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PHYSICAL AND CHEMICAL ANALYSIS OF NONEQUILIBRIUM PROCESSES OF SYNTHESIS OF NANOSTRUCTURED CONSTRUCTION MATERIALS AND COATINGS

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The paper testifies that for non-equilibrium processes of synthesis of materials and coatings at different levels, it is reasonable to extend the basic principles of physicochemical analysis. The principle of continuity should be complemented by considering the dissipation of energy when structures and phases are formed. The principles of correspondence and compatibility should be extended on the basis of fractal representations of geometric patterns and the study of possible ways of the system evolution. The principles of transformation of fractals under the synthesis of materials determine the advisability of multifractal parametrization for determining the mechanisms of formation of nanostructures in multicomponent materials and coatings.

***Keywords*:** nanostructured constructional materials, nonequilibrium process, fractal dimension, fractal parametrization, percolation, multifractal analysis.

Introduction

The synthesis of nanostructured construction materials and coatings implies the maximum use of technological opportunities for structure control and, as a result, of a complex of structurally dependent properties and optimization of the operational parameters of alloy quality [1]. Therefore, the creation and study of the physicochemical bases for controlling the properties of such materials and coatings during the synthesis process is of great importance at the stage of implementation of the developed technologies into industrial production [2-4]. Because of the nonequilibrium of high-speed processes of synthesis of nanostructured materials and coatings, their state diagrams are metastable [5]. The analysis of state diagrams is complicated by the fact that the processes run during short time period, in a very limited extent, under high pressure and temperature gradients, and are accompanied by active impurities and modifiers [6]. As a consequence, in the state diagrams it is difficult to determine not only the positions of points and lines describing phase transitions, but also their number, which increases as a result of the formation of intermediate phases or transition structures.

The aim of the work is to consider basic principles of the analysis of physical and chemical diagrams for studying nonequilibrium processes of formation of structures and phases of nanostructured materials and coatings at macro-, meso-, micro- and nanostructured levels as well as description of the processes of formation of surfaces separating structures, phases and layers of obtained products with complex micro-, meso-, and macroreliefs.

1. Thermodynamics of nonequilibrium processes.

For the analysis of a closed, equilibrium physicochemical system, the Gibbs phase equation is intended. At the same time, it is also applicable for an open system, when external flows of energy and matter are dissipated by dissipative structures. The dissipation function ψ and the entropy production σ at absolute temperature T:

$$\psi = T\sigma = T\, d\varepsilon/d\tau,$$

by virtue of the second law of thermodynamics, they increase ($\psi \geq 0$, $\sigma \geq 0$) for τ time.

Under closed conditions, in the process of evolution with $d\varepsilon \geq 0$, the system moves towards an equilibrium state, in which $\varepsilon = \max$, $d\varepsilon = 0$; in this case, the entropy production does not increase $d\sigma \leq 0$. In an open system, the evolution condition is preserved $d\sigma^* \leq 0$, and the equilibrium condition assumes $\sigma = \min$, $d\sigma = 0$; with the derivative with respect to time: $d\sigma/d\tau \leq 0$.

According to the Prigogine-Glensdorff fundamental theorem, with time evolution τ to a stationary state, arbitrary systems with time-invariant boundary conditions satisfy: $d\sigma \leq 0$ – the evolution condition; $d\sigma = 0$ – stationarity condition; $\delta\sigma \geq 0$ – the stability condition.

As a result, the Gibbs equation with restrictions with respect to the production of entropy, according to the Prigogine-Glensdorff theorem, allows us to consider open nonequilibrium systems.

2. Fractal dimension of a dissipative system.

Due to the sensitive dependence on the initial conditions (SDIC), the state of the physicochemical system can be rationally represented as an attractor. The SDIC requires the dimension of an attractor satisfying the inequality for the number of degrees of freedom, $C > 2$. At the same time, in order to have an SDIC, a three-dimensional flow in the phase space should provide $C < 3$, since in the case of a dissipative system volumes in the phase space decrease in the course of time. An attractor that can represent a chaotic regime should be so that the inequality $2<C<3$ holds. The attractors satisfying this inequality have a non-integer fractal dimension.

Thus, it is fair to say that a dissipative dynamical system can become chaotic if the dimension of the phase space is greater than two. As a result, in order to avoid unpredictability of the mode of behavior of deterministic energy and matter flows during their dissipation, the system should be provided with less than three degrees of freedom.

3. Fractal parameterization and percolation

The description of structures in the synthesis of structural materials and coatings until recently has been based on their representation by geometric objects with integer dimensions. Justified in a number of cases, such approaches are insufficient to describe systems with a complex and heterogeneous structure, such as nanoprocesses and nanomaterials.

One of the promising ways of quantitative description of the structures of materials and their surfaces is parameterization, based on the use of fractal theory. Fractals are used to generate objects of a quasi-periodic character, and their use allows modeling irregular in time and space processes or those of chaotic character. The theory of fractals reflects well the specific structure of clusters and is promising for describing the properties of highly heterogeneous materials.

In its initial formulation, it is similar to the theory of percolation, designed to describe the behavior of systems near topological phase transitions. Typically, a percolation model is considered for a lattice system in which nodes or bonds are selected with a probability of *x*. At small x, the separated nodes are mostly isolated, but with their increasing concentration, there appear clusters

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i.e. groups of connected separated particles. With further growing x, the aggregation become avalanche-like and occurs simultaneously according to several schemes:

particle – particle, particle – cluster, and cluster – cluster.

The most important characteristic of a percolation system is the percolation threshold, passing through which the quantity transforms into quality; and in a system of selected nodes the connectivity caused by the appearance of a percolation hypercluster becomes global.

4. Multifractal analysis of structures

Self-similar dissipative structures cannot be easily analyzed on the basis of the study of geometric self-similarity alone using the value of a fractal dimension. All structures are considered as potentially multifractal with some degree of adequacy of the application of the multifractal description. The basis of the multifractal approach to the quantitative description of structures is the construction, using one way or another, of a measure of the set approximating the structure under study. Dividing the Euclidean space covering the structure under study into units, each unit can be assigned its own measure (weight) according to the feature of the object (mass fraction, area, energy, etc.).

According to theoretical and experimental studies, for quantitative parameterization it is expedient to use such multifractal characteristics as generalized entropies (dimensions) of Renyi Dq and effective quantitative characteristics of homogeneity fq and ordering Δq. Based on the change in these characteristics it is possible to obtain additional information on the rates of the processes of structure formation, the change in the mechanisms of formation of structures, etc.

5. Transformation of fractals on the interfaces

The analysis of fractal dimensions at a change in the base and increase in its complexity, made it possible to form basic principles of transformation of fractals, their percolation and degeneration in the formation of interfaces of structures, phases and layers of a product.

From the structural-energy standpoint, an expedient sequence of stages in the development of interfaces of structures, phases and layers is determined: the growth of surface fractal structures; an increase in the number of elements of the fractal basis; complication of fractal meanders; percolation of layers at the interface; degeneration of fractals. In this case, the change in the mechanisms of transformation of interfaces in the material due to the complication of fractals, through their percolation to degeneracy, as a result of multiscale aggregation, at all stages is accompanied by both fractal growth and an increase in the number of basic elements, and by the possible complication of fractal meanders.

Conclusion

To study the nonequilibrium processes of synthesis and application of materials and surfaces of a product at macro-, meso-, micro- and nanostructured levels, it is advisable to extend the basic principles of physicochemical analysis:

continuity – by considering energy dissipation in the formation of structures and phases;

correspondence – by fractal representations of geometrical images;

compatibility – by studying possible ways of evolution of the system.

The development of the principles of physical and chemical analysis makes it possible to analyze quantitatively the transient processes and structures described by non-integer values of the D – degrees of freedom of the system and the multifractal parameters of the F– forming phases.

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