

THE EFFECTS OF NITROGEN ATMOSPHERE PRESSURE, CONSTANT AND HIGH-VOLTAGE PULSE POTENTIALS OF THE SUBSTRATE ON THE STRUCTURE AND PROPERTIES OF VACUUM-ARC ZrN COATINGS

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ZrN-phase coatings with a cubic lattice (NaCl structure type) were produced by the method of vacuum-arc evaporation of a Zr cathode in nitrogen atmosphere at pressures P_N between 0.02 and 0.64 Pa. The pressure increase at a bias potential of -150 V leads to formation of the growth texture [111] or to appearance of the bitextural state with the axes [111] and [311]. Additional pulsed-mode supply of high-voltage negative potential $U_{ip} = 800 \dots 2000$ V, with pulse duration of 10 μ s and frequency of 7 kHz, stimulates the emergence of texture [110]. At the substrate level, the U_{ip} supply causes the microstrain relaxation and the crystallite size growth with increasing pressure. The observed changes are attributed to increased particle mobility and nitride formation activity under the action of U_{ip} . The hardness increases with increasing pressure and reaches a value of 43 GPa. The U_{ip} supply leads to a shift of the maximum hardness towards higher pressures.

INTRODUCTION

By the present time titanium nitride and TiN-based coatings deposited by both physical (PVD) and chemical (CVD) methods are most extensively studied among the nitrides of the 4th group metals [1–10]. Titanium nitride exhibits high hardness, fine corrosion resistance, and is widely used for coating of cutting tools and for other kinds of treatment. However, in the past few years attention is being increasingly focused on zirconium nitride coatings [11, 12]. Having high erosion resistance and strength in combination with a sufficiently high hardness, zirconium nitride coatings (ZrN) find their application when handling nonferrous metals. An intensive development of radiotechnologies may also account for a keen interest in ZrN coatings as a radiation-resistant material.

In this connection, it appears most topical to solve the materials science problem in structural engineering of vacuum-arc ZrN coatings with an aim of predictive attainment of the required functional physical-and-mechanical characteristics.

1. COATING FORMATION CONDITIONS AND RESEARCH TECHNIQUES

To solve the structural engineering problem using the upgraded setup "Bulat-6", which is equipped with an additional generator of high-voltage pulses supplied to the substrate during the process of deposition, ZrN coatings were obtained at nitrogen atmosphere pressures P_N ranging between 0.005 and 0.7 Pa. In the process, the negative constant bias potential, $U_b = (-5 \dots -300)$ V, and the high-voltage pulse potential, $U_{ip} = (-0.8 \dots -2.0)$ kV, with the pulse frequency of 7 kHz and the action time of 10 μ s (~7% of the total deposition time), were supplied to the substrate. The duration of the deposition process varied between 1 and 2 hours. Stainless steel 12Kh18N10T plates, measuring 18x18x2 mm, and

copper foils were used as substrates. The coating microphotographs were taken with the scanning-electron microscope JEOL JSM840.

The coatings were deposited onto 0.2 mm thick copper substrates. Structural studies of the samples were performed by the X-ray diffraction technique using the DRON-3M apparatus. The Cu- K_α radiation was used in all the experiments. To determine the orientation dependence of the coatings, the photography was carried out with Bragg-Brentano focusing in the θ -2 θ configuration. The size of grains-crystallites (coherent scattering region) in the nitride films was determined by the method of diffraction curve shape-fitting technique [13].

The sample hardness was determined at room temperature by the use of the "Micron-gamma" installation [14] equipped with the Berkovich diamond pyramid (the load being up to 0.5 N).

2. RESULTS AND DISCUSSION

2.1. MICROSCOPICAL STUDIES

The examination of ZrN coating morphology has shown that the coatings formed at a relatively low bias potential, -100 V, have a substantial amount of the drop phase on their surfaces (Fig. 1,a). The increase in the constant bias potential up to -300 V causes an essential decrease in the number of macroparticles on the coating surface (see Fig. 1,b). This decrease in the drop phase content can be explained by the fact that the drop component takes on the negative (floating) potential and is repelled by the surface, to which the negative potential is supplied (substrate surface in our case) [15].

A substantial drop-phase decrease is also observed with an increase in the nitrogen atmosphere pressure. It is apparent from Fig. 2 that unlike the coatings formed at $P_N = 0.02$ Pa (see Fig. 2,a,b), where a substantial content of drop-phase inclusions is noticeable, in the

coatings formed at $P_N=0.66$ Pa the drop phase is practically absent on both the surface (see Fig. 2,b) and in the bulk (side thin section in Fig. 2,d), and the

structure of the coating formed presents crystallites of columnar type (see Fig. 2,b).



Fig. 1. ZrN coating surface morphology ($P_N = 0.6$ Pa): a – $U_b = -100$ V; b – $U_b = -300$ V

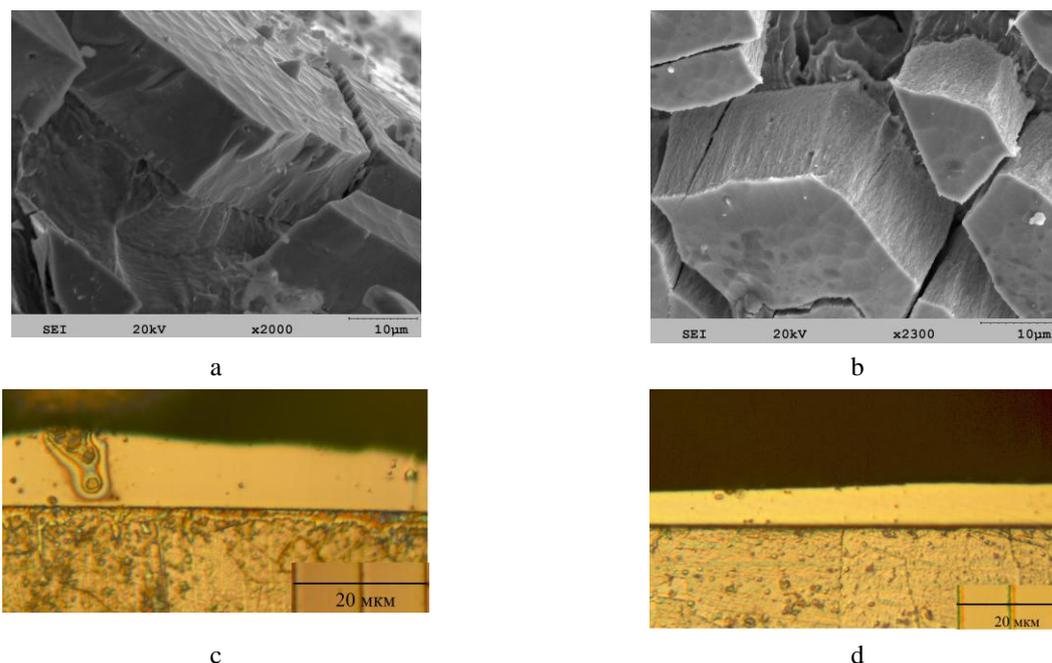


Fig. 2. Fracture morphology on the copper substrate (a, b) and cross sections (c, d) of ZrN coatings formed at a constant bias potential of $U_b = -150$ V on steel 12Kh18N10T substrate: a, c – $P_N = 0.02$ Pa; b, d – $P_N = 0.66$ Pa

At the lowest pressure of $2.7 \cdot 10^{-3}$ Pa, the spectrum shows the reflexes from pure Zr (ICDD PDF-2 No 500665), and also, a small amount (up to 5 vol.%) of the Zr_2N phase (ICDD PDF-2 No 46-1204).

The crystallites of Zr have the preferred orientation with the axis [110] perpendicular to the growth plane. Their size is comparatively large, exceeding 200 nm.

At pressures above 0.02 Pa, a single-phase state of ZrN is formed, having the cubic lattice of NaCl-structure type (JCPDS 35-0753). The arrangement of crystallites with practically no preferred orientation at a pressure of 0.02 Pa changes to give rise to the preferred crystallite orientation with the axes [111] and [311] (bitextural state) perpendicular to the growth plane at pressures ranging from 0.07 to 0.4 Pa, and finally at a higher pressure, to a practically uniaxially oriented texture [111] (the relative intensity of texture peaks of the family of planes {111} makes up more than 80% of the total intensity of all the peaks at angles $2\theta = 25 \dots 80^\circ$).

2.2. THE EFFECTS OF NITROGEN ATMOSPHERE PRESSURE ON THE PHASE COMPOSITION, STRUCTURE AND MECHANICAL CHARACTERISTICS OF ZrN COATINGS

Fig. 3 shows the diffraction spectra of ZrN coatings deposited at different nitrogen pressures $P_N = (2.7 \cdot 10^{-3} \dots 0.64)$ Pa and at constant $U_b = -150$ V.

The analysis of substructural characteristics (microstrain and size of crystallites) as functions of P_N at deposition shows that at a low pressure (0.02...0.1 Pa), when the formation of the solid-solution state of Zr(N) (i.e., lower zirconium nitride or zirconium nitride having the cubic lattice and biaxial texture) takes place, the general trend is seen toward the decrease in the microstrain of crystallites and size as the pressure increases. This behavior may be due to the process of polygonization at a higher mobility of atoms deposited at a low pressure. In this case, a comparatively low nitrogen-atom occupation density of octahedral

interstitial sites makes it possible to considerably relax the lattice microstrain that arises during deposition, owing to dislocation motion and formation of new boundaries.

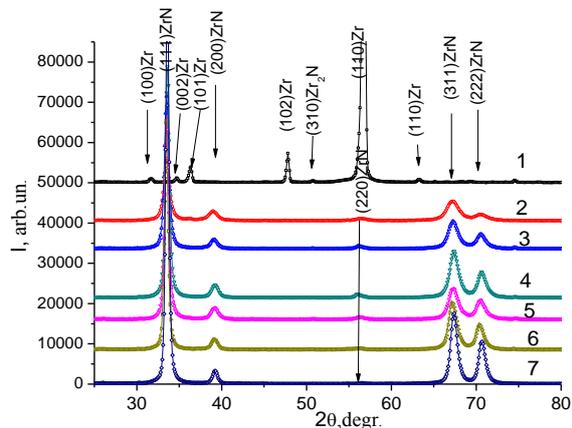


Fig. 3. Diffraction spectrum plots of ZrN coatings formed at a constant negative potential of $U_b = -150$ V and at different nitrogen atmosphere pressures, P_N , Pa: 1 – $2.7 \cdot 10^{-3}$; 2 – $2.7 \cdot 10^{-2}$; 3 – $6.7 \cdot 10^{-2}$; 4 – $9.3 \cdot 10^{-2}$; 5 – 0.13; 6 – 0.4; 7 – 0.64

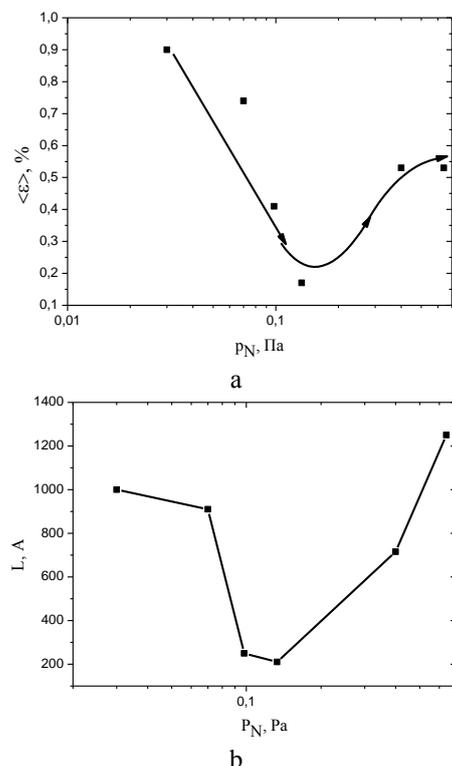


Fig. 4. Microstrain (a) and crystallite size (b) as functions of nitrogen pressure during deposition of ZrN coatings

The second spectrum plots observed at pressures exceeding 0.2 Pa is characterized by approach of the microstrain curve to a practically constant level of 0.50...0.55%, and also, by a considerable increase in the average crystallite size in the direction of film-forming particle incidence. It should be noted that in this case columnar-type crystallites are formed (see Fig. 2,b) with the preferred growth orientation axis [111] (see Fig. 3, spectra 6, 7).

The variation of substructural characteristics observed at high pressures can be related to the total saturation of the nitrogen atom-formed coating to stoichiometric and superstoichiometric compositions in nitrogen atoms. The last-mentioned composition provides the attainment of the constant lattice microstrain value and the stability improvement of larger crystallite formations.

The use of microhardness as the major express criterion of mechanical characteristics shows (Fig. 5) that in correlation with substructural data the hardness-nitrogen pressure relationship can be divided into two sections. The first section up to $P_N = 0.1$ Pa with the hardness increase from 5.8 GPa up to 42 GPa as P_N increases, may be attributed to the saturation of bonds with nitrogen atoms at simultaneous decrease in the average size of crystallites. The second section at a higher pressure 0.1...0.64 Pa with the hardness remaining practically at a level of 37...38 GPa, may be due to the action of two mutually competing processes, which are opposite in their influence on the hardness. These are the coating saturation by nitrogen atoms with formation of strong covalent nitride bonds, and the substantial increase in the average size of the crystallites.

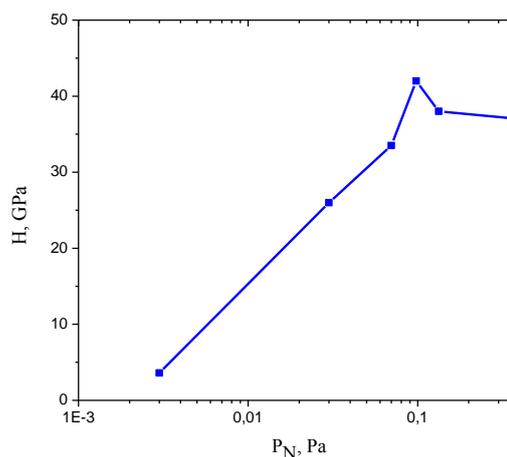


Fig. 5. ZrN coating hardness versus working atmosphere (nitrogen) pressure during deposition

2.3. THE EFFECTS OF HIGH-VOLTAGE PULSE AMPLITUDE ON THE PHASE COMPOSITION, STRUCTURE AND MECHANICAL CHARACTERISTICS OF ZrN COATINGS

The influence of high-voltage pulse potential on the phase composition and structural state was investigated at three different pulsed modes with amplitudes (U_{ip}) at 800, 1200 and 2000 V.

Fig. 6 shows the plots of diffraction spectra obtained for the coatings deposited at different pressures under the action of 800 V-amplitude pulse stimulation.

It is obvious that the tendency for the transition from the bitextural state (with the texture axes [311] and [111]) to the monotextural state (the texture axis is [111]) with increasing pressure (by analogy with the deposition mode without pulse stimulation) holds in this case, too. At that, the action for 7% of time with the $U_{ip} = -800$ V has led to a small relative increase in the peak intensity from the plane (220). A similar effect is

enhanced with increasing U_{ip} , and at the bias amplitude of -2000 V the peak from the plane (220) becomes apparent for the coating deposited at the highest pressure of 0.64 Pa (see Fig. 6,c, spectrum 6).

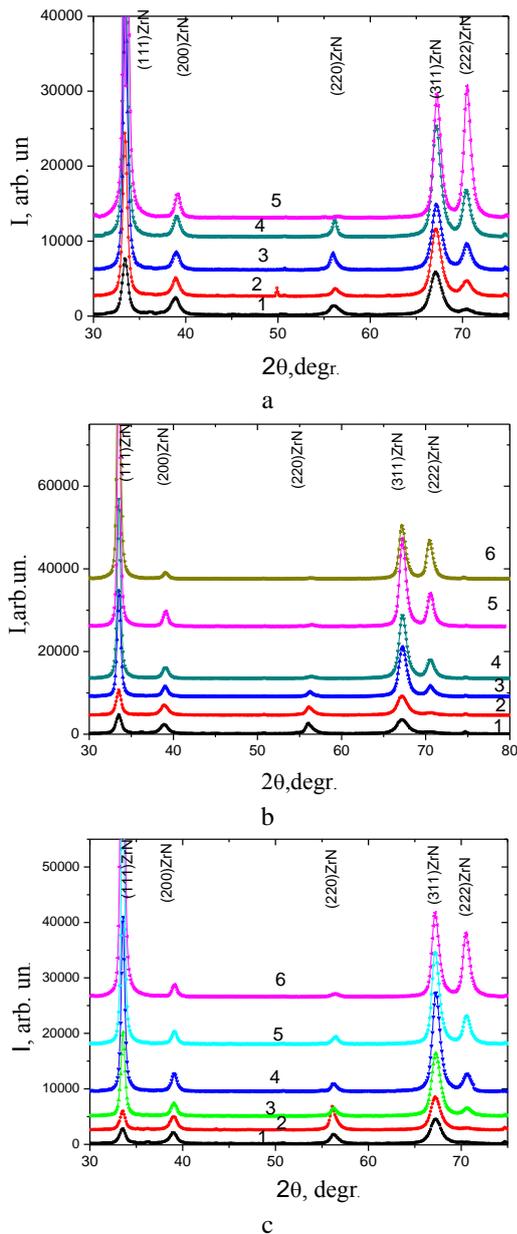


Fig. 6. Plots of X-ray diffraction spectra for ZnO coatings formed at $U_b = -150$ V, $U_{ip} = -800$ V (a), $U_{ip} = -1200$ V (b) and $U_{ip} = -2000$ V (c) at P_N : 1 – 0.027 Pa; 2 – 0.07 Pa; 3 – 0.098 Pa; 4 – 0.133 Pa; 5 – 0.40 Pa; 6 – 0.64 Pa

At a substructural level, the supply of a high-voltage pulse potential during coating formation leads to microstrain reduction at low pressures (Figs. 4,a and 7,a) and to a smoother attainment of values close to $0.5...0.6\%$. In this case, as U_{ip} increases, the deviation from the average microstrain value decreases in the whole range of pressures. As mentioned above, the attainment of a practically constant value of microstrain at high pressures is specified by occupation of octahedral interstitial sites by nitrogen atoms, which impede the deformation due to strong bonds formed with metal atoms of the lattice. The

supply of high-voltage pulses stimulates activation of physico-chemical reactions; that leads to intensification of the process of nitride formation at comparatively low pressures, and thus, to the attainment of practically constant microstrain values at a level of $0.5...0.6\%$ throughout the pressure range ($0.02...0.64$) Pa (see Fig. 7,a, curve 3).

The U_{ip} supply leads to a qualitative change in the behavior of the function $L(P_N)$. It can be seen (see Figs. 4,b and 7,b) that unlike the pulse-free mode, which is characterized by the crystallite size reduction at pressures between ($0.02...0.13$) Pa, the supply of high-voltage pulses leads to the increase in the mean crystallite size with increasing P_N . The observed variations at high-voltage pulsed ion stimulation can be explained by a higher energy transferred to deposited particles, and accordingly, by their higher mobility and chemical activity at nitride formation. That specifies the improvement in the perfection of the structure with nitrogen atmosphere pressure increase. At the same time, the crystallite size reduction at high pressures ranging from 0.4 to 0.64 Pa with the highest impulse excitation amplitude (-2000 V), is evidently caused by the radiation action, which is specified by a high energy (sufficient for cascade formation) of the particles deposited under the action of HV pulse potential. In combination with the coating supersaturation with nitrogen atoms at high pressure, this leads to the increase in the number of nucleation sites, thereby decreasing the average size of coating crystallites (see curve 3 in Fig. 7,b).

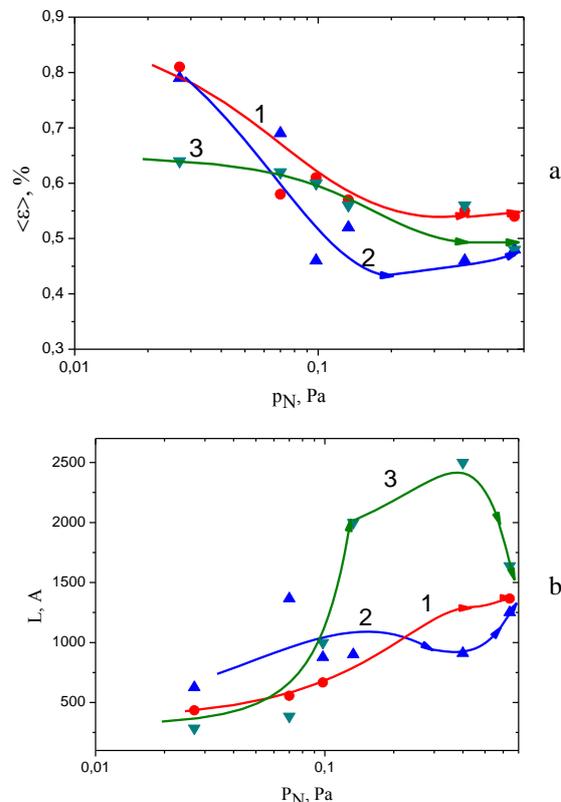


Fig. 7. Substructural characteristics of ZnO coatings (microstrain (a), crystallite size (b)) versus nitrogen atmosphere pressure for deposition at $U_b = -150$ V and at high-voltage pulse potentials U_{ip} : 1 – 800 V; 2 – 1200 V; 3 – 2000 V

The increase in crystallite size with simultaneous improvement of nitride formation efficiency, as well as the supply of U_{ip} with pressure increase are acting as mutually opposite factors that exert influence on the mechanical properties of coatings. This is manifested in a small change of hardness throughout the entire range of pressures used (Fig. 8). Leaving unchanged the maximum hardness value 40...43 GPa, the particle energy increase during coating formation due to negative constant potential (applied to the substrate) leads to the displacement of the maximum position on the pressure scale, i. e., with increasing U_{ip} the hardness peak value is shifted to the region of higher nitrogen atmosphere pressures during coating formation (see curves 1 to 3 in Fig. 8).

The increase in the average crystallite size due to the pulsed high-energy action is likely to be the governing factor in the decrease of hardness at higher pressures. Note, however, that the use of pulsed conditions makes it possible to avoid a dramatically considerable grain growth, which deteriorates the mechanical properties, as it might be expected in the case of high-energy action of particles accelerated with supply of a constant high-voltage bias potential.

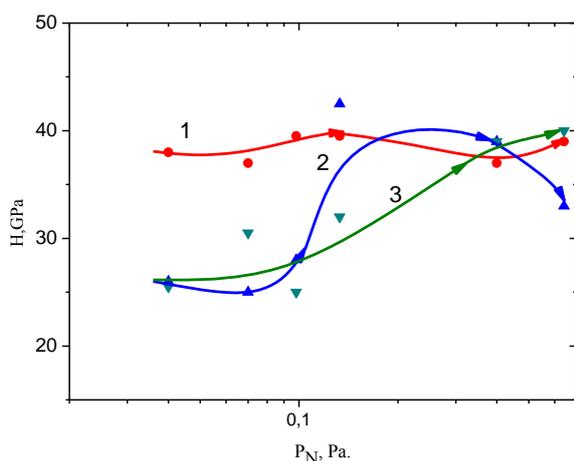


Fig. 8. Microhardness of ZrN coatings versus working atmosphere (nitrogen) pressure at deposition with HV impulse action U_{ip} :
1 – 800 V; 2 – 1200V; 3 – 2000 V

In this regard, the observed crystallite size reduction at a high pressure (curve 3 in Fig. 7,b) is evidently the main factor responsible for a certain increase in hardness revealed for the coatings of this type at high pressures (curve 3 in Fig. 8).

CONCLUSIONS

1. With an increase in the nitrogen atmosphere pressure from 0.002 up to 0.02 Pa during deposition, the phase composition of coatings formed through vacuum-arc evaporation of the zirconium target varies from multiphase (Zr, Zr_2N and ZrN) to single-phase structure (ZrN). At a higher pressure during deposition, structural changes take place in the single-phase ZrN coating. They show up as a formation of preferred orientation of the crystallite growth with the texture axes [111] and [311]. At the highest pressure (0.64 Pa), the [111] texture becomes determinant.

2. In the pressure range between 0.02...0.4 Pa, the supply of an additional high-voltage pulse potential gives rise to the texture with the axis [110]. As U_{ip} increases, the [110] texture is formed in the coatings produced at higher pressures P_N .

3. At a substructural level, the pressure P_N increase in the range 0.02...0.1 Pa causes reduction in both the microstrain and the crystallite size; that corresponds to the process of polygonization. At a higher pressure the microstrain value attains practically a constant level of 0.5 to 0.6% at a continuous increase in the crystallite size.

4. The supply of a negative high-voltage pulse potential, which enhances the particle mobility and the nitride formation activity, results in the reduction of the microstrain and in the attainment of constant microstrain values at low P_N (0.1...0.2 Pa). The crystallite size increase in this case with P_N is determined by the formation of nitrides directly on the growth surface during deposition.

5. The present ZrN coatings refer to superhard coatings with the hardness reaching 43 GPa. The supply of a high-voltage pulse potential, which increases the average particle energy, causes the shift of the hardness peak value to the region of higher pressures.

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ВЛИЯНИЕ ДАВЛЕНИЯ АЗОТНОЙ АТМОСФЕРЫ, ПОСТОЯННОГО И ВЫСОКОВОЛЬТНОГО ИМПУЛЬСНОГО ПОТЕНЦИАЛОВ ПОДЛОЖКИ НА СТРУКТУРУ И СВОЙСТВА ВАКУУМНО-ДУГОВЫХ ПОКРЫТИЙ ZrN

О.В. Соболев, А.А. Андреев, В.А. Столбовой, В.Ф. Горбань, Н.В. Пинчук, А.А. Мейлехов

Методом вакуумно-дугового испарения Zr-катода в азотной атмосфере при давлении $P_N = 0,02 \dots 0,64$ Па получены покрытия ZrN с кубической (структурный тип NaCl) кристаллической решеткой. Повышение давления при потенциале смещения -150 В приводит к образованию текстуры роста [111] или появлению битекстурного состояния с осями [111] и [311]. Дополнительная подача высоковольтного отрицательного потенциала $U_{ни} = 800 \dots 2000$ В в импульсном режиме с длительностью 10 мкс и частотой 7 кГц стимулирует появление текстуры [110]. На субструктурном уровне подача $U_{ни}$ приводит к релаксации микродеформации и росту размеров кристаллитов при повышении давления азота. Наблюдаемые изменения связываются с повышением подвижности частиц и активности нитридообразования в условиях действия $U_{ни}$. Твердость возрастает с увеличением давления и достигает значения 43 ГПа. Подача $U_{ни}$ приводит к смещению максимальной твердости в сторону больших давлений.

ВПЛИВ ТИСКУ АЗОТНОЇ АТМОСФЕРИ, ПОСТІЙНОГО І ВИСОКОВОЛЬТНОГО ІМПУЛЬСНОГО ПОТЕНЦІАЛІВ ПІДКЛАДКИ НА СТРУКТУРУ І ВЛАСТИВОСТІ ВАКУУМНО-ДУГОВИХ ПОКРИТТІВ ZrN

О.В. Соболев, А.О. Андреев, В.А. Столбовой, В.Ф. Горбань, Н.В. Пинчук, А.А. Мейлехов

Методом вакуумно-дугового випаровування Zr катода в азотній робочій атмосфері при тиску $P_N = 0,02 \dots 0,64$ Па отримані покриття ZrN з кубічною (структурний тип NaCl) кристалічною решіткою. Підвищення тиску в умовах дії негативного потенціалу зсуву -150 В призводить до утворення текстури росту [111] або появи бітекстурного стану з осями [111] і [311]. Додаткова подача высоковольтного негативного потенціалу $U_{ни} = 800 \dots 2000$ В у імпульсному режимі з тривалістю 10 мкс і частотою 7 кГц стимулює появу текстури [110]. На субструктурному рівні высоковольтний імпульсний вплив призводить до релаксації мікродеформації і зростання розмірів кристалітів при підвищенні тиску азоту. Спостережувані зміни пов'язуються з підвищенням рухливості частинок і активності нитридоутворення в умовах дії $U_{ни}$. Твердість зростає із збільшенням тиску і досягає значення 43 ГПа. Подача $U_{ни}$ призводить до зсуву максимальної твердості в бік великих тисків.