

Structural Engineering Multiperiod Coating ZrN/MoN

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Using the method of structural engineering by changing the thickness of the layers in a multiperiod ZrN/MoN system investigated the effect of the phase-texture state of the crystallites and their size on the hardness of the vacuum-arc coating. It is revealed a determining influence on the formation of ZrN layers preferential orientation growth [100] axis with a small layer thickness 7-20 nm (the deposition of 3 to 10 seconds). At high layer thickness determines the texture [311] crystallites are γ -Mo₂N phase formed in the Mo-N layers. Pulsed high-voltage stimulation without changing the type of structural states for different layer thicknesses, leads to partial disorientation texture in thick layers. Hardness of coating with thick (80 nm) layers is 35-37 GPa. In small thickness layers pulse stimulation of atoms motility causes the formation of a planar structure with an average crystallite size of 4-9 nm in the layers, which is accompanied by increased hardness of up to 44 GPa.

Keywords: Multilayer coating ZrN/MoN, The thickness of the layers, The bias potential, Structure, Crystallite nanosize, Hardness.

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1. INTRODUCTION

Numerous studies conducted in recent years [1-6] showed that by creating a composite coating of the multi-element nitrides [7-10] or alternating two or more layers of nitrides of transition metals [11-14] can largely improve the functional properties of the surface (to the greatest extent achieved improvement in the mechanical characteristics).

Among the multilayer systems, the highest mechanical properties compared to single components (Ti, Al)N/VN [15, 16] and TiN/VN [17-19]. Moreover primarily on the properties of these coatings are influenced by the thickness of the layers [20, 21] (most high properties were obtained when the thickness of the layers in the nanometer range). It is assumed that the basis for such an increase in properties of multilayer systems is retaining (quenching spread) the ability of the interlayer boundaries to crack propagation, and hence a high wear resistance values measured from the H/E ratio [22, 23]. The unique properties and structural states MoN coating in the form of single-layer coatings [24, 25], and in multilayer compositions [26-30] in the first instance determined by the possibility fibrewise strain relief [24], which is a very important parameter in the formation of a multilayer composition. On the other hand, in recent years an enhanced interest has been shown by coatings based on ZrN [31], which is largely due to the high resistance of such coatings to oxidation and radiation resistance.

Therefore, as one of the most promising multilayer systems can be considered MoN/ZrN system, which used a combination of nitride allows a high hardness and wear resistance combined with good resistance to oxidation and other influences in aggressive environments.

The aim of this work was to study the influence of such parameters as the thickness of layers on the phase composition, structure and mechanical properties (hardness) of the coatings deposited at a different negative potential bias supplied to the substrate ($-U_b$), that provides a difference in energy of the particles deposited.

2. MODES OF RECEIVING COATINGS AND METHODS OF RESEARCH

Coatings were obtained by vacuum-arc method on the modernized installation "Bulat-6" [32]. Pressure of working (nitrogen) atmosphere during deposition was $P_N = 4 \cdot 10^{-3}$ Torr, the deposition speed was about 2 nm/sec. Deposition was carried out from two sources (Mo and Zr) at a predetermined time delay or continuous rotation fixed on substrates of samples at 8 rev/min.

The deposition process is carried out under the following processing conditions. After the deposition of the first layer the two evaporator turned off, turning the substrate holder by 180° and again at the same time included both evaporators. The arc current during the deposition was 85 ... 90 A, the distance from the evaporator to the substrate – 250 mm, the substrate temperature (T_s) was in the range of 250 ... 350 °C.

The total coating thickness was about 10 microns with the hourly time deposition. In the process of deposition on the substrate was fed a constant negative potential value $-U_b = -110$ V and -200 V.

Multilayers nanostructured coatings MoN/ZrN with simultaneous ion implantation in the deposition process deposited when applying for a substrate holder along with a negative constant potential and pulse potential with a pulse duration of 10 ms, repetition frequency of 7 kHz and an amplitude of up to 2 kV.

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The main advantage of the method of plasma ion implantation and deposition (PBII & D-method) at two-phase synthesis of nanostructures MoN/ZrN is to substantially reduce synthesis temperature (below 200 °C), which would block an appreciable diffusion mixing components.

The phase composition, structure and substructural characteristics were investigated by X-ray diffraction (DRON-4) using Cu-K α -radiation. For monochromatic detected radiation used graphite monochromator, which is installed in the secondary beam (front of the detector). The study of phase composition, structure (texture, substructure) produced by conventional methods by X-ray diffraction by analysis of the position, intensity and shape of the diffraction reflexes profiles [33]. To decrypt diffraction patterns used tables International Centre for Diffraction Data Powder Diffraction File.

Microindentation performed on the installation "Micro-gamma" with a load of up to $F = 0,5$ N Berkovich diamond pyramid with an angle of 65°, to automatically perform loading and unloading for 30 seconds.

3. RESULTS AND DISCUSSION

Analysis of the morphology of the fracture of multilayer coatings show reasonably good planarity of them (Fig. 1), which is typical for all investigated precipitation regimes.



Fig. 1 – The lateral cross-section of the multilayer coating with the duration of the overlay layer $\tau = 40$ sec

The phase-structural condition substantially depends on the mode used. Fig. 2 shows plots of the diffraction spectra of coatings deposited at constant $-U_b = -110$ V without pulse stimulation rate (Fig. 2a) and the pulse stimulation during growth (Fig. 2b).

One can see that for small time deposited layers (and thus the thickness of layers to 20 nm) of the coatings obtained without pulse stimulation (Fig. 2a), there is a change of the preferential orientation of the crystallites on the [100] at the least thickness to [311] at the maximum thickness layers (shown by the arrows of the Fig. 2a). The last occurs simultaneously in both ZrN, MoN and the layers (where this texture is determined by the growth of crystallites γ -Mo $_2$ N phase lattice type NaCl). From the analysis of the results of previous studies [24, 30] texture of [311] can be considered in determining these conditions growth in layers γ -Mo $_2$ N phase, while for the formation of ZrN characteristic texture with the [100] or [111].

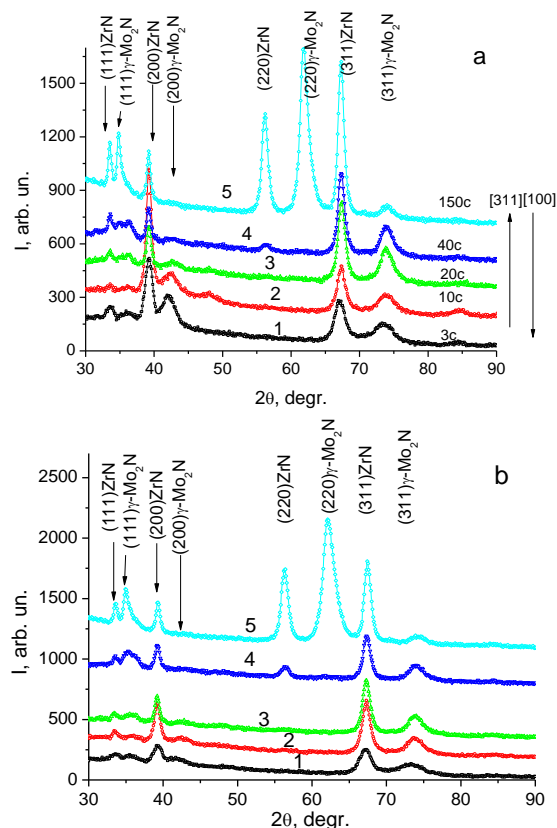


Fig. 2 – Plots diffraction spectra of coatings obtained at a constant potential -110 V without bias pulse stimulation (a) and with pulse stimulation (b) when τ , sec.: 1 – 3, 2 – 10, 3 – 20, 4 – 40, 5 – 150

Therefore, we can assume that at small thicknesses of the layers, specifying the preferred orientation of growth is the texture layers of ZrN (ie in the layers determines the largest radiation damage due to the heaviest Zr atoms). With increasing thickness of the layers is determined primarily by the growth of crystallites it becomes a layer of γ -Mo $_2$ N. This change may be due to the contribution of the growth factors deformation as the thickness of the layers.

If we compare the diffraction spectra of the coatings obtained without pulse stimulation (Fig. 2a) and with pulse stimulation (Fig. 2b), we see that if the general trend of pulse high impact results in greater disorientation of crystallites growth axes, reducing the degree of texturing, and at most to the thickness translates texture characteristic radiation factor action (with [110] axis perpendicular to the growth plane) [7].

This increase in the permanent capacity to $-U_b = -200$ V at least thin layers of a thickness of about 7 nm ($\tau = 3$ sec) leads to increased texture [100] axis, which can be associated with an increase in the mobility of atoms. The latter is a consequence of the increase in the average energy of film-forming charged particles with increasing $-U_b$ to -200 V.

The analysis of crystallite sizes carried out on the broadening of the diffraction reflexes showed that ZrN layers crystallites have a greater dimension in the direction of growth with increasing deposition time (thickness) of layers from 3 to 150 seconds, a crystallite size (L) is increased by 7 to 15 nm. The crystallite size

in the layers of γ -Mo₂N considerably smaller and varies in the range of 3.1-4.5 nm (Fig. 3, the dependence of 1 and 2). A lower value of the average crystallite size of γ -Mo₂N phase may be associated with a tendency to its shear deformation due to the relatively low power communication Mo-N (and, accordingly, the heat of formation).

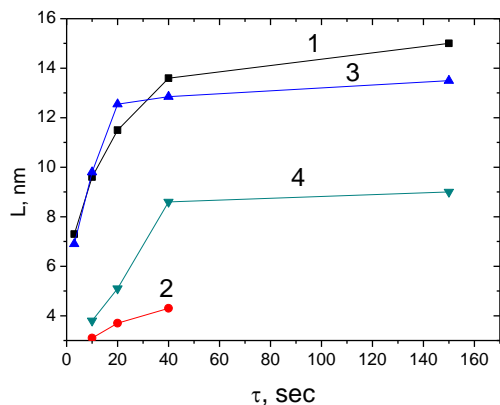


Fig. 3 – Changing the size of crystallites in the layers, depending on the deposition time: 1 – ZrN (without pulse stimulation) 2 – Mo₂N (without pulse stimulation), 3 – ZrN (pulse stimulation), 4 – Mo₂N (pulse stimulation)

Additional pulse stimulation is not a determining effect on the growth of ZrN crystallites (Fig 3, the dependence 3). But due to increasing mobility significantly increases the average size in the γ -Mo₂N layers (4 to 8.5 nm) with an increase of 3 to τ 150 sec (Fig. 3, 4 dependent).

Possibilities of structural engineering on different layers of preferential orientation of the crystallites and their size would greatly change the mechanical properties of multilayer ZrN/MoN coating. The most universal criterion of the mechanical characteristics refers the working surface microhardness. Fig. 4 shows the generalized results Microindentation. One can see that increasing $-U_b$ to -200 V, while a strong texture

formation stimulated with [100] axis, but leads to a drop in the hardness of the system up to 30 GPa.

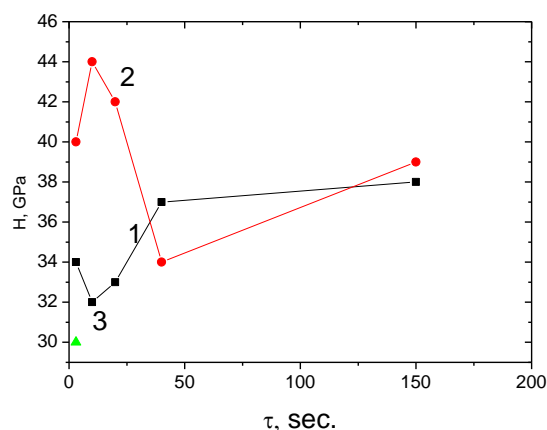


Fig. 4 – Dependence of change microhardness of the coatings at the time of deposition of layers: 1 – $-U_b = -110$ V, without pulse stimulation, 2 – $-U_b = -110$ V, with a pulse stimulation, 3 – $-U_b = -200$ V, with a pulse stimulation

The hardness of coatings obtained by $-U_b = -110$ V without pulse stimulating nonuniformly varies in the range of 32-34 GPa at a low layer thickness, with a further increase to 37 GPa with an increase in the average crystallite size of 10 nm and a perfect texture growth axis [311]. The hardness of such coatings do not significantly change with the greatest layer thickness (about 300 nm) and education bitextural state with axes [311] and [110]. In the coatings obtained by $-U_b = -110$ V and pulse stimulation of the mobility by potential to 2 kV, a hardness similar to that of thick layers of coatings obtained without stimulation and is 35-37 GPa. With a relatively small thickness layers stimulation pulse due to increased mobility of the atoms at their deposition leads to an increase of hardness up to 44 GPa, apparently due to the growth with the planarity of the interlayer boundaries and formation of texture with the axis [311].

Структурна інженерія багатоперіодних покриттів ZrN/MoN

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Використовуючи метод структурної інженерії шляхом зміни товщини шарів в багатоперіодній системі ZrN/MoN досліджено вплив фазово-текстурного стану кристалітів і їх розмір на твердість вакуумно-дугових покриттів. Виявлено визначальний вплив ZrN шарів на формування переважної орієнтації зросту з віссю [100] при малій товщині шарів 7-20 нм (час осадження 3 -10 сек). При великій товщині шарів визначальним текстуру [311] є кристаліти γ -Mo₂N фази, що формується в Mo-N шарах. Імпульсна високовольтна стимуляція не змінюючи тип структурних станів для різних товщин шарів, призводить до часткової разорієнтації текстури при великій товщині шарів. Твердість покриттів з товстими (80 нм) шарами становить 35-37 ГПа. У шарах малої товщини імпульсна стимуляції рухливості атомів призводить до формування планарної структури з середнім розміром кристалітів в шарах 4-9 нм, що супроводжується підвищенням твердості до 44 ГПа.

Ключевые слова: Багатоперіодні покриття ZrN/MoN, Товщина шарів, Потенціал зсуву, Структура, Нанорозмір кристалітів, Твердість.

Структурная инженерия многопериодных покрытий ZrN/MoN

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Используя метода структурной инженерии путем изменения толщины слоев в многопериодной системе ZrN/MoN исследовано влияния фазово-текстурного состояния кристаллитов и их размера на твердость вакуумно-дуговых покрытий. Выявлено определяющее влияние ZrN слоев на формирование преимущественной ориентации роста с осью [100] при малой толщине слоев 7-20 нм (время осаждения 3 -10 сек). При большой толщине слоев определяющим текстуру [311] являются кристаллиты γ -Mo₂N фазы, формируемой в Mo-N слоях. Импульсная высоковольтная стимуляция не меняя тип структурных состояний для разных толщин слоев, приводит к частичной разориентации текстуры при большой толщине слоев. Твердость покрытий с толстыми (80 нм) слоями составляет 35-37 ГПа. В слоях малой толщины импульсная стимуляция подвижности атомов приводит к формированию планарной структуры со средним размером кристаллитов в слоях 4-9 нм, что сопровождается повышением твердости до 44 ГПа.

Ключевые слова: Многослойное покрытие ZrN/MoN, Толщина слоев, Потенциал смещения, Структура, Наноразмер кристаллитов, Твердость.

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