікроскопії, рентгеноструктурного аналізу та наноіндентування вивчені: склад, структура, а також механічні властивості отриманих покриттів. Показано, що покриття володіють ОЦК-структурою з розміром ОКР від 16 до 30 нм. Однокомпонентні покриття володіють стовбчастою структурою. Введення до складу W-покриття Ta (5…38 мас.%) призводить до припинення стовпчастого росту і формуванню конденсату з більш равновісними структурними елементами. Покриття з такою структурою володіють кращими механічними властивостями (H/E – 0,7...0,77).