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# Mixing on the Boundaries of Layers of Multilayer Nanoperiod Coatings of the $TiN_x/ZrN_x$ System: Simulation and Experiment

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Using the complex of methods for attestation of the structural state in combination with computer simulation and measurement of mechanical properties (hardness), the influence of the period Λ on the mixing process on the interlayer boundaries of multilayer coatings $TiN_x/ZrN_x$ is studied. The formation of two phases (TiN and ZrN) with one type of crystal lattice (structural type NaCl) is identified in the layers of multiperiodic compositions $TiN_x/ZrN_x$ with a period of Λ = 20 ... 300 nm. At Λ = 10 nm, the formation of a solid solution (Zr, Ti)N, as well as a small volume of the TiN phase is revealed on XRD spectras. The presence of TiN component is due to the larger initial value of the layer based on titanium nitride. To explain the results obtained, the results of computer simulation of damage at the atomic level during bombardment by ions accelerated in the $U_b$ field are used. The critical thickness of mixing (about 7 nm) in the $TiN_x/ZrN_x$ system is determined upon condition that $U_b = -110$ V. It is established that a decrease in the period from 300 to 20 nm leads to increase in hardness. The highest hardness of 44.8 GPa corresponds to the superhard state.

It is established that the critical thickness of radiation-stimulated defect formation has a significant effect on the stress-strain state and hardness of coatings with a small Λ ≈ 10 nm. In this case, relaxation of the stress-strain compression state occurs and the hardness decreases. However, the formation of a solid solution, while retaining part of the unreacted layer of titanium nitride at Λ = 10 nm, makes it possible to obtain an ultrahigh (44.8 GPa) hardness of the coating.

**Keywords**: Vacuum arc, $TiN_x/ZrN_x$, Period, Bias potential, Phase composition, Structure, Stress-strain state, Solid solution, Computer simulation, Hardness.

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## 1. INTRODUCTION

Structural engineering of composite vacuum-arc coatings is a relatively young direction of surface engineering, but for a number of systems it has become possible to obtain materials with very high functional characteristics [1]. In this case, the state of the boundary between the layers is the determining factor of many operational characteristics [2] and for the strengthening of the boundaries, their doping with atoms (both in the form of separate elements [3] and as constituents of new phases [4]) with strong cohesion [5, 6] is used. This can occur both during the formation of the coating [7] (sometimes accompanied by the formation of metastable phases [8]), both in the process of exploitation by separating such atoms from the matrix because of their low solubility [9].

Also effective way to increase the hardness, thermal stability, functional properties of the vacuum plasma coating is a transition to the multielement (5 or more elements) coating [10]. However, despite its attractiveness the transition to multielement coatings prevented sufficiently solve the problem of the formation of the critical cracking and catastrophic (on the entire thickness of the coating) coating fracture [11]. As shown by studies in recent years, multiperiod composites are very promising as a material for solving this problem. In these materials, the phase boundaries between layers provide relaxation of destruction concentrators preventing crack propagation [12].

Multiperiod composite coatings show significantly higher hardness and toughness than the individual components of the layers due to the presence of plurality of interphase (interlayer) boundaries and the reinforcing effect of the inner layers (the formation of dislocations is suppressed by nanoscale thickness of the layers and the difference in the modulus of elasticity of different components contacting layers inhibits portability of dislocations) [13].

In recent years, multilayer coatings of nitrides of transition metal with high functional properties have been obtained. For example CrN/NbN [14], TiN/NbN [15], TiAlN/TiN [16] and others.

Among the multi-period coatings obtained, the $TiN_x/ZrN_x$ system has recently been of increasing interest due to high functional properties (hardness, corrosion resistance and high tribological properties [17-20]). This determines the good prospects for the industrial use of multi-layer nanocrystalline coatings $TiN_x/ZrN_x$ as protective and wear-resistant for machines tools, blade tools, as anticorrosion coatings for critical elements in power engineering [21-23], as well as coatings for bioimplantation applications [24].

In this case, the use of a different multi-layer architecture [25], as well as the reduction in the thickness of

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the component layers to several nanometers in order to prevent cracking and increase in hardness, led to the revealed effect of a decline in properties at small layer thicknesses (8 nm or less) [26, 27]. A similar effect of a decrease in hardness with a layer thickness of less than 8 nm was noted for other systems: TiN/SiN [28], TiN/VN [29], TiN/NbN [15], NbN/TaN [30] and others [31].

As was noted in works [26, 27], when the bilayer period (Λ) is less than 8 nm, the hardness and modulus of elasticity decrease abruptly. According to the assumptions made in works [32, 33], such a decrease in properties for a small thickness of the layers can be associated with radiation-stimulated mixing.

As follows from work [34], the TiN/ZrN system (given that the discrepancy between the lattice spans TiN and ZrN is about 7 %) cannot be considered as a superlattice with a coherent interface. Therefore, the mechanical behavior in the layers of the multi-period coating cannot be interpreted using a coherent deformation model [15]. Since the heats of formation of TiN and ZrN are close (ΔHf (298) = – 87.3 kcal/mol for ZrN and ΔHf (298) = – 80.4 kcal/mol for TiN), it is possible to form a mixed intermediate layer of $Ti_xZr_{1-x}N$ between the layers TiN and ZrN under radiation-stimulated diffusion of atoms during deposition. This is indicated by the preservation of high functional properties of coatings at Λ more than 15 nm [34]. The same conclusion can be reached on the basis of the results of work [35] in which it was shown that in the nano-sized period, not only the hardness and modulus of elasticity decrease, but also related to plastic deformation and cracking the critical loading parameters $L_{c1}$ (from 15 to 7 H) and $L_{c2}$ (from 28 to 18 N) are significantly reduced.

Thus, the purpose of this paper was to study the influence of the thickness of the layers of multilayer nanoperiodic coatings of the $TiN_x/ZrN_x$ system (obtained by the vacuum arc method) on the phase composition, structure, stress state and hardness, and also to compare the obtained data with the results of computer simulation of radiation-stimulated processes at interphase borders.

## 2. SAMPLES AND METHODS OF RESEARCHES

Multilayer two-phase nanostructured coatings $TiN_x/ZrN_x$ were deposited in a vacuum-arc unit "Bulat-6" [1]. The following cathodes materials were used: titanium BT 1-0; low-alloyed zirconium; active gas - nitrogen (99.95 %). Coatings were applied to the surface of samples (20 × 20 × 2 mm) made of steel 12Cr18Ni10Ti (analog of stainless steel SS 321) prepared by standard grinding and polishing methods. Before deposition, the vacuum chamber was evacuated to a pressure of $10^{-5}$ Torr (a negative potential of 1 kV was applied to the rotary device with a substrate holder, the evaporator was turned on and the surface of the substrates was cleaned by bombardment with zirconium ions for 3 ... 5 min). Then both evaporators were simultaneously turned on, nitrogen gas was supplied to the chamber of the "Bulat-6" unit and the first layer was deposited on one side of the ZrN, and on the opposite side – TiN. After the first layer was deposited, both evaporators were turned off, the substrate holder was rotated at 180°, and both evaporators were turned on simultaneously. The arc current in the deposition process was 100 A, the nitrogen pressure ($P_N$) in the chamber varied in the range $10^{-5}…5·10^{-3}$ Torr, the distance from the evaporator to the substrate was 250 mm, and the substrate temperature ($T_s$) was in the range 250... 350 °C. A coating thickness of about 10 μm was obtained. During deposition, a constant negative potential $U_b$ = – 110 V was applied to the substrate. The formation time of the layers was 300 s., 150 s., 80 s., 40 s., 20 s., 10 s., and about 3 seconds (with continuous rotation).

The phase composition, structure, and substructural characteristics were studied by X-ray diffractometry (DRON-4) using Cu-Kα radiation. For monochromatization of the recorded radiation, a graphite monochromator was used, which was installed in a secondary beam (in front of the detector) [8]. The study of the phase composition, structure (texture, substructure) was carried out using traditional X-ray diffractometry techniques by analyzing the position, intensity, and shape of the diffraction reflection profiles [7]. To decode the diffractograms, tables of the international diffraction data center – Powder Diffraction File were used.

To study the macrostress-strain state, the method of multiple inclined surveys ($\sin^2\psi$ method) was used [12].

The morphology of the cross section of multi-period structures was studied with a scanning electron microscope JEOL JSM840. For electron-microscopic studies, coatings were deposited on copper substrates 0.2 mm thick.

Microindentation was carried out at the Micron-gamma unit with a load up to $F$ = 0.5 N with a Berkovich diamond pyramid with cutting angle of 65°, with automatic loading and unloading for 30 seconds.

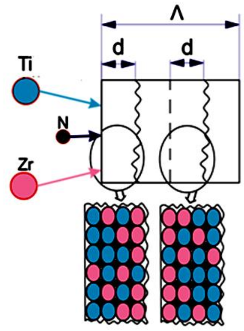



Fig. 1 – Scheme of radiation-stimulated mixing in layers during the formation of a multilayer composition of $ZrN_x/TiN_x$

To understand the spatial distribution of radiation-stimulated changes in the boundary (interlayer) regions during the deposition of high-energy particles, computer simulation was used in the work. To do this, we used a program based on the approximate method of double collisions, TRIM, which is based on the Monte Carlo method for describing the trajectory of the incident particle and the damage created by this particle. The TRIM program used the maximum exposure parameters determined by the density of the medium, the constant mean path between collisions [12] in the approximation of the formation scheme shown in Fig. 1.

## 3. RESULTS AND DISCUSSION

A comparison of the scanning electron microscopy data upon condition of coating application showed that on electron microscopic photographs the lighter layers correspond to titanium-based nitrides. These layers are about 1.6 times thicker than dark layers based on zirconium. Thus, the deposition rate of zirconium-based layers is lower than that of titanium-based layers. Figure 2 shows shots of the breaks of the coating from 13 periods, where each of the layers was deposited for about 300 s. With a total coating thickness of about 13 μm (13 layers based on titanium and 13 layers based on zirconium), the thickness of the layer based on titanium is about 600 nm, and on the basis of zirconium – about 400 nm. While the deposition time of each layer was about 300 seconds – the deposition rate of layers based on titanium is 2 nm/s, and on the basis of zirconium – about 1.4 nm/s. Then, for a minimum deposition time of 3 s, the thickness of the Ti-based layers is about 6 nm, and on the basis of Zr is about 4 nm, and the period Λ is about 10 nm.

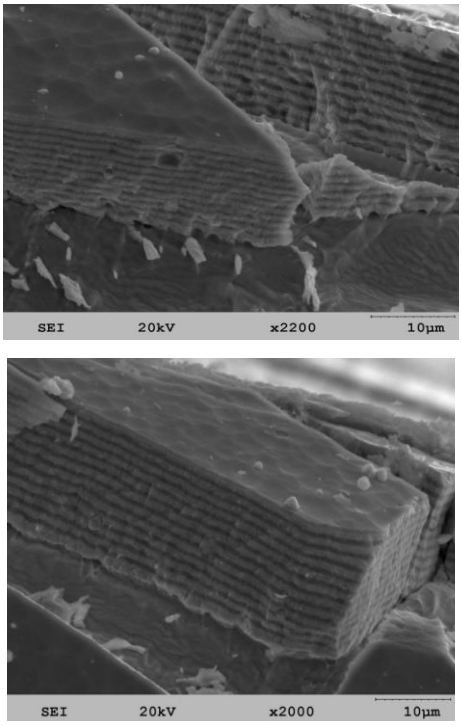



Fig. 2 – Two projections of the morphology of the fracture of a multilayer coating $TiN_x/ZrN_x$ with the number of layers 13 obtained at a deposition time of each layer of 300 sec

The X-ray diffraction (XRD) spectra of the multiperiod system $ZrN_x/TiN_x$ coatings are shown in Fig. 3. The use of the complex profile separation program showed that at a large Λ (about 300 nm), two systems of diffraction peaks from ZrN and TiN phases (card PDF 38-1420) Figure 4, a, c) are identified.

The high relative intensity of the peaks from the plane system {111} indicates the formation of a predominant orientation of the crystallites with the axis [111] perpendicular to the growth surface. With a decrease in the thickness of the layers (spectra from 4 to 2 in Fig. 3), the degree of texture with the axis [111] decreases (as evidenced by the relative decrease in the intensity of the peaks from the plane system {111}) [7]. A qualitative change in the form of the spectrum occurs for the coating with the thinnest layers (spectrum 1 in Fig. 3). As can be seen on the diffraction spectra after their separation, a low intensity peak from the TiN phase is observed only at medium angles (Fig. 4b). At high angles (Fig. 4c), peaks are detected only from the crystal lattice of the ZrN phase with a reduced (in comparison with the tabulated values for ZrN) period 0.4523 nm. The reason for the reduction in the period can be the formation of a solid solution (Zr, Ti). In such a solution, the replacement of zirconium atoms (having a larger atomic radius) by titanium atoms (which has a smaller atomic radius) should lead to compression of the lattice and a decrease in its period.

Thus, the transition to the nanoscale layer of a multilayer coating $ZrN_x/TiN_x$ with a period of about 10 nm leads to the formation of a solid solution phase. This is possible because of the similarity of the lattices of nitrides formed on the basis of zirconium and titanium

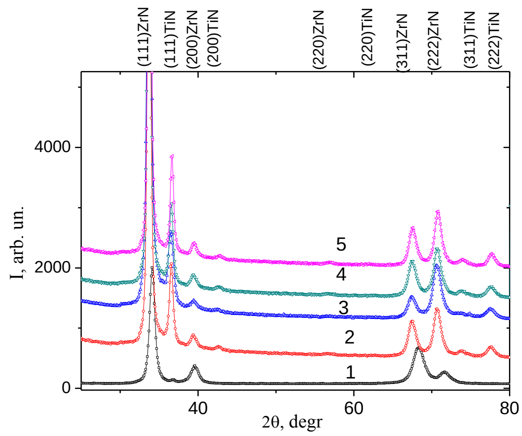
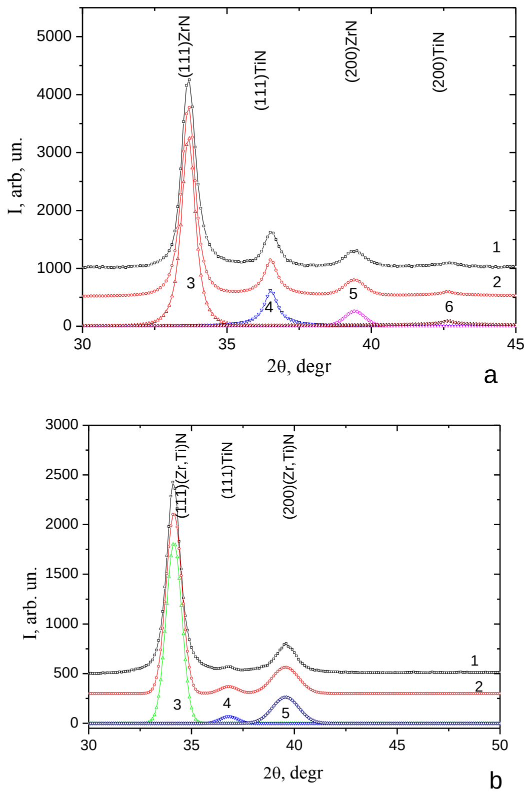



Fig. 3 – XRD-spectrums of coatings $ZrN_x/TiN_x$ with different Λ: 1 – 10 nm; 2 – 20 nm; 3 – 80 nm; 4 – 150 nm; 5 – 300 nm



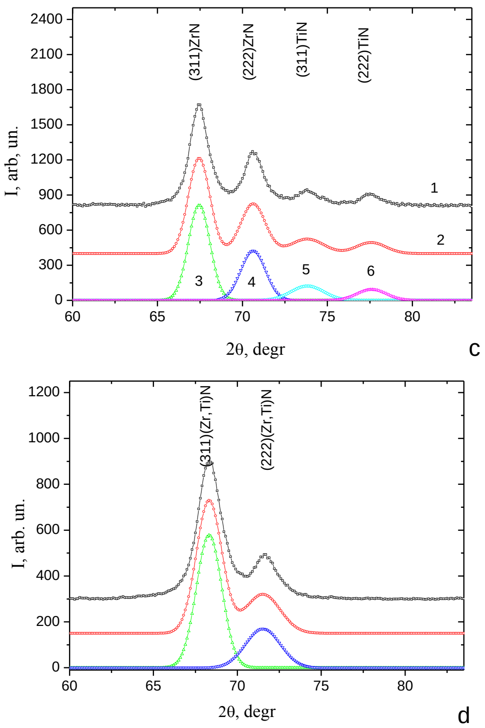



Fig. 4 – XRD-spectrums of coatings $ZrN_x/TiN_x$, after separation of complex profiles into components at medium (a, b) and distant (c, d) corners. For the system with Λ = 300 nm (a, c) and 10 nm (b, d)

(structural type NaCl). At the same time, because of the greater relative thickness of the TiN component, part of the titanium nitride layer remains unreacted. This indicates the formation of a solid solution precisely at the interface between the layers during growth.

Determination of the phases in the coatings by the XRD method makes it possible to apply the X-ray method to determine the stress-strain state in each of the phases separately. For this purpose, the method of multiple inclined surveys ($\sin^2\psi$-method) was used in this work. As a basis planes, the (422) and (511) planes were used located in the optimal angular range $\theta$ = 60-75° for the precision survey.

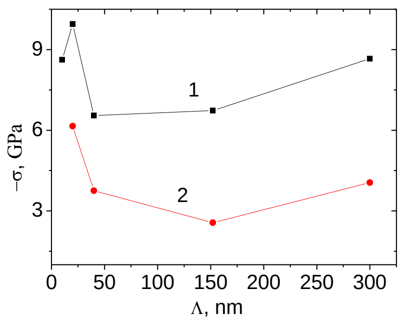



Fig. 5 – Dependence of compressive stresses (– $\sigma$) in the layers ZrN (1) and TiN (2) on the period Λ of multilayer coatings of the ZrN/TiN system ($U_b$ = – 110 V)

It can be seen that large compressive stresses develop in layers based on zirconium nitride. This is apparently determined by the higher heat of formation (and binding energy) in the Zr-N system. With a decrease in the thickness of the layers, the range of stresses does not change monotonically. This is most seen when Λ is less than 40 nm. The formation of a solid solution (at Λ about 10 nm) contributes to partial stress relaxation, which is usually associated with ordering [2].

The most important factor in the multilayer composition is the state of its interphase boundary [10, 11]. As was shown above, the formation of a solid solution occurs precisely at the interphase boundary and is associated with the action of radiation-stimulated processes. This necessitates the simulation of processes that can occur at the border. This is especially important for the nanometer scale of layers, when the radiation effect is comparable to the thickness of the layer. Using the software package TRIM, simulation showed that in the case of irradiation with ions with an average energy of 110 eV, which corresponds to deposition under the action of $U_b$ = – 110 V, in the $TiN_x/ZrN_x$ system, the penetration depth of Ti ions is larger in comparison with Zr (as more straggling, Fig. 6). For accelerated ion energy of about 100 eV, the average penetration depth of Ti ions is 1.9 nm (the number of vacancies initiated is 0.35 vacancies per ion, the total depth of action reaches 3.5 nm), and for Zr ions is 1.8 nm (the number of vacancies initiated is 0,46 vacancies per ion, the total depth of exposure reaches 2.9 nm).

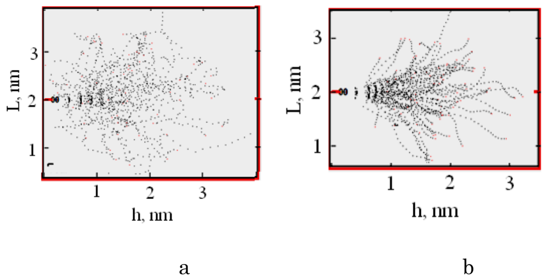



Fig. 6 – Depth of penetration of titanium ions (a) and zirconium ions (b), $TiN_x/ZrN_x$ system (100 iterations)

Thus, in the case of the $TiN_x/ZrN_x$ system, the total depth of impact can reach 6-7 nm in the border region. This is, apparently, the determining factor in the appearance of shifted diffraction peaks from the solid solution in the spectra of Figures 3 and 4.

The most universal and express characteristic for evaluating mechanical properties is indentation [4]. The results obtained of indentation for coatings with different Λ are shown in Fig. 7. It is seen that in coatings with a small period Λ an ultrahard state is reached. The highest value of 44.8 GPa was obtained for a $ZrN_x/TiN_x$ system with a layer thickness of about 10 nm. With a smaller thickness, the hardness slightly decreases, yet leaving coatings in the region of the superhard state. When Λ values are greater than 20 nm, a distinctive decrease in hardness occurs with an increase in the size of the structural elements [10].

Thus, despite the formation of a solid solution in the mixed interlayer region of the $TiN_x/ZrN_x$ system, the hardness of the coating with Λ about 10 nm remains sufficiently high, exceeding the hardness of similar coatings with a longer period (Λ more than 50 nm).

It is important to note that a comparison with the

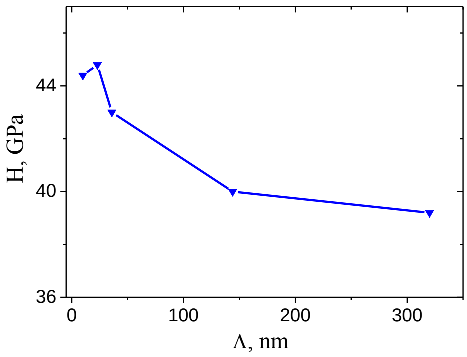



Fig. 7 – Dependence of the hardness of coatings (*H*) on the thickness of the bilayer period (Λ) for multilayer coatings of the $TiN_x/ZrN_x$ system

results of the investigation of the stress-strain state indicates the existence of a correlation between the increase in hardness and the increase in the magnitude of compressive stresses developing in the coating. This effect is understandable, since the compressive stresses are stimulated by a greater specific atomic density and thus contribute to an increase in bonding forces and hardness.

## 4. CONCLUSION

The formation of two phases (TiN and ZrN) with one type of crystal lattice (structural type NaCl) in the layers of multi-period compositions $TiN_x/ZrN_x$ with a period of Λ = 20 ... 300 nm is identified.

1. At Λ = 10 nm, the formation of a solid solution (Zr,Ti)N, as well as a small volume of the TiN phase revealed on XRD spectras. The presence of the TiN component is due to the larger initial value of the layer based on titanium nitride.
2. Using the simulation method of radiation-induced damages of material during irradiation with ions makes it possible to determine the critical mixing thickness in the $TiN_x/ZrN_x$ bilayer system. This thickness is about 7 nm at $U_b$ = – 110 V.
3. It is established that the critical thickness of radiation-stimulated defect formation has a significant effect on the stress-strain state and hardness of coatings with a small Λ ≈ 10 nm. In this case, relaxation of the stress-strain compression state occurs and the hardness decreases. However, the formation of a solid solution, while retaining a part of the unreacted layer of titanium nitride at Λ = 10 nm, allows to reach the ultrahigh (44.8 GPa) coating hardness.

## Перемішування на границях шарів багатошарових наноперіодних покриттів системи $TiN_x/ZrN_x$: моделювання та експеримент

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Використовуючи комплекс методів атестації структурного стану в поєднанні з комп'ютерним моделюванням і вимірюванням механічних властивостей (твердості), досліджено вплив величини періоду Λ на процес перемішування на міжшарових границях багатошарових покриттів $TiN_x/ZrN_x$. У шарах багатоперіодної композиції $TiN_x/ZrN_x$ з величиною періоду Λ = 20 ... 300 нм виявлено формування двох фаз (TiN і ZrN) з одним типом кристалічної решітки (структурний тип NaCl). При Λ = 10 нм на рентгендифракційних спектрах виявляється утворення твердого розчину (Zr, Ti)N, а також малого об'єму TiN фази. Наявність TiN складової обумовлена більшою вихідною величиною товщини шару на основі нітриду титану. Для пояснення отриманих результатів використані результати комп'ютерного моделювання пошкоджуваності на атомному рівні при бомбардуванні прискореними в поле $U_b$ іонами. Визначено критична товщина перемішування (близько 7 нм) в системі $TiN_x/ZrN_x$ при дії $U_b$ = – 110 В. Встановлено, що зменшення періоду від 300 до 20 нм призводить до підвищення твердості. Найбільша твердість 44,8 ГПа відповідає надтвердому стану.

Встановлено, що критична товщина радіаційно-стимульованого дефектоутворення істотно впливає на напружено-деформований стан і твердість покриттів з малим Λ ≈ 10 нм. При цьому відбувається релаксація напружено-деформованого стану стиснення і зменшується твердість. Однак утворення твердого розчину при збереженні частини шару нітриду титану при Λ = 10 нм, який не прореагував, дозволяє отримати надвисоку (44,8 ГПа) твердість покриття.

**Ключові слова:** Вакуумна дуга, $TiN_x/ZrN_x$, Період, Потенціал зміщення, Фазовий склад, Структура, Напружено-деформований стан, Твердий розчин, Комп'ютерне моделювання, Твердість.

## Перемешивание на границах слоев многослойных нанопериодных покрытий системы $TiN_x/ZrN_x$: моделирование и эксперимент

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Используя комплекс методов аттестации структурного состояния в сочетании с компьтерным моделированием и измерением механических свойств (твердости), исследовано влияние величины периода Λ на процесс перемешивания на межслойных границах многослойных покрытий $TiN_x/ZrN_x$. В слоях многопериодных композиций $TiN_x/ZrN_x$ с величиной периода Λ = 20…300 нм выявлено формирование двух фаз (TiN и ZrN) с одним типом кристаллической решетки (структурный тип NaCl). При Λ = 10 нм на рентгендифракционных спектрах выявляется образование твердого раствора (Zr,Ti)N, а также малого объема TiN фазы. Наличие TiN составляющей обусловлено большей исходной величиной толщины слоя на основе нитрида титана. Для объяснения полученных результатов использованы результаты компьютерного моделирования повреждаемости на атомном уровне при бомбардировке ускоренными в поле $U_b$ ионами. Определена критическая толщина перемешивания (около 7 нм) в системе $TiN_x/ZrN_x$ при действии $U_b$ = – 110 В. Установлено, что уменьшение периода от 300 до 20 нм приводит к повышению твердости. Наибольшая твердость 44,8 ГПа соответствует сверхтвердому состоянию.

Установлено, что критическая толщина радиационно-стимулированного дефектообразования оказывает существенное влияние на напряженно-деформированное состояние и твердость покрытиях с малым Λ ≈ 10 нм. При этом происходит релаксация напряженно-деформированного состояния сжатия и уменьшается твердость. Однако образование твердого раствора при сохранении части непрореагировавшего слоя нитрида титана при Λ = 10 нм позволяет получить сверхвысокую (44,8 ГПа) твердость покрытия.

**Ключевые слова:** Вакуумная дуга, $TiN_x/ZrN_x$, Период, Потенциал смещения, Фазовый состав, Структура, Напряженно-деформированное состояние, Твердый раствор, Компьютерное моделирование, Твердость.

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