

Structural Engineering of Vacuum-plasma Interstitial Phase Coatings

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The analysis of possible structural states defined by nonequilibrium processes in vacuum-plasma methods for obtaining interstitial phase coatings has been carried out in the work. It is shown that nonequilibrium deposition conditions from ion-plasma fluxes significantly expand the range of possible structural states of the formed material: from amorphous like to highly ordered crystalline. A high thermalization rate determines the formation of phases with a cubic crystal lattice (in most cases of NaCl structural type). The conditions and mechanisms of the transition from a metastable state with a cubic lattice to the equilibrium state with a hexagonal crystal lattice are shown by examples of W-C and Ta-N systems with a hexagonal lattice type in the equilibrium state. The transition is performed by diffusion-shear transformation with the formation of stacking faults in the alternation of the most densely packed planes along the [111] axis. The formation of stacking faults is facilitated by a small shear region in nanocrystalline materials and the presence of vacancies, and the shear transformation itself (through the formation of stacking faults) is accompanied by a sharp relaxation of structural stresses.

Based on the atomic mobility criterion, the mechanisms of structural transformations in vacuum-plasma coatings and the necessary physical and technological conditions for directed structural changes at the deposition and high-temperature annealing stage are discussed.

Keywords: Structural engineering, Vacuum plasma coating, Interstitial phases, Metastable, Diffusion, Structural transformation, Shift mechanism, Stresses.

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1. INTRODUCTION

A high thermalization rate of particle energy in vacuum-plasma methods for obtaining coatings predetermines a wide range of the formed structural states including nonequilibrium in phase composition, as well as amorphous-like and clustered in structural types [1-5].

The main criterion determining the type of the formed structural state is the mobility of the deposited particles [6, 7]. When the deposition rate is 1 monolayer/s that is typical for ion-plasma methods by the magnetron circuit and corresponds to the average flux density of $3 \cdot 10^{15}$ atoms/cm²·s, then in order to form a nucleus of a close-packed plane of crystallite orientation (111) consisting of 3 atoms, the necessary atomic mobility should ensure the displacement over, at least, 2 interatomic distances that is about 0.45 nm. In this case, the surface diffusion coefficient of film-forming atoms should be not lower than $4 \cdot 10^{-16}$ cm²/s that is typical for deposition of particles with the electron-volt energy at a substrate temperature of 300-400 °C [7].

In order to form a nucleus of a more complex form, in particular, nuclei of 3D configurations that is necessary when the crystallites of low-symmetry lattices grow, the atomic mobility should be much higher that is achieved only with increasing substrate temperature in deposition higher than 800 °C [8].

A low homological temperature determines the formation of highly porous condensates that stimulates the formation of tensile stresses. The achievement of the mobility necessary for planar filling of the growing surface may not result in ordering with long-range crystalline order in the case of a large difference in the atomic radii of substitution elements (for example, Si is this alloying element for transition metals). The amorphization process is stimulated in the case of the formation of interstitial phases with such interstitial elements as B and O in the transition from a base metal of group IV to metals

of group VI, and also in the case of the addition of metallic components with low binding energy [9-16].

If at a relatively low deposition temperature the particle energy allows them to form the long-range crystal lattice for phases of the MeX type (Me is the transition metal, X is the interstitial element B, C, N, O), then the simplest lattice type, namely, the fcc-lattice of the NaCl structural type is mainly formed [9, 17, 18].

A high-entropy base of ordering into simple (of cubic system) crystal lattices is most clearly manifested for high-entropy alloys and coatings on their basis, where the inhomogeneity associated with a variety of atoms leads in most cases to the formation of a cubic crystal lattice of the fcc type [19].

The aim of this work was to elucidate the mechanism of the crystal lattice transformation in nanocrystalline MeX condensates, for which the formed phase with the NaCl structural type is metastable in equilibrium conditions corresponding to the deposition temperature.

2. EXPERIMENTAL

The carbide coating samples were fabricated by magnetron sputtering of the α -WC target in an argon atmosphere at an operating pressure of $2 \cdot 10^{-3}$ torr and a discharge power of 30-300 W. At that, the film deposition rate was 0.12-1.8 nm/s that corresponded to the flux density of the deposited particles of the metallic component (tungsten) $j_W = 1.2 \cdot 10^{15} - 1.8 \cdot 10^{16}$ cm⁻²·s⁻¹. Al₂O₃ and Si plates of 180 μ m and 370 μ m thick, respectively, were used as substrates. Annealing of the samples was performed in a specially designed vacuum installation at a residual pressure less than 10^{-5} torr. Heating was carried out by halogen lamps to 600-1300 °C temperatures followed by exposure for 1 hour at these temperatures.

The nitride samples were produced by magnetron sputtering in SaNEL lab [20] in an Ar + N₂ atmosphere (for different ratios) and a total pressure of $5 \cdot 10^{-3}$ torr.

A bias potential (U_s) of -100 , -200 and -300 V was applied at deposition. The deposition temperature was about 550 °C.

The study of the phase composition, lattice constants and substructural characteristics, as well as the stress state, was performed by X-ray diffractometry. The investigations were conducted in filtered $\text{Cu-}k_\alpha$ radiation.

The processing of the results obtained was carried out by both classical methods [21] and using the multi-parameter cross-section technique [22].

The electron microscopic studies were performed on the electron microscope PEM-125K at a magnification of up to $450\,000$ at a voltage of 100 kV.

3. RESULTS AND DISCUSSION

As known [23, 24], an increase in the deposition temperature transforms the coating material structure formed from vacuum-plasma fluxes into a more equilibrium state. For most interstitial phases, 900 - 1000 °C is such a temperature, at which the state of the formed structure can be considered close to equilibrium [1, 7]. Moreover, ordering in the displacement cascades under high-energy impact can result from the metastable to a more equilibrium state [2].

The W-C and Ta-N systems with the element content close to the equiatomic one have phases with non-cubic crystal lattices in the temperature range of 20 - 300 °C in the equilibrium state, and therefore phases with a cubic lattice formed in non-equilibrium conditions are metastable that makes it possible by their example to study in detail the transition conditions and mechanisms from the metastable to the equilibrium state.

β -WC metastable phase with a cubic crystal lattice of the NaCl structural type is formed in the W-C system at a deposition temperature lower than 700 °C [7].

The Auger electron elemental analysis showed that when the deposition rate varied from 0.12 to 1.8 nm/s that corresponded to the total flux density of the deposited particles $j_W = 1.2 \cdot 10^{15}$ - $1.8 \cdot 10^{16}$ $\text{cm}^{-2} \text{s}^{-1}$, then the C/W atomic ratio in the coating varies from close to 1.1 to 0.8 (see Fig. 1).

The X-ray diffraction studies of micron thick coatings showed that at flux densities of the deposited particles less than $j_W \approx 8 \cdot 10^{15}$ $\text{cm}^{-2} \text{s}^{-1}$ they are single-phase (the β -WC phase) (Fig. 2, spectra 1-2). With increasing flux density, there is a redistribution of the intensity of the diffraction curves from different planes in the direction of increasing relative intensity of the peaks from $\{100\}$ planes and also the appearance at $j_W > 9 \cdot 10^{15}$ $\text{cm}^{-2} \text{s}^{-1}$ of the diffraction peaks from equilibrium α -W₂C phase with the hcp lattice, which is carbon depleted compared with the sputtered target (Fig. 2, spectra 3-4).

If consider the ratio of the peak intensity of the reflections from the (111) and (200) planes as a criterion of development of the preferred orientation of crystallites, then at low flux density of the deposited particles the ratio $I_{(111)}/I_{(200)}$ is approximately equal to 1 (Fig. 3) that indicates the formed at low flux density of the deposited particles preferred orientation of crystallites with the axis $[111]$ perpendicular to the growth face. It should be noted that the formation of such preferred orientation is observed at some excess of interstitial atoms in comparison with the stoichiometric composition (see Fig. 1).

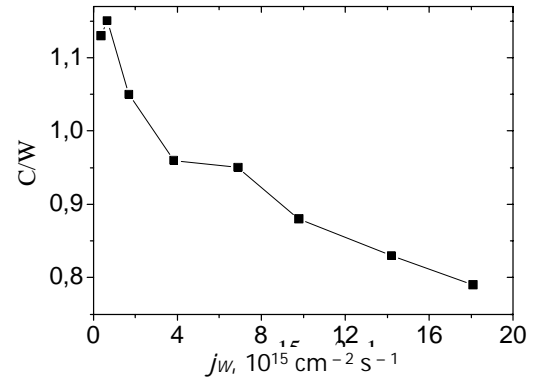


Fig. 1 – Dependence of the carbon-to-tungsten atomic ratio in tungsten carbide condensates on the flux density of the deposited particles

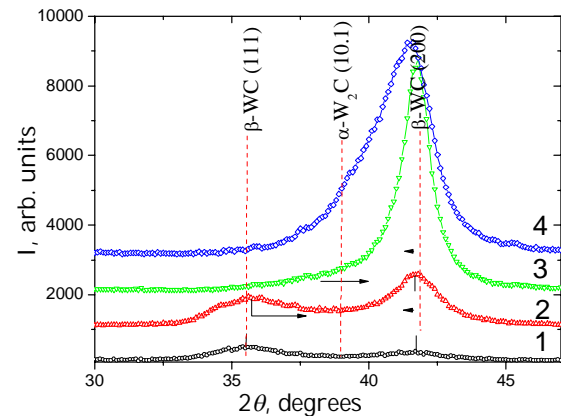


Fig. 2 – Regions of the diffraction spectra from tungsten carbide condensates obtained at different flux densities of the deposited particles j_W : 1 – $1.2 \cdot 10^{15}$ $\text{cm}^{-2} \text{s}^{-1}$, 2 – $5.2 \cdot 10^{15}$ $\text{cm}^{-2} \text{s}^{-1}$, 3 – $1.4 \cdot 10^{16}$ $\text{cm}^{-2} \text{s}^{-1}$, 4 – $1.8 \cdot 10^{16}$ $\text{cm}^{-2} \text{s}^{-1}$

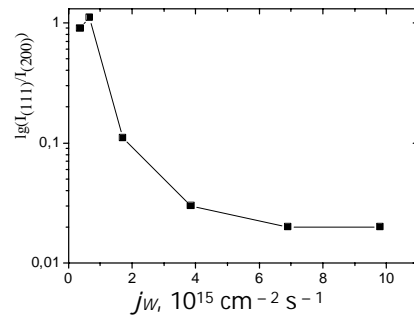


Fig. 3 – Dependence of the relative change in the intensity of (111) and (200) line of the β -WC phase

At $j_W > 9 \cdot 10^{15}$ $\text{cm}^{-2} \text{s}^{-1}$, the appearance of preferred orientation with the $[100]$ axis leads to a sharp drop in the ratio $I_{(111)}/I_{(200)}$.

In order to estimate the concentrations of the α -W₂C and β -WC phases in the films, the calculation method [7] by the following formulas was applied:

$$\frac{C_\beta}{C_\alpha} = \frac{S_\beta Q_\alpha}{S_\alpha Q_\beta P_{hkl}^n}, \quad Q = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \cdot |S_{hkl}|^2 \cdot \rho \cdot N^2,$$

where $S_{\alpha\beta}$ is the area of the diffraction line of the α and β phases, S_{hkl} is the structure factor, N is the unit cell number, θ is the reflection angle, ρ is the repetition factor.

Due to the presence of a texture in the β -WC phase, the pole density factor P^{hkl} was introduced in the formula. Since only one line is detected for the α -W₂C phase, it is assigned a pole density of 1. Because of the proximity of the rocking curve width of the compared diffraction lines, the texture coefficient was not introduced. The estimation of the concentrations was carried out by two pairs of lines (111)- β -WC, (101) α -W₂C and (200)- β -WC, (101) α -W₂C for the modes $j_W \approx 1.4 \cdot 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ and $j_W \approx 1.8 \cdot 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ taking into account the fact that $C_\alpha + C_\beta = 1$. As shown by the calculations performed for both pairs of lines for a lower flux density, the content of the α -W₂C phase is about 3%. For the highest flux density (spectrum 4 in Fig. 2), the content of the α -W₂C phase increased to 27%.

Analysis of the spectra obtained in Fig. 2 shows that with increasing j_W , the β -WC \rightarrow α -W₂C transformation occurs through the displacement of the (111) and (200) peaks of the β -WC toward each other (arrows in Fig. 2) that is typical for the formation in the alternating planes along the [111] direction of a stacking fault of the subtraction type (see Fig. 4).

The manifestation of stacking faults is also evident in high-resolution electron microscopic images (circles in Fig. 5).

In order to elucidate the mechanism of this transformation accompanied by the formation of stacking faults, high-temperature vacuum annealing was performed and showed that a noticeable change in the diffraction peak profiles from the lattice planes of the β -WC occurs at an annealing temperature higher than 700 °C, when according to the data of [25] the diffusion coefficient of carbon atoms $D_C \rightarrow_{WC}$ is approximately $10^{-14} \text{ cm}^2/\text{s}$, and the diffusion coefficient of tungsten atoms $D_W \rightarrow_{WC}$ is close to $10^{-19} \text{ cm}^2/\text{s}$.

Therefore, a detailed study of the structural changes was conducted in the temperature range of hourly annealing of 750-800 °C. As seen from the diffraction spectra illustrated in Fig. 6, an almost complete transformation β -WC \rightarrow α -W₂C, which is accompanied by a shift of the diffraction peaks associated with the formation of stacking faults (an arrow in Fig. 6), occurs as a result of the annealing.

The magnitude of the volumetric change occurring at β -WC \rightarrow α -W₂C (fcc-hcp) shear transformation can be estimated by the change in the interplanar distance using the relation [26]

$$\frac{\Delta V_{fcc-hcp}}{V_{fcc}} = \Delta_1 + 2\Delta_2,$$

$$\text{where } \Delta_1 = \frac{d_{002} - d_{111}}{d_{111}}, \Delta_2 = \frac{d_{110} - d_{220}}{d_{220}}.$$

$\Delta V/V = -4.8\%$ for the carbide composition β -WC_{0.8} determined in the work at $j_W \approx 1.8 \cdot 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$.

Ta₂N phase with a hexagonal lattice (PDF 26-0985) is the equilibrium phase in the Ta-N system at a temperature of 20-300 °C in the nitrogen content range of 35-50 wt. %. Tantalum nitride, as well as in the case of β -WC phase, has a metastable cubic modification TaN of the NaCl structural type with the lattice constant of 0.433 nm (PDF 32-1283).

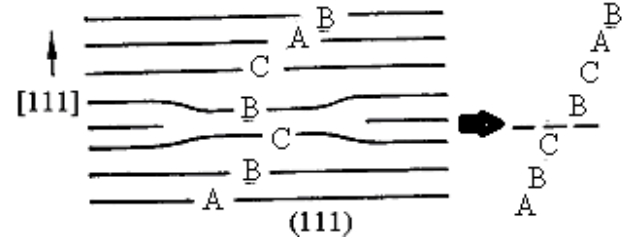


Fig. 4 – The scheme for the formation of stacking faults of the subtraction type when the most densely packed planes in the fcc lattice (111) are mixed

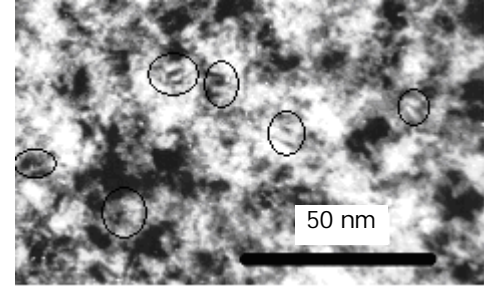


Fig. 5 – The electron microscopic image of tungsten carbide obtained at $j_W \approx 1.8 \cdot 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$

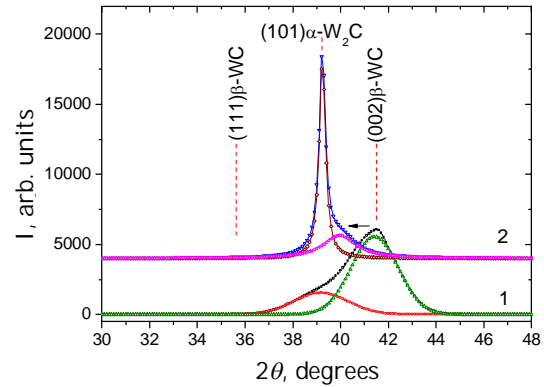


Fig. 6 – The regions of the diffraction spectra with the selected components of the diffraction profiles for the coating obtained at $j_W \approx 1.8 \cdot 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ in the initial state (a) and after hourly annealing at 800 °C (b)

As seen from the X-ray diffraction spectra [20] shown in Fig. 7, an increase in the nitrogen component in the sputtering atmosphere leads to a transition from the hexagonal structure of the Ta₂N phase with the preferred orientation (101) to the development of the texture (100) and a transition to the cubic crystal lattice of the TaN phase with the preferred orientation (111) with blurred peaks similar to that observed earlier in a transition in the W-C system (see Fig. 2 and Fig. 6).

The wavelength scanning for coatings obtained at a constant concentration of N₂ in the working atmosphere at a level of 5 vol. % when varying U_s showed that with increasing U_s that stimulates a decrease in the relative content of the light nitrogen component in the coating due to secondary sputtering processes [7], there is also a transition from a cubic to a close packed hexagonal structure (Fig. 8, spectra 1 and 2), which passes through the approach of reflexes that corresponds to the approach along the interplanar distances of the structures during the fcc \rightarrow hcp transition.

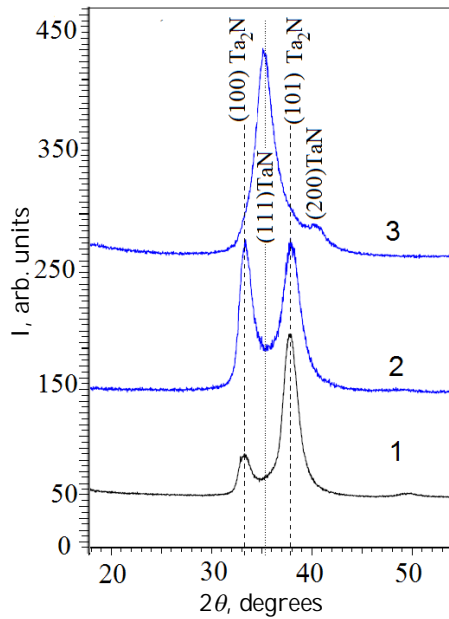


Fig. 7 – Regions of the diffraction spectra of tantalum nitride coatings obtained in the Ar + N₂ working atmosphere with the concentration of N₂, vol. %: 1 – 2.5; 2 – 5; 3 – 7 ($U_s = -200$ V)

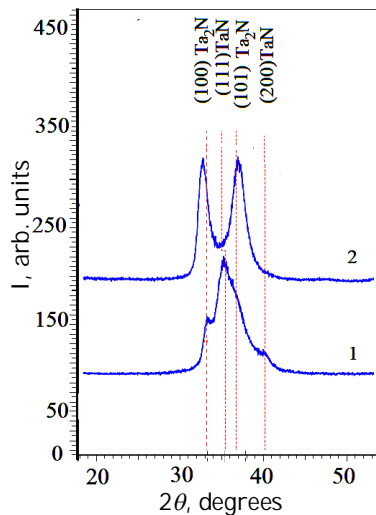


Fig. 8 – Regions of the diffraction spectra of tantalum nitride coatings obtained in the working atmosphere with 5 vol. % of N₂ at U_s : 1 – 100 V, 2 – – 200 V

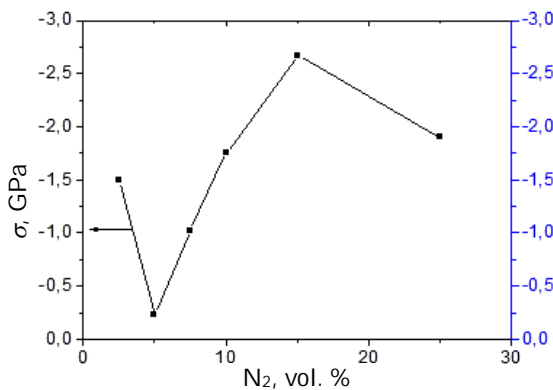


Fig. 9 – Dependence of the compressive stress on the nitrogen percentage in the working atmosphere

If consider the change in the macrostress state of the coatings, then its sharp drop (Fig. 9) is observed in the region of the structural phase transition (about 5 vol. % of N₂) that is typical for coordinated shear relaxation [7].

It should be noted that the development of compressive stresses in deposition is a consequence of the “atomic peening” effect [27], the essence of which is in the implantation of high-energy film-forming particles in the near-surface region proceeding with increasing specific volume and the development of compressive stresses in the coating bonded to the substrate.

Thus, the non-equilibrium conditions for the formation of material from ion-plasma fluxes predetermine the stabilization of simpler structural forms, which with increasing mobility of the deposited particles pass through the stages from an amorphous-like disordered state and cluster ordering to the long-range crystalline ordering. For the interstitial phases based on transition metals of IV-VI groups at a relatively low homological deposition temperature ($T_{depl}T_{ann} = 0.05-0.15$), that in practice corresponds to the substrate temperatures in the range of 20-500 °C, the formation of structures based on the fcc crystal lattice mainly occurs. In the case of the systems, for which more complex crystal lattice types are inherent in the equilibrium state, the formed structures are metastable, subjected to rearrangement with increasing temperature and, correspondingly, atomic mobility. In the case of deposition, the required energy (0.1 eV or more) for most systems is achieved even at a deposition temperature of 900 °C [7]. For the formed coatings, a larger energy (more than 0.15 eV) is required for rearrangement, and the rearrangement occurs at temperatures higher than 1100 °C, when the diffusion coefficient of the base metal element reaches 10^{-15} cm²/s.

A decrease in energy (and, thus, temperature) of the transition is facilitated by the presence of vacancies in the nonmetal sublattice that in the case of the systems considered in the work is accompanied by the appearance of preferred orientation of the crystallite growth with the [100] axis perpendicular to the growth plane.

The fcc → hcp transition (occurring with a decrease in the specific volume) is accompanied by a sharp decrease in the compressive macrostress state determined by the collective shear nature of this transition.

Thus, in nanocrystallites of vacuum-plasma condensates in the presence of vacancies in the nonmetal sublattice, the transformations when ordering are similar to the bainitic: at first, diffusion of interstitial atoms (for carbides – of carbon atoms, for nitrides – of nitrogen atoms) occurs with their ordering allowing in the future by shifting planes (by a martensite-like type) to pass through the transition to the equilibrium crystal structure.

The displacement of atoms during the transformation by a martensite-like type occurs by cooperative directed shift of entire atomic planes for a short time at distances not exceeding the interatomic ones. Deformation with an invariant plane, which is the common plane of the interfaces, leads to the displacement of atoms along the direction of the displacement vector, and the magnitude of this displacement is proportional to the distance from the invariant plane.

In the case of the interstitial phases with the fcc base of metal atoms and the interstitial elements located in

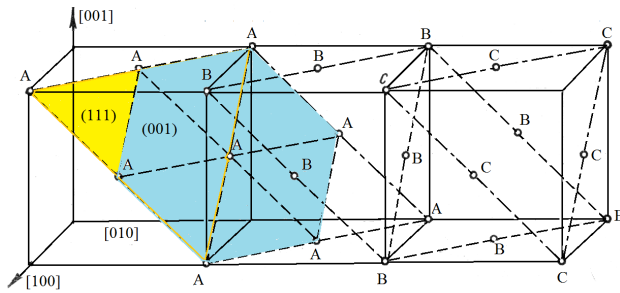


Fig. 10 – The scheme of the fcc \rightarrow hcp rearrangement by shift along the (111) plane. The positions marked A, B, C correspond to the basic atomic positions in Fig. 4

the octahedral interstitial sites along the [111] direction, there is an alternation of layers only of metal atoms and atoms of the interstitial elements; and the shift in the metal lattice is determining in such a structure. This process of rearrangement of the fcc lattice with the formation of the (001) nucleus-basis along its shifted (111) plane for the hcp crystal lattice is schematically shown in Fig. 10.

4. CONCLUSIONS

1. Non-equilibrium deposition conditions from ion-plasma fluxes significantly expand the spectrum of possible structural states of the formed material: from amorphous to highly ordered crystalline material.

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2. In the most commonly used temperature range of coating deposition of 20-500 °C without additional stimulation during the formation of interstitial phases based on transition metals, the atomic mobility is sufficient to form structures with a simple highly symmetric crystal lattice type (in most cases on the fcc metal base) and a high level of structural stresses.

3. A high deposition temperature (700-900 °C) transforms the structure into a more equilibrium state, which is facilitated by the formation of vacancies in the subsystem of the interstitial element.

4. In the case of the equilibrium phase with a hexagonal crystal lattice, the transition is performed by diffusion-shear transformation with the formation of stacking faults in the alternation of the most close packed planes along the [111] axis. The formation of stacking faults is facilitated by a small shear region in nanocrystalline materials and the presence of vacancies, and the shear transformation itself (through the formation of stacking faults) is accompanied by a sharp relaxation of structural stresses.

5. The type of transformation associated with the rearrangement of the crystal lattice is similar to the bainitic one: at first, diffusion of interstitial atoms (for carbides – of carbon atoms, for nitrides – of nitrogen atoms) occurs with their ordering that allows in the future by shifting planes (by a martensite-like type) to perform the transition to the equilibrium crystal structure.