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STRUCTURE AND PROPERTIES OF WEAR-RESISTANT ION-BEAM VACUUM COATINGS

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The work investigates the structure and properties of coatings, formed by ion-beam spraying in vacuum of composite targets based on chromium with addition of ultradisperse diamonds and nanodisperse particles of Al_2O_3 and ZrO_2. It is shown that the ion-beam spraying method allows transferring target material on the product in form of coating keeping the composition and stoichiometry of the compound. A structural model of ion-beam vacuum coatings based on chromium with addition of ultradisperse diamonds Al_2O_3 and ZrO_2 was developed. 1 Ref., 5 Figures.

Keywords: *ion-beam vacuum coatings, nanosized particles, structure, properties*

One of the relevant directions in the field of science and technology is modification of surface of the structural and tool steels in order to increase the service characteristics of machine and mechanism parts operating under excessive wear and aggressive media. Today the enterprises of machine-building and metal-working industries widely use the different methods of surface modification such as deposition of wear-resistant coatings by vacuum physical and chemical methods, different types of thermochemical treatment.

The method of ion-beam spraying is the most efficient among the physical methods of functional coating formation for deposition of multicomponent material films. Currently, one of the most perspective ways to increase the efficiency of wear-resistant coatings is addition to a spraying target a small amount (up to several percent) of nanosized particles of oxides of some metals as well as ultradisperse diamonds (UDD). Since ion-beam spraying provokes complete transfer of composition and stoichiometry of multicomponent material of spaying target into the coating, this method can be used for obtaining the thin composite coatings with additives of nanosized particles, introducing the materials mentioned above in the spraying target.

Materials and investigation procedure. The ion-beam coatings based on chromium with 1 and 5 wt.% of ZrO_2 and Al_2O_3 additives, respectively [1] as well as 1 and 5 wt.% of UDD additives. Size of ZrO_2 particles made 50 nm, that of Al_2O_3 was 20 nm. The time of spraying made 2 h. Coatings were formed on St.3 grade steel.

Investigations of surface morphology of coating surface was carried out on scanning electron microscope (SEM) of high resolution Mira of Tescan Company (Czech Republic), resolution of which makes 1.7 nm (at 30 kV) and 3.0 nm (at 5 kV) as well as atomic-force microscope NT-206 (ODO Microtest-machines, Gomel). Resolution of AFM makes: vertical — 0.2 nm; horizontal — 2 nm.

Phase composition of ion-beam coatings was examined using electron backscatter diffraction (EBSD) method with add-on device to scanning electron microscope HKL. A principle of EBSD-analysis is based on formation of Kikuchi bands as a result of electron backscatter diffraction.

A value of load on indenter of Knoop type in microhardness measurement made 0.02–0.03 N.

Adhesion strength was determined using a special block, in which Rockwell type indenter was moved over the surface with 5 mm/min speed at smoothly increasing loading. A value of adhesion strength was determined on a value of normal load, at which coating detachment takes place on acoustic emission signal.

Wear-resistance was determined at loading on indenter 0.2 N and path 10 m. The indenter in form of 3 mm diameter ball reciprocates over the sample surface without lubricant. A length of single pass over the sample surface made 10 mm. A friction coefficient was determined during wear-resistance tests.

Chromium-based ion-beam coatings. Chromium is a material of increased wear resistance. The technology used for production of these coatings develops pore-free coating, which is virtually inaccessible for effect of the most severe and aggressive chemical agents. Therefore, in this case the etchant of the next composition, namely 50 % HCl + 50 % HF was used for determination of corrosion resistance.

Structure of the ion-beam chromium coating presents itself a three-layer composition. It consists of a

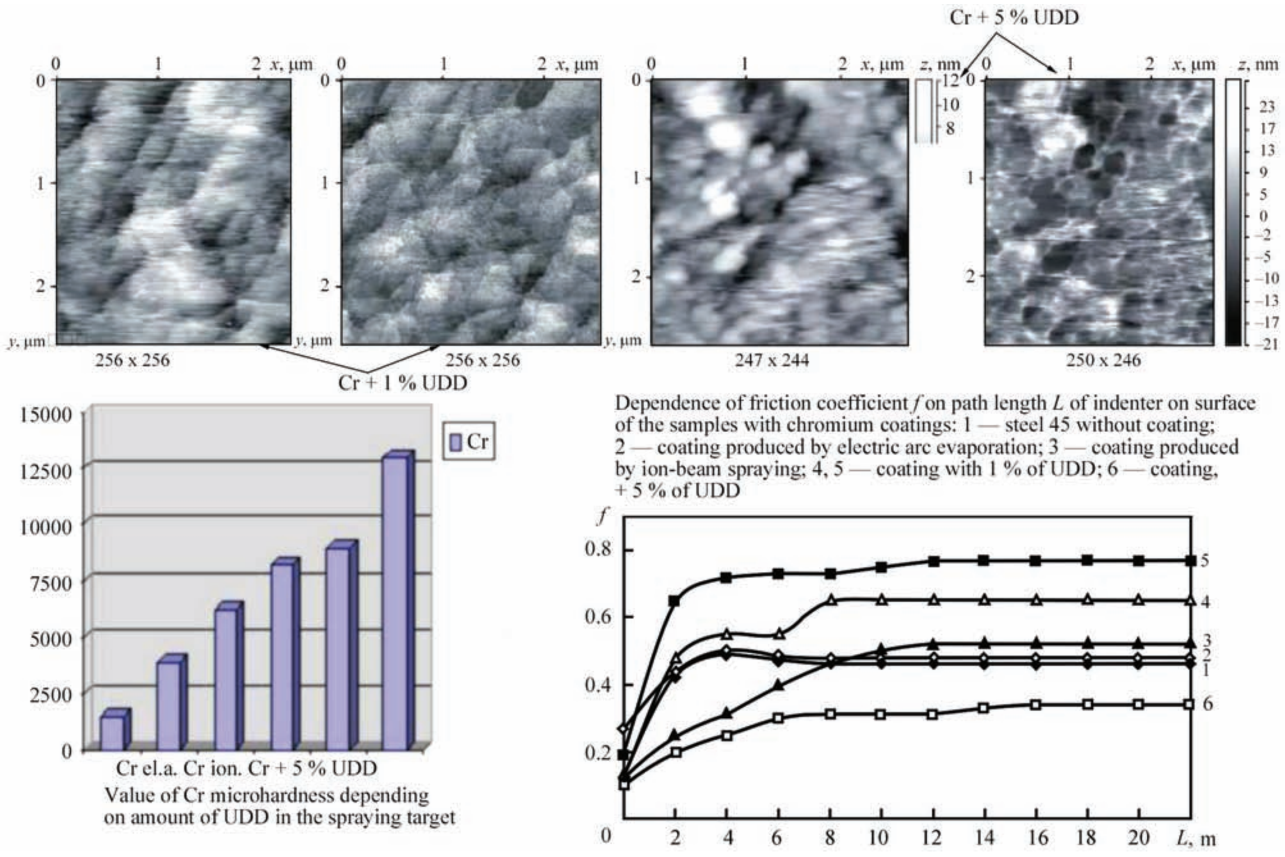


Figure 1. Microstructure, microhardness and coefficient of metal friction of Cr-based ion-beam coating with 1 and 5 % of UDD additives

very thin surface layer, middle layer, having columnar branched structure, and formed under it a layer of grain structure. Addition of 1 % of UDD into the spraying target increases coating resistance to etchant effect. Only some areas have got the etching pits, characterizing dislocation accumulation areas. A surface of chromium coating with 1 % of UDD is virtually completely free from the single etching pits, however, a fine grain structure (Figure 1) starts its development. An analysis of coating cross-section structure showed that addition of 1 % of UDD promoted absence of obvious columnarity in the cross-section structure.

Examination of morphology of the surface of ion-beam coatings based on Cr + UDD 5 % is much more complex. The etching pits even at very long etching appear as separate accumulations in form of sparse chains and single dots. In some instances, when etching on defect structure has reached the basis, it was possible to reveal coating cross-section structure based on chromium. Photos of the structure (Figure 1) clearly show columnar structure of the coating middle layer, moreover, this structure is laminar, but very dense. There are virtually no defects in it. Size of separate structural constituents does not exceed 10 nm. Very fine and absolutely structureless for SEM resolution film is observed on the coating surface. It seems as the coating columnar structure grows in it.

A morphology of surface of the ion-beam chromium coating, obtained using atomic-force microscope has the following characteristics, namely grain height does not exceed 40 nm, and it size varies in 100–150 nm limits (Figure 1).

Addition of 1% of UDD into the chromium spraying target promotes refining of the coating grain structure. An average grain size makes 70 nm, and grain height does not exceed 15–20 nm. The grain boundaries are weakly revealed. The grain boundaries close to the coating develop more clearly when adding 5% of UDD in the spraying chromium target. An average size of grains reduces from 40 to 50 nm, and height does not exceed 10 nm. In this case the grain boundary hardening using the phase contrast mode can be well seen (Figure 1).

The interesting results were obtained in microhardness measurement of the chromium ion-beam coatings. The values of microhardness of chromium ion-beam coatings with different content of UDD make:

- microhardness 16500 MPa in the case of addition of 1% of UDD into the spraying target;
- microhardness 25900 MPa (Figure 1) in the case with UDD 5 %.

It is known that the coatings, produced by ion-beam spraying method are brittle, as a rule. High hardness of the coatings can promote their cracking and further delamination. Therefore, the tribotechnical tests of these coatings have been carried out. The analysis of dependence of friction coefficient on a length of indenter path over the surface of samples with chromium coatings showed (Figure 1) that they can be divided into two steps.

The first step corresponds to friction surfaces running-in. At that, all samples demonstrate increase of the friction coefficient. It is explained by low roughness of the initial surface of examined coatings. During running-in the smooth initial surface is broken and equilibrium structure of coating surface layers with roughness exceeding the initial one is formed.

The second step is set wear-out. The friction coefficient at this step is not changed. The path of indenter until reaching the set wear-out can be one of the criteria for coating wear resistance evaluation. Addition of UDD into the spraying target increases the length of path before running-in, value of which reaches the maximum in the coating containing UDD 5 %. The minimum friction coefficient corresponds to this coating. The classical third step of change of the friction coefficient, namely breaking of the coating and friction over substrate, is absent in all examined samples after 22 m of path.

Thus, the examinations showed that the composite chromium coatings formed by the method of ion-beam spraying have sufficiently good wear resistance. An important index of wear-resistance is morphology of wear surface in a mode of set running-in. The largest part of the wear surface of coating, produced by spraying of powder chromium target with 1 % of UDD, is free of any traces of intender impact. At the same time, on separate sections of friction paths there are sufficiently deep grooves, probably, being the result of incorporation of chipped particles of the coating.

Addition of UDD in the spraying target except for direct transfer of diamond phase provokes its partial decomposition and formation of chromium carbides. They are located along the grain boundaries and prevent emergence of the dislocation on the surface, simultaneously increasing hardness of the coating. Rise of diamond phase up to 5 % allows forming a network virtually along the whole coating surface. It completely blocks the possibility of dislocation emergence on the surface. The processes of diffusion dislocation climb from the base into the coating on interphase boundaries and processes of formation of grown-in dislocations do not stop in coating formation. Formation of dislocation networks additionally strengthens the coating. It is proved by microhardness data.

In the coating with 5 % of UDD $H_\mu = 25\,900$ MPa. However, the level of structural constituent refining affects the value of microhardness in addition to dislocation processes and formation of the network.

The ion-beam chromium-based coatings with addition of 1 % of ZrO_2 particles of 50 nm size into the spraying target are characterized with developed surface relief (Figure 2). There can be observed grain structure, moreover, grain size is varied from 50 to 200 nm. After etching in acid mixture (HNO_3, HF, HCl) it can be clearly seen a columnar structure of the coating, besides, it is more dense in the upper layers and more porous in the base.

When comparing the coatings formed with addition of 5 % of ZrO_2 particles of the same size (50 nm), then in this case more dispersed structure will be observed, the grain size will refine and become more uniform (Figure 2). The grain size varies in the limits of 20–30 nm. An exposure in characteristic X-ray radiation indicates that ZrO_2 is mainly located along the grain boundaries.

Spraying of the targets with 5 % of ZrO_2 results in grain size refinement. It can be clearly seen that in both cases zirconium dioxide is mainly located along the grain boundaries.

Measurements of coating microhardness showed: 17759 MPa for targets with 1 % of ZrO_2 and 17800 MPa for targets with 5 % of ZrO_2.

Examination of the surface using atomic-force microscopy method were carried out for the samples formed of chromium targets containing ZrO_2 (Figure 2) as well as the targets containing additives of aluminum oxide (Figure 3).

As it was shown by carried examination, spraying of chromium target with 5 % of ZrO_2 provides homogeneous structure with small grain size. Homogeneity of structure is proved by an image in lateral force mode. The grain size varies from 60 to 100 nm (Figure 2).

Decrease of content of ZrO_2 to 1 % results in coarsening of chromium coating grain. Grain size in the coating of the target with ZrO_2 particles of 50 nm size varies from 50 to 200 nm (Figure 2). At that it has the largest inhomogeneity of surface in the lateral force mode. There are two phases in the surface structure, moreover, one of them is divided on subgrains of 40 nm size. Grain structure for the coating formed using chromium target containing 5 % of 50 nm size ZrO_2 particle is homogeneous and grain size varies in 50–100 nm range.

Obtained date can be explained in the following way. Grain size in the chromium ion-beam coating depends on density of nucleation centers in solidification of coating, to which ZrO_2 particles are referred to among the others.

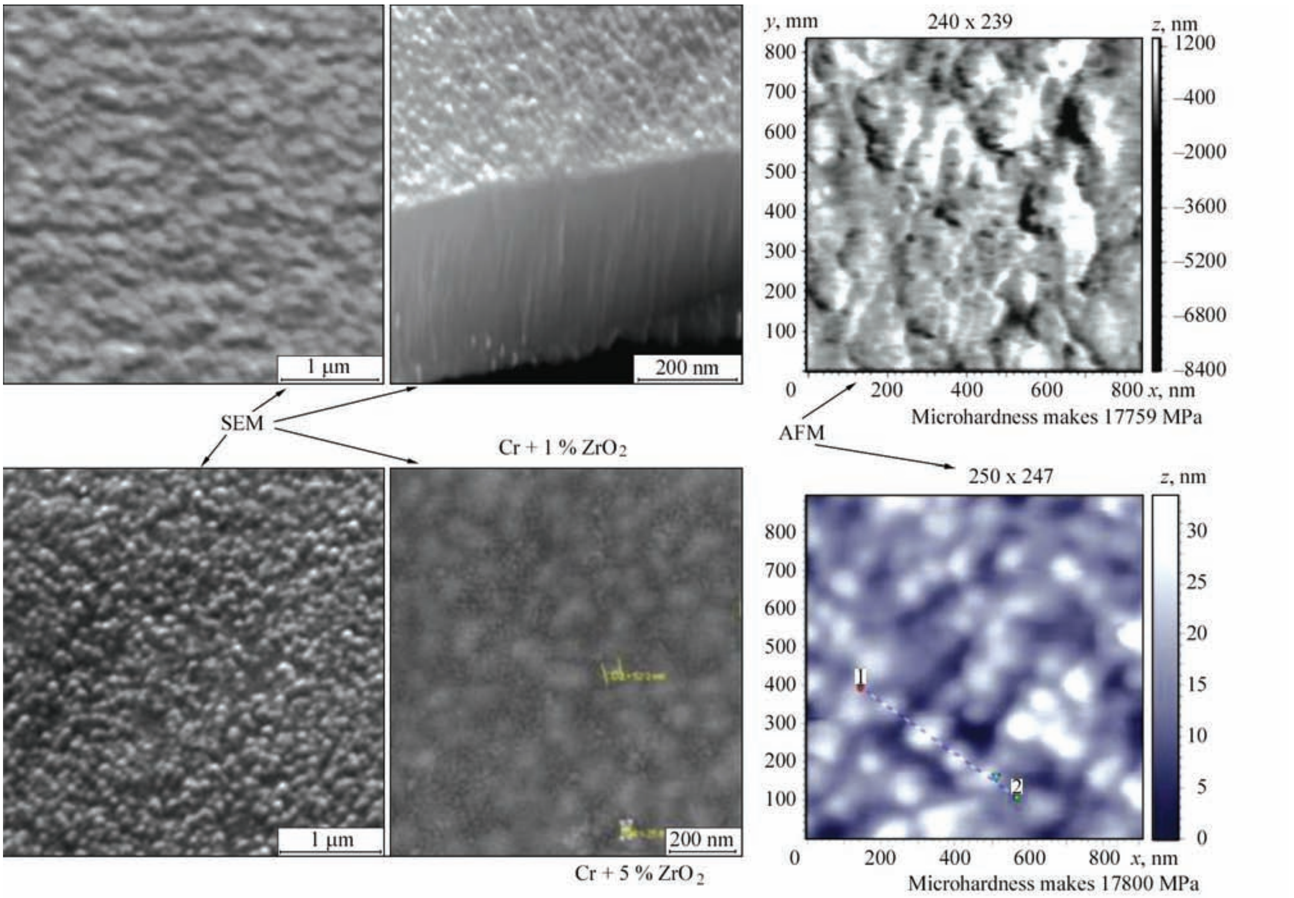


Figure 2. Microstructure of ion-beam chromium-based coating with 1 and 5 % of ZrO_2 additives

A size range of ZrO_2 particles in 5 % amount forms the optimum conditions for generation of homogeneous nanosized structure with 60–100 nm grain size. Content of 1 % of ZrO_2 oxide does not already guarantee sufficient number of nucleation centers for formation of nanosized grain in the coating.

Examination of surface of the ion-beam coating formed by spraying of chromium target with 5 % of Al_2O_3 additive showed that it has grain structure. Grain size varies from 50 to 70 nm. Etching in acid mixture revealed appearance of the coating columnar structure.

In examination of the coating formed with the help of Cr + 5 % Al_2O_3 target on the field of 4x4 μm it is possible to determine that a relief was formed by multiple deepenings, roughness R_a makes 9.1 nm. On the field of 2×2 μm it was found that the surface was formed by deepenings of 100–400 nm diameter and separate projections of 100–200 nm diameter. In «Torsion» mode the surface has one color, therefore, it is single-phase.

Addition into the spraying chromium target of 5 % of Al_2O_3 allows rising microhardness of the coating up to 29640 MPa. For these coatings the microhardness results differ by good stability.

The ion-beam chromium coatings without additives of different materials into the spraying target have microhardness values of around 7600 MPa. Addition of aluminum oxides into the spraying target allows forming on the samples' surface the coatings having almost two-three times higher microhardness.

Scratch test was used to determine the adhesion strength of titanium coatings. Normal loading on indenter in scratch increases from 0 to 90 N, indenter movement speed over the surface made 5 and 10 mm/min. Wear resistance was evaluated on wear-out value, which was determined on area of a crater on profilograms across the friction pathes. The largest wear-out was registered in coatings of the target «Cr + + 1 % ZrO_2 of 50 nm grain size», for which $K_{fr} = 0.7$ was determined. High value of wear-out and K_{fr} as well as low value of adhesion strength are explained by coating damage. The best results were registered for coatings formed from the target «Cr + 5 % ZrO_2 of 50 nm grain size», in this case $K_{fr} = 0.17$. Absence of pronounced wear craters indicates formation in the friction zone of the transferred layers.

Analysis of phase structure of the ion-beam coatings was carried out by method of electron backscatter diffraction (EBSD) with the help of add-on device to scanning electron microscope HKL. A principle of EBSD-analysis is based on formation of diffraction pattern, which is generated as a result of electron backscatter diffraction. The information embedded in the diffraction pattern contains data on symmetry of crys-

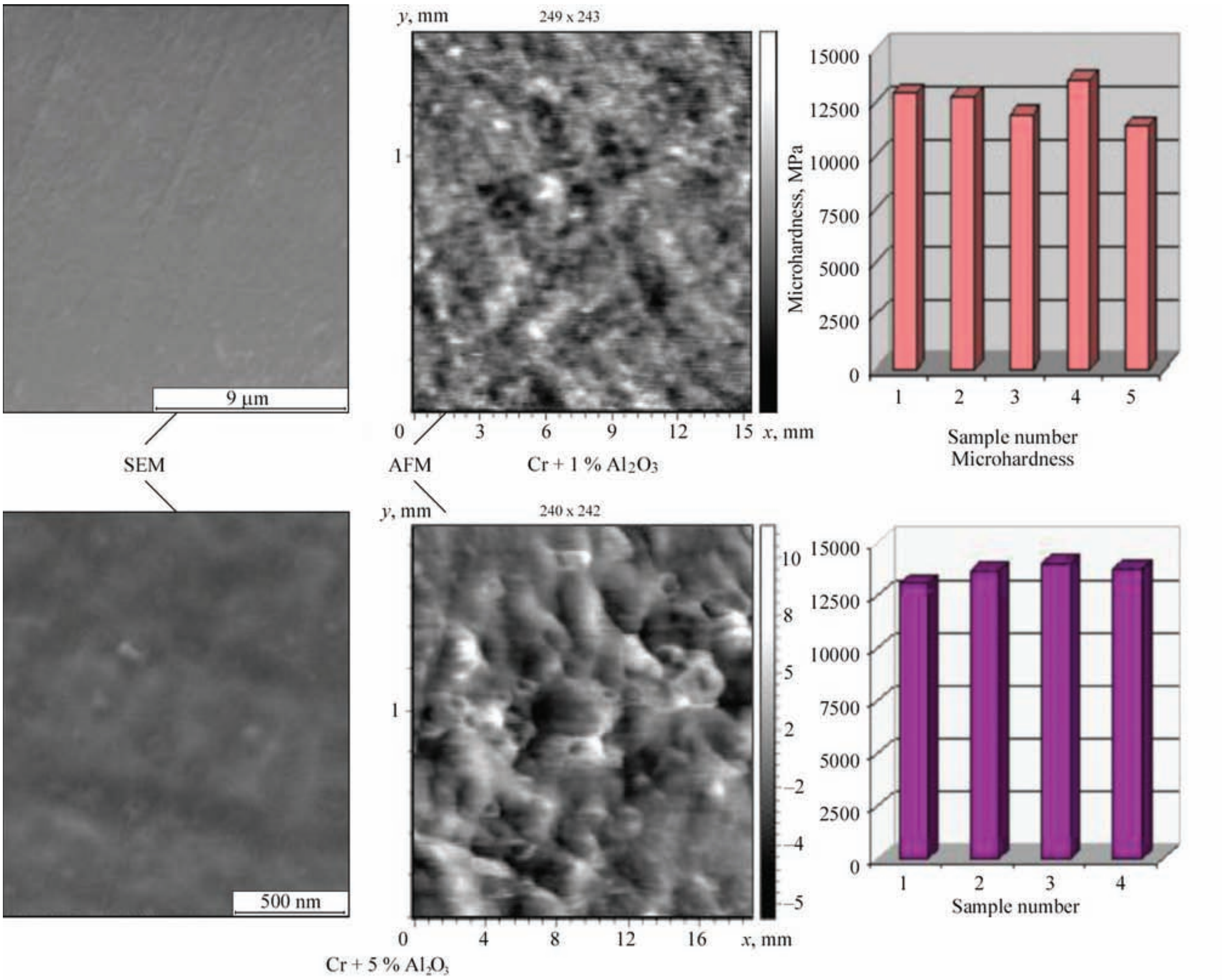


Figure 3. Microstructure and microhardness of ion-beam Cr-based coating with 1 and 5 % additive of Al_2O_3

tal and its orientation. Since the angles between the planes and axes of the zone are explicitly determined by crystal symmetry and parameters of its lattice, then information taken from the diffraction pattern is used for determination of phases contained in the sample.

The results of point X-ray phase examination of the ion-beam coatings are presented in Figure 4. Kikuchi bands were assigned with Miller indices in accordance with crystalline planes, which formed them, and the intersection points of bands are marked with the symbols of zone axes. The coating structure was examined in the several points (areas) of the coating.

Collision of the particles of gas phase with the substrate surface took place on the first stage, after what the particles can firmly attach on the substrate or in some time evaporate or elastically reflect from the surface.

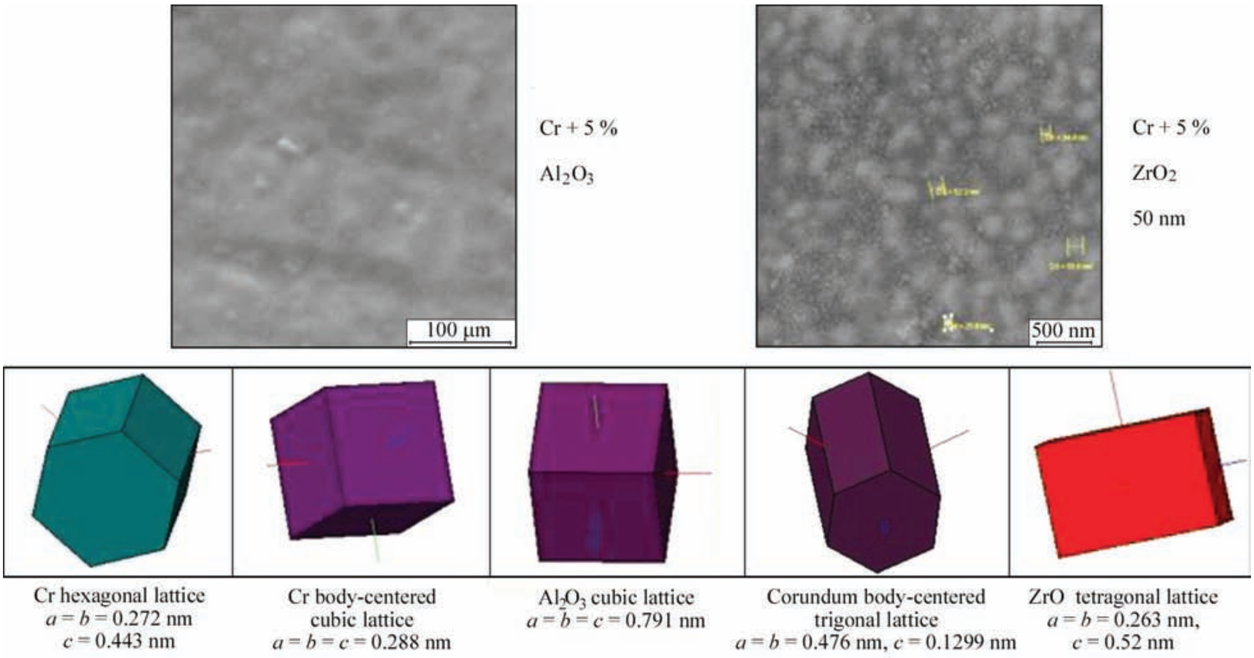
Following the results of X-ray phase analysis, different phases of target metal as well as nanodisperse additives can be formed in the process of formation of the ion-beam coatings.

Thus, for example, in spraying of the target with ZrO_2 additives, chromium and titanium there can be formed hexagonal, cubic or tetragonal lattice.

ZrO_2crystalline lattice in the coating can be rhombic and monoclinic. Al_2O_3 forms a face-centered cubic lattice and body-centered trigonal lattice, formation of rhombic lattice is also possible.

Analysis of obtained results allows concluding that three types of crystalline lattices, namely cubic, hexagonal and body-centered cubic are formed by chromium in the process of ion-beam spraying independent on composition and amount of additives. Besides, it is determined that common cubic lattice and body-centered cubic lattice have different interplane distances — 0.288 nm for common cubic and 0.459 nm for body-centered cubic. Hexagonal lattice has $a = b = 0.272$ nm, $c = 0.443$ nm (Figure 4).

Application of EBSD method allowed proving that ZrO_2 and Al_2O_3 are transferred from the target on the coating in form of cluster crystalline structures during the process of ion-beam spraying. Thus, ZrO_2 in the chromium-based coatings was found in form of three crystalline lattices, i.e. tetragonal with interplane distances $a = b = 0.363$ nm, $c = 0.520$ nm and rhombic with similar interplane distances. Al_2O_3 in a coating composition has three crystalline lattices, name-



Cr hexagonal lattice $a = b = 0.272$ nm $c = 0.443$ nm

Cr body-centered cubic lattice $a = b = c = 0.288$ nm

Al_2O_3 cubic lattice $a = b = c = 0.791$ nm

Corundum body-centered trigonal lattice $a = b = 0.476$ nm, $c = 0.1299$ nm

ZrO tetragonal lattice $a = b = 0.263$ nm, $c = 0.52$ nm

Figure 4. Morphology of surface of ion-beam coating based on Cr with different additives and HKL data

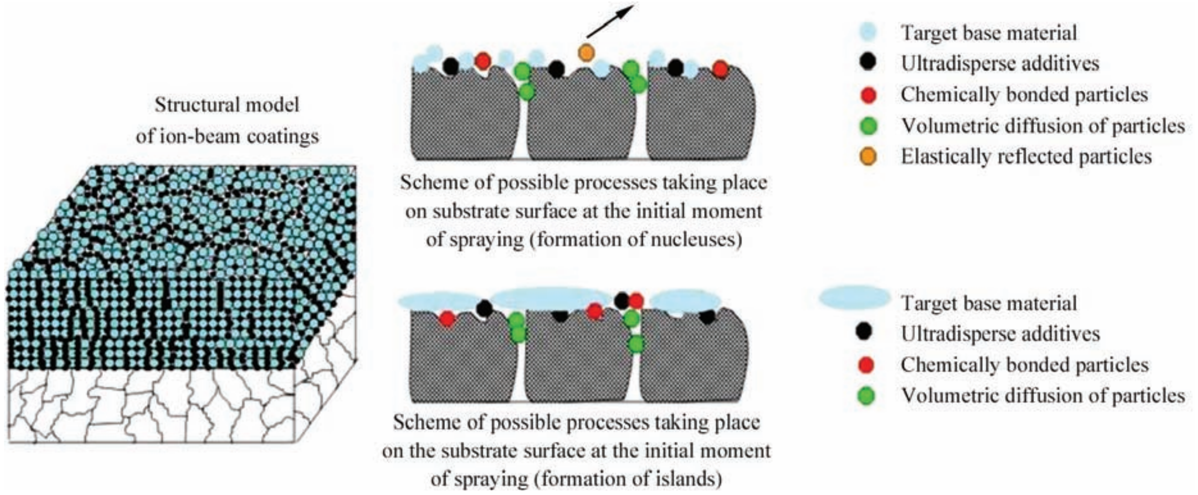


Figure 5. Structural model of ion-beam coatings formed based on chromium with UDD additives, Al_2O_3 and ZrO_2

ly face-centered cubic, rhombic and body-centered trigonal lattice typical for corundum (Figure 4).

The reasons of formation of different crystalline phases in process of ion-beam coating formation require further investigation.

Conclusions

Carried investigations allowed making a conclusion that the method of solid body surface modification using coating deposition by ion-beam spraying provides the possibility in wide limits to change purposefully the surface properties of structural and tool materials.

Carried examinations of Cr-based ion-beam coatings with ultradisperse diamond additives proposed a concept of mechanism for these coatings formation. Examination of the Cr-based ion-beam coatings with addition of metal oxides verifies proposed mechanism. Let’s in short words describe the main stages of formation of ion-beam coatings.

The process of formation of thin films independent on metal transfer method and its composition takes place in several stages (Figure 5):

- nucleation of new phase particles;
- growth of particle size without their number change;
- formation of islands and further increase of islands’ size;
- coalescence of islands in the solid film.

On the first stage collision of the particles from gas phase with the substrate surface takes place after what the particles can strongly fix on the substrate or can be elastically reflected from the surface.

The substrate before coating formation is subjected to cleaning with ion beam that results in appearance of the defects on it, which determine behavior of the particles entering the surface during spraying. These are so-called dislocation tubes (areas of dislocation accumulation), located, as a rule, along the grain boundaries. Particles of the sprayed material, captured in such tubes, penetrate deep into the substrate, and in this case so-called volumetric diffusion takes place. Part of the particles is kept on the substrate due to surface attraction force, part of the particles forms chemical bond with coating material. Part of the particles can be elastically reflected from the base surface.

Growth of thin films after formation of nucleuses can develop on three possible mechanisms, namely layer-by-layer, island or mixed.

A layer-by-layer growth is a successive filling of the substrate with monocluster layers. An island growth takes place, if bonding of the particles in the islands is more than with the particles in the neighbor islands that result in prevailing upward growth of the islands. The processes of layer-by-layer and island growth can get simple physical interpretation.

In the first case, there is complete wetting of the surface. Attachment of the particles to the nucleus side edges is thermodynamically preferred up to complete filling of the first layer.

In the second case, accumulation in a drop is better for the nucleus. In the process of growth, the conditions of good wetting can be disturbed, and then change of layer-by-layer to island mode will take place.

After the islands consisting of two-four adsorbed particles on the coating surface approach to bonded particles and particles caught in the dislocation tubes, their coalescence and formation of the coarse islands take place. The next step is formation of coating monolayer. Later on this layer becomes a basis for growth of the next layers. It is determined that ion-beam coatings have mixed growth mode. It means that after some initial time of spraying (10–20 s) bonding between the particles in the islands becomes higher then between the particles of the neighbor islands. In this case islands start upward growing and columnar structure is formed. Besides, the columnar structural constituents themselves have lamination. Presence of columnar structure can promote appearance of coating nanoporosity.

Nanodisperse particles of zirconium and aluminum oxides added to the chromium spraying targets adsorb on the substrate surface. The nanodisperse particles of oxides prevent coalescence of the chromium particles into coarse structural constituents, and this, in turn, results in coating structure refinement. Part of nanodisperse particles is located over defects of crystals of sprayed materials and part over the boundaries of chromium grains. Carried examinations using EBSD method showed that in the process of formation of ion-beam coatings there is complete transfer of target material into the coating.

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