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Morphology and genealogy of structural defects in vacuum ion-plasma coatings

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Introduction. The main work objective is systematization and analysis of structural defects of vacuum ion-plasma coatings; on this basis, their classification principles are developed and given in the paper. Another important part of the work is the experimental study on one of the specific defects of coatings, which the authors propose to call “defect of substructural origin”.
Materials and Methods. PVD coatings of various nitride and metal systems 1.5–9.0 μm thick were used as an object of the research. Coatings were applied in vacuum installations using arc and magnetron evaporators. The research results were obtained by high resolution electron microscopy, energy dispersive analysis and indentation.
Results. Various types of defects in ion-vacuum coatings are presented as the research results. They include discontinuities, deformation of crystallites, and structural inhomogeneity. The principles of their systematization are validated. It is proposed to classify defects into droplet, substructural, and growth defects (depending on the causes of their nucleation), as well as regular and stochastic ones (depending on their distribution in the coating volume). The study of “substructural defects”, classified by the authors as stochastic, is given special consideration. These micrometric defects are shaped like a cylinder with a conical “head”. Their main axle is oriented perpendicular to the surface of the coating. They can be “extruded” (tore away) by the coating. The paper validates the dislocation mechanism of their nucleation and the helicoid growth principle.
Conclusions. The inference is summarized that the proposed systematization of defects in ion-plasma coatings has the character of an intermediate result of research in this scientific area. At this, the “substructural defects” do not have a fatal effect on the structure and properties of the coating due to a small size.

Keywords: metal ceramic coatings, vacuum ion-plasma deposition, microstructure, structure defects, scanning electron microscopy.

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Introduction and Problem Statement. Obtaining ion-plasma coatings is one of the most rapidly developing research areas. Despite the high publication activity of scientists working in this area, the authors failed to find thorough fundamental studies on the defects of ion-plasma coatings. The problem of defects is usually rated as technological, and, in this case, it is considered not in the content-related part of a scientific publication, but only in the methodological one. In this regard, when performing this work devoted to the problem of defects in ion-plasma coatings, two objectives have been set:

— to suggest classification principles for defects of this type of coating on the basis of a small review;

— to conduct a study on one of the specific types of such defects, which we propose to call "defects of substructural origin".

Materials and Methods. To obtain coatings, vacuum ion-plasma spraying units were used: two-cathode system PLATIT π^{80} equipped with two arc evaporators; modernized TINA-900 unit equipped with magnetron evaporators. The operating modes of coating deposition were as follows: deposition temperature — 300−450ºC; pressure in the vacuum chamber — $(1.3-4.7)\times10^{-2}$ mbar; bias voltage — 100−150 V. In accordance with the given parameters of the vacuum ion-plasma technology, the resulting coatings are classified as PVD. The coatings of various nitride and metal systems with a thickness of 1.5−9.0 μm have been investigated. The basic results on the study of substructural defects were obtained on Ti-Al-N coatings. The coating hardness of the selected systems exceeded 12−15 GPa, which allows them to fall into the category of wear-resistant.

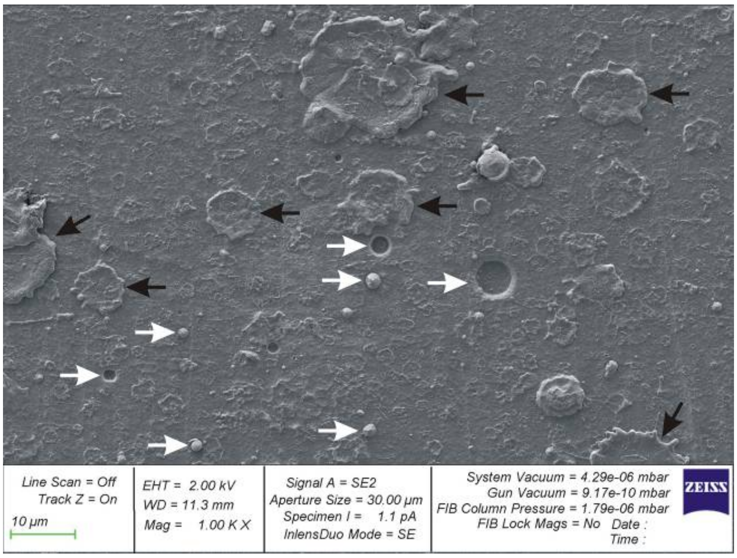
Samples from various structural steels were used as a substrate. The impact of the composition, structure, and properties of the substrate on the parameters of the coatings was not taken into account. Before coating deposition, the sample surface was cleaned in a vacuum chamber by a continuous flow of Ar ions for 5 min. To provide high adhesion of the coatings, a sublayer of the first metal in the system was applied to the sample surface cleaned by the ion beam.

To study the microstructure of the coatings and their surface relief with high resolution, we used a scanning dual beam (electron/ion, SEM/FIB) microscope ZEISS CrossBeam 340 with an integral energy-dispersive X-ray detector X-Max EDAX (Oxford Instruments).

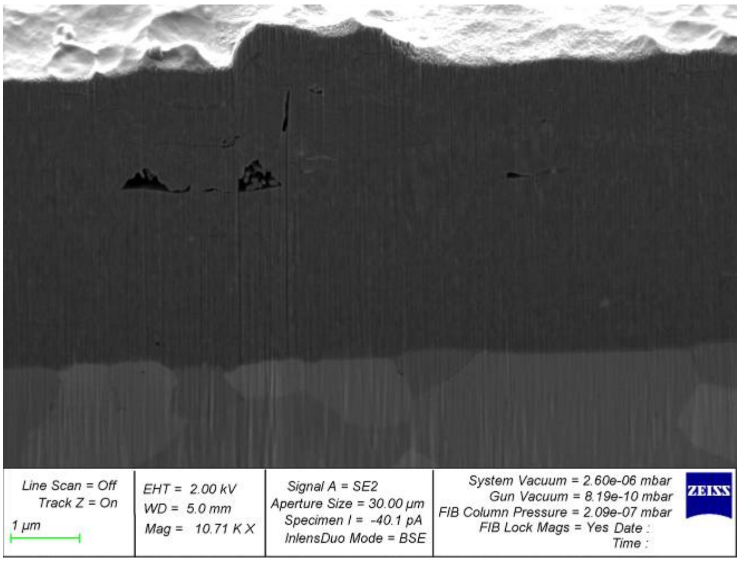
Results and Discussion. One of the basic conditions for zero-defect coatings obtained using the ion-plasma technology is the minimum branching of the substrate surface relief. To implement the procedure, according to the normative requirement to the surface relief, roughness should have the parameters not lower than $R_a \leq 0.12$ μm; $R_z \leq 0.6$ μm. Failure to comply with these conditions can cause the formation of "regular growth defects" in the coating during deposition in the form of porosity, deformation of crystallites and lattice, internal stresses, etc. Microroughnesses located separately on a tolerably smooth substrate relief cause disorientation of the axes of growing crystallites, which induces their deformation and forms incoherent, often porous, intercrystalline boundaries. High density of microroughnesses causes the formation of a large volume of porosity near the coating and substrate interface. Large waviness of the substrate surface, for example, during rough grinding, forms high stresses in the coating, which, under weak cohesive bonds in the coating, can induce its delamination, and under poor adhesion — complete delamination of the coating. Coatings with such defects, as a rule, do not meet even the most moderate operating requirements in terms of protecting products from wear, corrosion and similar actions.

If the specified requirements for the substrate surface roughness are met and the coating is uniform in density and structure, this does not exclude the appearance of random defects in it: those of substructural origin and due to the presence of a droplet phase.

Since the appearance of both types of defects in a specific microvolume of the coating is of a random nature, then, in contrast to "regular growth defects", it is logical to combine them into a class of "stochastic defects". Among them, "droplet defects" are mainly formed when using powerful thermal evaporators of a vacuum installation, as well as during the deposition of fusible coating elements. "Droplet defects" can be almost completely eliminated through magnetron evaporation. Examples of "drop stochastic defects" of ion-plasma coatings are shown in Fig. 1. On the surface, they have a characteristic shape with a flaky configuration, which is marked in Fig. 1 a with dark arrows. Getting on the surface of the coating during its application, the droplet phase violates the laminar dynamics of the normal growth of the coating, which manifests itself in the form of irregular pores in the cross section of the coating (Fig. 1 b). In multilayer coatings, pores and structural inhomogeneity formed in the droplet phase zones can have an elongated shape at the boundaries of the coating layers during the transition from a layer with refractory components to a layer with a fusible element (Fig. 1 c).



a)



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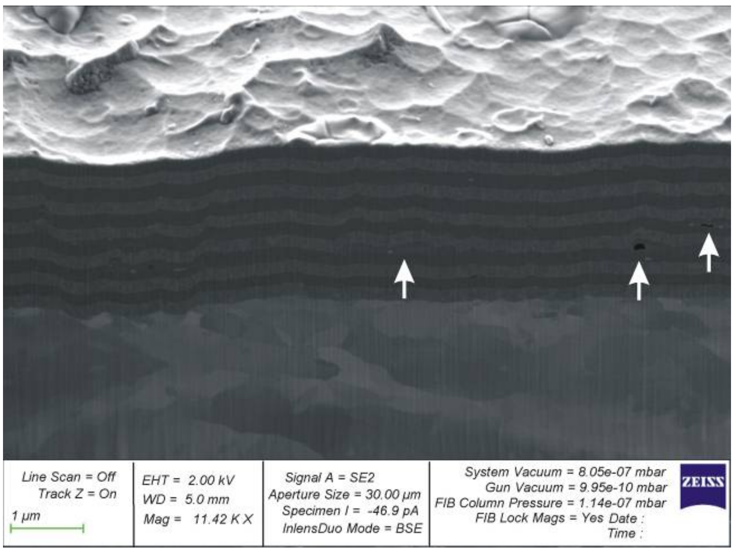


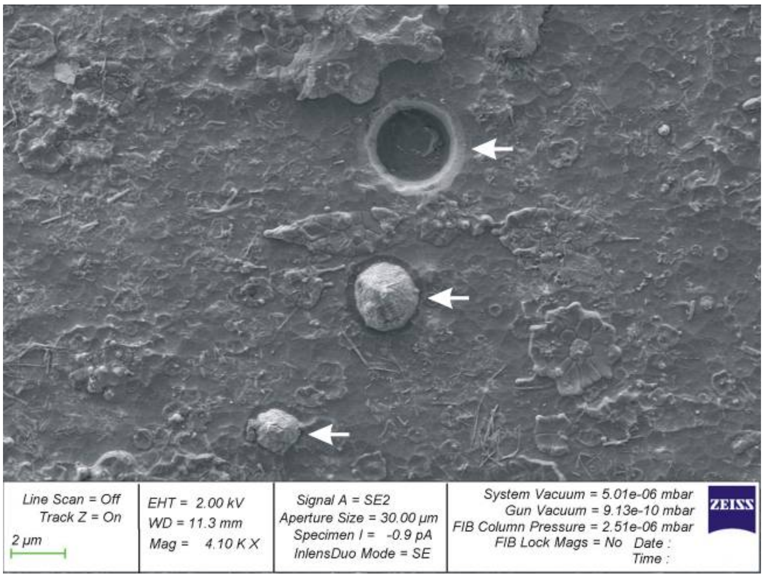
c)

Fig. 1. Examples of droplet defects in TiAlN coatings, SEM: *(a)* on the coating surface (marked with dark arrows); *(b)* in the cross section of a monolayer coating; *(c)* in the cross section of a multilayer coating (marked with light arrows)

In general, all of the coating defects discussed above are of technological origin. Their appearance can be excluded or limited through optimization of the process variables of the ion-plasma method and equipment. With regard to defects of substructural origin, the regulation or exclusion of their appearance in the coating seems unlikely since they are due to the very nature of the actual coating material. The results of studying such defects are the subject matter of this work.

Examples of the studied defects of substructural origin are shown in Fig. 1 *a* (marked with light arrows) and in Fig. 2. They have a characteristic geometric shape. In the body of the coating, there is a cylindrical part of the defect, and a conical part protrudes above the surface of the coating. Under certain conditions, the formed defect is rejected through undergoing extrusion, i.e., extrusion by the coating, leaving cylindrical depressions of the correct geometric configuration in place of its localization. If the coating process continues, the cavity is filled with the deposited ions of the coating material at a higher rate than the rest of the flat surface. This is probably due to the “edge effects” of the electromagnetic field formed by the bias voltage on the substrate. As a result, the cylindrical depressions are “healed” during the application process, and the coating is sufficiently uniform in this area. If the considered defects are extruded from the coating immediately before the end of the process of its application, then the remaining cylindrical niches are clearly visible on the surface (Fig. 1 *a*, and 2 *a* – 2 *d*).

Fig. 2 shows a complete microscopic picture of various stages of the life cycle of substructural defects in the PVD coating of the Ti-Al-N system. Normal projection shows three defects of different sizes located at a distance of several micrometers from each other (marked with arrows). The conical shape of the protruding part of localized defects and the cylindrical niche of the extruded defect are clearly visible. In Fig. 2 *b* – 2 *d*, these stages of the existence of defects are presented in a three-dimensional picture. Conical “heads” protruding from the coating are designated by number 1, cylindrical niches — by number 2; and number 3 in Fig. 2 *d*, shows the place of the niche at the stage of “healing”. The volumetric image was obtained through preparing the FIB cross-section, perpendicular to the coating surface, and then tilting the sample towards the detector by 15–28°. Fig. 2 *b*, 2 *c*, show only the cross section of the coating and its surface, and Fig. 2 *d* — the entire cross-section in block. The preparation of cross-sections provided obtaining a cross section of the investigated defects (Fig. 2 *b*, 2 *c*). It is clearly seen that their lower base is flat, being located inside the coating at different depths, and morphologically not related to the coating structure or to the substrate relief. Almost all visible in Fig. 2 defects have different diameters and heights, while the angle at the apex of the conical “head”, i.e., the ratio of its diameter to height, changes insignificantly. This suggests that defects grow as the coating grows. Defects originate at a certain point on the surface of an already existing “growing” coating and subsequently increase their diameter and height further on with time. The growth of the coating and the defect occurs simultaneously and at the same rate, with the exception of the advanced growth of the “head” of the defect, since until the moment of extrusion, the “head” has to always be above the level of the coating surface.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InlensDuo Mode = SE
System Vacuum = 5.01e-06 mbar
Gun Vacuum = 9.13e-10 mbar
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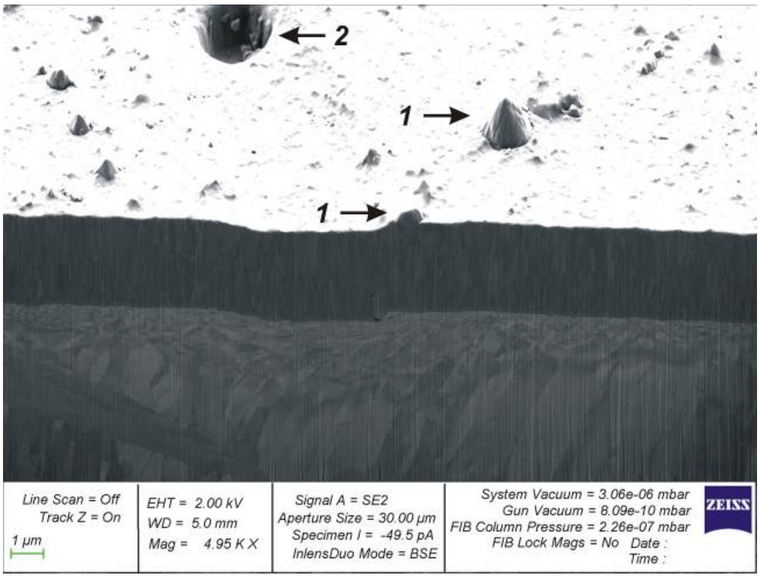
a)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WD = 5.0 mm
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InlensDuo Mode = BSE
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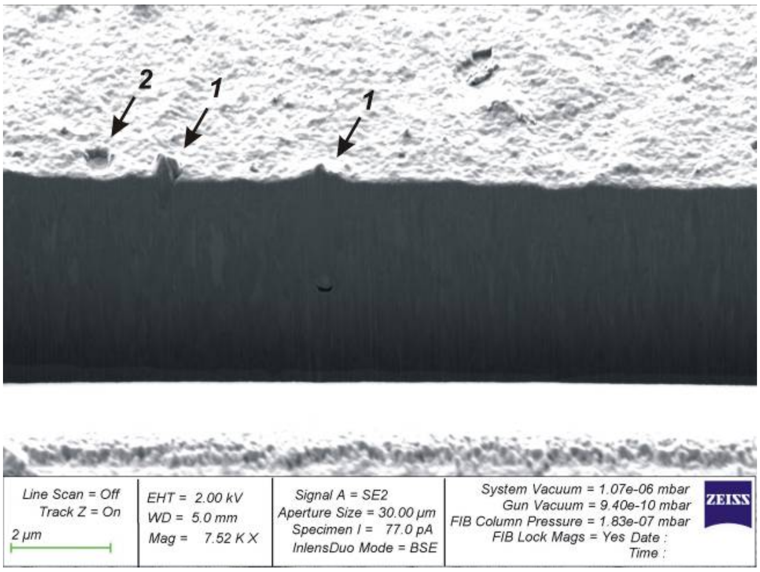
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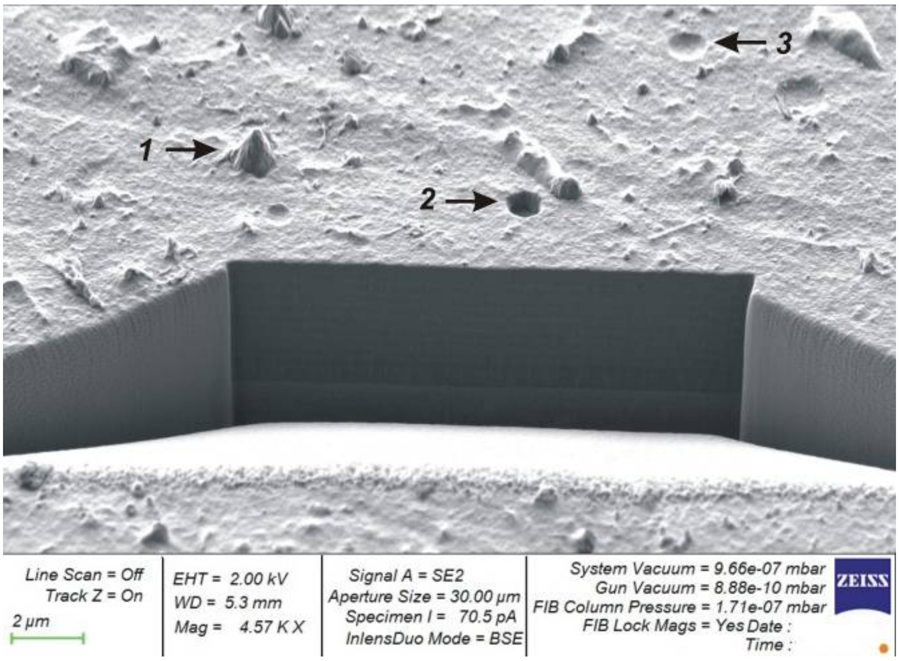

d)

Fig. 2. Substructural defects of ion-plasma TiAlN coatings, SEM: (*a*) on the coating surface in normal projection (marked with arrows); (*b*)–(*d*) on the surface of the coating and in cross-sections FIB

In the literature, both scientific and technological, concerning the formation of ion-plasma coatings, the substructural defects under discussion are often attributed to a droplet origin. It is assumed that the droplet phase formed in the chamber, when getting on the coating surface, burns it through and is fixed in the surface layer. When a drop crystallizes, its volume decreases, and it falls out leaving a cylindrical niche. This mechanism of formation of the defects under consideration contradicts the kinetics of their growth described above, based on the presented micrographs, and is also refuted by the experimental fact that defects of such geometry are observed not only during thermal evaporation, when the presence of a droplet phase cannot be avoided, but also during magnetron evaporation, whose regime eliminates the formation of drops in the chamber. Moreover, the morphology of the described defects under the arc and magnetron evaporators is identical. In addition, in the coatings obtained through the magnetron evaporation, these defects occur also in the case when all the components of the coating are infusible and temperature of their transition to the liquid state cannot be obtained under the applied coating modes [1, 2].

On the basis of the experimental data presented in [3], the authors put forward and validated a hypothesis on the endogenous (internal with respect to the coating) origin of the defects considered. Its physical essence is as follows. As you know, there are no real defect-free materials including coatings. In the process of formation of the crystal structure of the coating, inherent defects of various geometries are also formed: point, linear, surface, volumetric. Even the densest PVD coatings with an ordered structure, for example, monolayer thin films, contain various defects in the crystal structure [4–8]. The formation of dislocations under the growth of coatings, as in any crystallization process, is natural. Taking into account the nature of the deposition of ion-plasma coatings, when the modes of shear stresses in the coating are practically absent, the formation of screw dislocations is most likely. If such a dislocation reaches the coating surface, it forms a helical step. During deposition, as a result of the attachment of ions to a non-growing step, the latter will move along the surface rotating around a fixed axis. This is how the well-known mechanism of spiral (helical) crystal growth in the direction of the dislocation axis is implemented [9]. The dislocation growth mechanism is also used to explain the formation of “crystal whiskers”.

At a high density of screw dislocations on the surface, the distance between them is small, and the atomic layers formed on adjacent steps merge. In this case, the growth of the surface occurs in a cohesive way and gives a tolerably flat coating plane [10–12]. Dislocations distant wide apart form single cones. This is due to the fact that the portions of the step located closer to the dislocation axis rotate around it faster and require a smaller amount of deposited ions per unit time for growth than the distant portions. Thus, the twisting of the spiral under the screw growth occurs from the periphery to the dislocation axis, which determines the conical shape of the protruding part (“head”) of the growing crystal (Fig. 2). The shape of the helicoid spirals, that is, the size of the steps, is determined by the rate of their growth, which, in turn, depends on the concentration of the components in the growing crystallite. The shape of the areas of growing spirals at a fast growth rate and, accordingly, high over-saturations, is close to circular; at a lower growth rate and, accordingly, low over-saturations, it is polygonal. With an increase in the growth rate (with an increase in over-saturation), the angle of the growth cone becomes steeper, and the height of the steps in such spirals is large [13–16].

These features of helical growth suggest that the considered defects of ion-plasma coatings (Fig. 2) are formed at a high growth rate. This is indicated by the cylindrical shape of their “base” recessed into the coating, and a sharp conical shape of the “head” protruding above the coating surface. These geometric features also assume enrichment of conical crystallites in one of the coating components. Apparently, the higher growth rate of the spiral faces of the considered defect in comparison with the surrounding volume of the coating is the key reason for the isolation of the considered substructural defects in the coating and their subsequent extrusion.

Thus, from the terminological point of view, the defects of PVD coatings considered by us are substructural in origin, since:

— they originate at dislocations;

— for the place of localization, they are stochastic since the occurrence of dislocations in the coating is a random process;

— by morphology, they are helicoid since they are formed on screw dislocations and develop according to the mechanism of spiral growth.

Statistical data on the geometric characteristics of substructural defects in the Ti-Mo coating are shown in Fig. 3. Under the statistical analysis, the maximum diameter of the “head” measured over the coating surface was considered as the diameter of the defect *d*.

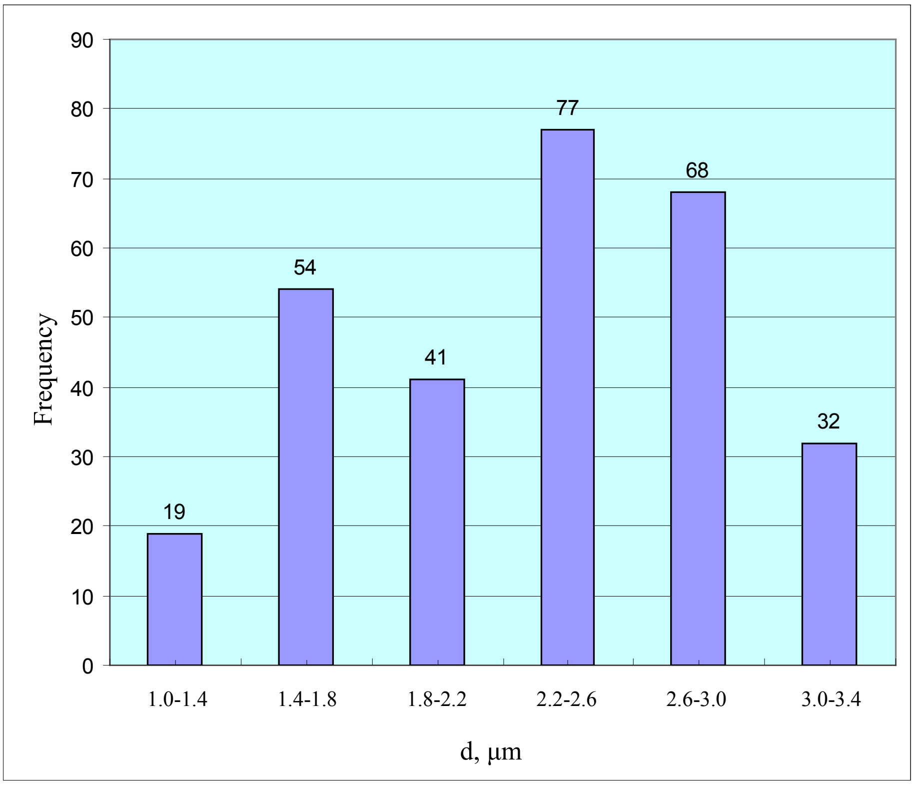

Fig. 3. Diameter *d* distribution of substructural defects in Ti-Mo coatings

The scatter of *d* values is quite significant and amounts to 0.95 – 3.3 µm, the average value is $d_{cp.}$ = 2.26 µm. For coatings of the Ti-Al-N system, the values of similar statistical parameters are: *d* = 1.2 – 4.0 µm; d_{cp} = 1.91 µm. The average statistical value of the parameter d/h_0, where h_0 is the height of the conical "head" of the defect protruding above the coating surface; for all studied coating compositions was 1.48, which corresponds to the angle at the apex of the "head" cone — 73°.

A similar statistical analysis based on the results of electron microscopic studies of the diameters of extruded defects (niches) d_e, has shown that the spread in d_e values is too large to assert that the extrusion of a defect occurs when a certain fixed critical value d_e is attained. Fig. 4 shows that in the coating of the Ti-Al-N system there are extrusions of various diameters, whose range of values is d_e = 1.3 – 4.6 µm. This interval overlaps with the interval of *d* values, and average values of the compared parameters are also close: d_{cp} = 1.91 µm and d_{ecp} = 2.17 µm.

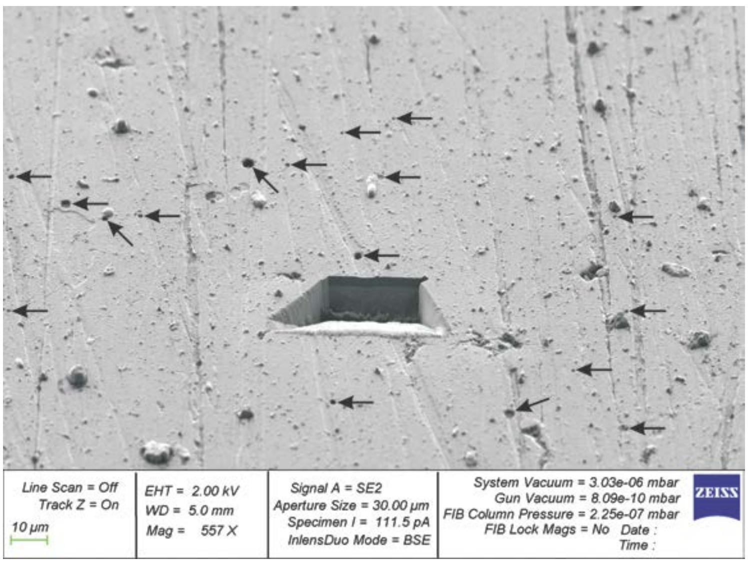

Fig. 4. Surface of TiAlN coating with substructural defects, SEM: arrows indicate extrusion defects;
in the center there is rectangular FIB cross-section

The available experimental data do not explain at what geometrical parameters of a growing substructural defect it is extruded from the coating, but they establish the baseline for further theoretical study on this aspect, for example, based on the classical theories of dislocation and nucleation.

Conclusion. Within the framework of the objectives set by the authors, the study gives certain intermediate results both on the classification characteristics of defects in ion-plasma coatings and on the investigation of defects of substructural origin. The substructural defects considered by the authors are found in coatings of various compositions and structures. Therefore, they can, despite their stochastic nature, claim to be a "systemic error of technology", which, however, does not have a fatal effect on the structure and properties of the coating due to the smallness of its size. Thus, they can, despite their stochastic nature, pretend to be a "systemic error of technology," which, however, does not have a fatal effect on the structure and properties of the coating due to the smallness of its size. More or less fully, the authors have studied this type of defects only in coatings of the Ti-Al-N system; therefore, the logical development of this research area involves expanding the range of coating composition.

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Claimed contributorship

O. V. Kudryakov: underlying concept and research plan; development of conceptual classification principles for defects in vacuum ion-plasma coatings; analysis of the experimental data; theoretical underpinning of the hypothesis

of the formation of “substructural defects” of coatings; academic advising; editing of the text of the paper. V. N. Varavka: formulation of the research objectives and tasks; organization and support of the methodological and experimental part of the research; preparation and formation of the text of the paper, results and conclusions. I. Yu. Zabiyaka: experimental studies using scanning electron microscopy, energy dispersive analysis and nanoindentation. Eh. A. Yadrets: sample preparation for research; participation in the application of experimental ion-plasma coatings; participation in obtaining the required experimental data. V. P. Karavaev: analysis of literary sources and own data on the subject area of the work; recordation and textualisation of the experimental data; preparation of illustrations for the paper.

All authors have read and approved the final manuscript.