Nanostructure Superhard Coatings and Technological Design of Gradient-Packed Macrostructures

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Abstract – In this work there are given research results proving the possibility of technological design of gradient-pack macrostructure which contains ion-plasma nanocrystalline Ti-N-Si-B or Ti-N-Al-Si coatings with the hardness of about 60 GPa. The possibilities of purposeful gradient-pack designing are defined by technological methods and apparatus which we created. They are the following: 1) the use in ion-plasma sputtering of multi-component cathodes made by powder metallurgy methods and high-temperature synthesis; 2) purposeful and, if required, continuous changing the elemental composition of coating layers by means of variation of type, quantity and discharge current value of sputtered cathodes; 3) the use of gas plasma generator based on arc discharge with hot cathode for prior ion-plasma doping of near-surface layer (e.g. nitriding), and also for assisted influence on structure-phased state and properties of deposited magnetron and electroarc coatings.

Pack technological design of generated multilayer coatings with purposeful distribution (gradient) of elemental composition, structure and properties is realized on the hybrid plant "Composite-3," completed with multi-component cathodes of different composition and containing magnetron sputtering system of planar type with two sputtering targets (cathodes), two electroarc evaporators and gas plasma-generator "PINK" in vacuum chamber.

1. Introduction

From the beginning of using technologies of deposing protecting and strengthening coatings for industrial applications the creators have offered the following recommendations [1, 2]:

- to provide good adhesion bond and working capacity, the deposited coating must have some affinity with the substrate, particularly, in crystallographic structure, similarity of hardness values, coefficients of thermal expansion, heat conductivity coefficients, etc.
- external layer of deposited coating must have specific purposes, for example, provide high thermal stability, prevent seizure of conjugate surfaces, have small shearing strength and, correspondingly, small friction coefficient;
- interlayer, defining time of coating functioning, must have high strength and wear resistance.

Obviously, only one kind of coating material can't provide meeting all above-mentioned requirements. That is why, the most progressive tendency in the development of the technology of instruments and machine details surface strengthening has become the designing of structures and methods of the formation of multilayer coatings [3, 4], every layer of which works according to its specific task which allows, to some extent, to approach the solution of a denoted problem. For example, in two-layer TiC+TiN coating, deposing on WC-alloyed instruments, inner layer TiC provides good adhesion bond with substrate and anticipates decarburization (loss of strength) of its near surface layer. External layer TiN is more inactive in contact interaction with medium-carbon steel; it prevents adhesion bond with this steel and reduces cutting force [3]. According to basic notions of tribology [5, 6], technological ways of providing normal behavior of external friction (without adhesion bond, burrs, cohesive damage, etc) and decreasing of wear as a whole are based on the formation of surface coating structure with positive gradient characteristics, i.e. producing weak layer, localizing shear deformation, on the strengthened sublayer. For example, one of the ways of increasing the time of working of high-loaded friction units is laying films (coatings) having small shear strength, e.g. from polymeric materials or soft metals [5], on their surface. At the same time, it's necessary to provide great hardness of a sublayer to anticipate the effects of plowing, microcutting or cohesive failure.

Rapid developing technologies of nanomaterials and nanocomposite coatings creation make the tasks of optimization of protecting and strengthening surface structures with their use, to be of great relevance. It is connected with great difference of structure-phased state of nanocrystalline films from traditional materials (steels, metals, alloys) and also with fundamental difference in their physical and mechanical properties, first of all, hardness and elastic modulus. The purpose of presented work was to create ion-vacuum nanocrystalline coatings with great hardness values and, at the same time, to define the possible fields of practical use of obtained results taking into account basic notions of tribological engineering. According to it there were set the tasks of studying mechanisms and developing the principals of creation of protecting and strengthening macrostructures, containing nanocrystalline superhard coatings, corresponding technological equipment and units, methods of their formation.

Unlike the known methods of producing multilayers coatings in our work the following special features are realised: 1) Multilayer structure was formed by gradual changing the composition of layers from superhard nanocomposite (H>40GPa) to amorphous-crystalline which are characterised by the hardness about 30–35 GPa. The amorphous component in the layer was aimed at decresing of internal stress, increase of viscosity of coating and minimisation of gradients lattice parameters, coefficients of thermal expansion and hardness. 2) Gradient-layer structure gave the possibility of neutralizing column growth effect and forming equiaxed grains in the coating.

2. Equipment and Experimental Methods

The structure and physico-mechanical characteristics of ion-vacuum nanocryctalline films are influenced by the type and relation of components, value of partial pressure and the composition of gas mixture, value of ions current and their energy, temperature parameters of the process [7–10]. In our research the accounting of enumerated factors and expansion of the band of their variation has become possible due to existed scientific beginning, i.e. the results we got in the 90-s which were based on deposition of composite coatings with sputtering of multiphase cathodes made with the method Self-propagating High-temperature Synthesis (SHS) [11], and working on deposing coatings with assisted influence of high-density low-energy gas plasma [12, 13], formed by plasma generator on the basis of arc discharge with hot cathode [14].

The deposition of magnetron coatings was made on the industrial plant MIR-2 completed with gas plasma generator "PINK" [14]. As a working gas there was used the mixture of argon and nitrogen according to the proportion Ar:N=4:1. Gas mixture was being given either through the circular magnetron anode in case of traditional variation of magnetron deposition or through gas plasma generator in case of deposition with the assisted influence of gas-discharge plasma. Working pressure in all cases was equal to $1{,}3\cdot10^{-1}$ Pa. As sputtering targets (cathodes) there were used titanium alloy VT 1–0, composite material Ti-B-Si made by SHS method, powder alloy Al-Si, made by hot compaction method.

Coatings were deposited either by sputtering of only one cathode of duplex magnetron or by sputtering of two cathodes of different composition with variation of their discharge current value. Because of variation of relation of discharge value there changed the relation of elements in deposited coating Ti-Si-B-N. The potential of the substrate in all cases was equal to –100 V. Deposition of electroarc coatings Ti-N, Ti-Si-Al-N, Zr-Nb-Si-Al-N was made on the industrial plant NNV 6.6-I-1, completed with gas plasma generator, also in two variations – without assisted influence of "PINK" and with it. The potential of substrate in all cases was equal to –200 V. As sputtering cathodes titanium (VT 1–0) and zirconium-niobium (2% Nb) alloys and also powder alloy Al-Si. As working gas commercial acid nitrogen was used. Working pressure was equal to $3\cdot10^{-1}$ Pa. Changing of components relation in deposited coatings was gained by variation of evaporators discharge rate, and also by changing the location of substrate in regard to centroidal axis of sputtering flow – angularly 90 or 45°.

Coatings were simultaneously deposited on mechanically polished samples made from hard metal T15K6 (to measure hardness), noncorrosive steel 12X18H10T (for electron microscopic research), steel H12M (to measure the friction coefficient). Measuring of coatings microhardness was made with the help of an attachment to the optical microscope Neophot-2 with the loading of 0,2 N on diamond pyramid. Nanohardness was measured on the NHT-S-AX-000X device. Electronic microscopic studying [15] of coatings in fine foil was conducted on microscopes EM-125 and Phillips CM30. Scanning electron microscopy of torn samples with the coatings and X-ray Spectroscopy of coatings component were made on the microscope SEM-515. Measuring of friction coefficient was made on the device of "Cyclometer" type according to the scheme stationary indenter – rotating disk with coating. As an indenters the changeable polished beads 3 mm in diameter, made of hardened steel ShM-15 were used. Loading on the indenter was equal to 0,15 H. The speed of disk rotation – 300 rpm.

3. Results and Discussion

First of all there was studied the influence of compsition on the hardness of two types of coatings: 1) Ti-Si-B-N deposited by traditional magnetron sputtering at the substrate temperature of less than 200 °C with different content of Si in regard to Ti; 2) Ti-Si-Al-N and Zr-Nb-Si-Al-N deposited by electroarc traditional method at the substrate temperature equal to 6000 C with different content of Si and Al in regard to Ti or Zr. Then there was carried out the research of assisted influence of plasma gas discharge of PINK on microhardness of magnetron and electroarc coatings of the same composition and deposited at the same temperature (<200 °C and 600 °C). The results of comparative measuring of hardness are given in the table 1. It is clear from the table data analysis that the influence on microhardness of coatings is exerted both composition and assisted influence of plasma PINK (coating Zr-Nb-Si-Al-N in this case wasn't studied because of relatively low values of its initial hardness in comparison to Ti-Si-Al-N coating).

Table I.Values of microhardness of composite coating depending on the relation of constituent elements and assisted influence of plasma PINK

The composition of coatings	The relation of elements	H_{20}, GPa without Pink	H_{20}, GPa with PINK
Ti-Si-B-N	Si:Ti=0,14	23,2	24,2
Ti-Si-B-N	Si:Ti=0,077	29,2	34,9
Ti-Si-B-N	Si:Ti=0,04	40,6	45,0
Ti- Si-Al-N	Si:Al:Ti=0,1:1,0:93,0	51,4	54,9
Ti- Si-Al-N	Si:Al:Ti=0,6:1,5:91,8	58,8	59,6
Zr-Nb-Si-Al-N	Si:Al:Zr=4,8:0,8:76,5	35,0	--
Zr-Nb-Si-Al-N	Si:Al:Zr=6.4:0,5:76,9	45,9	--

At the same time it is noted that microhardness of magnetron coatings deposited at low temperature (<200 °C) increases in a more remarkable way and rises by 4,3–19,5 % depending on the composition and assisted influence of PINK plasma. Evident assisted influence of PINKplasma on microhardness of low-temperature magnetron coatings was also confirmed on Al-Si-N coating. Its microhardness at all other similar parameters of deposition increased in case of assisted influence of PINK plasma from 28 to 34 GPa, i.e. 21,4% more.

Less noticeable effect of increasing microhardness at assisted influence of PINK can be seen on electroarc Ti-Si-Al-N coating (1,4 и 6,8 % more). We assumed that this quantitative difference of PINK influence on hardness of magnetron and electroarc coatings is connected, firstly, with difference in the temperature of deposition (<200 °C and 600 °C), i.e. with the difference under the condition of synthesis of compound on the substrate. Comparative research of electroarc coatings, deposited at a lower temperature equal to 400 °C, confirmed our supposition. In this case when deposition by a traditional way (without using PINK), microhardness of Ti-Si-Al-N coating with reduced content of silicon and aluminum was 43,9 GPa, whereas with increased content of these doping elements – 49,8 GPa. The hardness of coatings slightly decreased in comparison with the case of high temperature deposition. (see table 1). At the same temperature of deposition (400 °C) but with simultaneous assisted influence of PINK, hardness of these coatings increased up to 56,0 and 59,1 GPa correspondingly, i.e. by 27,5 % and 18,7 %. It is to be mentioned that reached values of hardness, in this case, practically coincide with the values of hardness of high temperature coatings (see table I). Undoubtedly, such decrease of deposition temperature (from 600 to 400 °C) owing to assisted influence of gas-discharge plasma PINK has a great practical importance in case of applying the coating on the pieces of hardened alloy, for example, on instruments of high-speed steel. As you can see in the table 1, maximum value of microhardness of magnetron coatings deposited with the assisted influence of PINK at the temperature of less than 200 °C is 45 GPa. This value was fixed at the relation Si:Ti=0,04, provided by the relation of discharge current values of two cathodes of duplex magnetron (of powder alloy Ti-Si-B and titanium alloy VT1-0) equal to 1:5. Due to the increase of the current of arc gas discharge when assisting from 10 to 50 A and, correspondingly, the substrate temperature up to 4000C, microhardness of coating with the same relation cathode discharge current values (1:5) increased up to 60 GPa. High values of coating of this composition were additionally confirmed by the method of nano indentation on the NHT-S-AX-000X device[15]. Exposed to the loading of 0,008 N on the indenter the average value of nanohardness is 70 GPa at the following dispersion of its value – from 62 to 86 GPa. Difference in values of microhardness and nanohardness can be caused by a softer substrate influence when measuring microhardness with relatively large loading on adamantine pyramid (0,2 N) and little thickness of deposited coating (about 1 mm).

Conducted electron microscopic studying of magnetron Ti-Si-B-N coatings showed that their structure state considerably depends on the relation of components [15]. For example, at Si:Ti=0,077 relation coating has nanocrystalline structure with the grain size about 10 nm. Besides, increased diffuse background which indicates the presence of amorphous component in the coating can be seen in micro-diffraction patterns [15]. When increasing the thickness of deposited coating, together with areas which are about the size of a grain of 10 nm, there can be found rather extended areas where the grain size is even smaller (they are almost not defined on the dark field),and sufficient broadening of micro diffraction rings allows to call this structure an amorphous-crystal one. With the decrease of relation Si:Ti up to 0,04 in coating Ti-Si-B-N another more sophisticated structure is formed. Firstly, electron microscopy finds particles (grains of titanium nitride) of submicron size equal to 0,1–0,2 μm, which are fragmented to the areas of 10–15 nm with small-angle off-orientation, i.e. double-level structure is formed. Secondly, isolated superfine grains of 20–25 nm are found in the coating. So, the structure of this coating is a mixture of two-level and nanocrystalline structure [15]. Similar structures have been also observed during the electron microscopic research of the electroarc coatings of the system Me-Si-Al-N, where Me is Zr or Ti.

It is necessary to mention that unlike the first Ti-Si-B-N coating with the relation of Si:Ti=0,077, where there is a lack of any preferred orientation of

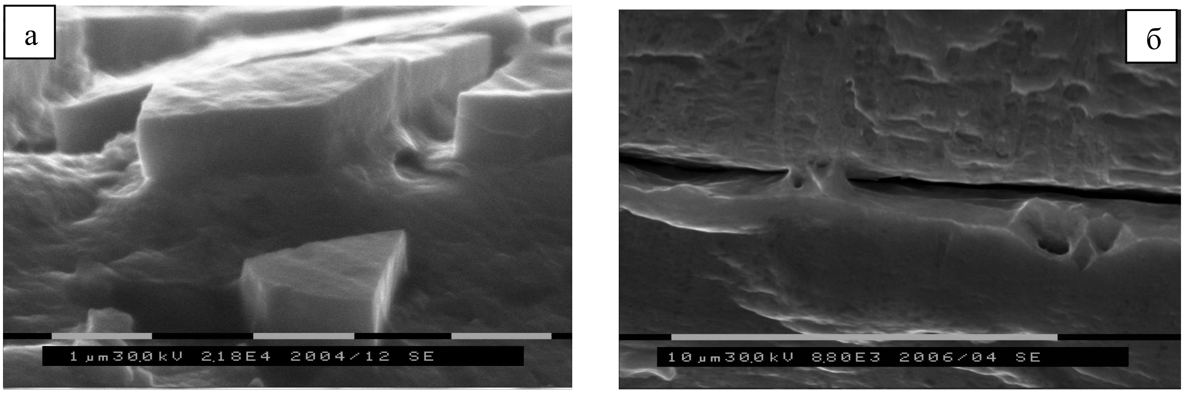

Fig. 1. Scanning electron microscopy of a torn sample with the coatings Ti-Si-B-N: a) with the relation Si:Ti=0,04 (epitaxial connection of the coating and substrate); b) with the relation Si:Ti=0,077 (absence of epitaxial connection of the coating with the substrate)

crystallographic planes at the coating with the relation Si:Ti=0,04 near the substrate, crystallographic planes of the growing layer are parallel to the corresponding crystallographic planes of the substrate, i.e. there occurs epitaxial nucleation. At the border substrate-coating crystal grains orientation of the coating iterates the substrate orientation, and during their growing the texture with the gradual changing of crystallographic orientation of the grain is formed. This fact is of great practical importance. It is known that adhesion (adherence of coating with a substrate) is defined by the nature of the separation borders of the coating-substrate. Fig. 1 shows the results of scanning electron microscopy of torn steel samples with the coatings of two relations Si:Ti deposited in other similar conditions.

Photos distinctly show that on the coating with the relation of Si:Ti=0,077, where there is absence of epitaxial connection, adhesion is weak and at the place of breakage there is an evidently seen crack between the coating and substrate (fig. 1, *b*). Existence of epitaxial connection with the substrate (in case of coating with the relation Si:Ti=0,04), determines greater adhesion. It can be seen (fig. 1, *a*) that there is no crack between the coating and substrate in this case.

The influence of high-density low-energy plasma of PINK on the phase composition of deposited coatings has been confirmed by the method of electron diffraction investigation. Electron-diffraction research has shown that in case of traditional magnetron sputtering at the substrate temperature of less than 200 °C in the coating composition, the titanium silicide can be found. With the additional assisted influence of PINK at other similar conditions of deposition, this phase component of coating disappears. Seemingly, high ionization of nitrogen plasma PINK and its intensive energy-radiation influence on the deposited layers and diffusion processes change the character of plasma-chemical reactions on the substrate, in particular, increase the possibility of nitride formation.

Nowadays, the most accepted is the dual nature model of friction interaction of the surfaces [5, 6]. According to molecular-mechanical model of Kragelskiy I.V. [5], friction force F may be represented as follows:

$$F=f_{mol.}\cdot S_{f.mol.}+f_{mech.}\cdot S_{f.mech.}, \quad (1)$$

where $f_{mol.}$ and $f_{mech.}$ – friction force components of molecular and mechanical nature, $S_{f.mol}$ and $S_{f.mech.}$ – factual area of molecular and mechanical interaction. Earlier, we demonstrated the abilities of active influence (by changing the doping elements content and assisted influence of PINK) on structure and hardness of deposited nanocrystalline coatings, and, consequently, on mechanical component of friction force. Molecular component depends, firstly, on chemical-phased composition of the surface, which interacts with the opposite material during the friction. In the table II the results of measuring of friction coefficient of magnetron coatings Ti-N and Ti-Si-B-N (with greatest possible relation of elements Si:Ti=0,2), deposited at different values of current of assisted PINK discharge and the temperature of substrate. Friction coefficient has been measured together with hardened and polished steel ShM-15 at minimum loading on indenter 0,15 H during the first 30 seconds of frictional interaction, i.e. in conditions of little contact loadings and smooth contacting surfaces, when determinative contribution to the friction force is made by a molecular component [5]:

Table II. Values of the coefficient of friction f of the coatings of different kind together with the steel ShH-15

Type of the coating	Ip of PINK, A Temperature, °C	Value f
Ti-N	20 A, 200 °C	0,19–0,20
Ti-N	40 A, 300 °C	0,15–0,17
Ti-N	70 A, 400 °C	0,12–0,16
Ti-Si-B-N	20 A, 200 °C	0,09–0,10
Ti-Si-B-N	40 A, 300 °C	0,08–0,09
Ti-N... Ti-Si B-N	40 A, 300 °C	0,10–0,11

Preliminary measuring of microhardness has shown that in the researched range of values of discharge PINK current and the temperature of the substrate the hardness of the deposited coatings is changing insignificantly and is of 27–28 GPa for the coatings Ti-N and 35–36 GPa for the coatings Ti-Si-B-N. At the same time analysis of the table data indicates that with the increase of discharge PINK current and, correspondingly, temperature of the substrate, coefficient of friction f of both types of coatings changes considerable. According to above mentioned information on changing phase composition of Ti-Si-B-N coatings deposited with and without assisted influence of PINK, taking into consideration considerable changing of the Ti-N coatings colour with the increase of the assisted arc discharge current (from gently yellow to saturated yellow with bronze tone); obtained results confirm the potential abilities of gas plasma-generator as an effective means of influence on plasma-chemical synthesis reactions, and, consequently, on the functional properties of deposited coatings.

The ability of purposeful changing the composition of deposited coatings and controlling their tribotechnical characteristics is tested on gradient-pack coating, with the following reference designation Ti-N...Ti-Si-B-N (see table II). In this case the sublayer of titanium nitride (Ti-N) by means of magnetron sputtering of only one cathode (target) of titanium alloy VT 1-0 initially deposited. After some time, together with the first cathode of duplex magnetron, there began to sputter the second one, made of Ti-Si-B alloy with the gradual increase of the current of its discharge up to the maximum possible value. After it there began the decrease of discharge current of the first titanium cathode, till full extinction of its discharge. At he final stage (after disabling the titanium cathode) on the surface during some time there was deposeted the external layer of the Ti-Si-B-N composition with the greatest possible relation of Si:Ti=0,2. The measuring of microhardness of gradient composition (gradient-packed) coating indicated that its value was 30,6 GPa and it was between the hardness indexes of Ti-N and Ti-Si-B-N coatings. As we can see from the table II, gradient-pack coating is also characterized by intermediate value of the friction coefficient in the initial 30 seconds of friction interaction. More long-term friction testing (during 5 minutes) has shown that a relatively low coefficient of gradient coating friction (not more than 0,14) remained during the whole period of testing. Coefficient of the friction of Ti-N coating deposited at the same temperature 300 °C, at the end of the 3d minute of testing increased to 0,35, and at the end of the 5th minute the process of seizure of friction surfaces with the chaotic changing of the friction coefficient from 0,45 to 0,58 became obvious.

Friction coefficient of Ti-Si-B-N coating, deposited at 300 °C increased up to 0,24 at the end of the third minute of testing and the process of seizure began also fix at the fifth minute. Most likely, in case of Ti-N coating it is possible to explain seizure by the low hardness of the coating (of 27 GPa order), its relatively high frictional interaction with the ShM-15 steel and rather big wearing by the fifth minute. In case of Ti-Si-B-N coating the seizure effect is presumably explained by poor adhesion (adherence) with the steel substrate which leads to the relatively early flaking of this coating in condition of repeated friction loading. Features of local flaking have been observed visually on the wearing path at small optical magnification on microscope MBS-10. And only gradient-pack, including Ti-N sublayer which is responsible for good adhesion of the whole coating with substrate, interlayer with gradient content of Si,B doping elements and antifriction Ti-Si-B-N external layer (according to Auger- spectral analysis – with the maximum content of Si and B), has provided high tribotechnical characteristics during the testing time without any sign of wear and flaking of tested coatings.

We suppose that potential abilities of gas plasma-generator of PINK type when solving the tasks of gradient-pack structures are not restricted only to its assisted application in the process of electroarc or magnetron coating deposition with the positive influence on plasma-chemical synthesis reactions in growing layers. In case of superhard coatings on a steel (relatively soft) substrate there naturally appears the need of additional strengthening of its near surface layer to provide gradual changing of hardness from the base to the coating with the purpose of preventing its early fracture failure under the conditions of shock and cycling mechanical loading. Great possibilities of gas plasma generator in solving the tasks of strengthening the steels of different degrees of doping (37G2S, 25H5M, R6M5) using the method of ion-plasma nitration were discovered [13]. At the same time it was stated that due to the variation of arc gas discharge current (and, correspondingly, temperature of a substrate), potential on the substrate, which defines the energy of ion nitrogen, and time of the process it is possible to control the degree of strengthened near surface layers and profile (gradient) of distributing the hardness according to thickness. So, the preliminary nitrated near surface layer of the steel base may also be included into gradient-pack macrostructure which is formed with the following depositions of superhard layers of nanocrystalline coatings on it.

4. Conclusion

1. On basis of obtained results of physical research there are defined the main principals of techno-

logical design of gradient-pack macrostructures containing superhard nanocrystalline coatings. One of the variations of such structure with magnetron deposition of Ti-N...Ti-Si-B-N composition have been successfully approved under conditions of simulated friction process and wearing.
2. For realization of gradient-pack technological design in the industrial purposes the hybrid plant "Composit-3" completed with multicomponent cathodes of different composition was created. The plant has two electroarc evaporators, planar magnetron with two independently sputtering cathodes, generator of gas plasma of PINK type in one vacuum chamber.
3. On the plant "Composit-3" the strengthening of pilot lots of cutting tool is made by forming gradient-pack structures of Me-N...Me-Si-Al-N type (where Me-Ti or Zr) which are tested in factories "ROLTOM" (Tomsk) and "Stepnogorsk Bearing Plant" (Kazakhstan Republic).

5. Acknowledgements

This work has been performed within the of Project support by Russian Fund of Research Financing Grant № 05-08-01277.

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