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A Computer Simulation of Radiation-Induced Structural Changes and Properties of Multiperiod ZrN_x/MoN_x System

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Influence of the period value Λ (at different negative potential U_b that supplied during deposition) on phase composition, structure, stress-strain state and hardness of multiperiod coatings ZrN_x/MoN_x is investigated by using complex methods of validation structural state at combined with microindentation. Formation in layers ZrN_x and MoN_x the phases with cubic lattice and preferred orientation of crystallites with axis [100] is established. Stress-strain state of compression with increasing U_b is amplified and reaches maximum value (– 6.7 GPa) at Λ = 20 nm and U_b = – 110 V. Hardness of coating increases with decreasing Λ from 300 to 20 nm. Coatings that obtained with Λ = 20 nm and U_b = – 110 V have the highest hardness 44 GPa. Relaxation of structural compressive stresses and decreasing hardness is happening at smaller Λ and larger U_b = – 110 V (as a result of radiation-stimulated forming defect and mixing).

Data of computer modeling of defectiveness at atomic level at bombardment of ions that accelerated in field U_b are used to explain the results.

Keywords: Coatings, ZrN_x/MoN_x, Period, Potential of bias, Phase composition, Structure, Stress-strain state, Solid solution, Computer simulation, Hardness.

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1. INTRODUCTION

Deposition of vacuum-arc coating is happening in conditions of action radiation factor because of interaction of charged accelerated particles with surface of material [1, 2]. Most typical types of radiation damages in surface layers at bombardment of accelerated ions are shown in Figure 1. Such interaction is characterized by various physical phenomena: forming cascade and subcascade defective areas [3], forming grid of dislocations, disintegration of solid solution, phase transformations [4] and other effects.

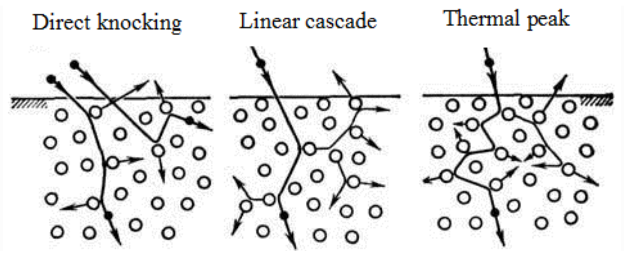

Fig. 1 – Types of effect of accelerated particles on atomic structure of subsurface layers

Defect formation leads to forming new types of structures [5], preferential arrangement of structural elements [6] and development of structural stresses [7] in coatings at their deposition. Forecasting and control of stresses in PVD (physical vacuum deposition) coatings has continued interest [8]. This is due to determining influence of texture and stress-strain state on number of important technological properties of material [9, 10]. In particular, as has been shown in several researches [e.g., 11] stresses that developing during deposition process in coatings, stresses determine its strength of adhesion with substrate, forming various types of fractures [12, 13] or formation on surface of self-assembled structural formations [14, 15].

Therefore aim was determined at article: effect of value period of multi-layer structure (at different negative potential U_b that supplied during deposition) on phase composition, structure and stress-strain state with using complex methods of validation structural state (including XRD method of multiple slanted surveying ($\sin^2\psi$- method) and method of computer simulation radiation-induced structural changes at ion implantation). Analysis of the results was carried out in comparison with the mechanical properties (hardness) coatings.

Multilayer system ZrN_x/MoN_x, in which ZrN component has high negative heat of forming nitride – 366.6 kJ/mol, and MoN – relatively low ΔH^0_{298} = – 34 kJ/mol been used as a base in this research.

2. SAMPLES AND METHODS OF RESEARCHES

Coatings were deposition by vacuum-arc method on modernized installation "Bulat-6" [4]. Molybdenum and zirconium that obtained by method of electron beam

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melting been used as materials of cathodes; reactive gas – nitrogen (99.95 %). Pressure of working (nitrogen) atmosphere during deposition was $P_N = 4 \cdot 10^{-3}$ Torr, deposition rate was about 2 nm/sec in this case. Deposition was carried out from two sources on surface of samples with dimensions $20 \times 20 \times 2$ mm from austenitic steel 12Cr18Ni10Ti (analog of stainless steel SS 321).

Thickness of layers in coating (h) was determined by holding time at source and an average for layer amounted to 5, 10, 20, 40, 75 and 150 nm that corresponds to bilayer period Λ with average thickness 10, 20, 40, 80, 150 and 300 nm.

Constant negative bias potential (U_b) with value of – 70 or – 110 V was supplied during deposition of substrate.

Phase composition, structure and substructural characteristics been studied by method of X-ray diffractometry (DRON-4) with using Cu-Kα-radiation. Graphite monochromator, which was installed in secondary beam (front of detector) was applied to monochromatization of registered radiation. Study of phase composition, structure (texture, substructure) was carried out by traditional methods of X-ray diffraction through analysis of position, intensity and form of profiles diffraction reflections [5, 17]. Tables of International Centre Diffraction Data Powder Diffraction File been used to decrypt diffractograms.

Method of multiple slanted surveying ($\sin^2\psi$ method) been used to research macrostresses-strain state [17]. Scheme for biaxial stress-strain state (Fig. 2), at which deformation of lattice related to voltage by equation been used [13]:

$$\varepsilon_{\varphi,\psi} = \frac{d_{\varphi,\psi}-d_0}{d_0} = \frac{1+\nu}{E}\sigma_\varphi sin^2\psi - \frac{\nu}{E}(\sigma_{11}+\sigma_{22}) \qquad (1)$$

where d_0 – grating period in unstressed state, $d_{\varphi,\psi}$ – grating period in stressed state, σ_φ – stresses in direction φ, that is determined by plane of cover, ψ – tilt angle, σ_{11} and σ_{22} – principal stresses in plane, E – elastic modulus, υ – Poisson's ratio of coating material.

Stresses σ_φ (along direction φ) can be calculated from equation (1) using following equation:

$$\sigma_\varphi = \frac{E}{(1+\nu)sin^2\psi}\left(\frac{d_{\varphi,\psi}-d_{\varphi,\psi=0}}{d_0}\right) \qquad (2)$$

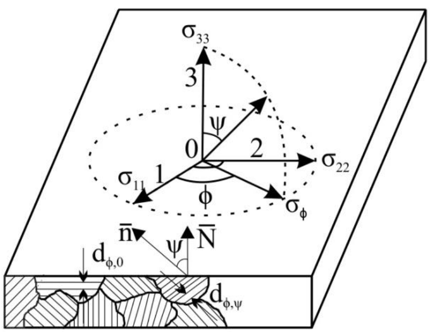

Fig. 2 – Scheme of determining of basic parameters using $\sin^2\psi$-method to determine the stress-strain state of coatings which are in plane stress. ***N*** – normal to the surface, ***n*** – normal to the planes.

Equation (2) allows to calculate stresses in any direction on plane and stresses in direction φ. Value $d_\psi = 0$ been used to simplification of calculations instead of d_0. This change introduces an error of less than 0.1 % in determination of the voltages values.

Study morphology of lateral shear of multiperiod structures was performed on raster electron microscope JEOL JSM840. Coatings were deposited on copper substrates with thickness of 0.2 mm for electron microscopy studies.

Microindentation was performed on installation "Micron-gamma" with load up to $F = 0.5$ N by diamond Berkovich pyramid with angle of sharpening 65°, with automatically accomplished loading and unloading during 30 seconds [18].

Computer simulation been used at research to understanding spatial distribution of radiation-stimulated changes in border (interlayer) areas during deposition of high-energy particles. Program that based on approximate method of double collisions, TRIM, which is based on Monte Carlo method to describe trajectory of incident particle and damages that formed by this particle been used at research for this [19]. TRIM uses maximum parameters of exposure that determined by density of environment and constant mileage between clashes [20].

3. RESULTS AND DISCUSSION

Negative constant potential of displacement with value – 70 or – 110 V that are standard modes to provision of good adhesion was supplied at receipt of multiperiod system ZrN_x/MoN_x [8, 21].

Analysis of morphology fracture of multilayer coatings shows reasonably good their planarity (Fig. 3) that is typical for all investigated regimes of deposition. Layers ZrN_x are light, and MoN_x – dark (refer to images).

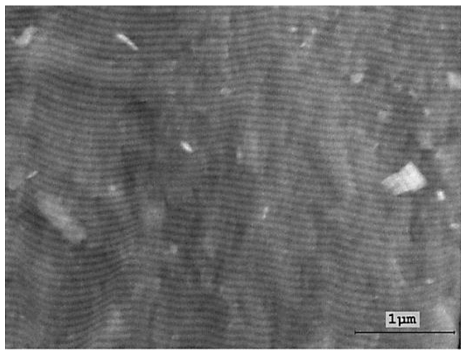

Fig. 3 – Cross section of multilayer coating ZrN_x/MoN_x that obtained at $U_b = -110$ V with period Λ = 80 nm

Phase composition of layers was determined by XRD-method. As seen from the obtained diffraction spectra in coatings formed isostructural phase (structural type of NaCl) ZrN_x и γ-Mo_2N. Crystallites with preferred orientation (axis [100] is perpendicular to plane of growth, axial texture) are formed at lowest potential $U_b = -70$ V coating layers [5]. Degree of perfection of texture increases at increasing of layer thickness (Fig. 4, spectrums 3 and 4). Preferential orientation of crystallites almost no detected in coatings that are deposited at higher $U_b = -110$ V

(Fig. 4, spectrums 1 and 2). Thus average crystallite size that determined according to Scherrer formula [16] crystallites ZrN_x is about 5 nm, and crystallites γ-Mo_2N phase is significantly less (with size of about 2.3 nm).

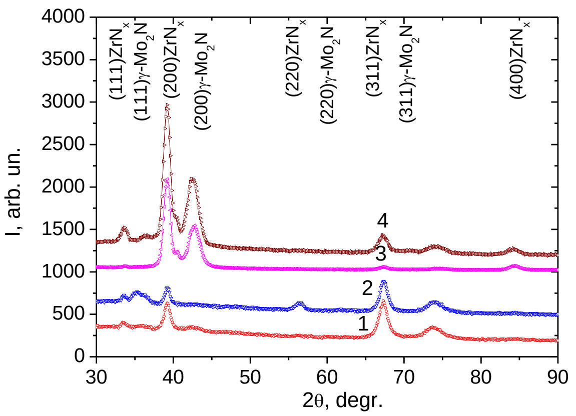

Fig. 4 – Diffraction patterns spectrums of coatings that obtained at $U_b = – 110$ V (1 and 2) and $U_b = – 70$ V (3 and 4) with period 20 (1 and 3) and 80 nm (2 and 4)

Ability to allocation of separate phases in coatings by using XRD method allows to use X-ray method also to determination of stress-strain state in each phase separately. Method of multiple slanted surveying ($\sin^2\psi$-method) been used at research for this. Planes (422) and (511) that located in optimal angle range $\theta = 60$-$75°$ for precision surveying, been used as basic at researches. Surveying was carried out in angular ranges of inclination of sample $\psi = 0$-$60°$ (Fig. 2) with standard subsequent processing of received data [17].

Maximum value of resilient compressive stress (– 6.7 GPa) is achieved in layers ZrN_x at largest $U_b = – 110$ V (Fig. 5a). Increasing $– \sigma$ with decreasing Λ (less than 70 nm) is characteristic to all systems. But decreasing of compression stress is observed for coatings that obtained at larger $U_b = – 110$ V with lowest Λ = 10 nm.

Compressive stress in its magnitude becomes close to constant at thickness of layers $\Lambda \geq 100$ nm.

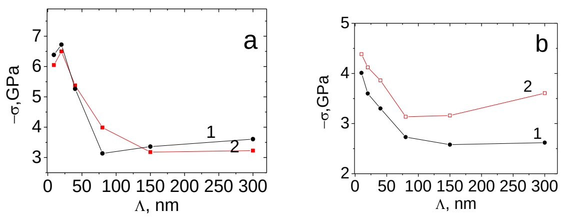

Fig. 5 – Dependence value of compression stress ($– \sigma$) from size of period of coatings Λ for constituting of system ZrN_x/MoN_x: 1 – ZrN_x, 2 – MoN_x (a – $U_b = – 110$ V, b – $U_b = – 70$ V)

Also of note is revealed regularity – forming compressive stresses in both layers of bilayer composition. Such effect could be due to structural character of formed stress-strain state in layers.

State of interphase boundaries is factor that to greatest extent determines stability of structure and properties of multiperiod composite coatings [7, 22]. Modeling of processes that may occur at border at nanometer size of layers is based on radiation-stimulated processes during deposition. Analytical decisions on depending defect distribution in space at obtaining coatings is sufficient difficult. Computer simulation is necessary to use to determine spatial and temporal development of cascade. Program that based on approximate method of double collisions (TRIM), in which Monte Carlo method is used to describing trajectory of incident particle and damage that generated by this particle been used at research.

Modeling has shown that in case of ion irradiation with average energy 110 eV (corresponds to deposition at exposure $U_b = – 110$ V), in system ZrN_x/MoN_x at bombardment by ions Mo coating ZrN (Mo → ZrN) according to calculations the value maximum of concentration introduced particles should be at depth ≈ 0.9 nm at total depth of exposure to 2 nm. At considering of exposure Zr → MoN: maximum of ion distribution is also at depth ≈ 0.9 nm at total depth of exposure ≈ 1.85 nm.

Thus layer of thickness about 2 nm (in which decisively affecting of radiation-stimulated mixing) is formed on borders during deposition of coating. Total depth of impact of radiation defect formation in period is about 4 nm, because two such boundaries in period Λ.

Indentation is most versatile and express characteristic of determining mechanical properties. Summary results according to change hardness of multiperiod coatings from Λ are shown on Figure 6. From the results obtained can be seen that highest hardness (≈ 41 GPa) is achieved in coatings with least Λ at small $U_b = – 70$ V (Fig. 6, curve 1). Hardness of coatings decreases with increasing Λ. Decrease of hardness is observed at large $U_b = – 110$ V (unlike low U_b, Fig. 6, curves 1 and 2) and smallest period Λ.

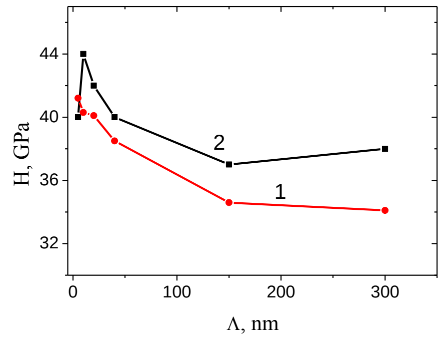

Fig. 6 – Dependence of coatings hardness (*H*) from thickness of bilayer period (Λ) for multilayer coatings of system ZrN_x/MoN_x that obtained at $U_b = – 70$ V (1) and $U_b = – 110$ V (2)

This effect may be associated with small size of crystallites in layers MoN (about 2.5 nm), at which transition from relaxation of deformed in shear to rotational relaxation is happening. Rotational relaxation usually leads to decrease of hardness [23] that is observed in our case.

Characteristic decrease of hardness with increasing the size of structural elements in nanometer range is happening in the field of Λ > 20 [24-26]. It is important to note that matching with results research of stress-strain state indicate the existence correlation between increasing hardness and increasing magnitude of compression stress that are formed in coating. This effect is understandable, because compressive stress is stimulated by higher specific atomic density and contributes to improving strength and links of hardness.

4. CONCLUSION

1. Formation of two phases (ZrN_x and γ-Mo_2N) in layers of multiperiod composition ZrN_x/MoN_x with magnitude of period Λ = 10 ... 300 nm is revealed.
2. Preferential orientation of growth crystallites with axis [100] that perpendicular to plane of growth is formed at low potential U_b = – 70 V. Change of axis to [311] is happening at large U_b = – 110 V.
3. Using modeling method of radiation-induced damages of material at irradiation by ions allowed to determine critical thickness of mixing in bilayer composition ZrN_x/MoN_x. This thickness is about 4 nm
4. It is found that critical thickness of radiation-stimulated defect formation has significant effect on stress-strain state and properties in coatings with low $\Lambda \leq$ 10 nm. Relaxation of stress-strain state of compression is happening in this case and hardness is decreasing.

Комп'ютерне моделювання радіаційно-стимульованих структурних змін і властивості багатоперіодної системи ZrN_x/MoN_x

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Використовуючи комплекс методів атестації структурного стану в поєднанні з мікроіндентуванням досліджено вплив величини періоду Λ (при різному негативному потенціалі U_b, що подається при осадженні) на фазовий склад, структуру, напружено-деформований стан і твердість багатоперіодних покриттів ZrN_x/MoN_x. Встановлено формування в шарах ZrN_x і MoN_x фаз з кубічної решіткою і переважною орієнтацією кристалітів з віссю [100]. Напряженно-деформований стан стиснення зі збільшенням U_b посилюється, досягаючи максимального значення (– 6,7 ГПа) при Λ = 20 нм і U_b = – 110 В. Твердість покриттів збільшується зі зменшенням Λ від 300 до 20 нм. Покриття, отриманні при Λ = 20 нм і U_b = – 110 В мають найбільшу твердість 44 ГПа. При меншому Λ і великому U_b = – 110 В (в результаті радіаційно-стимульованого дефектоутворення і перемішування) відбувається релаксація структурних напружень стиску та зменшення твердості.

Для пояснення отриманих результатів використані дані комп'ютерного моделювання пошкоджуваності на атомному рівні при бомбардуванні прискореними в поле U_b іонами.

Ключові слова: Покриття, ZrN_x/MoN_x, Період, Потенціал зміщення, Фазовий склад, Структура, Напружено-деформований стан, Твердий розчин, Комп'ютерне моделювання, Твердість.

Компьютерное моделирование радиационно-стимулированных структурных изменений и свойства многопериодной системы ZrN_x/MoN_x

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Используя комплекс методов аттестации структурного состояния в сочетании с микроиндентированием, исследовано влияние величины периода Λ (при разном отрицательном потенциале U_b, подаваемом при осаждении) на фазовый состав, структуру, напряженно-деформированное состояние и твердость многопериодных покрытий ZrN_x/MoN_x. Установлено формирование в слоях ZrN_x и MoN_x фаз с кубической решеткой и преимущественной ориентацией кристаллитов с осью [100]. Напряженно-деформированное состояние сжатия с увеличением U_b усиливается, достигая максимального значения (– 6,7 ГПа) при Λ = 20 нм и U_b = – 110 В. Твердость покрытий увеличивается с уменьшением Λ от 300 до 20 нм. Покрытия, полученные при Λ = 20 нм и U_b = – 110 В имеют наибольшую твердость 44 ГПа. При меньшем Λ и большом U_b = – 110 В (в результате радиационно-стимулированного дефектообразования и перемешивания) происходит релаксация структурных напряжений сжатия и уменьшение твердости.

Для объяснения полученных результатов использованы данные компьютерного моделирования повреждаемости на атомном уровне при бомбардировке ускоренными в поле U_b ионами.

Ключевые слова: Покрытия, ZrN_x/MoN_x, Период, Потенциал смещения, Фазовый состав, Структура, Напряженно-деформированное состояние, Твердый раствор, Компьютерное моделирование, Твердость

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