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Structural Engineering of the Multilayer Vacuum Arc Nitride Coatings Based on Ti, Cr, Mo and Zr

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The possibilities of structural engineering of multi-period vacuum-arc coatings based on nitrides of transition metals Ti, Cr, Mo, and Zr have been investigated by structural studies (X-ray diffraction and electron microscopy) in combination with measurement of hardness by indentation. The formation of phases with a cubic crystal lattice under nonequilibrium conditions under vacuum arc method of production. The supply of a negative bias potential of – 200V in mononitrides leads to the predominant formation of texture of crystallites with the [111] axis. The introduction of thin (about 10 nm) metal layers leads to a decrease in texture perfection [111] and texture formation [100]. This effect is associated with a change in the stress-strain state of nitride layers. It is determined that the composite multiperiod coatings (Me_1N/Me_2N)/(Me_1/Me_2) have a greater hardness and greater resistance compared to MeN/Me. For a multiperiod system with damping metal layers – (ZrN/CrN)/(Zr/Cr), superhard coatings with a hardness of 46 GPa were obtained.

Keywords: Vacuum-arc method, Multiperiod coatings, Structural Engineering, Stress state, Hardness, Strength.

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1. INTRODUCTION

Nowadays, a structural engineering is one of the more sought-after scientific and technical areas of materials science. Due to the use structural engineering is already at the development stage manage to predict the functional parameters derived materials [1]. In the area of production of coatings - structural engineer determines the possibility of the directional selection of physical and technological conditions of deposition and the subsequent impact on the condensate to produce the desired structure of the design that determines the achievement of the required performance properties [2 – 4]. A result of using of the structural engineering can be obtained, as a new phase states [5] as well as the most effective structure [6] and the stress-strain states [7].

The most promising technology industrial obtaining coatings is vacuum-arc PVD method. This method is widely applied to obtaining coatings TiN [8], HfN [9], MoN [10, 11], ZrN [12], CrN [13, 14], NbN [15], and lately multicomponent (TiAl)N [16], (TiCr)N [17], (MoAl)N [18] and multiple element high-entropy materials [19]. However, the highest operational characteristics of manages to reach by engineering composite multilayer periodic structures. Among the most investigated in this direction compositions can be attributed TiN/Cu [20], TiN/CrN [21], HfN/VN [22], TiN/α-Ti [23], (Ti, Al)N/VN [24, 25] and TiN/VN [25, 26], etc., from materials as compatible with each other, so [27] and incompatible [29]. Results of investigations are prove that multicomponent and especially multilayer coatings considerably exceed coatings TiN by properties [7, 19].

In this work task was to identify opportunities for structural engineering multiperiod structures when used as constituent elements of the most promising transition metals. According to this, the aim of this study was to establish the regularities of formation of phase composition, structural conditions and their influence on the hardness of the multilayer vacuum-arc nitride coatings based on Ti, Cr, Mo, and Zr.

2. SAMPLES AND METHODS OF RESEARCHES

Multilayered two-phase nanostructured coatings were precipitated in vacuum-arc installing "Bulat-6". By way of materials of cathodes are used: titanium BT 1 – 0; low-alloy zirconium, chromium and molybdenum; active gas – nitrogen (99,95 %). Coatings were deposited on surface of the samples (20 × 20 × 2 mm) from steel 12X18H10T that prepared by standard methods of grinding and polishing. Procedure of deposition of multilayer coatings is included following operations. Vacuum chamber was evacuated to a pressure of 10^{-5} Torr. Then to swivel apparatus with substrate holder were fed negative potential of 1 kV, were included evaporator and were produced purification of surface of first of the two substrates by bombardment of ions of chromium during 3 – 5 min. Thereafter substrate holder was rotated 180 ° and was carried out same purification of second substrate.

In forming multilayer coatings after deposition of first layer are both evaporators were turned off, were turning substrate holder for 180° and again concurrently have included both evaporators. Arc current during the deposition was 100 A, nitrogen pressure (P_N) in the

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chamber was varied in the interval $3 \cdot 10^{-3}$ Torr, distance from the evaporator to the substrate – 250 mm, substrate temperature (T_s) was in the interval 250 – 350 °C. Coatings of thickness about 10 microns were obtained. At the time of deposition on a substrate was fed constant negative potential $U_b = -70 - -200$ V.

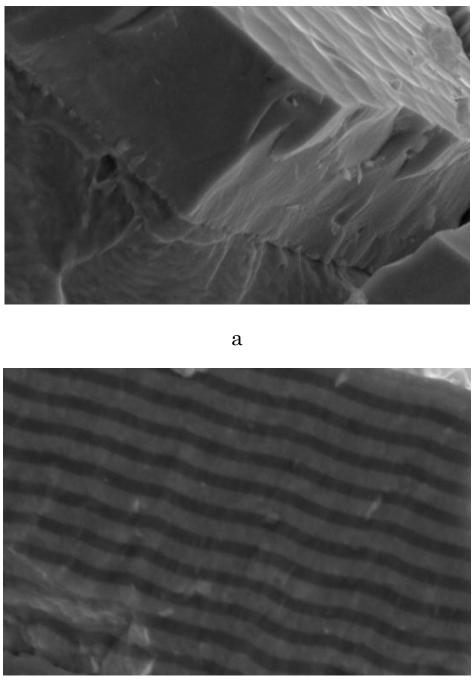
Phase composition, structure and substructural characteristics have been studied by method X-ray diffractometry (DRON-4) with use Cu-K_α - radiation. For monochromatisation of registered radiation was used graphite monochromator, which was installed in a secondary beam (ahead of the detector). Study of phase composition, structure (texture, substructure) were produced by means traditional methods of ray diffractometry through the analysis of position, intensities and forms of profiles of the diffraction reflexes. For decryption of diffractograms were used tables of International Centre for Diffraction Data Powder Diffraction File. Substructure characteristics were determined by method approximation.

Stress-strain state determined $\sin^2\Psi$-method for cubic lattice [29] under the assumption of a plane-strained state of the coating.

Microindentation was performed on installing "Micron-gamma" at a load till $F = 0{,}5$ H diamond pyramid Berkovich with an angle of sharpening 65 °, with automatically execution loading and unloaded throughout 30 seconds [30].

3. RESULTS AND DISCUSSION

Comparison of the morphology of the fracture nitride coatings in a single layer and multi-layer state (Fig. 1) shows that at the transition from single-layer to multilayer structure is maintained good planarity of the layers. Trickle metal phase as inside coating monolayer so and multilayer compositions practically not detected. Changes associated with the factor thickness for the layers affect the structural and substructure levels, as well as the stress-strain state.



a

b

Fig. 1 – Morphology fractures of the vacuum arc coating mononitride ZrN (×2000) (a) and system ZrN/Zr (×20000) (b)

In order to study structural state in the work the method of X-ray diffraction. Fig. 2 shows comparative diffraction spectra for the two types of systems: mononitrides and multiperiod bilayer systems "mononitride – metal". For all mononitrides systems at their deposition in highly non-equilibrium conditions (typical of the vacuum-arc method) there is a formation phases with a cubic crystal lattice structure type NaCl. This type of lattice corresponds to high temperature conditions for Mo and Cr deposition system at a temperature of about 500 K is a non-equilibrium. Fig. 2 are designated plane for NaCl-type lattice structure corresponding detectable diffraction peaks.

From the spectra in Fig. 2 that the introduction of the interlayer of metal analog nitride component (average thickness nitride layer of 50 nm and a metal interlayer of about 10 nm) for all systems studied reduces the degree of texturing of the crystallites with [111] axis. This is manifested in a decrease in the relative intensity of the diffraction peaks of the family of the {111} corresponding planes texture. It must be noted forming another axis texture [100] in the system CrN/Cr (Fig. 2a, spectrum 2). Also singularities appear in the system on the basis of Mo (metal with the lowest heat of formation of nitride, among the studied systems in the work). Using this case, a large negative bias potential $U_b = -200$ V results in the formation in a single layer state (with a thickness of 7 microns) of composite material consisting of γ-Mo_2N phase with an crystal lattice NaCl type and α-Mo (Fig. 2d, spectrum 1). In the case of thin layers in a multi-period composition, phase structure formed determined by the action a secondary sputtering growth surface - light weakly bound nitrogen atoms [29]. This leads to the formation only of metal layers α-Mo (Fig. 2d, spectrum 2). Still another feature revealed in analyzing the data in Fig. 2 is a shift toward larger angles diffraction peaks coating system MeN-Me (where the Me- transition metal) relative to the peaks MeN coatings. This change is determined by the partial relaxation of condensation (structural), compressive stresses in the coatings [29]. Largest displacement is detected for the system ZrN-Zr (ie for a system based on zirconium nitride, where the bond between the metal and nitrogen highest among the studied systems).

According to the data the results of X-ray tensometry ($\sin^2\Psi$ – method) stress state varies ZrN layers of compression – 9.5 GPa (in the single-layer coating) to – 3.4 GPa (in thin layers of Multi-period ZrN coating ZrN/Zr).

To a somewhat lesser degree it changes the state of stress in the TiN layers at the transition from a single layer to the thin layers in a multilayer state. Thus in voltage TiN layers vary from – 7.4 GPa to 3.8 GPa. In molybdenum-based coatings is not observed displacement of the diffraction peaks associated with the change in the stress state (Fig. 2d), unlike ZrN and TiN, which is determined close to zero stress (as in the monolayers and in the composition) of preferential detention metal α-Mo phase [29]. The ZrN and TiN with a relatively large force bonds due to «atomic peening»-effect [7] implanted atoms stabilize the high compressive stress.

To create the bilayer state, both for the nitride and the metal components of coating, were prepared in the multiperiod composite system with 4 layers in each period. Two nitride layer on based on two different transition metals and two metal layers used as such layers. Schematically, such a composition can be described as (Me_1N/Me_2N)/(Me_1/Me_2) (represented as a circuit and a photo side surface in Fig. 3).

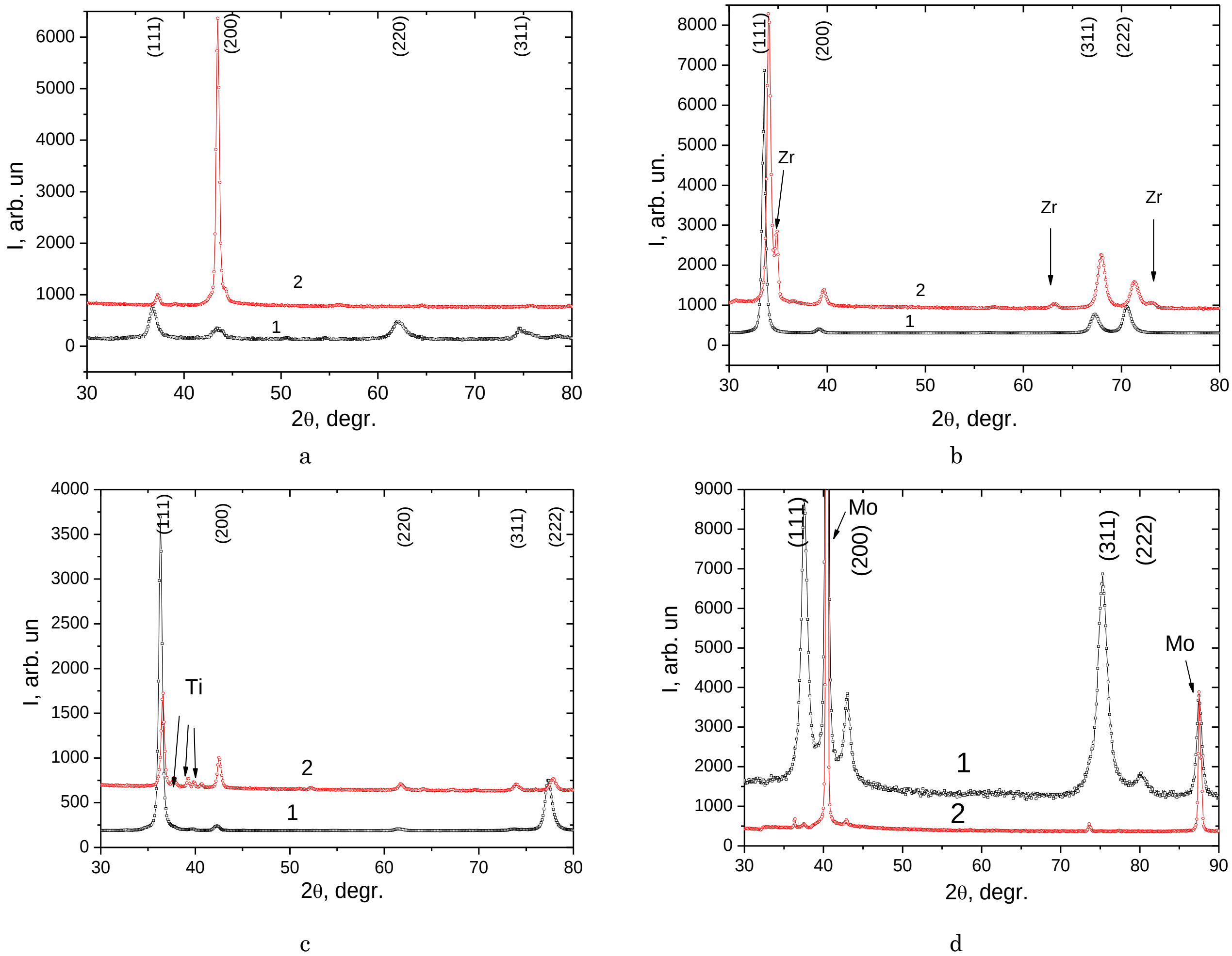


Fig. 2 – Diffraction patterns spectrums of mononitrides (1) and multiperiod bilayer "mononitride – metal" systems (2) on the basis of: a – Cr, b – Zr, c – Ti, d – Mo (diffraction peaks of metallic phases shown by the arrow)

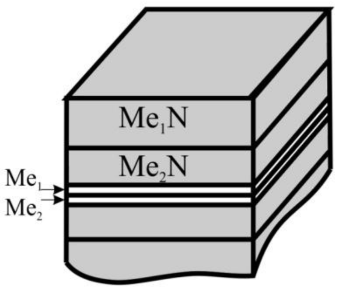


Fig. 3 – Scheme of the structure multi-period coatings (Me_1N/Me_2N)/(Me_1/Me_2)

X-ray diffraction spectra were obtained in investigations of this type of samples are shown in Fig. 4. It can be seen that the use of a composite system decreases the characteristic of preferential orientation in the texture with [111] axis of nitride layers. It is known that one of the main reasons for the formation of the surface parallel to the growth plane (111) is to reduce the strain factor of minimum free energy by the action of the compression stress [5]. Also, usually, the appearance of texture [111] under the influence of stress occurs when reducing the content of nitrogen atoms in the octahedral interstices in the f_{cc} lattice of metal atoms. According to this, a decrease in the degree of texture may indicate a relaxation of compressive stresses in growth of thin layers of nitrides with the introduction of metal composite interlayer. Usually in this case for all of the is the formation of a texture [100]. To the greatest extent this texture is manifested in a zirconium-based coatings (Fig. 4a, d). The Ti-based coatings formed bitextural condition: [100] and [111].

The most universal characteristic of the mechanical properties of the coatings is their hardness, which largely determines the resistance of the coating to abrasive wear. In Fig. 5 shows the hardness for monolayers and compositions of various types as histograms

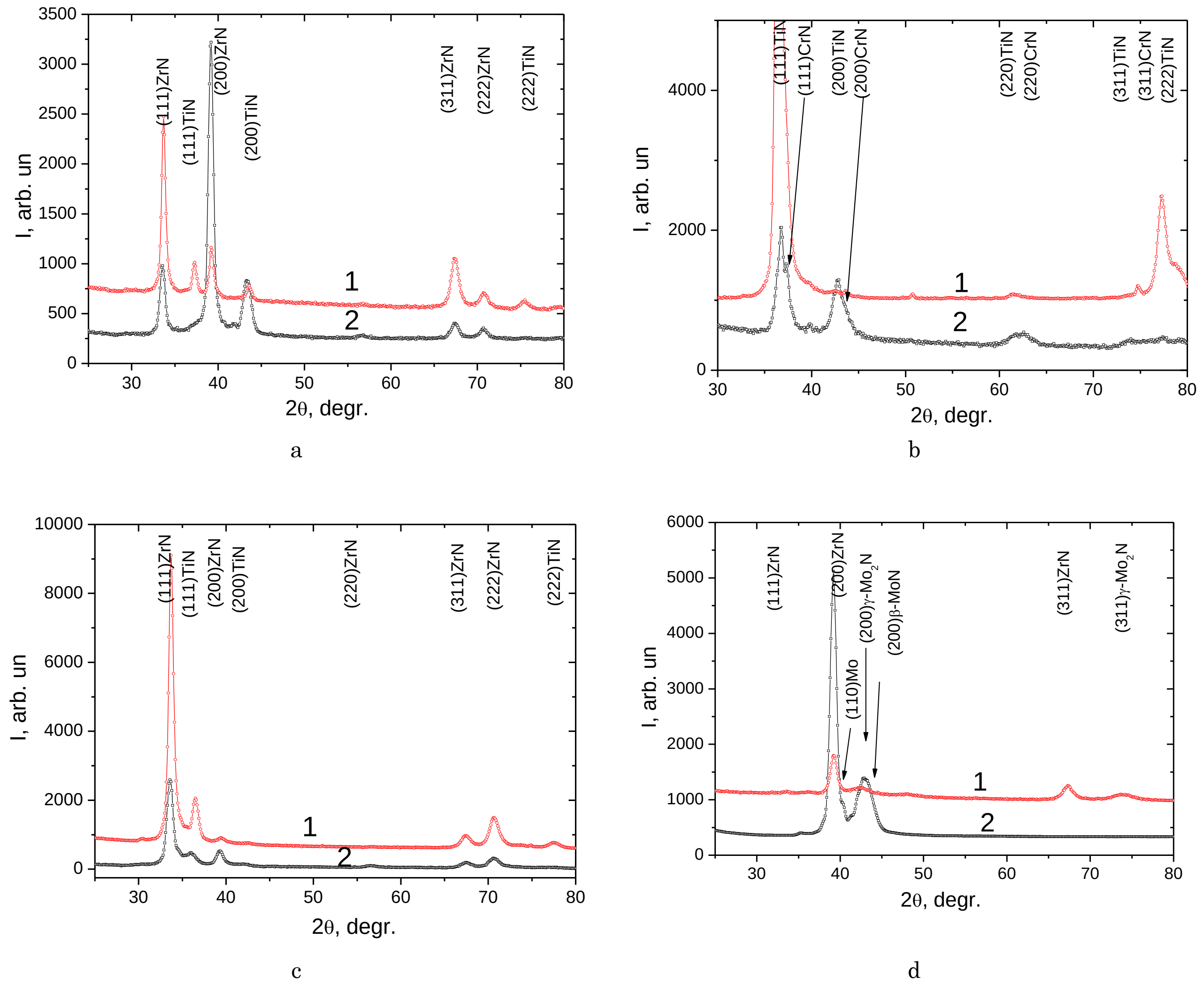


Fig. 4 – Diffraction patterns spectrums of composite multiperiod coatings of nitride bilayer (1) and the composition "bilayer-bilayer metal nitride" in the period (2): a – CrZr, b – CrTi, c – ZrTi, d – ZrMo

of distributions. It can be seen that the use of metal sublayers hardness for all systems does not exceed 27 GPa, which is 10 – 15% less than the hardness of the respective mononitrides.

In the case of alternating layers of nitrides is possible to achieve a hardness 41 GPa for composites TiN/CrN and ZrN/CrN. At thsit the introduction of metal composite interlayers in ZrN/CrN increases its hardness. It should be noted that the thickness of the metal sub-layers is about 10 nm, which corresponds to the optimal size in order to achieve maximum strength [20].

In the case of systems with Mo at large potential of – 200 V due to the formation of the metal phase does not exceed a hardness of 5 GPa. Only in the case of the periodic system with MoN/ZrN can achieve hardness of multi-period coatings – 34 GPa. Thus the introduction of the metal interlayers of nanometer thickness does not lead to a significant reduction in hardness. At the same time the metal interlayer serves as a good damper hindering the development of destructive cracks. As shown in schematically Fig. 6 in the case of destruction of multilayer coatings formed crack leads

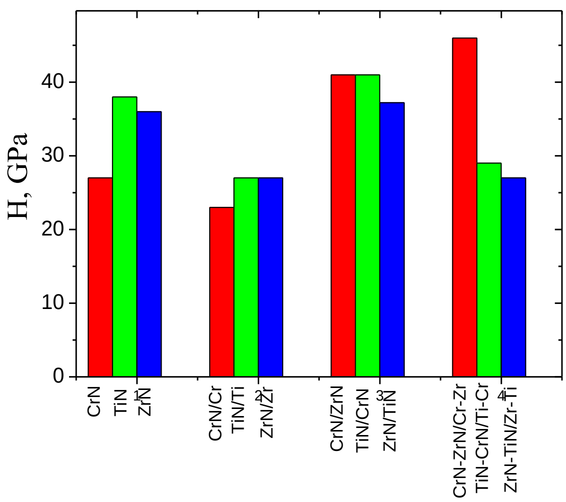


Fig. 5 – Histograms of hardness of coatings based on transition metal nitrides of four groups: 1 – mononitrides, 2 – "mononitride-transition metal", 3 – "mononitride Me_1-mononitride Me_2", 4 – "composition mononitrides-metal composition"

to the destruction of the coating as a whole (Fig. 6a). Use of the periodic system with a soft metal layer (i.e., in accordance with the Charpy principle – fatigue strength) results in development of cracks scattering peak by doing so, a more durable material.

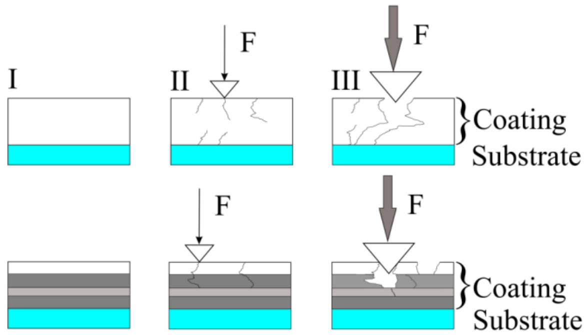


Fig. 6 – Scheme of the different stages of destruction coatings under the influence of the applied load: a – monolayer coating, b – multiperiod bilayer coating

Thus, for the parts and equipment, operating under multicycle loads (eg. seals and turbine blades) have a maximum working capacity (Me_1N/Me_2N)/(Me_1/Me_2) multiperiod system in which a relatively high hardness combined with resistance to destructive cracking.

4. CONCLUSIONS

1. The non-equilibrium conditions for obtaining coatings vacuum-arc method results (for the studied nitrides of transition metals Ti, Cr, Mo and Zr) to the formation of phases with a cubic crystal lattice.

2. In the nitride without metal interlayers upon edition of $U_b = -200$ V formed the preferred orientation of crystallites (face-centered cubic lattice) with the [111] axis perpendicular to the growth surface.

3. In the nitride systems with a Mo, having the smallest bond energy with the nitrogen upon edition of $U_b = -200$ V there is a formation of the metallic phase α-Mo, selective spraying stimulated loosely bound nitrogen atoms growth surface coatings.

4. Injection of the metal layers in multiperiod coatings with a period 60 nm impaired growth texture [111], and accompanied by a reduction of compressive stresses. Stability in this case the formation of coatings parameters indicative of the nature of the formation of a growth texture [111], stimulate the formation of compressive stress.

5. Compositional multiperiod coatings (Me_1N/Me_2N)/(Me_1/Me_2) have greater hardness and greater resistance compared to MeN/Me. For systems with multiperiod damping metal layers – (ZrN/CrN)/(Zr/Cr), obtained superhard coatings with hardness of 46 GPa.

Структурная инженерия многослойных вакуумно-дуговых нитридных покрытий на основе Ti, Cr, Mo и Zr

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Методами структурных исследований (рентгеновская дифракция и электронная микроскопия) в сочетании с измерением твердости индентированием изучены возможности структурной инженерии многопериодных вакуумно-дуговых покрытий на основе нитридов переходных металлов Ti, Cr, Mo и Zr. Установлено формирование фаз с кубической кристаллической решеткой в неравновесных условиях при вакуумно-дуговом методе получения. Подача отрицательного потенциала смещения -200В в мононитридах приводит к преимущественному образованию текстуры кристаллитов с осью [111]. Введение тонких (около 10 нм) металлических прослоек приводит к уменьшению совершенства текстуры [111] и формированию текстуры [100]. Этот эффект связывается с изменением напряженно-деформированного состояния нитридных слоев. Определено, что композиционные многопериодные покрытия (Me_1N/Me_2N)/(Me_1/Me_2) имеют большую твердость и большую стойкость по сравнению с MeN/Me. Для многопериодной системы с демпфирующими металлическими слоями – (ZrN/CrN)/(Zr/Cr), получены сверхтвердые покрытия с твердостью 46 ГПа.

Ключевые слова: Вакуумно-дуговой метод, Многопериодные покрытия, Структурная инженерия, Напряженное состояние, Твердость, Прочность.

Структурна інженерія багатошарових вакуумно-дугових нітридних покриттів на основі Ti, Cr, Mo і Zr

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Методами структурних досліджень (рентгенівська дифракція і електронна мікроскопія) в поєднанні з вимірюванням твердості індентуванням вивчені можливості структурної інженерії багатоперіодних вакуумно-дугових покриттів на основі нітридів перехідних металів Ti, Cr, Mo і Zr. Встановлено формування фаз з кубічною кристалічною решіткою в нерівноважних умовах при вакуумно-дуговому методі отримання. Подача негативного потенціалу зсуву -200В в мононітридах призводить до переважного утворення текстури кристалітів з віссю [111]. Введення тонких (близько 10 нм) металевих прошарків призводить до зменшення досконалості текстури [111] і формування текстури [100]. Цей ефект пов'язується зі зміною напружено-деформованого стану нітридних шарів. Визначено, що композиційні багатоперіодні покриття (Me_1N/Me_2N)/(Me_1/Me_2) мають високу твердість і високу стійкість в порівнянні з MeN/Me. Для багатоперіодної системи з демпфірувальними металевими шарами - (ZrN/CrN)/(Zr/Cr), отримані надтверді покриття з твердістю 46 ГПа.

Ключові слова: Вакуумно-дуговий метод, Багатоперіодні покриття, Структурна інженерія, Напружений стан, Твердість, Міцність.

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