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EMERGENCE DISSIPATIVE STRUCTURES WHEN FORMING PLASMA COATINGS

Yurov V.M.[1], Syzdykova A.Sh.[2], Eremin E.N.[3]

[1]Karaganda State University named after E.A. Buketov, Karaganda, Kazakhstan, exciton@list.ru
[2]Polytechnic College Corporation "Kazakhmys", Balkhash, Kazakhstan, aigul.syzdikova@gmail.com
[3]Omsk State Technical University, Omsk, Russia, weld_techn@mail.ru

Three stages of formation of plasma coatings were considered. In the first stage of nucleation of a new phase proposed to account for the size dependence of the surface energy. The equation for the third stage of coating formation was obtained. The formation occurs by plasma coating autowave law that corresponds to self substances. Methods for analyzing the conditions of formation of dissipative structures in the formation of plasma coatings were offered.

Keywords: plasma, coating, self-organization, dissipative structures

Introduction

Although methods for producing nanostructured materials and coatings are quite diverse [1], but they are all based on intensive energy dissipation mechanism, generalized in the three stages of formation. In the first stage in the process of nucleation, which is due to the lack of appropriate thermodynamic conditions, does not go into mass crystallization. The second stage is the formation around the nano crystal nuclei of amorphous clusters, which - in a third stage - are combined in the intergranular phase to form a dissipative structure.

Each of these steps is a complex process. Suffice it to point out the process of nucleation of a new phase, the theory of which has been developing for more than 100 years, and the main provisions of which were laid by Gibbs and then developed Volmer, Becker and Doring, Stransky and Kaishevym, Frenkel, Zel'dovich [2].

Despite various modifications and clarifications of the classical theory of nucleation, and it is quite correct qualitative description of nucleation, it is far from matching the experimental and theoretical data.

The stage of nucleation of a new phase

In the case of the crystallization of supercooled melt critical radius r_c of a nucleus can be expressed through the supercooling ΔT [2]:

$$r_c = 2M\sigma T_0/\rho q\Delta T, \quad (1)$$

where M - molecular weight; ρ - the density of the nucleus; q - heat of fusion; T_0 - the equilibrium temperature of the two phases of infinite radius, σ - interfacial tension of the crystal-nucleus.

Most of the work is believed that homogeneous nucleation of metallic crystals begins at supercooling $\Delta T = 0{,}2\ T_m$ the melting temperature. Assuming $T_m = T_0$, we get:

$$r_c = 10M\sigma/\rho q. \quad (2)$$

All values in the expression (2) (except σ) are determined experimentally with great precision and are given in the references. For pure metals surface tension value σ_0 is determined by us in [3]. The interfacial tension at the crystal - melt $\sigma \approx 1/3\ \sigma_0$ [4]. Then the calculation of the classical

formula (2) gives the value for the critical radius of the order of a micron or a fraction, which is three orders of magnitude of the experimentally observed values.

This is due to the following circumstances:

- classical theory is based on the rough assumption that the microscopic clusters of atoms possess macroscopic characteristics (in particular σ) and, in general, the equilibrium thermodynamic parameters;

- practically all works devoted to the initial stage of nucleation of a new phase (including the work of recent years), formation of the metastable phase is considered to be instantaneous.

In [5] to the surface tension of nanocrystals obtained by expression:

$$\sigma(r) = \sigma_\infty \left(1 - \frac{d}{r + d}\right), \tag{3}$$

where d - the critical radius, characterizing the size effects.

From (3) follows the conditions of homogeneous nucleation of crystals:

$$r_c = r \geq d/3. \tag{4}$$

Here, as above, the factor 1/3 arises taking into account the surface tension of the crystal - melt. Table 1 shows the value of the critical radius of the homogeneous nucleation of some pure metals obtained experimentally in [6]. In parentheses are the results of our calculations, taking into account the surface tension and the formulas (3) and (4).

Table 1 shows that our results agree well with the experimental. Thus, the classical theory of deviation from the experimental data due to not taking into account the size dependence of the surface tension and other physical quantities (melting point, etc.) to the nanometer range. Currently, the question of the size dependence of the physical properties of nanoparticles is obvious.

Table 1. Critical radius homogeneous formation of some metals

M	r_c, nm	M	r_c, nm	M	r_c, nm	M	r_c, nm
Ga	0,9 (0,3)	Ge	0,9 (1,3)	Cu	1,1 (0,8)	Pb	1,1 (0,8)
Sn	1,2 (0,7)	Ag	1,2 (1,0)	Bi	0,8 (0,5)	Hg	0,8 (0,4)

The third stage of coating formation and the problem of Stephen

Even more difficult is the third stage of the formation of the coating, when the growth of the film is determined by conditions on the moving phase boundary. Such tasks are called "Stefan problem", last reviewed in [7].

From a mathematical point of view of boundary value problems of this type are fundamentally different from the classical problems. Because of the size of the transfer area depending on the flow of time for this type of tasks do not apply the classical methods of separation of variables and Fourier integral, since, while remaining within the classical methods of mathematical physics, fail to agree on the solution of the equation with the movement of the phase boundary. Any attempts to get through the exact analytical solution of the problem in the field of generic type with boundary moving along an arbitrary law, leads to a system of integral equations of Volterra type II, which failed to resolve because of the complexity of the nuclei of the equation system. For infinite and semi-infinite domain with boundary moving along an arbitrary law, the problem has moved forward considerably in the 70s of the last century after the publication of a series of papers, G.A. Greenberg and colleagues [8].

With respect to our objectives, we use the solution of the Stefan problem, proposed in [9], replacing the electron flow in the flow of adatoms on the substrate surface. Then the flux of atoms or ions forming the coating, we obtain the following equation:

$$\rho(r,t)=\text{const}\cdot J_0\left(\frac{2r}{R}\right)\cdot\frac{1}{\beta(t)}, \quad (5)$$

where J_0 - the zero-order Bessel function; r - the current coordinate; R - geometrical size of the substrate; β(t) - speed interface. Schedule function ρ(r) is shown in Fig. 1.

From Fig. 1, and the formula (5) that the flux of atoms forming the coating decomposes to form "islands". Our result is consistent with the "insula" model of formation of ion-plasma coatings [1]. From (5) it also follows that increasing the growth rate of the coating β(t) of atoms flux density decreases and this leads to deterioration of the coating. This situation is typical in the case where the thermal parameters of the substrate and coating material are very different. To remedy this situation, it is necessary to use a composite (multi-element) cathode coating.

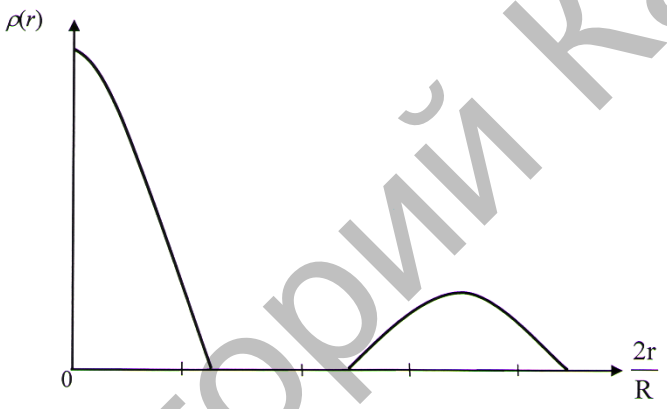


Fig.1. Graph of the function ρ(r) for r > 0

Autowave processes

The function ρ (r) describes some of the wave process. This is due to the fact that the whole order of the Bessel function can be expressed as the coefficients of the Fourier series. As an example, Fig. 2 shows the variation in microhardness coating on the sample area.

From the experimental studies should be that the formation of ion-plasma coating of spatial coordinates to be "quasi-periodic" law, i.e. corresponds to some of autowave processes (AWP). Under the AWP it is commonly understood as a self-sustaining in the active nonlinear medium wave process (including stationary structures), preserving their characteristics constant due to the distributed source of energy in the environment [10].

The very terms "autowave process" (AWP), "autowave" (AW) were offered an R.V. Khokhlov, although the theory was developed by mathematicians autowaves - works R. Fisher (1937), A.N. Kolmogorov, G.I. Petrovsky and I.S. Piskunov (1937), N. Wiener and A. Rosenbluth (1946), A. Turing (1952) - long before their experimental discovery [10]. Later, the theory of the AWP has become an integral part of the theory of self-organization and synergy.

One class of AWP include complex multi-phase environment in which non-equilibrium and AWPs supported by the energy of the laser radiation energy of the ion plasma in our experiments, thermochemical reactions and other sources. Similar phenomena are determined not only by diffusion and heat transfer and hydrodynamic flows, in particular convection, evaporation, boiling, surface tension. Education structures involving surface phenomena was considered in [11].

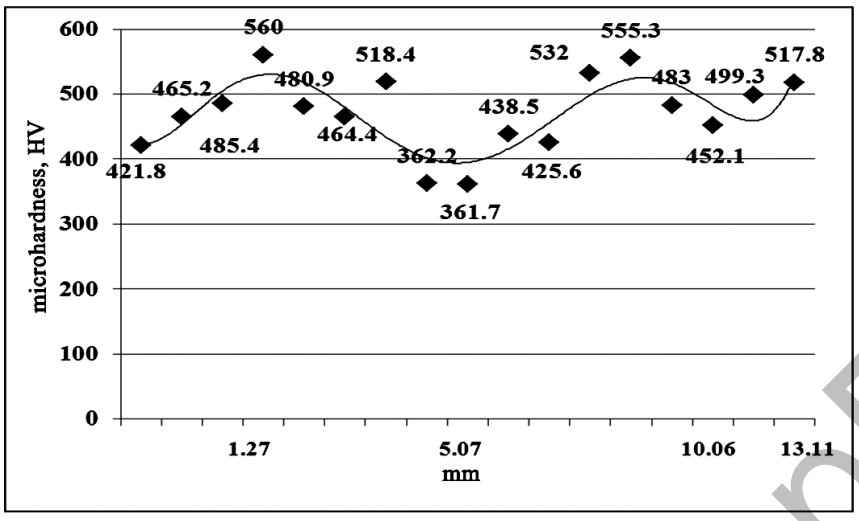


Fig.2. The change in surface area microhardness coating 12X18H10T+Ti, prepared in nitrogen atmosphere

In [12] an attempt to create a unified theory of dissipative structures Turing-Prigogine for systems of parabolic and hyperbolic equations with small diffusion. To this end, developed a special asymptotic methods of study of the problems of existence and stability of high-mode steady-state regimes in singularly perturbed systems, allowing to obtain a very subtle allegations of an unlimited increase in the number of stable dissipative structures (both stationary and periodic in time) with a decrease in the diffusion coefficients and fixed other parameters .

As a model system [12] is taken equation similar to the equation "point" model [10]:

$$\frac{\partial u}{\partial t} = \nu D \frac{\partial^2 u}{\partial t^2} + F(u). \qquad (6)$$

Here, the parameter $\nu > 0$ is responsible for the proportional change in the diffusion coefficients. The basic assumption of the problem (6) is that $u = 0$ - only its spatially homogeneous equilibrium is globally exponentially stable within a «point of the model».

However, this model contains an internal contradiction because the «point model» is applicable when $D_{ik} \to \infty$ [10]. Therefore, we will not dwell on the model (6). We note only that the theory of dissipative structures is still far from complete.

Non-linear properties of the medium, when there are conditions for the emergence of dissipative structures, can be obtained not only under the assumption that the nonlinearity of the function F in (6), and at imposing other conditions on the interval [0, L]. For example, setting an arbitrary law of motion of the boundary L. In this case, we arrive at a nonlinear Stefan problem, which also allow for solutions in the form of AWP (5).

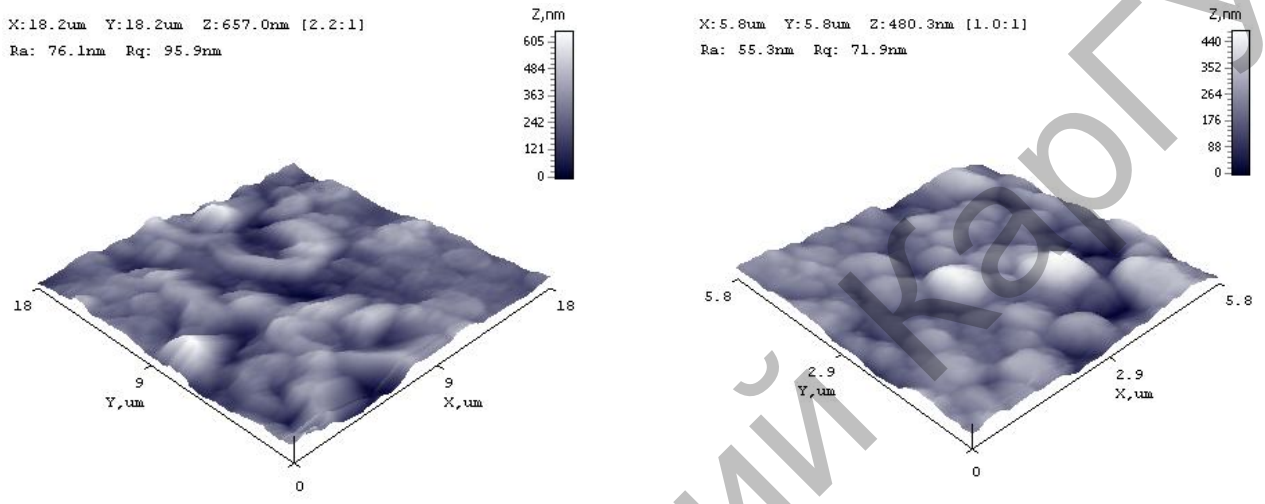
Control parameter in the formation of dissipative structures

Currently, examples of self-organization in nonlinear systems are many. Benard cells are one of the three standard examples of self-organization, together with the laser and the Belousov-Zhabotinsky reaction [13]. Self-control parameter is the temperature gradient.

In our case, the presence of a temperature gradient in the substrate - crystallized film is not in doubt, but to measure it in the coating process is problematic. The high thermal conductivity of the substrate and the coating must lead to a small temperature gradient, so that the control parameter in the formation of the cellular structure of the coating - a prototype Benard cells - it can hardly be.

More precisely (see [14]) in the analysis of processes in the system Benard as a control parameter is selected Rayleigh number $Re = gL^3bdT/va$, where g - acceleration of free fall, L - characteristic size, b - coefficient of volume expansion, dT - temperature gradient, ν - kinematic viscosity, a - coefficient thermal environment. Because the kinematic viscosity $\nu \sim 1/\sigma$, σ - the surface tension, then the above expression for the Rayleigh number, it follows that the control parameter in our case (and possibly in the case of Benar) is the surface tension.

Accounting for surface tension at the interface leads to a significant change in the kinetics of formation of coatings. Figure 3 shows the structure of the two coatings having different surface tension.



a) b)

Fig.3. AFM image of the surface coating Fe-Al (a) and Zn-Al (b)

Considering also that the formation of coatings is well described by the theory of dislocations, we can choose two control parameters - the dislocation density and surface tension. In this case, the process of forming the coating may be considered from the point of view of catastrophe theory. Disaster called abrupt changes in the form of a sudden response system to smooth changes in external conditions [15]. Catastrophe theory can be used in engineering problems for mathematical modeling of processes in which there may be a disaster. The growth of the coating film (the phase transition type I) is also a disaster. For mathematical modeling is possible to consider three sites:

1) the purpose of the operation,

2) one or two coordinates of the operation,

3) one or more control parameters, changing the course of which we manage the process.

In our consideration of the purpose of the operation - the formation of the coating, and coordinate this process, we take the rate of dissipation of free energy F, due to the formation of a film of $N >> 1$ clusters or islets. As control parameters take ρ dislocation density and surface tension σ. For one position $\dot{F}$ and two control parameters in the catastrophe theory, there is only one standard, canonical dependence for recording depending on the objective function

$$\dot{F}(N) = 0{,}25N^4 - 0{,}5\rho N^2 - \sigma N, \qquad (7)$$

where F (N) is the potential function, which is the energy of N clusters.

The disaster, which has a potential function, called the disaster of the "assembly" [15]. The assembly is in the subcritical region one stable equilibrium state (one hole of the potential function) and in the field after critical - two stable and one unstable equilibrium state (i.e. two holes separated by the hill).

Equation (7) gives a static model of the formation of the coating. For us it is important dependence of the rate of dissipation of free energy from the surface tension σ. From equation (7) it follows that the greater the surface tension, the smaller the rate of dissipation of free energy. This means that most of the input energy goes to the formation of the coating. Thus, as a rule, are formed honeycomb nanostructures having high hardness.

Experimentally, the rate of dissipation of free energy can be defined as follows: define the density of the coating standard method (the sample can be weighed before and after coating); determine the surface tension of the procedure [16]; the number of clusters is determined by the modified formula [17]:

$$N_0 = \left(\frac{1}{c} \cdot \frac{\ln n_0}{n_0} \cdot \frac{kG^0}{kT} \right)^{1/2}, \quad (8)$$

Make estimate of the number of particles in the cluster to cover the titanium nitride: G0 ≈ 410 kJ / mol; c ≈ 0,001; $\ln(n_0)/n_0 \approx 0{,}02$; k = 1,38 10^{-23}, T = 300K. Then $N_0 \approx 60$ titanium atoms. Our value is correlated with the number of N atoms in the bud in the homogeneous formation of nanoclusters of various metals [6]. The size of the cluster - r ≈ 1 nm. The number N is determined by the relation:

$$N = N_0 \cdot R / r, \quad (9)$$

where R-size coating particles (determined by electron microscopy).

Thus, in this paper we offer methods for analyzing the conditions of the formation of dissipative structures in the formation of plasma coatings.

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