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Structural Engineering of the Growth of Crystallites with a Predominant Orientation in Bilayer Multi-Period Vacuum arc Nitride Coatings

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The effect of the MeN (Me-Cr, Mo, Zr) layer composition in multi-period vacuum-arc (TiAlSi) N / MeN coatings with a nanoscale layer thickness on the predominant orientation of crystallite growth in layers and hardness was studied. It was found that phases with a cubic crystal lattice (structural type NaCl) in the layers of all types (TiAlSi)N/MeN coatings are formed, although for the MoN phase under equilibrium conditions a hexagonal crystal lattice is preferred.

The interrelation between the structure of MeN and (TiAlSi)N layers is revealed, as well as the effect of the structural state on the coating hardness. Defining influence of the MeN layer on the formation of three structural states types was found: with a preferential crystallite growth with the texture axis [111]; with the texture axis [100]; the formation of a non-textured state. The highest hardness of 47.8 GPa was achieved in the (TiAlSi)N/ZrN multilayer coating with the texture axis [111].

Keywords: Structural engineering, Nanoscale, Multiperiod coating, Structural state, Texture axis, Superhard.

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1. INTRODUCTION

Structural engineering has become in recent years the main way of obtaining materials with specified properties [1, 2]. The use of structural engineering principles has shown high efficiency during highly nonequilibrium conditions deposition of coatings [3, 4]. To such processes leads the use of ion-plasma [5] and vacuum arc technologies [6] coating deposition. The use of such technologies allowed creating nanocomposite structures with unique high mechanical characteristics. This was made possible by creating a special nanocomposite structure. Nanocomposites (i.e. composites based on nanoscale elements) were created on the basis of two structural approaches: by decay with ordering supersaturated solid solutions (mainly by spinodal-like mechanisms) and by creating multilayer composite materials [7]. These approaches have one common property: the basis for achieving high physicomechanical characteristics is determined by the interphase boundary properties (cohesion of grains, elastic characteristics, the ability to relax stresses, to block cracks spread, etc.) [8]. To increase the adhesion between grains, separate elements ("useful impurities" [8]) and various compounds (mainly in amorphous-like or nanocrystalline state with a thickness of 0.5-2 nm are used. For example, SiN_x in the Ti-Si-N system [9]). However, the greatest effect from the use of structural engineering was achieved in multilayer structures with nanoscale periods [10]. The properties of such systems depend on the structural state of phases in contact layers. In a number of cases, metastable states stabilization (mainly high-temperature phases with a simple cubic lattice, for example, the β-WC phase in the W-C system [11]) occurs in the ion-plasma multilayer coatings to minimize the energy at nanolevel. Considering the current tendency towards using multielement materials (for example, multielement high-entropy alloys are used to achieve high functional properties at high temperatures [12]), the structural state of contact layers becomes very important [10].

One of the most promising multi-element materials is Ti-Al-Si-N [13]. In most works, ion-plasma (magnetron-type) sputtering is used to produce nitride coatings of the Ti-Al-Si-N system [14]. At the same time, a mixture of Ar/N_2 gases is used as the atomizing atmosphere [15]. In this case, with a silicon content of less than 8 at. %, a single-phase solid solution state is formed with a predominant orientation of the crystallites with texture axis [111]. The crystallite size (at which the highest hardness is reached) is about 17 nm [14].

Coatings obtained by magnetron sputtering usually have a hardness of less than 40 GPa, even under optimum production conditions [13].

The work [16] states that the increased pressures of the nitrogen atmosphere (more than 0.5 Pa) with the magnetron method for obtaining coatings lead to a transition to the nanocomposite. At the same time, the metal coating AlTiSi deposited in the absence of reactive gas (nitrogen), demonstrated strong columnar growth [17, 18]. Columnar grains boundaries often serve as sites for nucleation and growth of cracks, which leads to the coatings destruction. Addition of nitrogen to the process gas leads to the creation of a nanocomposite structure consisting of crystalline TiAlN nanograins with a size of 2-3 nm surrounded by an amorphous Si_xN_y phase (and/or an AlN matrix) [16].

The use of the condensation method during ion bombardment (CIB) makes it possible to obtain coat-

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ings with higher hardness and good adhesion to various materials of the substrate [19]. For coatings obtained by this method, it was found in [20] that there is a transition from a nanocrystalline state (at a pressure up to 0.04 Pa) and a nanocomposite (0.04-0.66 Pa) to the amorphous state (0.66-1.1 Pa) as nitrogen pressure increases during deposition in the Ti-Al-Si-N system. At the same time, the highest mechanical characteristics and thermal stability were achieved by a coating having a nanocomposite structure with a low content of the amorphous phase.

This paper analyzes the possibility of obtaining different structural states in (TiAlSi)N layers by using various mononitrides in bilayer nanoscale period of multilayer vacuum arc coatings.

2. SAMPLES AND METHODS OF RESEARCHES

Samples were obtained by vacuum arc method using "Bulat-6" device. The pressure of nitrogen atmosphere during deposition (P_N) was $2.3\cdot10^{-1}$ Pa. The deposition was carried out from one (TiAlSi) or two (TiAlSi and (Mo or Cr or Zr)) ion sources with continuous samples rotation attached to the substrates (at a speed of 8 rpm). This made it possible to obtain layers with a thickness $d \approx 7 - 11$ nm, a period $\Lambda \approx 15 - 20$ nm and a total coating thickness $h \approx 9$ μm. The total coating deposition time was 60 minutes. During deposition, a constant negative potential $U_b = -110$ V or $U_b = -200$ V was fed to the substrate. Deposition was carried out on the samples of size 20 × 20 × 2 mm from 12Cr18Ni10Ti austenitic steel (analog of stainless steel SS 321).

The phase composition of coatings was investigated by X-ray diffraction analysis using DRON-4 system with Cu-K_α radiation (0.154 nm) according to the Bragg-Brentano scheme. A graphite monochromator was used to monochromatize radiation [15]. It was installed in a secondary beam (in front of the detector). 2Theta range varied from 20 to 80 degree with step duration of 0.05 degree. The tables of the international diffraction data center "Powder Diffraction File" were used to decipher the diffraction spectra. To determine the preferential crystallite growth orientation (texture), the integrated intensity of diffraction peaks from different planes was compared with the "Powder Diffraction File" data for the phases studied [21].

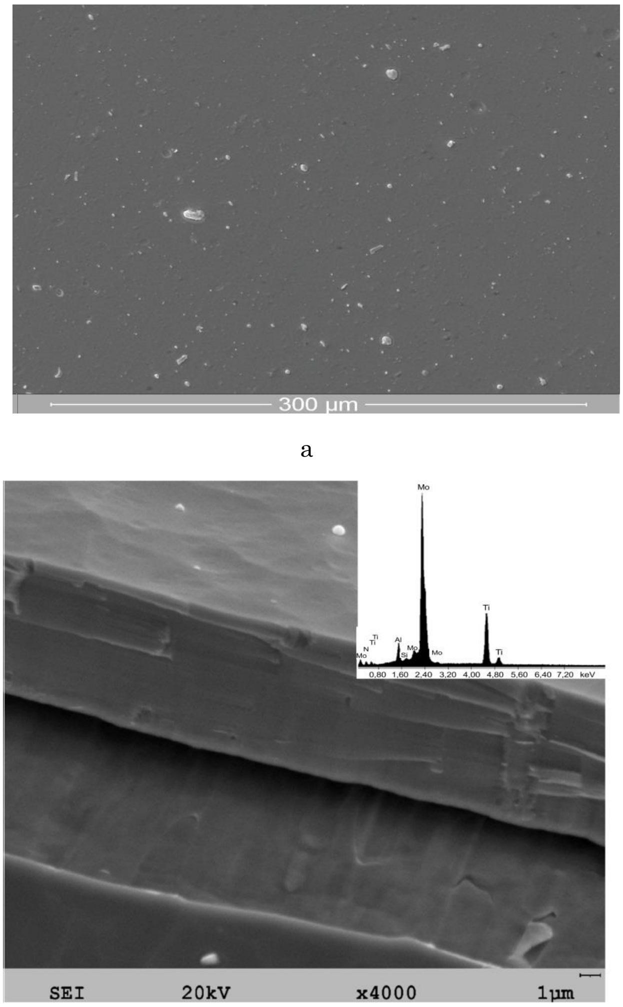
Microstructure and element composition investigations were done using scanning electron microscope (SEM) JEOL-7001F-TTLS equipped with an energy-dispersive X-ray spectroscopy (EDS) detector.

The microhardness was measured by the Vickers method at a load of 0.5 N. The average hardness value was determined from 10 measurements.

3. RESULTS AND DISCUSSION

Multiperiod coatings obtained by vacuum-arc evaporation have a fairly uniform morphology along the cross section. Drops are detected only on the surface and their number is small (Fig. 1).

Based on the energy-dispersive analysis findings, the nitrogen content in multiperiod systems coatings is 48.5-49.5 at. %. In a single-layer (TiAlSi)N coating, the Si content is about 3 at. %. In multilayer coatings (where (TiAlSi)N layer thickness is about half of total thickness Λ), the Si content is 1.31-1.67 at. %. The ratio of C_{Ti}/C_{Al} (where C_{Ti} is the content of Ti atoms and C_{Al} is the content of Al atoms) varies from 3/1 for ($U_b = -110$ V) to 5/1 for ($U_b = -200$ V).



a

b

Fig. 1 – SEM images of the surface morphology (a) and cross section with EDS pattern (b) of multilayer (TiAlSi)N/MoN coating

The phase composition and structural state were studied by XRD method and the results showed formation of phases with a cubic crystal lattice (structural type NaCl [5]) in the layers of all types coatings.

Fig. 2 shows the XRD spectra sections obtained for all types coatings of (TiAlSi)N/MeN systems studied in the paper. Spectra with designation "1" correspond to the coatings obtained at $U_b = -110$ V, and spectra with designation "2" correspond to the coatings obtained at $U_b = -200$ V.

The results indicated above show the existing regularity. Such regularity is a similar texture state for different layers in the bilayer system. As it can be seen from Table 1, three types of structural states are formed at small $U_b = -110$ V in the multilayer coatings. The first type is the formation of the texture axis

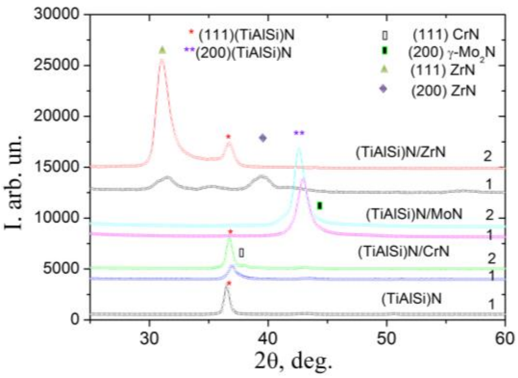


Fig. 2 – XRD patterns of various types coating based on (TiAlSi)N obtained at Ub, V: 1 – – 110, 2 – – 200

[111] in the layers of bilayer system (i.e. both in (TiAlSi)N and MeN layers). Such texture is formed in a single-layer coating (TiAlSi)N and observed for the system (TiAlSi)N/CrN (Table 1). The second type is the formation of the texture axis [100] in two layers. This type is preferred in the (TiAlSi)N/MoN system. The third type is the texture absence in the layers. This type can be observed in the (TiAlSi)N/ZrN system (i.e., the system where the heaviest element Zr is used as the metal in mononitride).

It should be noted that under equilibrium conditions a phase MoN with hexagonal crystal lattice (JCPDS data 25-1367, MoN phase with lattice periods $a = 0.5725$ nm, $c = 0.5608$ nm) should be formed in the (TiAlSi)N/MoN. Instead, γ-Mo_2N (JCPDS 25-1366) phase is formed with structural type NaCl (similar to the second component (TiAlSi)N in the bilayer) and texture axis [100].

Table 1 – Summarizes research results of the texture (axes of the preferential crystallite growth orientation) formed in the coatings

Coating type	Texture type			
	(TiAlSi)N		MeN	
	U_b = = – 110 V	U_b = = – 200 V	U_b = = – 110 V	U_b = = – 200 V
(TiAlSi)N	[111]	[111]	-	-
(TiAlSi)N/CrN	[111]	[111]	[111]	[111]
(TiAlSi)N/MoN*	[100]	[100]	[100]	[100]
(TiAlSi)N/ZrN	No texture	No texture	[111]	[111]

* nonequilibrium modification of γ-Mo_2N is formed in MeN layers

The decomposition of complex diffraction profiles showed (as an example in Fig. 3 shows the decomposition of the complex X-ray diffraction profile into components for (TiAlSi)N/MoN multilayer coating) that crystallite lattice periods in this type of coatings were 0.4233 nm ((TiAlSi)N) and 0.413 nm (γ-Mo_2N). Thus, there is a relatively small discrepancy between the crystal lattices periods in the layers of 2.5 %. In the (TiAlSi)N/CrN system this discrepancy reaches 3.2 %, and in the (TiAlSi)N/ZrN system it reaches 10.8 %.

At large $U_b = -200$ V, two types of structural states are formed. The first type is the formation of the texture axis [111] in two layers of the period. Such texture is formed in the (TiAlSi)N/CrN and (TiAlSi)N/ZrN systems.

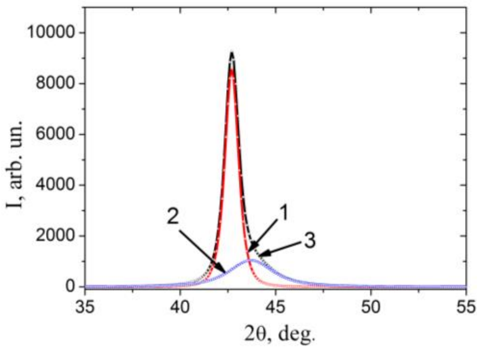


Fig. 3– Decomposition of the complex X-ray diffraction profile into components for (TiAlSi)N/MoN multilayer coating. 1 – (200) (TiAlSi)N, 2 – (200) γ-Mo2N, 3 – total complex profile

The second type of texture (with texture axis [100]) for the (TiAlSi)N/MoN system is the same as for the small $U_b = -110$ V.

Since multilayer coatings have a good prospect of being used as abrasive wear resistant coating on turbine blades, hardness is an important characteristic [6].

A study of multilayer coatings hardness showed that the greatest hardness was achieved in coatings with the texture axis [111] in the layers. The highest hardness of 47.8 GPa was achieved for the coating (TiAlSi)N/ZrN, obtained at $U_b = -200$ V. Also, great hardness was achieved in the multilayer composite (TiAlSi)N/MoN (hardness 44.3 GPa). It should be noted that the hardness, determined for the thickness of the layers 7-11 nm, was the greatest. For different thicknesses of the layers (TiAlSi)N/ZrN coatings, the hardness values were obtained: 47.8 GPa (layer thickness 7-11 nm), 39.7 GPa (average layer thickness 28 nm), 37.4 GPa (average layer thickness 45 nm), 35.9 GPa (average layer thickness 87 nm) and 32.75 GPa for an average layer thickness 170 nm.

4. CONCLUSION

Interrelated crystallites growth occurs in thin nanometer layers in multilayer (TiAlSi)N/MeN composites (where Me – Cr, Mo, Zr). A texture of crystallites with a common axis [111] is formed in systems with the lightest metal (Cr), at small $U_b = -110$ V. Such texture axis coincides with the axis for a single-layer coating (TiAlSi)N. The multilayer (TiAlSi)N/ZrN composite has relatively small mobility of the heaviest Zr atoms (in the ZrN mononitride layers). This stimulates the non-textured crystallites growth. Non-textured state is inherited in (TiAlSi)N layer (consisting of less heavy metal atoms).

γ-Mo_2N phase with structural type NaCl (similar to the second component (TiAlSi)N in the bilayer) is formed in the multilayer (TiAlSi)N/MoN composite, in which the phase with hexagonal crystal lattice should be formed under equilibrium conditions in the MoN layer. In this case, the texture axis [100] is formed. The formation of such texture, apparently, corresponds to the smallest free surface energy between the layers.

The highest hardness of 47.8 GPa was achieved in the (TiAlSi)N/ZrN multilayer coatings with the texture axis (the axis of preferential growth orientation) of crystallites [111].

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Структурна інженерія переважної орієнтації росту кристалітів в бішарових багатоперіодних вакуумно-дугових нітридних покриттях

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Досліджено вплив складу шару MeN (де Me – Cr, Mo, Zr) в багатоперіодну вакуумно-дугових (TiAlSi)N/MeN покриттях з нанорозмірною товщиною шарів на переважну орієнтацію росту кристалітів в шарах і твердість. Встановлено, що в шарах формуються фази на основі кубічної ГЦК металевої решітки (структурного типу NaCl), хоча для MoN фази в рівноважних умовах характерний гексагональний тип кристалічної решітки. Виявлено визначальний вплив MeN шару на формування 3-х типів структурних станів: з переважною орієнтацією зростання кристалітів з віссю текстури [111], [100] і формування не текстурованого стану. Найбільша твердість 47.8 ГПа була досягнута в багатоперіодному покритті системи (TiAlSi)N/ZrN з віссю текстури кристаллитов [111].

Ключові слова: Структурна інженерія, Нанорозмірна товщина, Багатоперіодне покриття, Структурний стан, Вісь текстури, Надтвердий стан.

Структурная инженерия преимущественной ориентациии роста кристаллитов в бислойных многопериодных вакуумно-дуговых нитридных покрытиях

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Исследовано влияние состава слоя MeN (где Me – Cr, Mo, Zr) в многопериодных вакуумно-дуговых (TiAlSi)N/MeN покрытиях с наноразмерной толщиной слоев на преимущественную ориентацию роста кристаллитов в слоях и твердость. Установлено, что в слоях формируются фазы на основе кубической ГЦК металлической решетки (структурного типа NaCl), хотя для MoN фазы в равновесных условиях характерен гексагональный тип кристаллической решетки. Выявлено определяющее влияние MeN слоя на формирование 3-х типов структурных состояний: с преимущественной ориентацией роста кристаллитов с осью текстуры [111], [100] и формирование не текстурированного состояния. Наибольшая твердость 47.8 ГПа была достигнута в многопериодном покрытии системы (TiAlSi)N/ZrN с осью текстуры кристаллитов [111].

Ключевые слова: Структурная инженерия, Наноразмерная толщина, Многопериодное Покрытие, Структурное состояние, Ось текстуры, Сверхтвердое состояние.

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