

Structure and Properties of Vacuum Arc Single-Layer and Multiperiod Two-Layer Nitride Coatings Based on Ti(Al):Si Layers

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The paper provides an analysis of impact of deposition conditions on structural and phase state and thermal stability of vacuum arc coatings based on Ti(Al):Si layers. We studied single-phase single-layer coatings, and multiperiod bilayer coatings with second phase nitride interlayers of one of the following three metals: Mo, Cr or Zr. It was established that hexagonal and cubic lattices may form in the coatings when transition to the cubic lattice occurs with Al content of about 25 at. %. Presence of second nanoscale (7-8 nm) layers in bilayer multiperiod compositions, which consist of one nitride from CrN_x, MoN_x or ZrN_x group, does not change the type of lattice in [Ti(Al):Si]N_x layers. Also, an *fcc* lattice with a strong or weak texture [111] forms in CrN_x and ZrN_x layers, while crystallites with hexagonal lattice form in MoN_x layers. High-temperature annealing at 700 °C during 40 minutes leads to a significant (by 23 % or up to $H_{\mu} = 47.56$ GPa) increase in microhardness of coating of the [Ti(Al)]N_x/ZrN_y system due to formation of a nano-size structure with an average size of crystallites of 3.6 nm in [Ti(Al)]N_x layers, and 6.3 nm in ZrN_x layers.

Keywords: Nitride coatings, Multilayers coating, Composition of elements, Structure, Microhardness.

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1. INTRODUCTION

The growing interest to high-temperature coatings has predetermined an intensive development of technology of formation of composite multielement multilayer coatings, in which high functional properties are obtained through correct choice of constituent ingredients [1-2]. The right structural condition, which is obtained through structural engineering techniques [3] under development, is another factor to ensure required properties of the material.

Nitride coatings based on TiN_x have high mechanical properties but comparatively low thermal stability [4, 5]. Their mechanical and tribological characteristics, as well as thermal stability and resistance to oxidation can be significantly improved by adding aluminum. Depending on the composition of elements, materials of the triple system based on Al, Ti and N can have either cubic or hexagonal structure. The [Al(Ti)]N_x metastable solid-state solution with the cubic face-centered (*fcc*) NaCl structure (B1 type) keeps stable up to $x = 0.6-0.8$ [6]. With the amount of titan exceeding the said upper limit, a crystal hexagonal lattice of ZnS type (wurtzite) forms. The coatings based on Al, Ti and N, unlike their analogues with *fcc* structure, have comparatively high thermal stability, but at temperatures higher than 900 °C they lose most of their mechanical properties and resistance to oxidation [7].

Silicon additives significantly change the structural and phase state, stereological characteristics and physical-chemical properties of nitride coatings, particularly, we observe increase in hardness and stability to

oxidation of nitride layers [8]. Segregation of silicon atoms on grain boundaries leads to formation of amorphous-like SiN_x phase, the interlayers of which segregate titan nitride or aluminum nitride grains and in such a way prevent their growth [9]. Such nanocomposite can have unique mechanical properties and thermal stability, and therefore it is a very promising material for high-temperature [10-12].

Another technique facilitating formation of the nano-structural state and therefore improving performance of the coating is creation of multilayer systems with a nanosized interlayer period. We believe that nitrides of transitional metals are promising materials for application in formation of the said structures.

The objective of this work was to carry out a feasibility study of structural engineering to improve high-temperature hardness of TiAl-based initial coatings by forming various nitride layers and multiperiod compositions based on them. In the course of this study, as a second layer in multiperiod systems, we formed three different nitrides with different enthalpies of formation: ZrN_x (– 365 kJ/mol), CrN_x (– 123.4 kJ/mol), MoN_x (– 37 kJ/mol).

2. SPECIMENS AND METHODS OF STUDY

We obtained coatings by vacuum-arc technique using an upgraded modification of Bulat-6 unit [13]. The working (ammonium) pressure in deposition (P) was 1×10^{-5} or 4×10^{-3} Torr. The deposition was carried out from one Ti(Al):Si composition or two sources. When two sources were used, the composition of the first one was just like in

the former case, i.e. Ti(Al):Si, while the second source was metallic. We applied one of the following three metals in various options: either Mo, or Cr, or Zr.

The coatings were deposited on $15 \times 15 \text{ mm}^2$ specimen plates which were 2.5 mm thick and made of X18H10T stainless steel.

In coating formation from two sources, specimens were fixed on a special platform which was constantly rotating during deposition shifting the specimens from

Table 1 – Modes of coating formation

Series No	Cathode(s)	I_a , A	I_f , A	U_{sp} , V	P , Torr
1	Ti(Al):Si	100	0,5	- 50	1×10^{-5}
2	Ti(Al):Si	100	0,5	- 110	4×10^{-3}
3	Ti(Al):Si	100	0,5	- 110	4×10^{-3}
	Cr	90	0,4		
4	Ti(Al):Si	100	0,5	- 110	4×10^{-3}
	Mo	150	0,4		
5	Ti(Al):Si	100	0,5	- 110	4×10^{-3}
	Zr	90	0,4		

one source to the other. With the rotation speed of 8 rpm, it took 1 hour to form a 9 μm thick coating. This coating consisted of 7-8 nm thick biphasic interlayers. In the process of deposition, the substrates were kept at a constant negative potential U_{sp} of 50 or 100 V. The specific modes of deposition are shown in Table 1 (I_a – arc current of the first and second cathode source, I_f – focusing current, U_{sp} – potential on the substrate during deposition, P – pressure of nitrogen atmosphere).

After deposition, the composites were annealed at 700 °C during 40 minutes in a VHT 8/22-GR Nabetherm GmbH vacuum furnace at a residual pressure of no more than 3×10^{-5} Torr.

The structure and phase analysis of obtained coatings was done by X-ray diffraction method in a radiation of Cu- α using a DRON-4 diffractometer. The profiles were separated with the help of the New Profile software package. To analyze the profiles, we used the New Profile software package.

The microhardness was measured by an AFFRI DM-8 using standard methods under an applied load of 50 g on the indenter.

The elemental composition was determined by energy dispersive spectra obtained on an EDAX X-ray microanalyzer, which was combined with a Quanta 200 3D scanning electron and ion microscope.

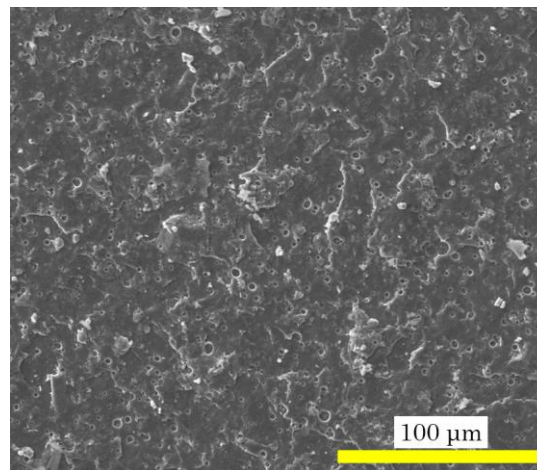
3. RESULTS AND THEIR DISCUSSION

The phase composition, structure and mechanical properties of [Ti(Al):Si] N_x coatings can be efficiently controlled by setting appropriate deposition parameters. Particularly, change of energy in falling particles substantially influences the mechanism of film growth and hence its properties. The process of vacuum arc evaporation provides highly ionized plasma with ions of metals which are in different states of ionization. Different ion charge states are characterized by different energy of particles, which may increase the impact energy of ions when they hit substrates. Such an increase of energy may be achieved without growth of bias voltage on the substrate. Besides, high energy of falling ions leads to thickening of coatings. Thus, with relatively insignificant bias voltages, we can form coatings with a dense structure and comparatively low porosity.

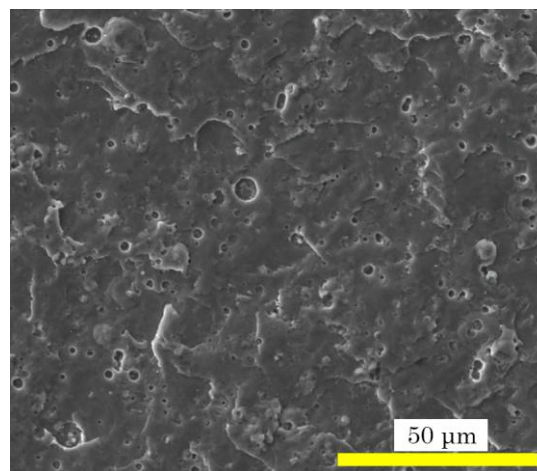
The electronic microscopy data (Fig. 1) show that [Ti(Al):Si] N_x -based coatings have a dense and practically droplet-free structure, whose homogeneity increases during annealing.

The elemental analysis of coatings was carried out on energy dispersive spectra which have a typical look in [Ti(Al)] N_x /Zr N_y systems (Table 1, Series 5) as shown in Fig. 2.

one source to the other. With the rotation speed of 8 rpm, it took 1 hour to form a 9 μm thick coating. This coating consisted of 7-8 nm thick biphasic interlayers. In the process of deposition, the substrates were kept at a constant negative potential U_{sp} of 50 or 100 V. The specific modes of deposition are shown in Table 1 (I_a – arc current of the first and second cathode source, I_f – focusing current, U_{sp} – potential on the substrate during deposition, P – pressure of nitrogen atmosphere).



a



b

Fig. 1 – Surface of [Ti(Al):Si] N_x coatings before (a) and after (b) annealing

The resulting data of the elemental analysis are provided in Table 2. It should be noted that the table shows metal atoms content in coatings excluding nitrogen atoms content which does not exceed 2 at. % for Series 1

specimens, while it is close to equiatomic contents for specimens of other series (one nitrogen atom per one metal atom).

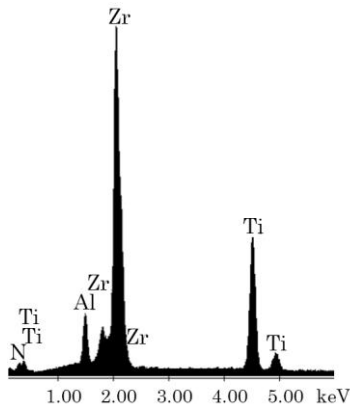


Fig. 2 – Energy dispersive spectra of Series 5 coatings, composition of $[\text{Ti}(\text{Al})\text{N}_x/\text{ZrN}_y]$

Table 2 shows that in the specimens obtained at low

Table 2 – Elemental composition and microhardness (H_{μ}) of specimens (series as shown in Table 1) before (a) and after (b) annealing

Series No		Content of Elements, At.%						Ti/Al	H_{μ} , GPa
		Ti	Al	Si	Cr	Mo	Zr		
1	a	74,09	23,27	2,64	–	–	–	3,36	6,65
	b	74,04	23,17	2,79	–	–	–	3,38	9,57
2	a	71,89	26,23	1,90	–	–	–	2,74	10,58
	b	70,78	26,50	1,85	–	–	–	2,67	9,85
3	a	44,10	15,29	1,27	39,25	–	–	2,88	27,25
	b	43,47	15,80	1,53	39,01	–	–	2,75	24,26
4	a	34,63	10,53	0,79	–	54,96	–	3,28	37,46
	b	33,30	10,74	1,11	–	54,81	–	3,10	37,74
5	a	39,67	12,20	–	–	–	47,80	3,25	37,90
	b	39,40	12,10	–	–	–	48,50	3,28	47,56

In case of multilayer systems with coating applied during rotation of the substrate between two sources, the Ti/Al ratio changes towards the primer (i.e. towards Ti/Al ratio ≈ 3.36). This may be caused by radiation effect of heavy accelerated charged metal particles, the depth of effect of which is comparable to the thickness of layers.

The X-ray research of the structure and phase state of specimens (Fig. 3) has shown that Series 1 coatings (Fig. 3a) are basically a one-phase solid-state solution based on *hcp* lattice. High-temperature annealing does not lead to a change of the lattice type but stimulates preferred orientation of crystallites with texture plane (101). This conclusion is based on the relative increase of reflection intensity (101) on spectrum curve 2 (Fig. 3a).

Coating deposition with an increased pressure of nitrogen leads to a change of the type of the formed crystal lattice from *hcp* (Series 1 metal coating) to *fcc* (Series 2 nitride coating), while the preferred orientation changes from (101) to (111) (Fig. 3b). Annealing does not basically alter the structural state, but leads to relaxation of condensing compressive stresses. On the diffraction spectra, this develops in a proportional spike displacement towards the high-angle region (projection in geometry $\theta - 2\theta$).

In multilayer coatings with interlayers 7-8 nm thick, the *fcc* lattice (NaCl structural type) is formed in two phases of making the coating layer in $[\text{Ti}(\text{Al})\text{:Si}]\text{N}_x/\text{CrN}_y$

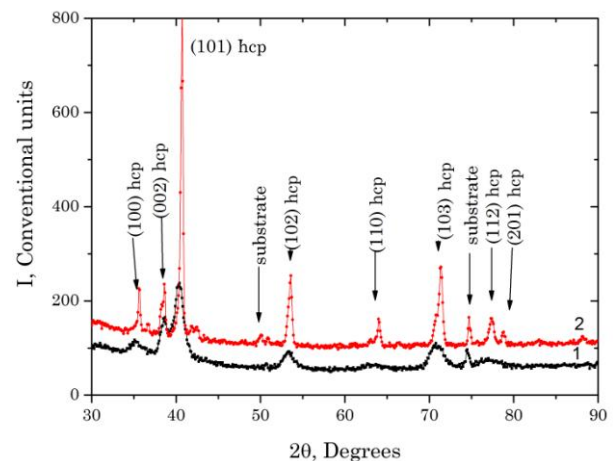
(1×10^{-5} Torr) pressure of nitrogen (Series 1, Table 1) and its small (less than 2 at. %) content in the coating, the atomic ratio Ti/Al makes 3.36, which corresponds to the content of Al in the coating in the amount of about 23 at. %.

The increase of nitrogen pressure in deposition up to 4×10^{-3} Torr leads to change of Ti/Al ratio towards increased content of Al, which corresponds with its content in the coating totaling about 26.5 at. %.

It is believed that almost all evaporated particles spontaneously interact with dissociated nitrogen forming nitride molecules Me-N (Me = Al, Ti) on the film surface [13]. These molecules (unlike weakly bound metal molecules) are much less subject to repeated sputtering even in relatively intense high-energy ion bombardment. Therefore the suggested cause for change of the Ti/Al ratio in the coating may be preferential formation of stable nitride complexes with Al in the plasma between the cathode and substrate. Compared to TiN, such formations are more resistant to secondary sputtering from the formed coating surface [14].

and $[\text{Ti}(\text{Al})\text{N}_x/\text{ZrN}_y]$ systems. It should be noted that in case of the $[\text{Ti}(\text{Al})\text{:Si}]\text{N}_x/\text{CrN}_y$ system, the coating has strong preferred orientation of crystallites on planes unchanged (111) (Fig. 3c), while for the $[\text{Ti}(\text{Al})\text{N}_x/\text{ZrN}_y]$ system, preferred orientation is practically not observed (Fig. 3e).

In the $[\text{Ti}(\text{Al})\text{:Si}]\text{N}_x/\text{MoN}_y$ system in $[\text{Ti}(\text{Al})\text{:Si}]\text{N}_x$ layers, preferred orientation changes for axial texture



a

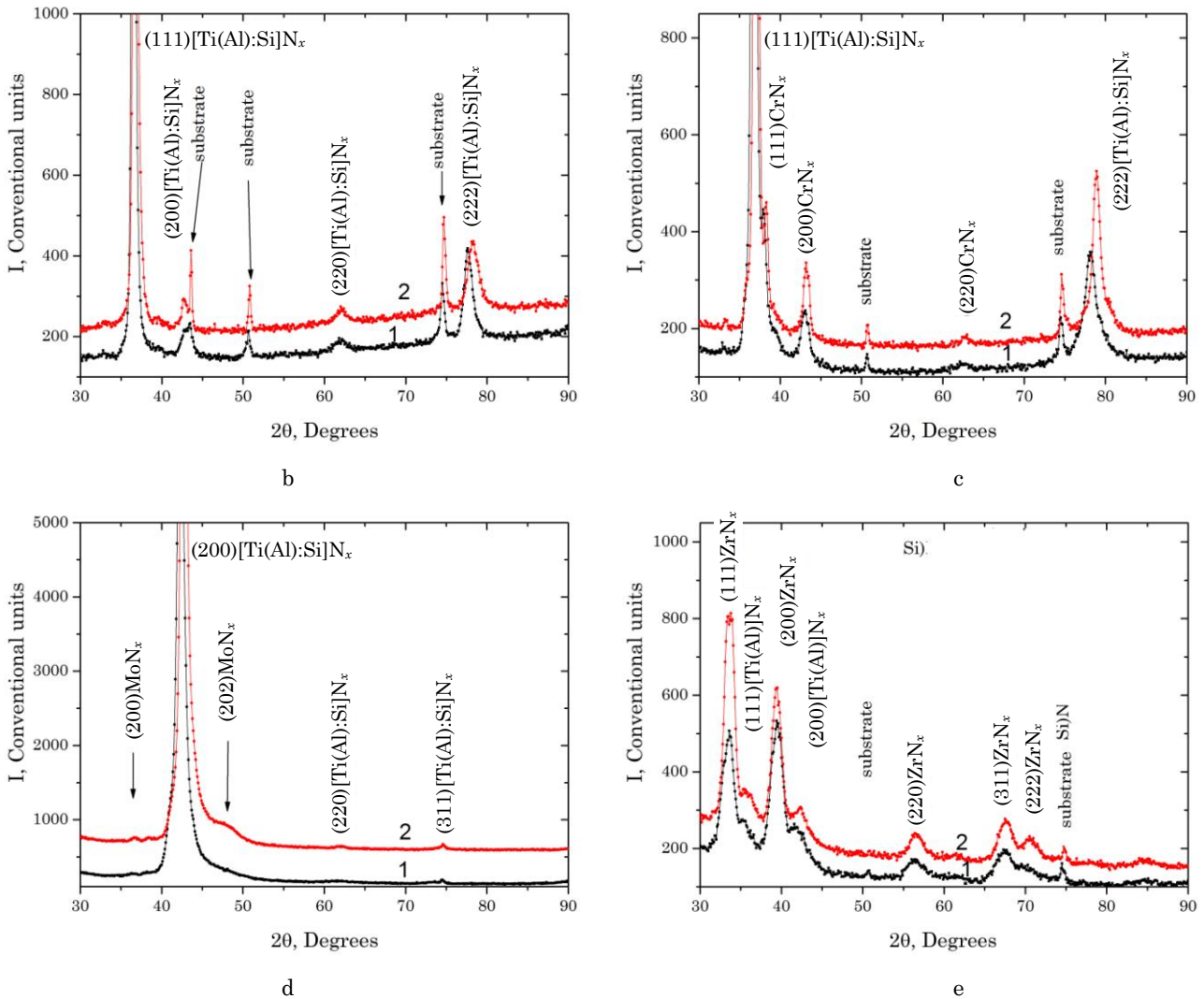


Fig. 3 – Areas of diffraction spectra of coatings before (1) and after (2) annealing of specimens of Series: a – 1, b – 2, c – 3, d – 4, e – 5 at 700 °C during 40 min

with axis [100] (Fig. 3d), Spectrum 1), while in MoN_x layers, formation of a phase with a hexagonal elementary cell (P6₃/mmc space group) takes place. Annealing does not alter the phase composition in layers of all studied systems, however it leads to relaxation of growth compressive stresses, which shows up in displacement of diffraction reflections on spectra towards the high-angle region (Spectra 1 and 2 in Fig. 1c, d, e).

We have made comparison of the obtained data on elemental composition and structural characteristics with the measurement data on coatings microhardness.

The observed increase of microhardness after annealing (Table 2, Series 5, 6) can be explained by strong texturing with preferred orientation of crystallite planes (101) parallel to the surface.

In [Ti(Al):Si]N_x coatings, as well as in the [Ti(Al):Si]N_x/CrN_y multilayer system, annealing is accompanied by some decrease of hardness owing to relaxation of the initial compressive stresses. In the stronger bound [Ti(Al):Si]N_x/MoN_y system, annealing at 700 °C does not practically change coating hardness (Series 4 in Table 2).

A quite significant increase of hardness after annealing (about 23 %) was observed for the [Ti(Al)]N_x/ZrN_y system. The detailed analysis of X-ray data with separation of components of complex spectra (Fig. 4) showed that annealing leads to practically no relaxation of the initial compression strain in this material. Displacement of diffraction peaks is not observed (Table 3), but their

Table 3 – Parameters of specimen diffraction peaks before (a) and after (b) annealing

Peak		Position, 2θ, Degrees	Intensity, Relative Units	Integral Breadth, Degrees
(111) ZrN _x	a	33,496	311,8	1,81
	b	33,643	578,7	1,51
(200) ZrN _x	a	39,413	351,0	2,00
	b	39,413	378,5	1,58
(111) [Ti(Al)]N _x	a	35,909	50,9	2,57
	b	36,071	95,1	2,17
(200) [Ti(Al)]N _x	a	42,014	93,0	2,74
	b	42,205	81,7	2,54

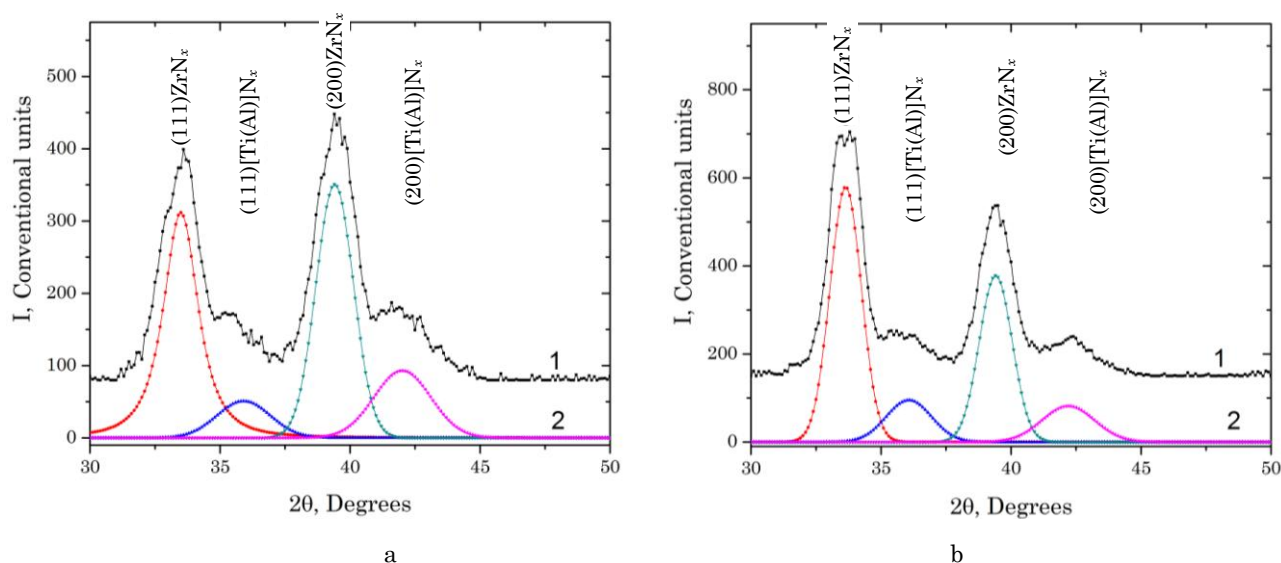


Fig. 4 – Areas of diffraction spectra of the $[\text{Ti}(\text{Al})\text{N}_x]/\text{ZrN}_x$ coating before (a) and after (b) annealing: 1 – initial spectrum, 2 – result of profiles separation into components

breadth changes considerably, which is the evidence of changes in the dislocation structure.

Average sizes of crystallites have been estimated by broadening of diffraction reflections using the Selyakov-Scherrer relation. It has been found that in $[\text{Ti}(\text{Al})\text{N}_x]$ layers, as a result of annealing, the average size of crys-

tallites changes from 3.4 to 3.8 nm, and in ZrN_x layers from 5.2 to 6.3 nm. Such a change of the average size of crystallites in a nanometer range leads to a transition from rotational strain to shearing strain [15], which eventually defines the observed increase of material hardness.

Структура и свойства вакуумно-дуговых однослойных и многослойных двухслойных нитридных покрытий на основе слоев $\text{Ti}(\text{Al})\text{:Si}$

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Проанализировано влияние условий осаждения на структурно-фазовое состояние и термическую стабильность вакуумно-дуговых покрытий на основе слоев $\text{Ti}(\text{Al})\text{:Si}$. Исследованы однофазные однослойные покрытия, а также многослойные бислойные покрытия с прослойками второй фазы из нитрида одного из трех металлов – Мо, Cr, Zr. Установлено, что в покрытиях могут формироваться решетки гексагонального и кубического типов, причем переход к кубической решетке происходит при содержании Al около 25 ат. %. Наличие в бислойных многослойных композициях вторых наноразмерных (7-8 нм) слоев, состоящих из одного нитрида из группы CrN_x , MoN_x или ZrN_x , не изменяет тип решетки в слоях $[\text{Ti}(\text{Al})\text{:Si}]\text{N}_x$. В слоях CrN_x и ZrN_x также формируется ГЦК решетка с сильно- или слабовыраженной текстурой [111], а в слоях MoN – кристаллиты с решеткой гексагонального типа. Высокотемпературный отжиг при температуре 700 °C в течение 40 минут приводит к значительному (на 23 % или до $H_v = 47,56$ ГПа) повышению микротвердости покрытия системы $[\text{Ti}(\text{Al})\text{N}_x]/\text{ZrN}_x$, вследствие формирования наноразмерной структуры со средним размером кристаллитов в $[\text{Ti}(\text{Al})\text{N}_x]$ слоях 3,8 нм, а в ZrN_x слоях – 6,3 нм.

Ключевые слова: Нитридные покрытия, Многослойное покрытие, Элементный состав, Структура, Микротвердость.

Структура і властивості вакуумно-дугових одношарових і багатоперіодних двошарових нітридних покриттів на основі шарів Ti(Al):Si

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Проаналізовано вплив умов осадження на структурно-фазовий стан і термічну стабільність вакуумно-дугових покриттів на основі шарів Ti(Al):Si. Було досліджено однофазні одношарові покриття, а також багатоперіодні бiшарові покриття з прошарками другої фази з нітриду одного з трьох металів – Mo, Cr, Zr. Було виявлено, що в покритті можуть формуватися ґратки гексагонального і кубічного типів, причому перехід до кубічної ґратки відбувається при вмісті Al близько 25 ат. %. Наявність у бiшарових багатоперіодних композиціях других нанорозмірних (7-8 нм) шарів, що складаються з одного нітрида з групи CrN_x, MoN_x або ZrN_x, не змінює тип ґратки в [Ti(Al):Si]N_x шарах. У шарах CrN_x і ZrN_x також формується ГЦК ґратка з сильно або слабовираженою текстурою [111], а в шарах MoN_x – кристаліти з ґраткою гексагонального типу. Високотемпературний відпал при температурі 700 °С протягом 40 хвилин призводить до значного (на 23 % або до $H_{\mu} = 47,56$ ГПа) підвищення мікротвердості покриття системи [Ti(Al)]N_x/ZrN_y внаслідок формування нанорозмірної структури з середнім розміром кристалітів у [Ti(Al)]N_x шарах 3,8 нм, а в ZrN шарах – 6,3 нм.

Ключові слова: Нітридні покриття, Багатшарові покриття, Елементний склад, Структура, Мікротвердість.

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