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FRACTAL STRUCTURE OF MULTI-ELEMENT COATINGS

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The paper shows that the surface layer of a metal is a nanostructure. This surface layer possesses nonlinear properties that depend on its size and all physical properties. The phenomenon of electron emission from a metal under the action of an external electric field is considered. Taking into account the dimensional dependence of the conductivity of the surface layer leads to the Mandelbrot equation. This result shows that the surface layer has a fractal structure. The study of fluctuations of the contact potential difference on samples made of structural metal alloys is carried out. It has been experimentally established that the magnitude of the fluctuation of the contact potential difference at one point of the sample does not depend on the surface roughness. Several mechanisms that lead to fluctuations in the contact potential difference are considered. The first mechanism is associated with the thermal motion of the atoms inside the sample. The second mechanism is related to the processes occurring on the surface of the sample. The third mechanism is related to the processes in the measuring instrument.

Keywords: coating, microstructure, fractal, microhardness, friction, surface tension

Introduction

In the second half of the 20th century, a mathematical content was found in all existing and observed material objects, in their geometry, structure and behavior. Thus the idea of the fractal geometry of Nature of Benoit Mandelbrot [1] arose. Fractal changed the philosophy of measures. Fractal relationships between scales, fractal parameters and conventional quantitative parameters are used in many studies to describe the subtle world of fractals from nucleation to growth, from micro-macro and from local to global.

In [2, 3] a fractal analysis of the basic elements of the microstructure, such as the arrangement of atoms or molecules, dislocations, grains, surface particles, boundaries, etc., was carried out. Since microstructures are closely related to the properties of solids, a qualitative description of the images of microstructures may be insufficient and incapable of requirements for the development of materials. Therefore, quantitative measurements of the basic elements become more and more necessary. A new classification of basic elements in microstructures is introduced in terms of fractal dimension, as well as introduction to digital imaging, image processing and measurement of parameters.

In work [4] theoretical and practical aspects of the tribological process with the use of synergistic, fractal and multifractal methods, as well as fractal and multifractal models of self-similar tribosystems, developed on their basis are considered. They provide a comprehensive analysis of their effectiveness, and also consider the method of flicker-noise spectroscopy with detailed parametrization of friction of the surface roughness. All models, problems and solutions are taken and tested on the basis of real examples of the oil and gas industry.

The paper [5] is the first systematic exposition of the theory of local iterated functional systems, local fractal functions and fractal surfaces and their connections with wavelets. In [6], for example, in Chapter 4, two- and three-phase fractal methods are used to develop models of capillary pressure curves that characterize the distribution of porous media in pore sizes. The theory of percolation provides a theoretical basis for flow and transport modeling in disordered networks and systems. Therefore, following Chapter 4, in Chapter 5, the fractal basis of the theory of percolation and its application in surface and subsurface hydrology is discussed. Chapter 6 shows that fault networks are modeled using fractal approaches. Chapter 7 presents various applications of fractals and multifractals for petrophysics and the corresponding field in petroleum engineering. In Chapter 8, we present the practical advantages of fractals and multifractals in geostatistics on a large scale, which are widely used in stochastic hydrology and hydrogeology. Multifractals are also widely used to model atmospheric characteristics, such as precipitation, temperature and the shape of clouds.

The analysis of time series over several decades was carried out in the fields of physics, hydrology, atmospheric research, civil engineering and water resources. Therefore, in Chapter 11 fractal, multifractal, and multifractal fluctuations are proposed, which can be used to study the temporal characteristics of a phenomenon, such as the discharge of a stream at a particular point in the river. Work [7] gives an idea of the advantages and limitations of using fractals in biomedical data. Also, the properties of biological data in relation to fractals and entropy are considered, as well as the connection with health and aging. The paper presents a detailed description of new methods of physiological signals and images based on fractal and chaotic theory. As follows from a brief and incomplete survey, fractals are used in materials science [2], tribology [4], hydrology [6], biology [7], etc.

In this paper, we consider the fractal structure and physical properties of the ion-plasma coating.

1. Experimental procedure

In this work we used multi element cathodes of Cr-Mn-Si-Cu-Fe-Al, Zn-Al, Mn-Fe-Cu-Al, obtained by induction melting, and Ti cathodes. Coatings were applied to steel samples by the ion-plasma method at the vacuum installation NNV-6.6I1. Electron microscopy was performed on a scanning electron microscope MIRA 3 from TESCAN. The investigations were carried out at an accelerating voltage of 20 kV and an operating distance of about 15 mm. For each sample, 4 images were taken from 4 surface points at different magnifications: 245 times, 1060 times, 4500 times and 14600 times. And also an energy-dispersive analysis was carried out at 4 points of the surface of each sample.

The optical microstructure was studied with the Epikvant metallographic microscope, and at the nanoscale with the NT-206 atomic force microscope. Investigation of microhardness of coatings was carried out on a microhardness meter HVS-1000A. Tribological studies were carried out on the installation described in [8]. The dependence of the microhardness of the deposited coating on its thickness is described by the formula [9]:

$$\mu = \mu_0 \cdot \left(1 - \frac{d}{h}\right), \qquad (1)$$

where μ is the microhardness of the deposited coating; μ0 is a massive sample; h is the thickness of the deposited coating.

The parameter d is related to the surface tension σ by the formula:

$$d = \frac{2\sigma\upsilon}{RT}, \qquad (2)$$

where σ is the surface tension of a massive sample; υ is the volume of one mole; R is the gas constant; T is the temperature.

In the coordinates $\mu \sim 1/h$ ($1/h$ - the inverse thickness of the deposited coating), a straight line is obtained, the tangent of the slope angle which determines d, and the surface tension of the deposited coating (σ) is calculated from formula (2).

Show that the structure under consideration is fractal, using the ratio of the perimeter and the area of the planar figures to the structures formed in the surface layer of the material. It is known [10] that for each family of flat geometric figures, the ratio of the perimeter L to the area remains constant and does not depend on the size of the figure:

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$$\gamma = \frac{L}{S^{1/2}}. \qquad (3)$$

However, if the structure is fractal, then, as shown in [10], it should be replaced by:

$$\gamma_D = \frac{L(\lambda)^{1/D}}{S(\lambda)^{1/2}}. \qquad (4)$$

where D is the fractal Hausdorff dimension of the structure under consideration.

The ratio (4) does not depend on the size of the fractal structure, but depends on the choice of the standard of length ℓ, since the length of the self-similar boundary of the fractal L (ℓ) depends on the length of the standard with which it is measured and L (ℓ) → ∞ as ℓ → 0. The area of the fractal remains finite as ℓ → 0 and is defined as:

$$S(\lambda) = N\lambda^2, \qquad (5)$$

where N is the number of cells of area ℓ2 necessary to cover a flat fractal.

In general, fractal structures with self-similar boundaries satisfy the perimeter and area ratio [10]:

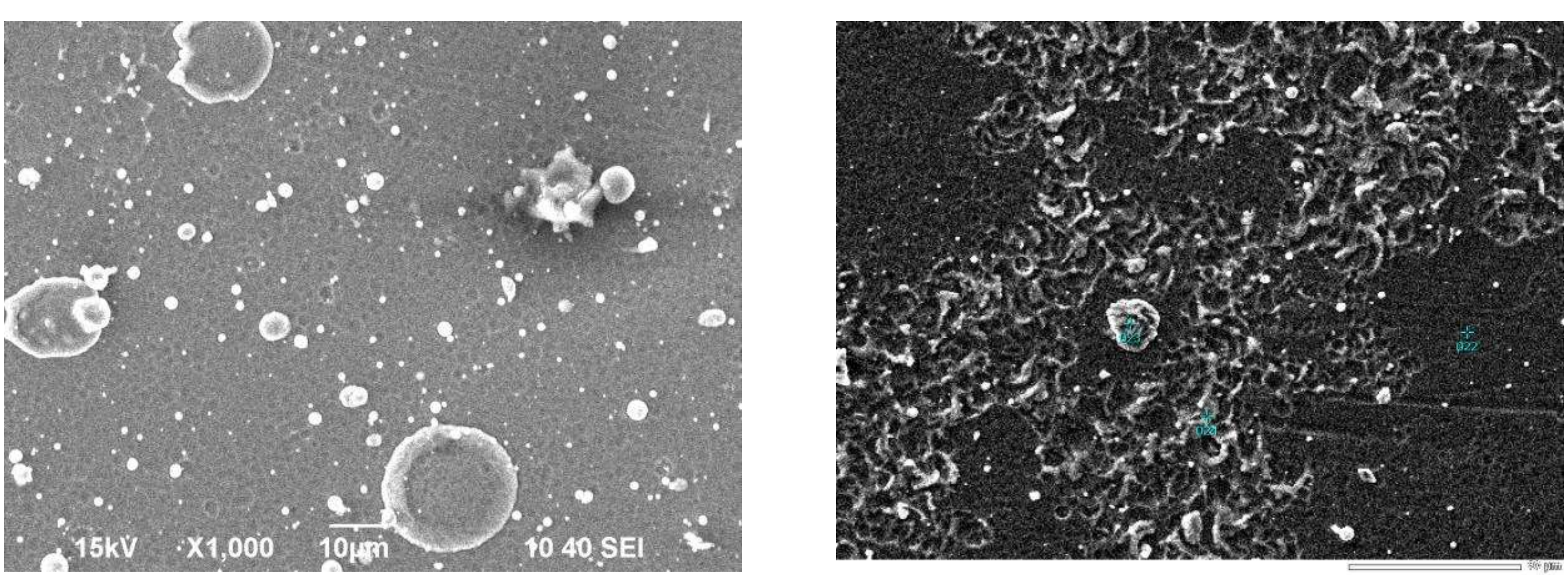
$$L(\lambda) = C\lambda^{1-D}\left[S(\lambda)\right]^{D/2}, \qquad (6)$$

where C is the coefficient of proportionality.

The relation (6) is satisfied for any standard of length ℓ sufficiently small to measure the smallest of the fractal sets. The fractal dimensions were calculated from the AFM images at the height of the median plane.

2. Results of the experiment and their discussion

Figure 1 shows, by way of example, an electron microscopic image of the Cr-Mn-Si-Cu-Fe-Al + Ti coating in argon and nitrogen. Titanium grains with a size of 1 to 10 μm in diameter are clearly visible. Materials with such a grain size are usually called large-crystal. In a nitrogen environment, the structure of the coating changes sharply (Figure 1 a), due to the formation of titanium nitride. In this case, the average grain size is 100-150 nm. Such coatings are called submicrocrystalline.



a) b)

Fig.1. Electron microscopic image of the Cr-Mn-Si-Cu-Fe-Al coating in argon (a) and nitrogen (b).

The results of the quantitative XPS - analysis of the Cr-Mn-Si-Cu-Fe-Al + Ti coating in a nitrogen medium showed that the chromium, titanium and nitrogen content are close to each other. This suggests that, in addition to the formation of titanium nitride, the process of formation and chromium nitride occurs. From Fig. 1 that the microcrystallites of titanium and chromium nitrides have a predominant orientation (presumably in the (200) direction), which is also different from the spherical symmetry of microcrystallites of pure titanium. Figures 2-7 show the AFM images and fractal structures of the metal composite films studied on steel X12.

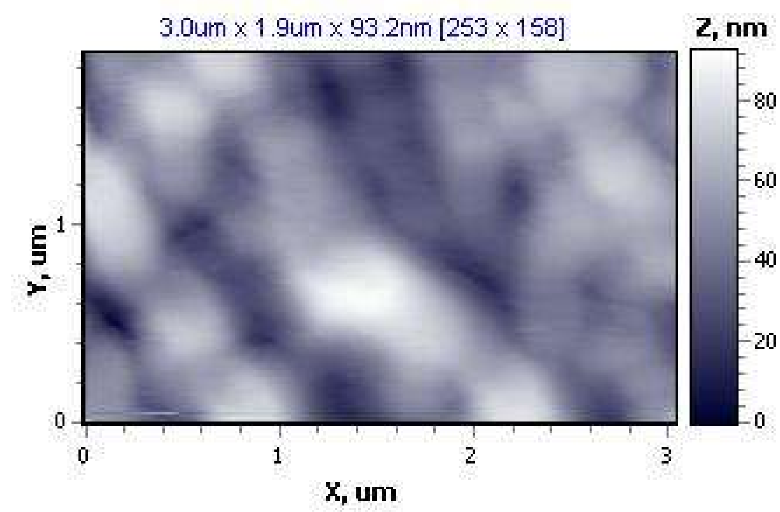


Fig.2. AFM image of the coating Cr-Mn-Si-Cu-Fe-Al+Ti

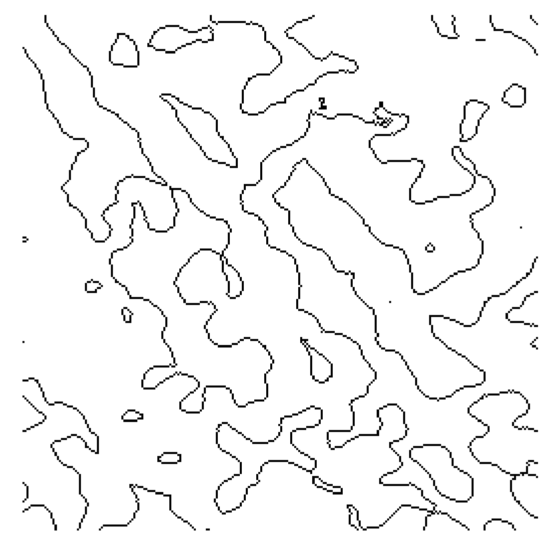


Fig.3. Fractal structure of the Cr-Mn-Si-Cu-Fe-Al+Ti coating

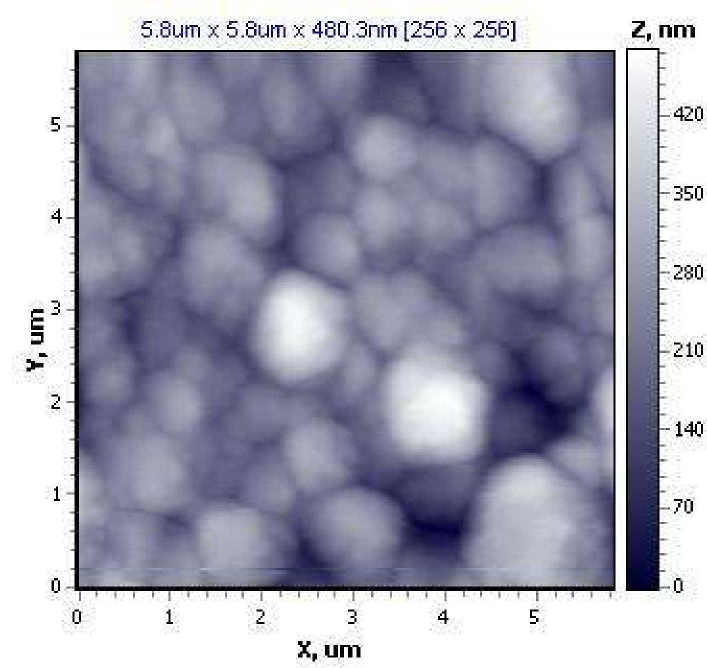


Fig.4. AFM image of the coating Zn-Al

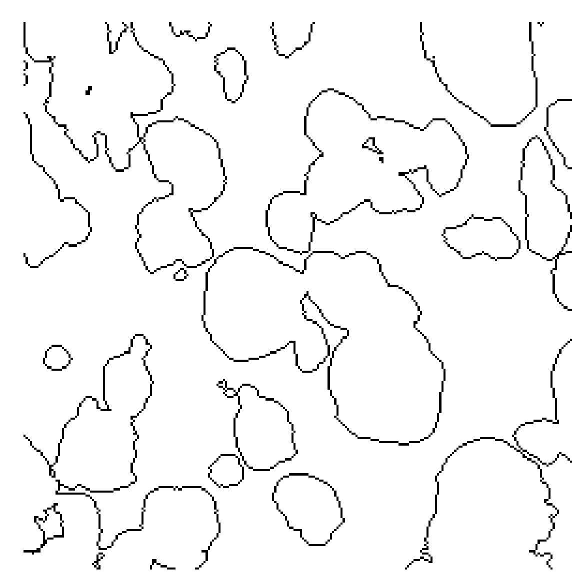


Fig.5. Fractal structure of the Zn-Al coating

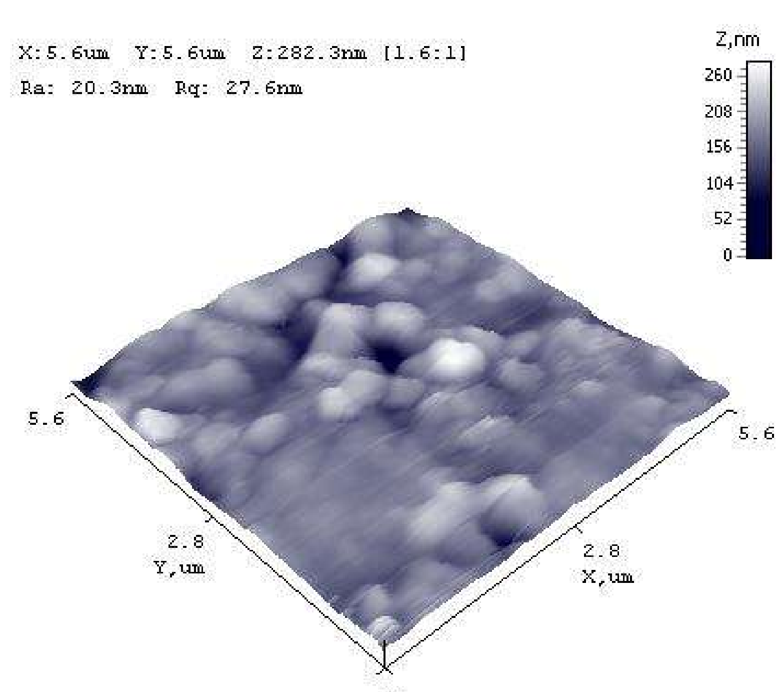


Fig.6. AFM image of the coating Mn-Fe-Cu-Al

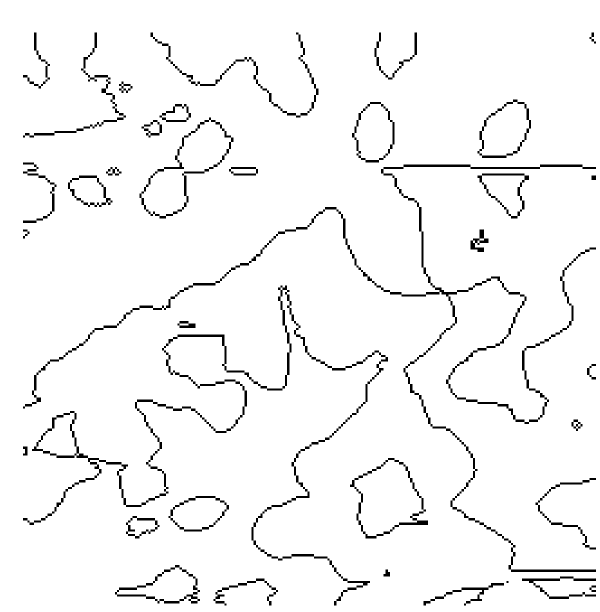


Fig.7. Fractal structure of the Mn-Fe-Cu-Al coating

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Table 1 - Roughness parameters and statistical characteristics of coatings

Electrode	Roughness R_a, nm	Dispersion R_q	Asymmetry R_{sk}	Excess R_{ku}	Fractal dimension of structure D_s
Cr-Mn-Si-Cu-Fe-Al+Ti	78.0	99.7	0.44	3.46	1.89
Mn-Fe-Cu-Al	29.89	41.42	0.15	8.97	1.81
Zn-Al	13.34	18.23	0.17	7.35	1.79

In [11], within the thermodynamic approach for the coefficient of dry friction, we obtained the following formula:

$$k_t = C \cdot T \cdot \frac{A}{\mu} \cdot \overline{N}, \quad (7)$$

where A is the work (energy) of destruction, T is the temperature, μ is the chemical potential of the metal, $\overline{N}$ is the average number of elementary carriers of destruction (proportional to the number of contacts), C is a constant.

From the formula (7) obtained by us, it follows that the coefficient of dry friction depends linearly on the work of failure of the contacts (roughnesses). Work A (J), spent on the destruction of contacts is proportional to the newly formed surface of the particles of the destroyed product:

$$A = \alpha \Delta S = K_R d^{D_s}, \quad (8)$$

where α is the time resistance to compression (Nm / m^2), ΔS is the area of the newly formed surface (m^2), K_R is the proportionality factor (Nm / m^2), d is the characteristic contact size (m), Ds is the fractal dimension.

Equation (7) can be rewritten as:

$$k_t = C \cdot K_R \cdot T \cdot \frac{d^{D_s}}{\mu} \cdot \overline{N}. \quad (9)$$

Taking the microhardness μ as the response function [11], we obtain

$$\mu = F \cdot \frac{d^{D_s}}{\mu} \cdot \overline{N}. \quad (10)$$

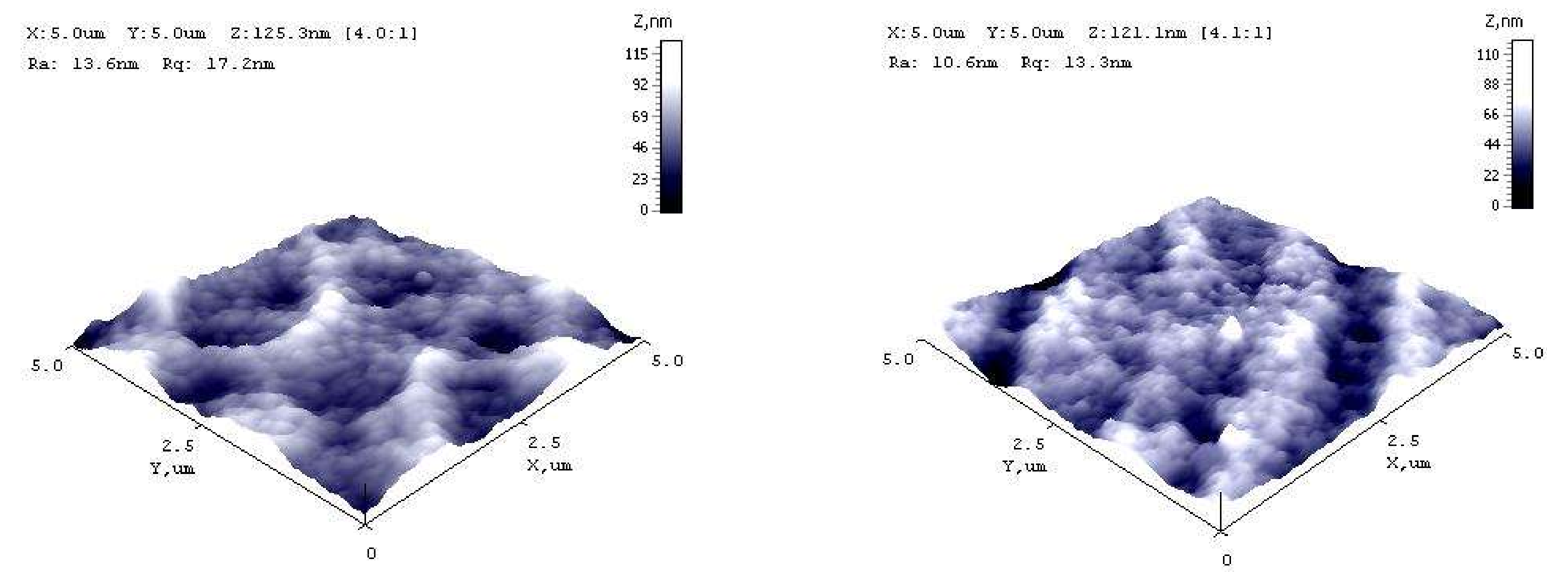
F = const.

Table 2 shows the fractal dimension of the coating and some surface properties. With a decrease in the fractal dimension, the surface tension, microhardness, and friction coefficient decrease. This agrees with formulas (9) - (10).

Table 2 - Fractal dimension and parameters of the coating

Electrode	Surface tension (J / m^2)	Microhardness HRC	Coefficient friction	Fractal dimension D_s
Cr-Mn-Si-Cu-Fe-Al+Ti	0.632	562.3	0.58	1.89
Mn-Fe-Cu-Al+Ti	0.342	420.4	0. 46	1.81
Zn-Al+Ti	0.238	268.8	0.29	1.79

Fractal dimension is a necessary condition for the manifestation of self-organization [12]. Figure 8, for example, shows a 3D image of Cr-Mn-Si-Cu-Fe-Al+Ti and Mn-Fe-Cu-Al+Ti coatings.



a) b)

Fig.8. AFM images of Cr-Mn-Si-Cu-Fe-Al+Ti (a) and Mn-Fe-Cu-Al+Ti (b).

For most of the coatings studied, a cellular structure is observed. A cellular substructure is often formed upon solidification as a result of the occurrence of concentration supercooling [13]. If the formation of a cellular structure at the crystallization front has a zone of a liquid melt enriched in an impurity, then the appearance of impurity segregation at the cell boundaries is due to the lateral diffusion flow of the impurity from the top of the growing protuberance. The amount of impurity that actually reaches the cell boundary is difficult to measure, but it depends on the depth of the notch between the cells. As the supercooling increases, the depressions between the cells become deeper, which should lead to an enrichment of the cell boundaries by an admixture due to the diffusion of the impurity from the top of the cell. The concentration of impurities on the boundaries can be several times greater than the concentration at the center of the cell.

Such a model is quite suitable for explaining the observed cellular structure, where the role of the dopant is played by titanium nitride. However, there remains the question of the cause of the self-organization of the crystallizing melt on the surface of the substrate.

To solve the problem of the self-organization of the structural units of coverage, we consider the model of Benard cells. Benard cells are the emergence of order in the form of convective cells in the form of cylindrical shafts or regular hexahedral figures in a layer of viscous liquid with a vertical temperature gradient (Figure 9) [14].

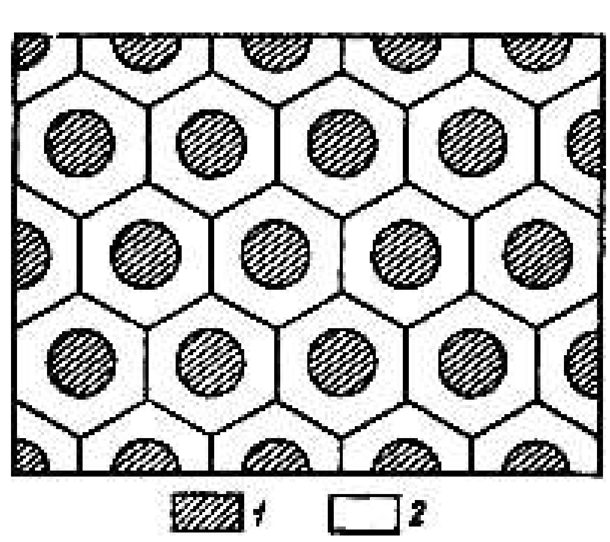


Fig.9. Diagram of Benard cells.
1 - upward movement, 2 - downward movement [14]

In the analysis of processes in the Benard system, the Rayleigh number is chosen as the control parameter: g is the acceleration due to gravity, L is the characteristic dimension, b is the coefficient of volumetric expansion, dT is the temperature gradient, v is the kinematic viscosity, and a is the thermal diffusivity coefficient of the medium. Since the kinematic viscosity is $\nu \sim 1 / \sigma$, σ is the surface tension, it follows from the above expression for the Rayleigh number that the control parameter in our case is surface tension (Table 2). In the process of ion-plasma coating deposition and during cooling in the latter, stress states are formed which can be sources of multiplication of dislocations throughout the deposited coating. Plastic deformation of crystals (and coatings) is accompanied by the formation of a deformation relief on their surface that reflects the process of localization of deformations in the crystal at the meso-, micro- and nanoscale levels [15].

It is believed that a cellular dislocation structure is a process of self-organization of dislocations under conditions of multiple slip. For its occurrence, it is necessary to fulfill a certain criterion (as in the case of Benard cells), which relates the coefficients of multiplication, immobilization, and annihilation of dislocations.

Conclusion

The experimental data obtained in principle fit into all the models considered here: the concentration super cooling associated with the presence of a radial gradient of the concentration of an impurity of titanium nitride; Benard cells, the occurrence of which is due to the presence of a vertical temperature gradient; cellular dislocation structure associated with the presence of plastic deformations in the coating. The final choice of the model and, accordingly, the control parameter has not yet been made. It is possible that the process of coating formation is influenced by all mechanisms in one or a degree.

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