The methodology of functional modifiers choice for nanocomposites based on industrial thermoplastics

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Abstract: *The methodological principles for the implementation of the concept of multilevel modification of polymer matrices by components with given energy parameters to obtain nanocomposites with a synergistic com-bination of performance characteristics have been developed. These principles based on:*

– *established crystal-chemical prerequisites for the natural and synthetic carbon-, metal- and silicon-containing semi-finished products choice for the directed formation of active nanosized particles with given structural, morphological and energy parameters under optimal technological impact (mechanical and chemical, thermal, laser);*

– *implementation of the conditions for the energetic compliance of nanomodifiers to the prevailing mechanism for the formation of the optimal structure of polymer, oligomer and blend matrices at various levels of organization – molecular, supramolecular and interphase;*

– *creating the conditions for the reveal of the prevailing mechanisms of interphase physical and chemical interactions of components with the formation of boundary layers of the optimal structure, which deter-mine the mechanisms of destruction of products from nanocomposites under various operational factors impact;*

– *achieving the conditions for the synergistic effect of structuring by using a complex of modifiers with a certain combination of parameters of dimensional, geometric and energy characteristics.*

KEYWORDS*: NANOCOMPOSITES, INDUSTRIAL THERMOPLASTICS, NANOSTATE, MULTILEVEL MODIFICATION, ENERGY AND TECHNOLOGICAL COMPLIANCE*

1. Introduction

In the brand range of modern engineering materials, a special place belongs to nanocomposites based on polymer, oligomeric and blend matrices, which for a variety of performance characteristics parameters are no alternative materials in the production of road transport, special, agricultural machinery and technological equipment for heat power engineering, petrochemical and processing road transport. At the same time, the potential of such matrices produced by the domestic industry in the creation of functional nanocomposites is not fully realized, although the base of its large-tonnage production is highly developed and enterprises have a lot of modern technological equipment.

The mechanism and kinetics of the processes of formation of the structure of composite materials at various levels of organization is determined by the activation energy, which depends on the parameters of the energy characteristics of the components at a given technological impact. Studies of domestic and foreign experts have shown the existence of the effect of the transition of a material particle when a certain size range is reached into a state with special parameters of energy characteristics, which according to the established terminology is called a nanostate. Obviously, the achievement of the nanostate by the component will have a significant impact on the structural processes in the composite material at different levels of organization, which determine the parameters of stress-strain, tribological, adhesive and other characteristics of products in metal-polymer systems [1–4].

At the same time, despite the experimentally established influence of energy parameters on structuring processes, there are no systemic studies of methodological approaches to the implementation of the nanostate phenomenon in materials science and the technology of nanocomposite materials based on industrial polymers. Therefore, the development of methodological approaches to the implementation of the phenomenon of nanostates at various levels of organization of the structure of nanocomposites is the actual problem of domestic materials science and polymer technology, which have a great scientific and applied importance.

2. Methods of research

The main objects of study were nanodispersed particles of carbon-containing (graphite, DND, CNT, shungite, carbon fibers), metal-containing (oxides, salts of organic acids) and silicon-containing (mica, tripoli, opal, clay) compounds obtained by technological impacts on natural and synthetic semi-finished products produced at industrial enterprises in Belarus and the Russian Federation. Nanosized components were obtained by mechanical crushing and heat treatment of dispersed semi-finished products at temperatures of 673–1473 K.

Two main types of thermoplastic materials were used as polymer matrices: the first, with a hereditarily high viscosity (HHV) of the melt due to the chemical structure of the chain and molecular weight: polytetrafluoroethylene (PTFE) and super high-molecular polyethylene (SHMPE); the second are materials with acquired high viscosity (AHV): industrial thermoplastic polymers such as polyamide PA 6, high density polyethylene (HDPE), ethylene-vinyl acetate copolymers (EVAC), polypropylene (PP), thermoplastic polyurethane (TPU), etc. with characteristic parameters of rheological properties that changed with the introduction of nanosized modifiers.

Polymer materials were used in the state of industrial delivery in the form of granules or powder obtained by cryogenic dispersion of granules at a temperature of 87 K.

The structure and properties of nanocomposite materials and products produced from its were investigated using modern methods of physical and chemical analysis: IR spectroscopy (Specord), electron paramagnetic resonance (EPR) spectroscopy (RE 1306, Bruker), X-ray diffraction (Dron 2.0, Dron 3.0), differential thermal analyzes (Q-1500), optical (MIM-10, MF-2), scanning electron (ISM-50A, Nanolab-7) and atomic force (Nanotope III) microscopy. The energy state of nanoscale modifiers and composite materials was assessed from the EPR spectra and the spectra of thermally stimulated currents (TSC) on the original equipment of the V.A. Belyi Metal-Polymer Research Institute of National Academy of Sciences of Belarus (MPRI NASB). The dielectric characteristics of materials after energy exposure (laser, ion, temperature) were determined according to the appropriate standardized methods. The regulation of the nanorelief of the surface layer of polymer samples and fillers was carried out using a short-pulse laser and accelerated ion irradiation with a given power density.

The parameters of the stress-strain characteristics of the developed materials were evaluated on standard samples in accordance with the relevant standards (GOST). Tribological characteristics were determined on universal or original friction machines (UMT, MI-2, SMC-2M, etc.) according to the "indenter – disk", "shaft – partial insert" schemes. Evaluation of the performance of products from the developed nanomaterials in the designs of automotive units for various purposes and technological equipment was carried out at the stands and in the process of virtual tests using the SKIF supercomputer and field tests. The test data processing was carried out by the methods of mathematical statistics using the standard software Microsoft Office 2020.

3. Results and discussion

Multicomponent materials based on high molecular weight matrices are systems the parameters of characteristics (stress-strain, tribological, adhesive, thermophysical, etc.) of which are determined by the structure at various levels of organization, formed by physical and physicochemical processes, the mechanisms and kinetics of which depend on the composition components and parameters of technological characteristics. In the interphase region of the system, a complex of physical and physicochemical reactions occurs simultaneously with the dominance of one or several, for which the most favorable conditions are realized, determined by the value of the activation energy. This dominant reaction, the kinetics of which is in accordance with the conditions of formation and operation of the system, determines the resistance of an element made of a composite or a metal-polymer system to the action of operating factors.

The methodological approach to the formation of composites based on the establishment of the dominant physicochemical reaction made it possible to establish a correlation between the parameters of the structure and the energy characteristics of the components (energy state) [5, 6, 8, 11].

To characterize the energy state a complex parameter was used, which is the cumulative result of the transformation of the initial individual parameters of the components (structure, composition, morphology, shape, size) under the influence of technological and operational factors. A feature of the proposed methodological approach is the ability to purposefully intensify the dominant interfacial reactions by forming the energy state of components with certain parameters of electrophysical characteristics.

Using the concepts of condensed matter physics, the conditions for the acquisition of a nanostate by a material object are determined, which can manifest itself when the size parameter L_0 is reached both by a single particle and by the components of the surface layer of a particle or substrate in the micro- and macro-range. For the analysis of various types of interphase interactions in systems based on the energy factor, the definition of "nanostate" has been proposed, which makes it possible to single out the main forms of its manifestation [9, 10].

The concept of energy and technological compliance of components for the formation of systems with optimized parameters of structural characteristics at various levels of organization has been developed [12, 13].

The energetic compliance of the components implies the possibility of achieving a total energy state by its that corresponds to the activation energy of the dominant physicochemical process, which ensures the formation of an optimal structure at the intermolecular, supramolecular, interfacial levels of organization in composites or metal-polymer systems.

To implement the principle of energy compliance of components, it is necessary not only a certain combination of initial parameters (thermophysical, dimensional, electrophysical, structural, elemental, etc.), but also the possibility of changing them in the specified ranges of values under technological influences on the components (deformation, temperature, ionizing, laser and etc.). When choosing an adequate technology for obtaining, preparing, mixing components or processing composites into products, conditions are created for changing the initial energy state and achieving a nanostate directly in the interphase interaction zone, which ensures the dominant physicochemical process of forming the optimal structure of the boundary layer [13].

The formation of an interphase (boundary) layer of the optimal structure indicates the technological correspondence of the components of functional materials and metal-polymer systems, which is understood as the possibility of achieving the specified energy parameters at a certain stage of the formation of a composite, product or structure, ensuring the dominant mechanism of interfacial interaction. The absence of such a compliance does not allow realizing the potential of individual components in the selected technological process of manufacturing the system, since it can manifest itself in various ranges of temperature, mechanical, physicochemical and other influences, not ensuring the achievement of the required value of the activation energy at a specific technological stage, leading to a negative a phenomenon called the structural paradox. The implementation of the principle of energy and technological compliance has made it possible to develop a methodology and practical technologies for the use of the phenomenon of nanostate in materials science of metal-polymer systems of various composition, design and functional purpose.

To develop methodological principles for creating optimized systems and algorithms for their implementation that are adequate to common technologies of polymer composites and systems, the factors that determine the nanostate of components (dimensional parameters and shape of individual particles, structure at various levels of organization, composition of components, morphology of the surface layer) are substantiated. Taking into account the selected factors, the analysis of the mechanisms of realization of the nanostates of dispersed particles and substrates of various compositions, structures and geometrical parameters for their practical applications in materials science and technology of nanocomposite materials based on industrial polymers was carried out.

Physical and physicochemical processes are caused by the transfer of electrons during the formation of intermolecular, supramolecular, interfacial structures, which led to the choice of the maximum value of the thermally stimulated current (TSC) in the temperature range adequate for the technological modes of obtaining, processing of composites and operation of metal-polymer units.

Analysis of the parameters of the energy state of dispersed particles of various composition, structure and production technology, which have found wide application in materials science of polymer nanocomposites (silicon-containing (clays, mica, talc, tripoli), carbon-containing (detonation nanodiamond (DND), carbon nanotube (CNT), carbon fibers (CF), shungite, colloidal graphite (CG)), metal-containing (particles of metals and oxides)), indicates the nonlinearity of the dependence of the TSC value on temperature, the presence of extrema in temperature ranges characteristic of each type of modifier, and instability $I = f(T)$ with a change in dimensional parameters, dispersion modes, the intensity of exposure to temperature, mechanical and other energy and technological factors. A typical form of the TSC spectra of particles of thermogasdynamic synthesis products (ultrafine polytetrafluoroethylene (UPTFE)), flint, shungite with a size of 50–100 μm is shown in Fig. 1 and 2. The nonlinearity of the $I = f(T)$ dependence is also typical for other organic and inorganic objects with different composition, structure and molecular weight.

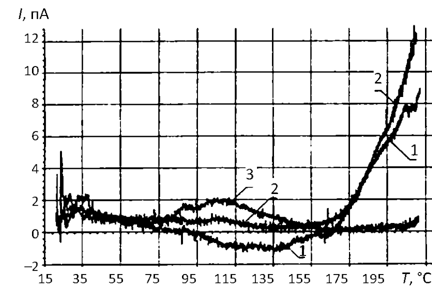

Fig. 1. *Typical form of the TSC spectrum of initial (1) and heat-treated at 373 K (2), 473 K (3) products of thermogasdynamic synthesis (UPTFE)*

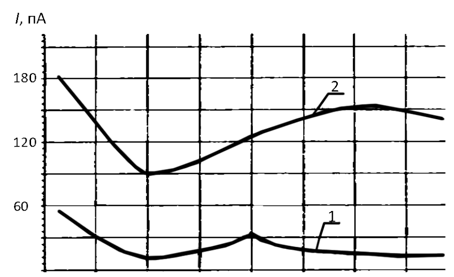

Fig. 2. *Dependence of the value of the maximum thermally*

stimulated current (TSC) on temperature for particles of silicon (1), shungite (2). Dispersion of particles is 50–100 μm

As follows from the research of prof. G. I. Distler, V. A. Goldade, L. S. Pinchuk, the parameters of the electrophysical characteristics of material objects are determined not only by their composition and structure, but also by the type of technological impact.

The feature of dispersed particles of most common modifiers of high molecular weight matrices is the presence of an uncompensated charge with a long relaxation time, which is confirmed by EPR spectroscopy data (Fig. 3). Along with the special parameters of the electrophysical characteristics, due to the peculiarities of the composition and structure, material particles can be in a nanostate, ideas about which were proposed by prof. P. von Weimarn, P. M. Ajan, I. P. Suzdalev, A. I. Gusev and others, with certain types of technological impact that change the size, geometric characteristics and morphology of the surface layer. The size range of the transition of material objects to the nanostate is individual for particles of different composition and structure and is determined by the analytical expression proposed by V. A. Liopo, according to which the limiting size is $L_0 = 230 \cdot \theta_D^{-1/2}$, where θ_D is the Debye temperature. The validity of the use of this expression for the analysis of the structure of polymer nanocomposites is confirmed by systemic studies, the results of which are summarized in monographs [5, 6, 8, 11].

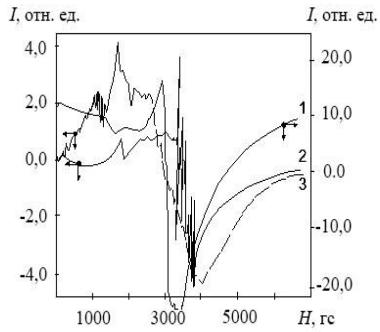

Fig. 3. *EPR spectra of opal (1) and clay minerals of various compositions (2, 3). Dispersion of particles is 50–100 μm*

An analysis of the morphological features of dispersed particles, widely used in the material science of polymer composites, by SEM and AFM methods, indicates the presence of nanosized components in objects of the micron range, which form the morphology of the surface layer (Fig. 4).

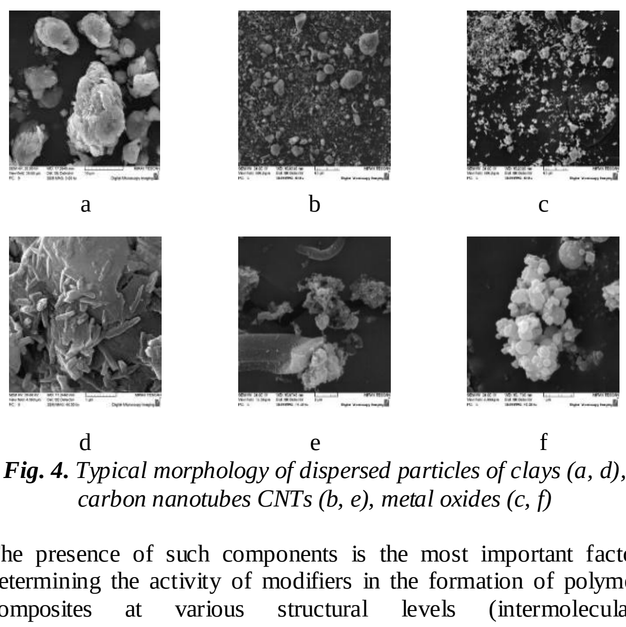

Fig. 4. *Typical morphology of dispersed particles of clays (a, d), carbon nanotubes CNTs (b, e), metal oxides (c, f)*

The presence of such components is the most important factor determining the activity of modifiers in the formation of polymer composites at various structural levels (intermolecular, supramolecular, interphase) due to the manifestation of the surface layer of particles of energy parameters characteristic of the nanostate. Therefore, the technologies for activating modifiers of polymer matrices should ensure the formation of nanosized components in quantities sufficient for the implementation of the determining process of the required intensity, by establishing the mechanisms of their formation under various types of technological impact on the semi-finished product.

Using the concepts of condensed matter physics on the basis of a barrier model of the formation of a juvenile surface, mechanisms of dispersion of layered minerals such as mica, talc, and kaolin with the formation of nanosized lamellar components are proposed. It has been established that the determining processes of degradation of particles of the micrometer range are dehydration and dehydroxylation, which cause the destruction of the initial layered structure and the formation of nano-sized lamellar elements in the active state with a long relaxation time sufficient for implementation in the technology of polymer nanocomposites [5, 6]. It has been experimentally established that the activity of such elements in the processes of interaction with the environment (system components) depends on its composition, temperature and time characteristics. To intensify the process of dispersion of layered minerals, it is advisable to use thermal impact at temperatures of 800–1000 K or diffusion saturation of interlayer regions with low molecular weight and oligomeric media based on carbon-containing products with low resistance to thermal degradation [6].

Model studies of the dispersion of layered minerals of the mica type (muscovite) have shown the possibility of the formation of nanoparticles with a size of 30–50 nm under a shock thermal effect on the initial semi-finished product at 1073 K for 5–20 min. The lamellar particles formed under thermal shock have an increased adsorption activity in the process of interaction with the environment, including polymer matrices in a viscous-flow state, and intensify the intermolecular structuring of the composite.

Dispersion of particles from layered silicates can be realized directly in the process of obtaining or processing composite materials under thermomechanical action on the components of the screws of mixers, extruders or injection molding machines. The formation of an intercalated or exfoliated structure of the nanocomposite provides a technically significant effect of increasing the parameters of stress-strain and tribological characteristics even with a doping content (0.1 ÷ 1.0 wt.%) of the modifier.

Thermal action on dispersed particles changes the energy parameters of not only layered silicates (clays, talc), but also framework and chain (silicon, zeolites) and multiphase natural (tripoli, shungite) products (Fig. 1, 2).

An effective technology for activating dispersed particles is its dispersion under mechanical or mechanochemical action. It was experimentally established not only an increase in the specific surface area, but also the formation of nanosized components in the surface layer of particles. Modifiers activated in this way retain their activity for a technologically significant time (up to a year) [14].

Nanoscale components of the structure of the surface layer can also be formed as a result of exposure of a semi-finished product to energy flows – ionizing, laser radiation. In this case, not only does the specific surface area of the particle increase, which provides the mechanical component of the interfacial interaction, but also the parameters of the characteristics that determine its nanostate, which affect the supramolecular structure and adsorption capacity of the surface layers of modified substrates (PET, PTFE, PP, HDPE, CF) (Fig. 5).

An energetic assessment of the nanostate of polycrystalline particles is carried out to establish the temperature equivalent of the geometric parameters. It is shown that for a nanoparticle, due to the increased role of surface energy in comparison with a bulk sample, there is a correlation between the particle size and its energy state, which can be estimated from the temperature factor.

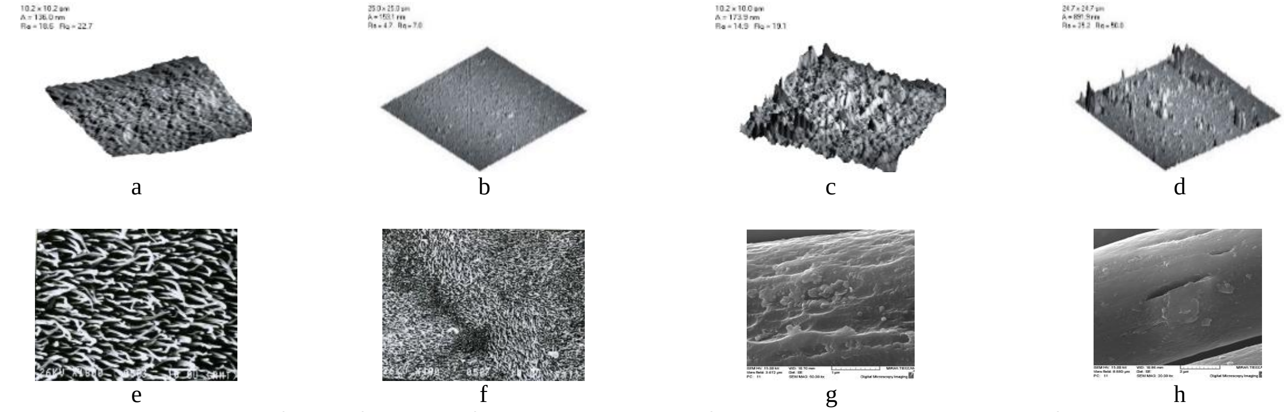

Fig. 5. *Typical morphology of the surface layer of the substrate PTFE (e, f), PET (b, d), HDPE (a, c), carbon fiber (g, h), initial (a, b) and exposed to nitrogen ions at a dose of 1016 ion/cm^2 (g, h), pulsed laser radiation with a power density of 2.0 W/cm^2 (c, d). AFM data (a – d) and SEM (e – h)*

When the particle size δ decreases by 1 %, the energy parameters increase by $\delta t = k\,(\delta T) \approx 3.5 \cdot 10^{-28}$ J. Therefore, the formation of nanosized particles or nanosized components in the structure of the surface layer of a macroparticle (substrate) is accompanied by an increase in the parameters of energy characteristics, estimated by the maximum value of the thermally stimulated current and the intensity of interfacial processes in the systems.

The carried out complex of studies on modeling the processes of formation of the structure of material objects with a pronounced manifestation of nano-state made it possible to determine the effective directions of its achievement in the technological processes of obtaining and processing nanocomposite materials based on industrial matrix polymers.

The choice of the conceptual direction of the technological embodiment of the phenomenon of nanostate is determined by a combination of materials science, technological, economic, and operational factors. An algorithm for the implementation of the methodological approach has been developed, which allows, on the basis of the factors that determine the nanostate of the components of a system of a specific purpose and design, to select the technology for their implementation at a specific stage of the process, taking into account the material, economic, ergonomic, environmental and other aspects.

The methodological principles of the implementation of the phenomenon of nanostate in materials science and technology of functional nanocomposites based on industrial polymer matrices and metal-polymer systems with its use, focused on the state of the domestic technological base of industrial enterprises, related mainly to IV and V techno-economic paradigms, are proposed (Fig. 6).

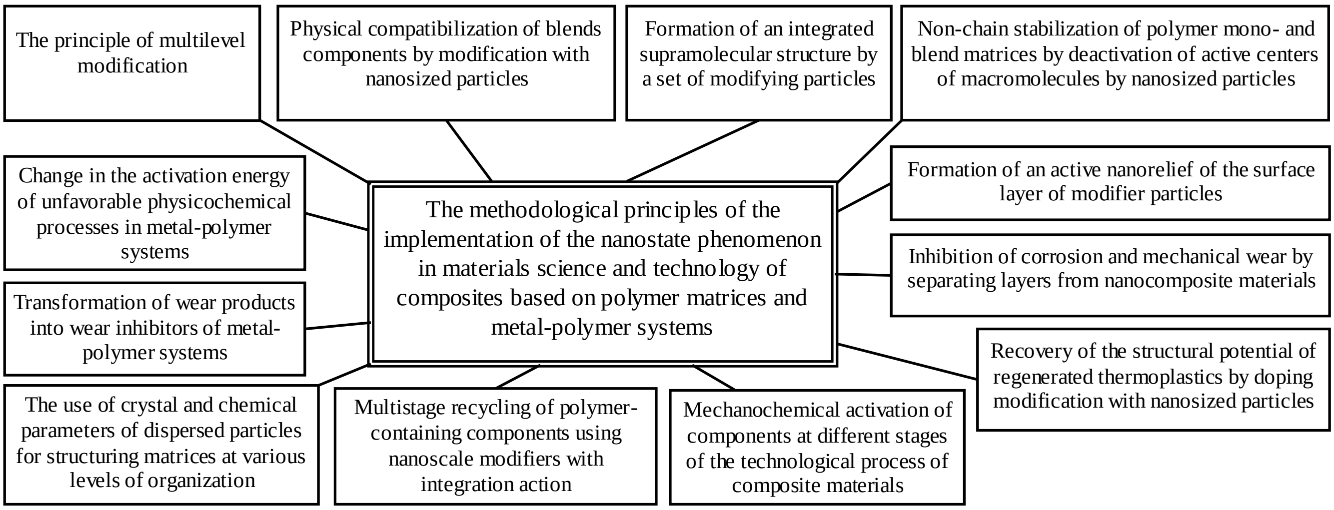

Fig 6. *The methodological principles of the implementation of the nanostate phenomenon in materials science and technology of composites based on polymer matrices and metal-polymer systems*

4. Conclusion

Based on a systematic analysis of the features of the morphological and energy parameters of dispersed components of condensed media of various compositions, its structure and production technologies, methodological approaches to the implementation of the phenomenon of nanostate in the formation of the optimal structure of composite materials and metal-polymer systems at different levels of organization have been developed. Scientifically-based foundation for the creating nanocomposite materials with increased parameters of stress-strain, adhesion and tribological characteristics based on industrial thermoplastics for functional metal-polymer systems and efficient technologies for its manufacture and processing into products are proposed.

The concept of energy and technological compliance of the components of functional composite materials and systems has been developed. This concept consists in the implementation of the parameters of energy characteristics of the components of functional composite materials and systems adequate to the value of the activation energy of the dominant structural process, which determines the optimal parameters of the stress-strain, adhesive and tribological characteristics under technological impact on the components in the process of obtaining composite and its processing. Theoretically and experimentally substantiated the reliability of estimating the parameters of the nanostate of material objects using an analytical expression to determine the limiting size of the transition to the nanostate of a particle or a component of the morphology of the surface layer according to the Debye temperature θ_D criterion. A definition of the nanostate of material objects is proposed. This definition characterizes the relationship between structural, morphological and energy parameters.

5. Acknowledgements

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