EVOLUTIONARY ROUTE IN THE SOLID STATE FORMATION OF BUILDING COMPOSITES

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We consider the evolutionary route of formation of solid and justified "arsenal nano" modification of the structure of building composites. We discuss the concepts and foundations nanomodification of structures of inorganic building materials in the problems of the development of their advanced technology. It is shown that the disclosure of the evolution of the structure on the nanoscale level is determined by a complex management tools. They include mechanisms play an important role, using a predefined nano-sized additives of different nature.

Keywords: system hardening, of building composites, nanomodification of structures

Building on the achievements of nanochemistry, and referring colleagues have obtained results, it is important to discuss with the concept of common positions and strategies of technology nanomodification construction composites structures. At the same time, using the nanoeffects and nanoscale phenomena consideration is required to systematize the fundamental laws governing the formation and evolution of the solid through all of the original initial and intermediate stages of a substantial change in its status , spatial and geometric characteristics in a multi-level scale (from nano- to macro-) structure. And then highlight the key features and areas of research for the development of applied nanotechnology management techniques synthesis of matrix structures systems of composites and composite structures themselves.

If we talk about the technology of building materials and stages of transition in the processes of structure formation of the solid phase state, it must be borne in mind hydration (lime, gypsum, cement), hydrothermal – synthesis (silicate – autoclave ones) system hardening, thermal – synthesis (ceramics, glass) methods for producing composites [1].

When the detection and analysis of general evolutionary model of formation of solid substance can follow interpretations I.V. Melikhova [4].

In line with modern concepts applicable to systems of any structure in the formation of solid, the following main stages in the evolution of substance: the emergence phase, particle growth, agglomeration, spontaneous transformation in time (Figure).

We should talk about the three evolutionary transitions between stages and, accordingly, on the phenomena of molecular, topological and morphological criteria. In the evolution of the solid can be realized (Figure) the two branches of the development process: the left, the corresponding small perturbations of the supersaturating, and the right, corresponding to large supersaturating of the phase-forming – guide macro component.

It is important to emphasize that each step corresponds to a specific range of the dimensions of the particles formed on it is solid. Shown in Figure dimensional scale illustrates the dimension geometric boundaries and limits. It is clear that the most significant "arsenal nano" we can use in the stages of nucleation and growth phase particles at other stages priorities are different physic- chemical methods of technology impact, affecting the micro and macro scale evolutionary process. The above should be considered in the development of methods of influence on each of the stages and transitions considered evolutionary route.

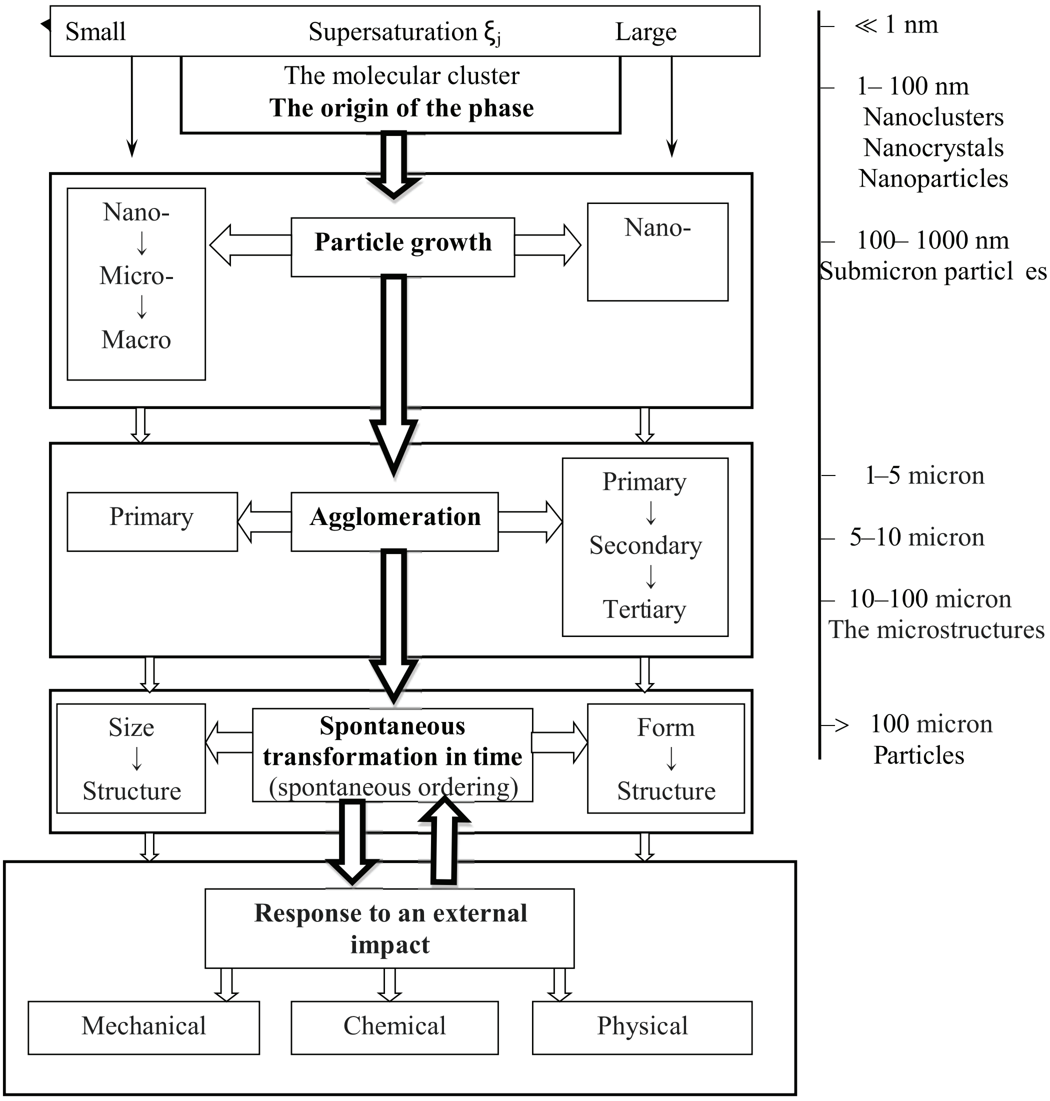
Stage of the emergence phase

According to thermodynamic theory Gibbs – Volmer [8] of a new phase can for a certain critical degree of supersaturating, which depends on the natures of the raw materials and the presence of condensation nuclei which can be introduced into the system and the outside. Nucleation is possible at a certain (critical) the degrees of supersaturating of the solution that substance whose molecules are involved in the formation of a new phase. Given the rate of supersaturating g can express the critical nucleus size, and write it in the form of:

$$r = \frac{2\sigma V_m}{RTln\gamma}. \quad (1)$$

Given this correlation equation of the total energy Gibbs nucleus of critical size will be:

$$\Delta G = \frac{16\pi\sigma^3 V_m^2}{3R^2T^2(\ln\gamma)^2}. \quad (2)$$



The evolutionary path of formation of solid substances and "dimensional scale" of its structural components

From (2) we conclude that the Gibbs energy of formation of nuclei in homogeneous condensation is equal to one -third of its surface energy, and the remaining two thirds of the energy is compensated with ethyl energetically favorable for the phase transition. From (2) it also follows that the energy of formation of the nucleus and the size of the critical nucleus depends on the degree of supersaturating of the system: the higher it is, the smaller the size of the resulting embryos are capable of further growth. Thus, bearing in mind the impact of technological capabilities, and in particular nanotechnology, on the generation stage of particles, above all, we should speak about of such factors as the creation of supersaturating control and the introduction of outside nuclei (nuclei) condensation.

Supersaturating can be created in two ways: increasing the concentration of molecules in a medium material and (or) its reduced solubility. Under the first method in flow administered molecules of the substance or reagent streams that are formed this substance is discharged by solvent evaporation or freezing, etc. When implementing the second system is cooled or added substance – salting-out agents. Variants of these two methods (and corresponding technology), there are many [2, 3]. Deepening the analysis of the issue substantiate the "arsenal of nano" should bear in mind the types of solid phase nucleation: nucleation in the gas phase, nucleic nucleation in a liquid medium, the nucleation on a solid surface, mechano-stimulated nucleation. Depending on the type of phase nucleation stage classification process can introduce solids synthesis methods, including in nanostate (Table 1).

the route of evolution solid "phase nucleation stage ® growth of particles". Against the background of reducing the free energy of the system it is developing phenomenon of the molecular screening, in which embryos are clusters of molecules that contain only a little different in structure and size of the molecule. Fouling of the particle phase-forming substance

Table 1

The main technological methods of synthesis of solids
and management factors depending on phase nucleation agents

Type inception phase of the substance / examples of systems	Technological methods of synthesis solid substance	Factors management
generation in the gaseous environment / nanosystems of metals and oxides metals	plasma chemical	● changes in the ionization energy of condensed matter; ● increase in the degree of ionization of condensed matter; ● increase the rate of condensation
	cryochemical	● changes in the concentration of inert gases; ● lowering the temperature of the deposition surface
nucleation in liquid environment / hydration and hydrothermal synthesis system hardening (lime, gypsum, cement)	sol – gel	● varying the chemical nature of the starting materials; ● changes in the initial pH of the medium; ● changes in the synthesis temperature; ● change the duration of the synthesis
	hydrothermal	● varying the chemical nature of the starting materials; ● changes in the synthesis temperature; ● reduce the length of the synthesis; ● increase the pressure in the system
nucleation on surface solid / nanosystems of metals and their compounds	electrochemical	● an increase in electrical potential; ● varying the nature of the materials and the solvent; ● changing the type and concentration of ions additives; ● changes in the adhesive properties of the deposited particles; ● changes in ambient temperature; ● changes in the conditions of diffusion of matter
mechano-stimulated initiation / thermal-synthesis system hardening (oxides, ceramics, glass)	mechanochemical	● increase the energy of impact; ● changes in the duration of exposure; ● change in the position of the functional groups in the molecules of the crystal
	ultrasonic	● change the frequency of the ultrasonic pulse; ● change the duration of the ultrasonic pulse; ● changes in the phase state of the system

Stage of the particle growth

Each particle originated while in supersaturated environments, attaches itself to the molecules of the medium more often than they were breaking away from the particles [4]. If the medium contains a plurality of different molecules, then the particles in significant quantities fixed first molecules having close crystal- structure. In fact, on the surface of the growing particle is controlled by molecular selection.

In this way, i.e. in the form of molecular screening is implemented the first transition in is facilitated if the space between the surface of the particles and clusters formed on it, there is a certain structural correspondence.

Form growing particles typically varies during the growth; the nature of changes of these depends on the structure and mechanisms of particle growth.

From the point of view of nanotechnology, it is possible and it is necessary to bear in mind the problem of changes of the concentration of crystallization conditions and the use of additives substances, in particular, nano-additives possessing similar to the nuclei of the crystal phase structure, and providing targeted acceleration of particle growth phase-forming substances [6], and their morphological modification.

According to V.B. Ratinova additives are divided into four classes:

1 – additives that alter the solubility of the system hardening and entering it into chemical interaction$

2 – additives that react with the curing to form insoluble compounds or malodissotsiruyuschih;

3 – additives, nucleating;

4 – additives, adsorbed on the grains of the solid [7].

Due to the marked our three global transitions in the evolution of the classification solid additives useful to clarify and separate the oversized on the basis of nano-sized, ultra-fine and micro particulates (Table 2). Based on theoretical considerations, it is believed that nanoscale additives and ultra 1–3 classes can actively participate in the processes of nucleation stage and grade 4 in the growth of the particles.

In general, the structure- modifying effect of participation and nanoscale modifiers may be the result of inter-related mechanisms. It should be emphasized that the incorporation of additives in curable system (most efficient in this case will be additive nanoparticles) may facilitate the formation of nuclei, as DG can thus reduce in accordance with equation (2).

Stage of agglomeration

In the course of evolution in the hardening system accumulate aggregates of particles of different size that are placed relative to each other in a certain order, resulting in aggregates become like colloidal crystals. The process can take place in several stages, forming the primary, secondary and tertiary aggregates

Table 2

Modifiers nano-, ultra-, micro-sized level of dispersion and their mechanism of action

Number	Type systems	The name and the chemical composition	Particle size and morphology	The mechanism of action
1	The nanosized	Nano-sized silica $SiO_2 \cdot nH_2O$	∅ = 5–10 nm spherical particles	1) Direct chemical involvement of nanoparticles (NP) in heterogeneous processes of phase formation of hydrated compounds; 2) the catalytic role NP as nucleation (growth of a new phase)
2		Sol $Fe(OH)_3$	∅ = 5–10 nm, spherical particles	
3		Sol $Al(OH)_3$	∅ = 30–50 nm, spherical particles	
4		Montmorillonite – a synthetic $(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$	~5–10 nm hexagonal plates	
5		Chrysotile nanotubes $[Mg_3Si_2O_5(OH)_4]$	∅ = 25–50 nm, l = 100–700 nm a tubular structure	
6		Carbon nanotubes fulleroids type carbon content ~ 99 %	∅ = 2 nm; l = 200 nm tubes of graphite cloth	Increased packing density of particulate addition, changing the porosity of the material structure
7		The zeolite sol – type zeolite NaX, ratio Si/Al = 1,3…1,5	∅ = 0,8–1,2 nm reticular structure	
8	Ultra dispersed	"Astralen – S" water-soluble fullerene analogue carbon content ~ 99 %	the average cluster size 300 nm a tubular structure	1) Increasing the packing density of the addition of dispersed particles; 2) zoning structure
9		Micro silica $SiO_2 \cdot nH_2O$	~ 100–300 nm	
10	Micro dispersed	Montmorillonite – natural $(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$	< 1 micron layered, leaf structure	Zoning structure hardening
11		Shungit – C 60–70 %; ash 30–40 %; SiO_2 – 35–50 %; Al_2O_3 – 10–25 %	0,1–10 micron graphite-like globules	
12		Bergmeal – SiO_2 – 70–85 %; Al_2O_3 – 5–13 %; Fe_2O_3 – 2–5 % и др.	0,01–0,001 mm spherical rounded opaline globules of silica	

to form complex hierarchies. After accumulating a sufficient number of particles of the system when the probability of meeting and fusion of the particles becomes commensurate with the probability of their molecular growth, the process of agglomeration. There comes a second evolutionary transition "growth ® agglomeration of particles". This phenomenon is the main selection topological ranked units consisting in the fact that the medium destroys and eliminates disordered aggregates and promotes ranked forms consisting of particles with similar morphologic parameters.

In real materials technology agglomeration step may be controlled by additives and surface-active agents (surfactants) are widely used plasticizers and superplasticizers (SP).

In this regard, it seems to us important structural systematics mechanisms modifying effect of plasticizers and superplasticizers agglomeration step in the evolutionary route of solid formation [1]. It should further be noted that the use of plasticizing additives action is often important and necessary condition furthermore the possibility of introducing the nano- and ultrafine particles in hardening since in normal conditions, these particles are chemically active and prone to spontaneous agglomeration prevents uniform volume of distribution in the material obtained. Same class of surfactant additives can solve this rather complex task nanotechnology.

Stage of spontaneous pattern formation

Evolutionary change a hardening system objectively linked to the third evolutionary transition "agglomeration radio ® spontaneous pattern formation". In the late stage of growth and agglomeration step system state far from equilibrium, so a certain period within the system simultaneously develop the redistribution of matter and energy, which leads to spontaneous ordering system. There is a phenomenon of morphological selection and there is a "change in the geometry of the system", ordered aggregates formed a certain shape and size of the place of less ordered forms. Processes leading to the approximation of the size and shape of the particles to equilibrium, and called morphological selection. Streamlining processes occur by two mechanisms: recrystallization and solid phase [5].

From a technological point of view of the stage management of spontaneous pattern formation can be based on the temperature and high-temperature treatment, the use of different types of compaction force pressing for the introduction of particulate additives, etc. As a result, nano-modification on the stage of spontaneous pattern formation can form ordered structures hardening close-packed crystals, increase the area of intergranular contacts in malignancy. This is achieved by varying the morphology of the resulting systems, which also determines the type of contact that occurs (private crystal – contact contiguity, fiber-needle – contact fusion, plate-and-prism – contact germination) can also be spontaneously dispersed reinforcement structure itself.

Conclusion

Thus, evidence-based principles of management structure at the nano – level is a key factor in the development of high-tech composites modified construction of a new generation. Possible "nanotools" to create high-quality building composites quite a lot, the approaches are very diverse and they can count on effective innovative technological solutions that are useful for a wide range of building materials.

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