Conditions and mechanisms of the defects formation in vacuum ion-plasma coatings

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Abstract. The results of studies of various structural features of vacuum ion-plasma PVD-coatings qualified by the authors as coating defects, are presented. Defects include a large volume of porosity, deformation of crystallites, exfoliation, etc. The systematization of defects is presented, depending on the nature of their nucleation (droplet, substructural, and growth defects) and on the character of their distribution in the coating (regular and stochastic). Coatings of various chemical composition were obtained by the method of ion-plasma deposition using both arc and magnetron evaporators. Experimental results are presented, the main array of which was obtained using a double-beam (ion / electron) electron microscope. A separate study on specific substructural defects was conducted. Statistical data on their geometrical dimensions and distribution in coatings is presented. Defects of this type have micron sizes (up to 5 μm in diameter) and a cylindrical shape with an axis perpendicular to the surface of the coating. A hypothesis about the dislocation mechanism of their nucleation on screw dislocations and the spiral mechanism of their growth has been put forward and substantiated.

1. Introduction

Obtaining of ion-plasma coatings is one of the most rapidly progressing scientific areas. Despite the high publication activity of scientists working in this field, we were not able to find deep fundamental research on the defects of ion-plasma coatings. The problem of defects is usually attributed to the category of technology and, if one wants to discuss it, not the substantive part of a scientific publication should be used, but a methodological one. Taking this consideration into account, for the present work devoted to the problem of defects in ion-plasma coatings, two aims were set: 1) to propose a classification basis for defects of this type of coating on the basis of a short review; 2) to conduct a study of one of the specific types of such defects, which is proposed to be called "defects of substructural origin".

To obtain coatings, vacuum-ion-plasma spraying units were used: the two-cathode system PLATIT π80, equipped with two arc evaporators, as well as the modernized TINA-900 unit, equipped with magnetron evaporators. The operating modes of the coating were the following range of parameters: deposition temperature was 300...450°C; pressure in the vacuum chamber was \((1.3...4.7) \times 10^{-2}\) mbar; bias voltage was 100...150 V. In accordance with the above parameters of vacuum ion-plasma technology, the resulting coatings belong to the category of PVD-coatings. The coatings of various nitride and metal systems were studied. The main results on the study of substructural defects were
obtained on TiAlN coatings. The coatings hardness had exceeding the level of 12…15 GPa, which allowed us to classify these coatings as wear-resistant.

Samples of steel 20Cr13, 08Cr18Ni10Ti, 38Cr2MoAl, 12Cr2Ni4 in a heat-treated state were used as substrates. The influence of the composition, structure, and properties of the substrate on the parameters of the coatings was not taken into account. Prior to coating deposition in the vacuum chamber, the surface of the samples was cleaned with a continuous stream of Ar ions for 5 min. To ensure high adhesion of the coatings, a sublayer of the metal was first applied to the sample surface cleaned by an ion beam.

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

2. Classification signs of defects in ion-plasma coatings

One of the main conditions for defect-free coatings deposition using ion-plasma technology is the minimum branching of the surface relief of the substrate. For the practical implementation of the technology, the roughness with parameters not lower than $R_a \leq 0.12 \mu m$; $R_z \leq 0.6 \mu m$ is considered a normative condition for the relief. Failure to comply with these conditions can lead to the formation of “regular growth defects” in the coating during deposition in the form of porosity, deformation of crystallites and lattices, internal stresses, etc. Separately located microroughness sites on a relatively smooth relief of the substrate lead to misorientation of the axes of the growing crystallites. It causes deformation of crystallites and forms incoherent intergranular boundaries with high porosity. A high density of microroughness sites leads to the formation of a large volume of porosity near the coating-substrate interface. A large macro-roughness of the surface of the substrate (for example, during rough grinding) forms high stresses in the coating. With weak cohesive bonds in the coating, it can lead to the coating delamination, and with weak adhesion, to the complete coating exfoliation. Coatings containing such defects generally do not meet even the most mild operating requirements in terms of protecting products from wear, corrosion, etc. impacts.

If the specified requirements for the surface roughness of the substrate are met and the coating is uniform in density and structure, this does not exclude the appearance of defects of a random nature in the coating. Such defects may include:

1) defects caused by the presence of a droplet phase;
2) defects of substructural origin.

Since the appearance of both types of defects in a specific microvolume of the coating is random in nature, unlike “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 low-melting coating elements. “Droplet defects” can be almost completely eliminated by magnetron evaporation. Examples of the droplet stochastic defects in ion-plasma coatings are shown in figure 1. On the surface, they have a characteristic shape with a flocculent configuration, which is indicated by dark arrows in figure 1 a. Getting on the coating surface during its application, the droplet phase disrupts the laminar dynamics of the normal growth of the coating, which manifests itself in the form of pores of irregular shape in the cross section of the coating (figure 1 b). In multilayer coatings, pores and structural inhomogeneities formed in the zones of the droplet phase can have an elongated shape. In this case, defects are located at the boundaries of neighboring layers saturated with a refractory and low-melting element (figure 1 c).

In general, all the coating defects considered above are of technological origin. Their appearance can be excluded or limited by optimization of the technological parameters of the ion-plasma method and equipment. As for defects of substructural origin, regulation or exclusion of their appearance in the coating seems unlikely, since they are caused by the nature of the real coating material. The results of the study of such defects are the main content of this work.
3. Defects of substructural origin

Examples of investigated defects of substructural origin are shown in the figure 1 a (shown by bright arrows) and in the figure 2. They have a characteristic geometrical shape: the cylindrical part of the defect is in the coating body, and the conical part protrudes above the coating surface. Under certain conditions, the defect that has formed is rejected (extruded, ejection) by the coating, leaving cylindrical recesses of the correct geometrical configuration in place of their localization. If the coating deposition process continues, the depression is filled with deposited ions of the coating material at a faster rate than the rest of the flat surface of the coating. Apparently, this is facilitated by the "edge effects" of the electromagnetic field generated by the bias voltage on the substrate. As a result, “healing” of cylindrical recesses occurs during the application process and the coating in this area is quite uniform. If the considered defects are extruded from the coating immediately before the end of the application process, the remaining cylindrical niches are clearly visible on the coating surface (figures 1 a and 2 a-d). Figure 2 shows a complete microscopic picture of the various stages of the life cycle of the substructural defects of the PVD coating of the TiAlN system.

Figure 2 a shows in a normal projection three defects of different sizes located at a distance of several microns from each other (marked by arrows). The conical shape of the protruding part of the localized defects and the cylindrical niche of the extruded defect are clearly visible. In figures 2 b-d
these stages of the existence of defects are presented in a three-dimensional picture: the conical “heads” protruding from the coating are indicated by the number 1, cylindrical niches by the number 2, and the number 3 in figure 4 c indicates the place of the niche at the “healing” stage. A volumetric image was obtained by dissecting the cross-section FIB, perpendicular to the surface of the coating, and then tilting the sample towards the detector by 15-28 degrees. Figures 2 b, c show only the cross section of the coating and its surface, and figure 4 d shows the entire cross section as a whole. The preparation of cross-sections made it possible to obtain a cross section of the studied defects (figures 2 b, c). It is clearly seen that their lower base is flat, located inside the coating at various depths and is not morphologically related to the structure of the coating or to the relief of the substrate. Almost all defects visible in figure 2 have different diameters and heights, while the angle at the apex of the conical “head” (that is, the ratio of its diameter to height) varies slightly. This gives reason to believe that defects grow as the coating grows: they nucleate at some point in time on the surface of an existing growing coating and subsequently increase their diameter and height over time; the growth of the coating and the defect occurs simultaneously and at the same rate, except for the outstripping growth of the “head” of the defect, since the “head” must always be above the level of the surface of the coating until extrusion.

In the literature, both scientific and technological, concerning the process of formation of ion-plasma coatings, the considered substructural defects are often attributed to the droplet phase. It is believed that the drop formed in the chamber, getting on the coating surface, burns through it and
“gets stuck” 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 considered defects contradicts the growth kinetics described above and based on the above micrographs. The droplet version is also refuted by the experimental fact that defects of a similar geometry are observed not only during thermal evaporation, when the presence of the droplet phase cannot be avoided, but also during magnetron evaporation, the regime of which eliminates the formation of droplets in the chamber. Moreover, the morphology of the described defects in an arc and magnetron evaporator is identical. In addition, for coatings obtained by magnetron evaporation, these defects are also encountered in the case when all the coating components are refractory and their transition temperature to the liquid state cannot be achieved under the applied coating conditions [1, 2].

Based on the experimental data presented, a hypothesis is stated forward about the endogenous (internal with respect to the coating) origin of the considered defects. A further part of the work is devoted to the substantiation of the hypothesis stated, which is based on the following physical model.

As you know, there are no real defect-free materials (including coatings). During the formation of the crystal structure of the coating, its inherent defects of various geometries (point, linear, surface, bulk) are formed, even the most dense PVD coatings with an ordered structure (for example, monolayer thin films) contain various defects in the crystal structure [3-6]. The formation of dislocations during coating growth is natural like any crystallization process. Given 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 comes to the surface of the coating, it forms a helical step. During deposition, as a result of the addition of ions to the step, the latter will move along the surface, rotating around a fixed axis. This implements a well-known mechanism of spiral (helicoidal) crystal growth in the direction of the dislocation axis. The idea of this mechanism — crystal growth without two-dimensional nucleation, — belongs to Sir Frederick Charles Frank (1949), like many creative points of the theory of dislocations. In 1951, F. Frank, W. Barton, and N. Cabrera proved the dislocation growth mechanism experimentally [7]. They also managed to explain the high growth rates of the crystal faces, their relief, many morphological features in the volume of crystals, their defects, physical properties, etc. Later, the dislocational growth mechanism was used to explain the formation of “crystalline whiskers”.

With 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 surface growth occurs as a united front and gives a relatively flat plane of the coating [8]. Dislocations remote over long distances form single cones. This is due to the fact that the sections of the step closer to the dislocation axis rotate around it faster and require a smaller amount of deposited ions (per unit time) for growth than the remote sections. Thus, spiraling during helical growth occurs from the periphery to the axis of dislocation, which determines the conical shape of the protruding part (“head”) of the growing crystal in figure 2. Schematically, the mechanism of spiral (helicoidal) growth with its main parameters is shown in figure 3. Growth spiral steps with sizes $\lambda$ and $h$ occurs in the direction of speed $\nu$, and the growth of the helicoid (conical "head" of the defect) — in the direction $\omega$. The shape of helicoid helices (i.e. step sizes) is determined by their growth rate, which, in turn, depends on the concentration of components in the growing crystallite. The shape of the areas of growing spirals at a fast growth rate (with large supersaturations) is close to circular, at a lower growth rate (with small supersaturations) polygonal. With an increase in the growth rate (with an increase in supersaturation), the angle of the growth cone becomes steeper; the height of the steps in such spirals is large [9-12].

The above features of helicoidal growth suggest that the considered defects of ion-plasma coatings, shown in Figure 2, are formed with a high growth rate. This is indicated by the cylindrical shape of their “base” buried in the coating and the sharp conical shape of the “head” protruding above the surface of the coating. These geometrical features also suggest the enrichment of conical crystallites with one of the coating components. Apparently, a higher growth rate of the spiral faces of the considered defect in comparison with the surrounding volume of the coating is the main reason for the isolation of the considered substructural defects in the coating and their subsequent extrusion.
Figure 3. Successive stages of step formation around the point of exit of a screw dislocation to the surface.

AO - the initial step formed by the exit to the surface of the screw dislocation; the dislocation line and its Burgers vector are located at point O perpendicular to the surface; the definition of the parameters in figures d and e are given in the text [13].

Thus, from a terminological point of view, the defects of PVD coatings that we are considering are substructural in origin, since they arise at dislocations; at the place of localization they are stochastic, since the occurrence of dislocations in the coating is a random process; according to morphology, they are helicoid, since they form on screw dislocations and develop according to the spiral growth mechanism.

Figure 4. Frequency size distribution of substructural defects in Ti-Mo coatings.

Statistical data on the geometrical characteristics of substructural defects in the Ti-Mo coating are shown in figure 4. In the statistical analysis, the maximum diameter of the “head” measured on the surface of the coating was considered as the defect diameter $d$. The scatter of $d$ values is quite
significant 0.95...3.3 μm, the average value was \( d_{med} = 2.26 \) μm. For TiAlN coatings, similar statistical results: \( d = 1.2...4.0 \) μm; \( d_{med} = 1.91 \) μm. The average statistical value \( d/h_0 \) (where \( h_0 \) is the height of the conical “head” of the defect projecting above the surface of the coating) for all investigated coating compositions was 1.48, which corresponds to an angle of 73 degrees at the apex of the cone “head”.

![Figure 5](image)

**Figure 5.** The surface of the TiAlN coating with substructural defects, SEM: arrows indicate extrusion defects; in the center – a rectangular cross-section FIB.

A similar statistical analysis based on the results of electron microscopic studies of the diameters of extruded defects (niches) \( d_e \) showed that the scatter of the \( d_e \) values is quite large to suggest that the extrusion of the defect occurs when a certain fixed (critical) value of \( d_e \) is reached. Figure 5 shows that extrusions of various diameters were found in the TiAlN coating, the range of values of which was \( d_e = 1.3...4.6 \) μm. This interval overlaps with the interval of values of \( d \), and the average values are also close: \( d_{med} = 1.91 \) μm and \( d_{e med} = 2.17 \) μm. However, the available experimental data do not answer the question “At what geometric parameters of a growing substructural defect does it extrude from the coating?” But they form the basis for further theoretical studies of this aspect, for example, on the basis of classical theories of dislocation and nucleation.

4. Conclusion

According to our aims, the work gives certain intermediate results both on the classification features of defects in ion-plasma coatings and on the study of defects of substructural origin. However, the first of these areas involves addition and discussion, and the second can develop in two directions. First, the substructural defects that we examined are found in coatings of various compositions and structures. Therefore, they can, claim the title of “systemic technology error”, despite their stochastic nature, which does not, however, have a fatal effect on the structure and properties of the coating due to its small size. We more or less fully studied this type of defects only in the TiAlN coatings; therefore, the first direction involves expanding the range of coatings. Secondly, the conducted studies leave open the question of the physical mechanism of extrusion of substructural defects. The high surface energy of the boundaries between the defect and the coating in the TiAlN system indicates their low strength, which facilitates the defect extrusion mechanism. But this does not reveal the physical nature of the mechanism itself. The issue of the mechanism requires a separate study, which is beyond the scope of this work because it lies more in the field of mesomechanics and computer modeling [14-17] than in the field of materials science.
Acknowledgments
The authors are deeply grateful to prof. L.M. Petrov (JSC “NIAT”) for a fruitful discussion of the topic and valuable comments. The work was carried out with financial support from Russian Foundation for Basic Research (project code 18-08-00546).

References
[1] Varavka V N, Kudryakov O V and Ryzhenkov A V 2015 Multilayered Nanocomposite Coatings for Anti-Erosive Protection Piezoelectrics and Nanomaterials: Fundamentals, Developments and Applications ed I A Parinov (New York: Nova Science Publishers) chapter 5 pp 105-132
[2] Kudryakov O V, Varavka V N, Zabiyaka I Yu and Morozkin I S 2016 Int. J. Res. 46 (4) 117-20
[3] 2006 Nanostructure Coatings eds A Cavaleiro, J T de Hosson (Springer Science+Business Media, LLC) 752 p
[4] Freund L B and Suresh S 2009 Thin film materials: stress, defect formation and surface evolution (Boston: Cambridge University Press) 750 p
[5] Cleland A N 2003 Foundations of Nanomechanics (Berlin, Heidelberg, New York: Springer-Verlag) 436 p
[6] Ilyin A A, Plihunov V V, Petrov L M and Spector V S 2014 Vacuum ion-plasma treatment (Moscow: INFRA-M) 160 p [in Russian]
[7] Burton W K, Cabrera N and Frank F C 1951 Phil. Trans. R. Soc. Lond. A 243 299
[8] Chernov A A 1980 Modern crystallography (Crystallization processes vol 3) ed B K Vainshtein (Moscow: Nauka) 408 p [in Russian]
[9] Rashkovich L N, Petrova E V, Shustin O A and Chernevich T 2003 Sol. St. Phys. 45 (2) 400-7
[10] Ester G R, Price R and Halfpenny P J 1999 JOP: Applied Physics 32 (10A) 128-33
[11] Ester G R and Halfpenny P J 1998 J. Cryst. Growth 187 (1) 111-7
[12] Murugakoothan P, Kumar R M, Ushasree P M, Jayavel R, Dhanasekaran R and Ramasamy P 1999 J. Cryst. Growth 207 (4) 325-9
[13] Available at: www.chem.msu.su/rus/teaching/materials/7cryst.pdf (accessed: 20.07.2019)
[14] Vasiliev A S, Sadyrin E V, Mitrin B I, Aizikovich S M and Nikolaev A L 2018 Rus. Eng. Res. 38 (9) 735-7
[15] Volkov S S, Vasiliev A S and Sadyrin E V 2018 MATEC Web of Conf. 226 03018
[16] Argatov I and Mishuris G 2016 Applied Mathematical Modelling 40 (4) 2541-8
[17] Śliwa A, Mikula J and Dobrzański L A 2010 Journal of Achievements in Materials and Manufacturing Engineering 41 (2) 164-71