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CHARACTERIZATION OF ARC-PVD ZrN NANOSTRUCTURED COATINGS BY USING THE FRACTALS THEORY

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Nanostructured ZrN coatings for hardening of a thin-walled cutting tools operating under cyclic loads conditions have been obtained and investigated. The structure and mechanical properties of nanocoatings have been examined. It was revealed that the ZrN coating improved the properties of thin-walled cutting tools. ZrN surface morphology was theoretically substantiated with the application of the fractals theory.

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INTRODUCTION

Nitride coatings obtained by the PVD method are widely used for cutting tools hardening. The general development trend of ion-plasma technologies during the past decades is the improvement of coatings functional characteristics. It requires not only equipment improvement but also an integrated approach to development of parameters of the application technology to obtain coatings with certain properties depending on the operating conditions. In this regard, it is important and relevant to study experimental and theoretical influence of the structure of coatings deposited at certain parameters on their physical and mechanical properties.

Zirconium nitride contains a mixture of ionic, covalent and metallic bonds that provide it with an unusual combination of performance properties, such as high hardness, wear resistance, corrosion resistance, higher fracture toughness, as well as high thermal conductivity. Due to these properties, such coatings are widely used as protective and bioinert layers in industry for cutting tools hardening, in medicine [1] (including implants [2]) as well as parts exposed to high temperatures [3].

To study the structure and evaluate the mechanical properties of such nanocoatings, various experimental methods such as optical and electron microscopy, X-ray diffraction, micro-X-ray spectral, micro- and nanohardness measurements, etc. are currently used. Theoretical studies of images using modern numerical methods with the solution of differential equations and the calculation of partial derivatives [4] make it possible to describe the processes of structure formation, both in the initial state, and to identify changes occurring during operating conditions. In [5], optical and mathematical analysis that describes the degree of variability in the identified phases is used to analyze the dispersion of structural components and estimation of the local heterogeneity of nanocoating. The authors [6] theoretically investigated the dependence of the defectivity (pore formations) of films on the conditions of their deposition. In addition, it is possible to use a fractal approach to study the influence of structure on physical and mechanical properties [7]. The reason for this is the geometric configuration of the structural elements of many materials, which is not always adequately approximated by Euclid's integer figures (circle, square, etc.) at various scale levels and is typical for semi-quantitative (point балловых) estimates. This leads to a loss of valuable information about the investigated structure and to a decrease in the accuracy of structure-property prediction models. The fractal approach is based on random choice of measurement metrics when calculating their fractal (fractional) dimension. From a physical point of view, fractal dimensionality describes the density of the filling of space by the object of study. Therefore, the fractal geometry of B. Mandelbrot [8] makes it possible to give a more differentiated estimation of structures of varying geometric complexity based on value of their non-integer dimension. Fractal formalism is successfully used in modeling the structure and properties of steels [9], cast iron [10], express prediction of the materials hardness [11], estimation of the influence of non-metallic parts on the mechanical properties of metals [12], ranking the quality criteria of multiparameter technologies [13], etc. The structure of zirconium surfaces is also successfully studied using non-quantitative dimension, which confirms the relevance of choosing a fractal approach in this paper. For example, the fractal nature of graphene ZrN in the visible and near-infrared ranges have been investigated in [14]. The fractal growth of zirconium nanoparticles at the induction stage of the sol-gel process is described in [15]. So this paper is devoted to studying of the influence of chemical composition and structure configuration on the ZrN nanocoating properties (obtained by the PVD method) using the fractal theory.

EXPERIMENTAL SETUP

The researches have been carried out on the example of a thin-walled cutting tools, installed on a semi-automatic sealer of corrugated boxes SIAT model S8 (manufactured by Italy), which are used in the food industry. The ZrN coating was deposited using Bulat-6 type facility. A pulsed voltage generator with adjustable amplitude, duration and frequency of repetition pulses was developed to prevent overheating of the thin-walled instrument. This made it possible to apply the nanostructured coating ZrN at a temperature of 150 °C.

The studies of instrument surface structure hardened by ZrN coating were carried out using a scanning electron microscope JEOL JSM-6390LV. The "Nanoindentor G200" device with a Berkovich diamond pyramid was used to determine the mechanical characteristics of the applied nanocoating ZrN.

The fractal dimension D was calculated using the developed technique [16] on the base of analysis of images of the applied ZrN nanocoating. The proposed technique increases the reliability of the fractal dimension of the identification object due to the application of cellular and point methods for its calculation.

Cellular dimension (1) was calculated following the formula of F. Hausdorff [17]:

$$D = -\lim_{\delta \to 0} \frac{\ln N(l)}{\ln l}, \qquad (1)$$

where N(l) is the number of cells with a linear size l into which the image of the structure is divided.

Point dimension (2) [18] was based on the estimation of the probabilities sum P (m, L) of cells with dimensions L, which contain the number of points m (pixels for computers). The fractal dimension is proportional to the average value of the cells Ñ(L)

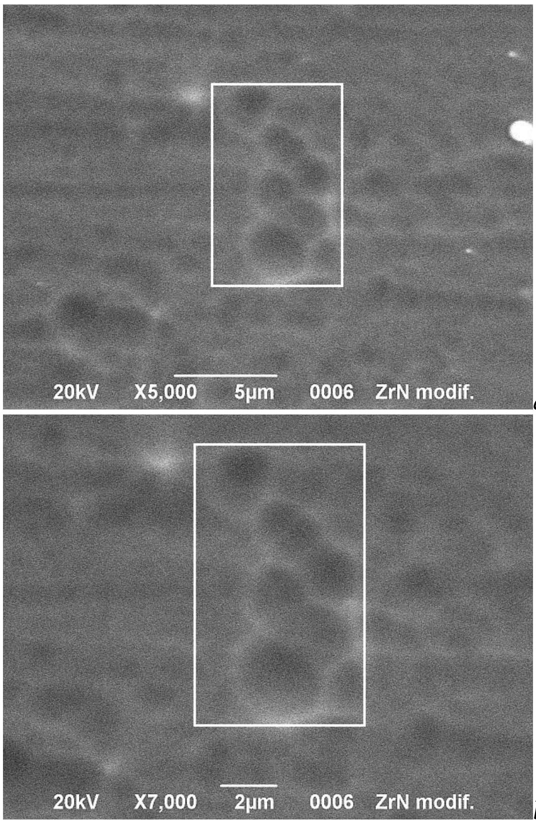
$$\tilde{N}(L) = \sum_{m=1}^{K} (1/m) P(m, L) \sim L^{-D}. \qquad (2)$$

RESULTS AND DISCUSSION

The analyses of received SEM images shown that ZrN coating deposited using the pulsed generator, has a honeycomb structure with a cell size of 0.2 to 2 µm (as seen in Fig. 1). At the same time, the hardened instrument surface contains a small number of macrodefects identified as droplets belonging to the cathode material. The maximal size of macroparticles in the ZrN coating does not exceed 5 µm (as seen in Figs. 2, 6).

The self-similarity of ZrN coating structure was estimated at a magnification of 5.000 times (white rectangle in Fig. 1,a) and 7.000 times (white rectangle in Fig. 1,b) for evaluation it belongs to fractal structures.

The difference in the values of fractal dimension is equal 0.012, that`s indicate the existence of a self-similarity of the structure, i.e. confirms its fractal nature. The difference in values of fractal dimension at different levels of the structure representation is obtained at analyzing the real structures of materials. Such a difference in dimensionality values can be explained from the point of view that when the scale of structure representation increases new details of the elements of the structure inherent in a given scale of its representation contribute to the change values of the fractal dimension, which are difficult to identify at a smaller increase.



a

b

Fig. 1. Fractal dimension of the selected (white rectangle) structure fragments 1.978 (a) and 1.990 (b)

Various structural components of ZrN coating at an increase of 5000 times (see Fig. 2) were investigated. The results of calculation of the structure fractal dimension are shown in Fig. 3. This indicator of the coating structure (matrix) was calculated on the basis of an average value of the cellular D1 (see green curve, Fig. 3) and point D2 (see purple curve, Fig. 3) dimensions and corresponds to the value of 1.904. The macrodefects (droplets) fractal dimension was also estimated on the basis of an average value of the cellular D3 (see red curve, Fig. 3) and point D4 (see yellow curve, Fig. 3) dimensions of light elements structure and is equal to 1.753.

Unlike the basic structure (matrix), macrodefects have 8.61 % lower values of fractal dimension, which from a physical point of view indicates their lower stability and is associated with non-equilibrium conditions for the formation of drip component.

The physical and mechanical properties of ZrN coating were investigated. The influence of the effect hardening on tool resistance increasing was also determined. Physical and mechanical characteristics showed that such a ZrN coating has indicators significantly higher than that of a similar nitride layer obtained under other deposition parameters. Such properties of ZrN coating will increase the wear resistance of the tool working surface layer.

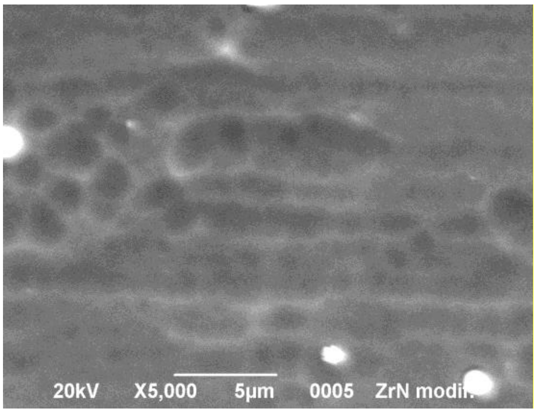


Fig. 2. SEM image of ZrN coating

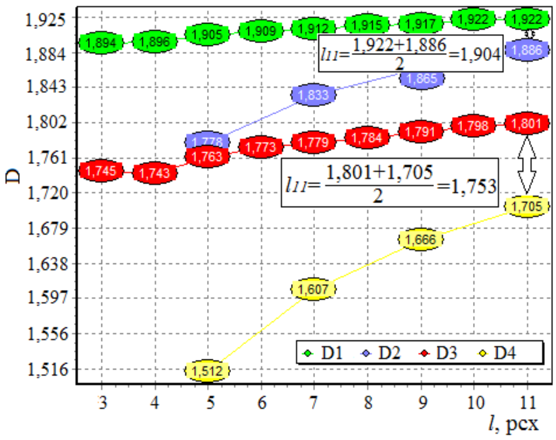


Fig. 3. Convergence of cellular and point dimensions

The nanohardness maximum value reaches 44.2 GPa [19] which is 32.8 % higher than that of the nanocoating of ZrN applied using a magnetic curvilinear filter and 39 % using an RF discharge [20]. The maximum elasticity modulus of deposited coating is 506.6 GPa and exceeds the values for ZrN coating by 23.3 % (using a filter) and 50.2 % (with RF discharge). The obtained difference in physical and mechanical characteristics is associated with the features of formed structure. The experimental data of mechanical properties (effective elastic modulus E*, shear modulus G, yield stress point σ_T, coefficient of resistance to plastic deformation H^3/E^{*2}, nanohardness H, elastic modulus E, plasticity index H/E) are shown in Table.

Mechanical properties of ZrN coating

N	Prop.					
	E, GPa	**H, GPa**	**H/E**	**H^3/E^{*2}**	**G, GPa**	**σ_T, GPa**
1	450.194	38.658	0.086	0.251	281.37	12.89
2	419.546	34.743	0.083	0.209	262.22	11.58
3	458.084	39.602	0.086	0.260	286.30	13.20
4	409.462	33.515	0.082	0.197	255.91	11.17
5	506.594	44.256	0.087	0.297	316.62	14.75
6	490.347	42.000	0.086	0.271	306.47	14.00
7	397.608	32.778	0.082	0.196	248.51	10.93

Theoretical calculations of fractal dimension were carried out in seven local sections of the coating to establish the relationship of the structural components of ZrN nanocoating with the level of mechanical properties (Fig. 4).

Relation between the fractal dimension of the ZrN coating and the mechanical properties are shown on Fig. 5. Analysis of constructed fractal models (R^2=0.8292... 0.8739) on Fig. 5 indicates the sensitivity of the studied properties of the coating to its fractal dimension. This fact points out an influence of the configuration of coating structure elements on the properties expressed through its fractal dimension. In all cases there is improvement of ZrN coating properties with an increase of the fractal dimensions of local areas. The maximal values are fixed in the fifth local area shown in Fig. 4 due to the structure configuration which contribute to an increase of fractal dimension of the analyzed area compared to the dimensions of other areas.

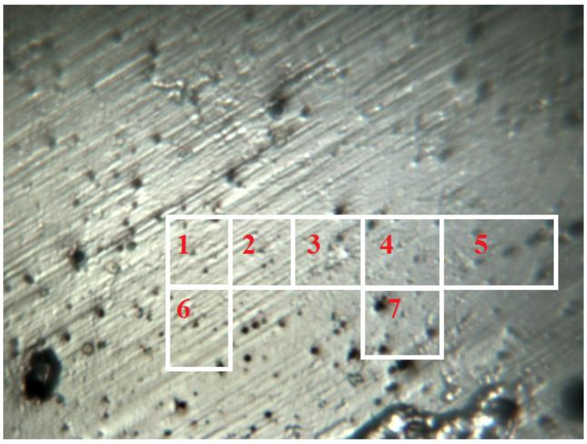


Fig. 4. Image of surface seven local sections of the ZrN coating for which were carried out theoretical calculations of fractal dimension. Magnification ×1000

As a result of the use of fractal analysis in combination with the use of nanoindentation method, it can be assumed that the coefficient H^3/E^{*2} of coating makes a significant contribution to the stability of structure and properties of surface layer. In confirmation of this, the maximal coefficient of pair correlation $R^2 = 0.8739$ for the indicator H^3/E^{*2}, which characterizes the resistance of ZrN layer plastic deformation (see Fig. 5,c) was obtained.

Thus, the positive effect of ZrN coating structure on increasing the physical and mechanical properties of the hardened surface of a thin-walled cutting tool has been theoretically substantiated using the theory of fractals. The determined relation between structure fractal dimensionality and coating properties indicate the importance of choosing a measurement metric when modeling them. The obtained results show the possibility of using fractal dimension as an indicator of structural changes in the coating surface. The effect of coating composition taking into account drops on its fractal dimension has been discussed in the paper.

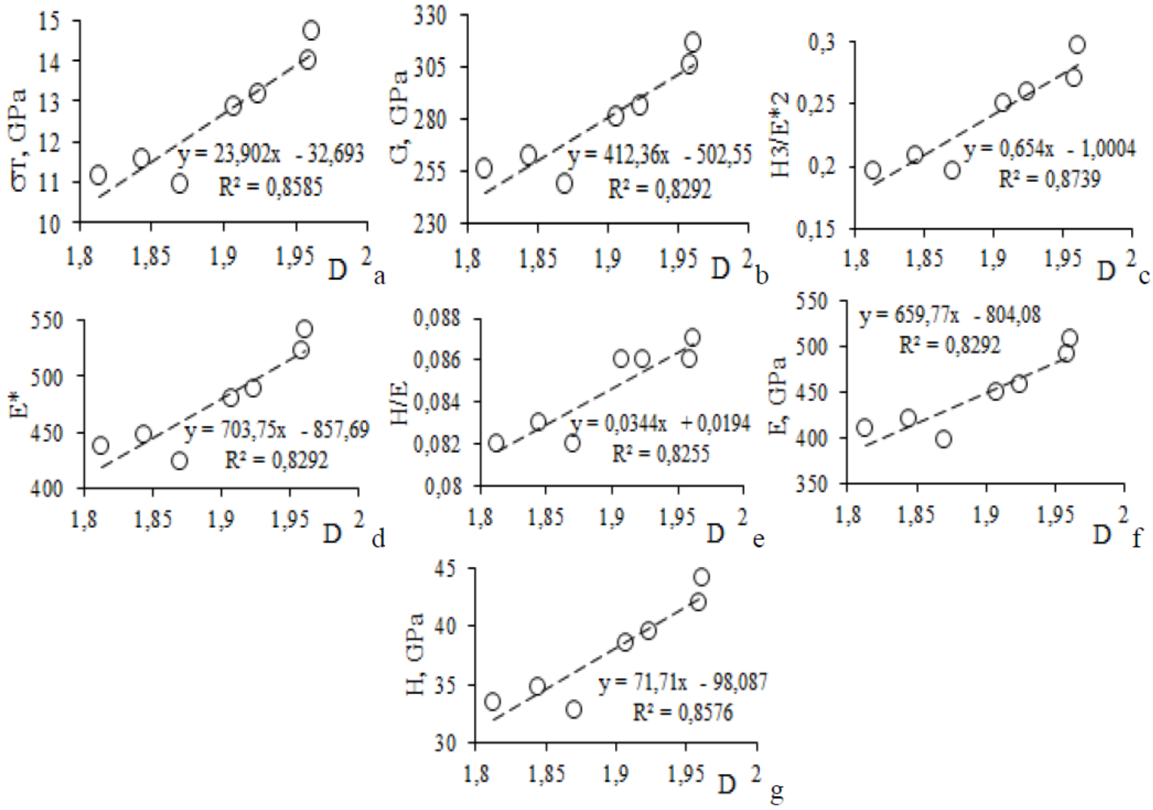
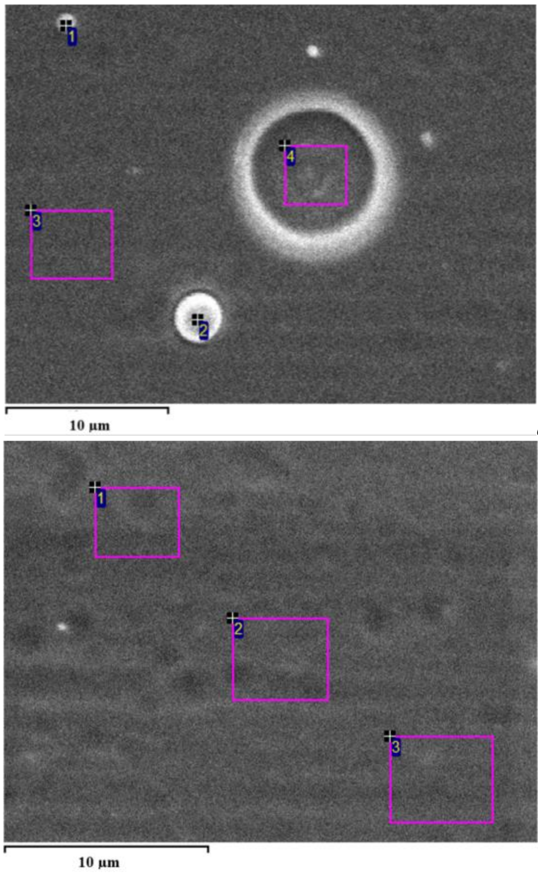


Fig. 5. Relation between the fractal dimension of the ZrN coating and the mechanical properties: yield stress point σ_T (a); shear modulus G (b); coefficient of resistance to plastic deformation H^3/E^{*2} (c); effective elastic modulus E (d); plasticity index H/E (e); elastic modulus E (f); nanohardness H (g)*

Two areas of the coating with droplets (area 1) and without droplets (area 2) were investigated (see Fig. 6). Fig. 6,a shows the composition of area 1, where spectra 1, 2 and 4 – characterize the regions with droplets. Spectra 3 Figs. 6,a,b correspond to the coating structure (matrix).

As calculations results showed the fractal dimension of the droplets increases with an increase in the oxygen content (Fig. 7,a) and zirconium (see Fig. 7,b) and decreases with an increase of carbon and nitrogen content (see Fig. 7,a). Change of the fractal dimension of the ZrN coating local areas is expressed through the influence of the chemical composition elements. These results confirm the conclusions of I.V. Tananaev [21], who developing N.S. Kurnakov's ideas about phase diagrams and diagrams composition – property, noted the need to replace the triad (composition – structure – properties) with a quadriga, which also includes structural characteristics and dispersion of the structure components. This approach allows to take into account the influence of the metal structure elements on its properties in order to clarify them. However, the difficulty in obtaining such results lies in the fact that many elements of the metal structure are difficult to quantify due to their complex configuration. In this case, a change of the geometric configuration of the structural components of local areas is associated with a change of their chemical composition. This provides new information about the composition-structure-property relation.



a

b

Fig. 6. SEM images of ZrN coating area 1 with droplets (a) and area 2 without droplets (b)

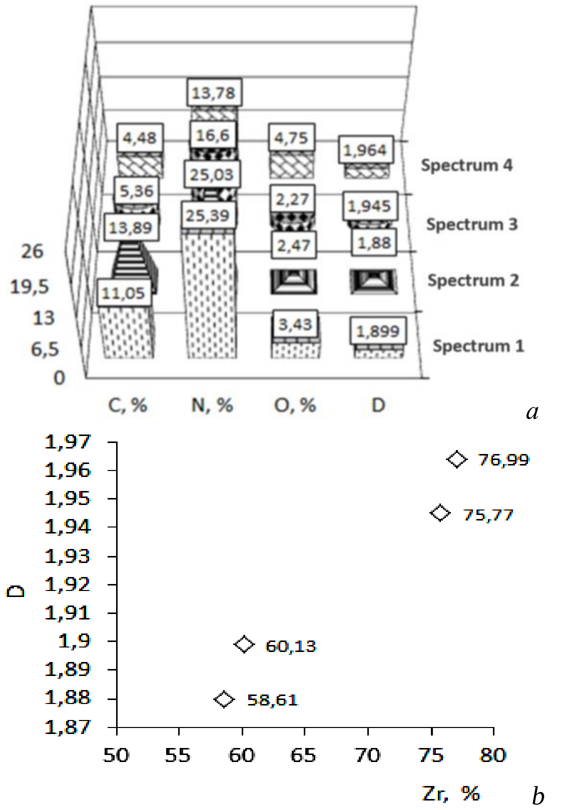


Fig. 7. Relation between fractal dimension D and composition C, N, O % (a), Zr% (b) of ZrN coating (Fig. 6,a)

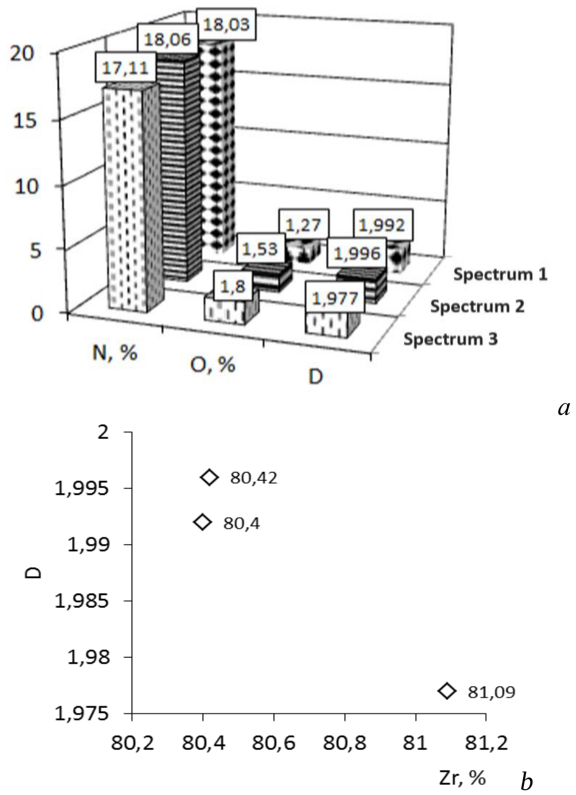


Fig. 8. Relation between fractal dimension D and composition C, N, O % (a), Zr% (b) of ZrN coating (Fig. 6,b)

The fractal dimension varied from 1.977 to 1.996 (Fig. 8), i.e. within of 0.01. Thus, it is confirm that structure is self-similarity. The sensitivity of dimensionality to changes in the content of chemical elements N, O (see Fig. 8,a) and Zr (see Fig. 8,b) was recorded. The influence of the elements content N, O (see Fig. 8,a) and Zr (see Fig. 8,b) on dimensional was recognized. In this case, the fractal dimension of areas 1–3 increases with increasing N content and decreases with increasing Zr content.

It should be noted that the fractal approach could be used in the study of the influence of the structure and chemical composition on the ZrN coating properties. Also, it could be applied to evaluate the influence of the contribution of individual macrodefects of the structure (droplets) on the properties.

CONCLUSIONS

1. The paper performed an ion-plasma coating technology using Bulat-6 type facility modernized by a pulsed voltage generator with controllable amplitude, pulse duration and repetition frequency. This allowed to deposit the nanostructured ZrN coating at a temperature of 150 °C and avoid overheating of the thin-walled tool.

2. ZrN nanocoating structure images obtained using an electron microscope (SEM) were analyzed on the basis of the fractals theory (based on the search for the convergence of cellular and point dimensions). A minimal difference in the analyzed indicator values D was revealed and it`s shown that it does not exceed 0.012. This makes it possible to evaluate the contribution of smaller structural components and testifies to its self-similarity.

3. It was also found that the hardening of ZrN nanocoating leads to the formation of a film on the working surface with effective mechanical characteristics. It is important to note that these characteristics are significantly higher than that of a similar nitride layer obtained under other deposition parameters, which provides an increase in the durability of food industry tools. The maximum nanohardness value reaches 44.2 GPa, which is 32.8 % higher than that of the ZrN nanocoating applied using a magnetic curvilinear filter and 39 % using a RF discharge. The elasticity modulus of the deposited coating is 506.6 GPa and exceeds the values for the similar ZrN coating by 23.3 % (using a filter) and 50.2 % (with RF discharge).

4. Dependence between mechanical properties and ZrN coating structure have been established theoretically. The fractal dimension D reaches 1.961 in analyzed structure areas with the maximum level of properties. At the same time, it was obtained that a significant contribution to stability of the structure (with a maximum coefficient of pair correlation $R^2 = 0.8739$) is made by the indicator H^3/E^{*2} which characterizes the resistance of ZrN layer plastic deformation. It has also been shown an influence of the elements of coating chemical composition on its nanoproperties.

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ХАРАКТЕРИСТИКА НАНОСТРУКТУРНИХ ПОКРИТТІВ ZrN З ВИКОРИСТАННЯМ ТЕОРІЇ ФРАКТАЛІВ

С.П. Романюк, В.М. Волчук, А.В. Таран, К. Новаковська-Лангер, О.В. Бирка

Отримано та досліджено наноструктуровані покриття ZrN для зміцнення тонкостінних ріжучих інструментів, що працюють в умовах циклічних навантажень. Досліджено структуру та механічні властивості нанопокриттів. Виявлено, що покриття ZrN покращує властивості тонкостінних ріжучих інструментів. Морфологія поверхні ZrN теоретично обґрунтована із застосуванням теорії фракталів.