Analysis of the structure formation processes of building composites by geometric methods

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Abstract. The work considers a method of structure formation modeling in composite materials based on geometric methods. For this purpose, a differential system is written for the fractions of the volume, surface, linear and point phase of the structure forming components of the material. To study it, a decomposition into a gradient and generalized-conservative component was used. Approaches to modeling of the processes of structure formation and destruction based on the theory of gradient systems, which take into account the structural potentials for the surface and volumetric components of the composite material, were proposed. The hypothesis according to which the formation of a high-strength structure of the material is associated with the implementation of the oscillatory mode for the indicator of the fraction of the volumetric phase was proposed. The mechanism of increasing the strength of the composite binder dough based on the selective preservation of the strongest intercrystalline contacts was discussed.

One of the main features of the processes of structure formation in dispersed systems and, in particular, in the binder dough of a composite material, is the appearance of new physicochemical objects - internal interfaces. Together with other structural elements - clusters of binder, filler and aggregate, they form an integral structure of the composite material [1]. All of these objects are geometrically complex, often fractal-like. One of the demonstrations of this complexity is a significant difference in the shape of the formed crystals of the new phase from the spherical one. The shape of the polycrystalline phase, like the crystals themselves, is characterized by the presence of edges and apexes, i.e. is a three-dimensional body with a certain volume, interface area, rib frame length, number of apexes (Fig. 1).

Fig. 1. Schematic representation of geometric features of the emerging new phase: S – surface area, L – linear skeleton, P – apex points.

The presence of geometric features affects the physical processes of the growth of crystals of the new phase, and their physicochemical characteristics. The research of structure parameters by geometric method, using the representation of the polycrystalline phase as fractal objects [2], can be implemented both in composites with a crystallization mechanism of structure formation (gypsum binders) and at a different scale level, for microcrystalline formations prevailing in cement binder dough.

To display the features of the structure formation of objects of complex (fractal-like) geometry, we consider the vector field specified by the coordinates \((y_0(t), y_1(t), y_2(t), y_3(t))\). Each of its components...
corresponds to the proportion of point, linear, surface and volumetric components of the dispersed system \[3\]. Hereinafter, in order to consider the dynamic processes of structure formation and destruction, the possibility of changing these values with time as a result of physicochemical processes was taken into account. In the case of mineral binders, hydration and crystallization processes will be the main ones. The corresponding \(n\)-dimensional vector field \((y_0(t), y_1(t), \ldots, y_n(t))\) is quite definite if the differential system (1) is given:

\[
\frac{dy_i}{dt} = f_i(y_0,\ldots,y_n), \quad i = 0,\ldots,n, \tag{1}
\]

and the corresponding initial conditions \(y(t_0) = y^0\). System (1) can be considered in the general case together with balance and stoichiometric equations. All values \(y_i\) are nonnegative and bounded from above by one; therefore, in the correctly constructed model (1) according to the Bohl-Brauer theorem, the system has at least one fixed point - the equilibrium state \[4\]. When studying system (1), it is useful to single out the gradient, corresponding to the term \(-\nabla V(y)\), and the generalized conservative component \(Q(y)\) (2):

\[
\frac{dy}{dt} = -\nabla V(y) + Q(y). \tag{2}
\]

Let condition (3) be satisfied:

\[
Q \cdot \nabla V(y) = 0. \tag{3}
\]

Generalized conservative component \(Q(y)\) associated with motion along the lines of the potential level \(V(y)\). Since from (1) and (2) it follows (4):

\[
Q(y) = f(y) + \nabla V(y), \tag{4}
\]

then for \(V(y)\) we find a partial differential equation (5) similar to the Hamilton-Jacobi equation:

\[
(f(y) + \nabla V(y)) \cdot \nabla V(y) = 0. \tag{5}
\]

In equation (5), the transition to vector designations was carried out. Equations (4) and (5) allow one to carry out expansion (2).

The system described using (1) has a rather general form: in addition to asymptotically stable (physically realizable) equilibria, unstable, as well as limit cycles, and strange attractors can exist in it.

The primary model of structure formation in composite materials can be built on the basis of the gradient representation (6)

\[
\frac{dy}{dt} = -\frac{\partial V(y,c)}{\partial y}. \tag{6}
\]

Equation (6) includes the potential \(V(y_2,y_3)\) for volumetric \((y_2)\) and surface \((y_3)\) components of the material, which is sufficient to consider many problems of structure formation. Considering for this case the expansion in a Taylor series, and carrying out a number of transformations associated with the diagonalization of the matrix of coefficients \[5,6\], we obtain as a result the equation of an umbilical surface, for example, hyperbolic (7):

\[
V(y_2,y_3) = y_2^3 + y_3^3 + wy_2 x_3 - uy_2 - vy_3, \tag{7}
\]

where \(w, u, v\) – control parameters that depend, for example, on the conditions of structure formation.
In some cases, for example, when discussing the problems of material destruction, it is sufficient to take into account one geometric parameter that serves as an order parameter for the system under consideration - the fraction of surface states $y_2$. Here the calculation is extremely simplified and the analogy with the theory of phase transitions is strengthened. Thus, using potential (8):

$$V(q) = \frac{q^4}{4} + \frac{uq^2}{2} + \nu q,$$

(8)

corresponding to an assembly catastrophe, it is possible to cover, at least on a qualitative level, such effects as the destruction of a material that is initially in a structurally metastable state (Fig. 2), and many similar effects.

![Diagram](image)

Fig. 2. Qualitative display of the material destruction process: the fraction of the surface component $y_2$ increases.

One of the possible models of material destruction obtained using the above approach is a sharp increase in the proportion of surface, linear and point components: $y_2$, $y_1$ and $y_0$ respectively.

If in a real system there is no energy supply, then one should expect the approximation and realization of some stable stationary regime, which happens during structure formation in material media. When energy is supplied from the outside, structural rearrangements can have a cyclic character, which corresponds to asymptotically stable limit cycles in system (1) (Fig. 3, C). The role of such an energy source can be played by physicochemical processes at the interface, for example, an increase in temperature during wetting, the phenomena of hydration and dissolution. In view of the considered decomposition procedure (2) of system (1), of interest is the Rebinder - Segalova theory associated with the interpretation of the slowdown in strength growth during hardening of gypsum binders, as well as the sometimes observed (especially for lime binders) appearance of secondary minima on the plastic strength plots. The processes of structure formation and destruction are presented in this theory as a single whole, with a sequential alternation of phases of the prevailing growth processes of a new phase: fouling of the primary framework of the coagulation-crystallization structure, the occurrence of internal stresses, partial destruction of the primary framework, secondary enhancement of the growth of neoplasms. Thus, near the "Rebinder point" corresponding to the minimum of the potential $V(y)$, corresponding to the structural equilibrium of the composite binder, the generalized conservative component $Q(y)$, corresponding to rotational motion around the equilibrium state, does not vanish (Fig. 3, A, B).
Fig. 3. Elements of the phase portrait of system (1): equilibrium states E (A-stable focus, B-center, C-realization of an unstable focus and limit cycle).

The generalization of the Rebinder-Segalova theory [7], taking into account the considered concepts, allows us to put forward a geometric hypothesis about the formation of binding properties, which are emerged both at the level of individual mineral binders and in composite mixtures. Next consider the ratio of the proportions of the volumetric and surface components of the binder in an individual form or in the compound of a composite material (9):

\[ y_{32} = \frac{y_3}{y_2}. \] (9)

The results of Rebinder's work considered above, the research of the hardening of lime binders indicate the oscillatory nature of the change in this value during the hardening period (Fig. 2). The proposed hypothesis is as follows: the formation of a stone-like body and the hardening of a composite binder is closely related to the processes of cyclic changes of the parameter. \( y_{32} \). Phase changes are associated with the dissolution of the original binder, the formation and growth of a new phase (decrease \( y_{32} \)), the formation of a primary coagulation-crystallization framework and the gradual accretion of gypsum binder crystals, overgrowth of the primary framework (increase \( y_{32} \)), its partial destruction (decrease \( y_{32} \)), the formation of a new framework (increase \( y_{32} \)) [8]. The stabilization of the disperse system corresponding to the hardened composite is thus carried out as a result of a damped oscillatory process (Fig. 4, 3), and the corresponding phase plane \((y_{32}, \dot{y}_{32})\) is characterized by the presence of a stable focus.

Fig. 4. The nature of temporary changes \( y_{32} \) during hardening.

According to this hypothesis, the processes corresponding to the trajectories (Fig. 4, 1 and 2) lead to the formation of a material of low strength. For the formation of a material of increased strength, it is necessary to carry out an oscillatory process for \( y_{32} \). One of the interpretations of the role of
Oscillations in the formation of strength can be based on the theory of the selection process [9,10]. The destruction of the formed primary crystallization framework occurs due to the destruction of mechanically unstable, weakened bonds between the growing crystals of the gypsum composite, which in the next phase of the oscillatory process are replaced by new ones.

The proposed hypothesis is confirmed, in particular, by the study of microscopic preparations of hardening gypsum G-5 as a model system (Fig. 5).

Fig. 5. Images of hardening gypsum preparations. The figures show the time from mixing (min.) of the binder dough and the scale.

By the method of computer image processing, the values of the volumetric component $y_3$ and surface component $y_2$ are obtained, and the corresponding ratio $y_{32}$ is determined. Its change in the process of binder hardening is reflected in the graph (Fig. 6).
Fig. 6. Variations in the parameter $y_{32} = V/S$ during hardening.

Figure 2 shows the initial phases of the oscillatory process. Since a high-density crystallization structure is formed during the hardening of the material (Fig. 1, 24 min.), the possibility of optical methods is significantly limited. It should also be noted that there is a significant difference in the geometric properties of the quasi-two-dimensional (micropreparation) and three-dimensional crystallization structures. For further registration of the oscillatory process, indirect measurements of the desired parameter $y_{32} = V/S$, are applicable, for example, based on the electrical characteristics of the binder dough and plastic strength.

Thus, consideration of the geometric properties of materials from a quantitative and dynamic point of view seems to be one of the ways to analyze the processes of structure formation of binders. On the basis of the proposed method of modeling structure formation, a hypothesis is considered, according to which the oscillatory modes of hardening of the composite binder dough are associated with the selection of bonds, which is accompanied by the formation of high-strength structures of the composite material.

Methods of geometric dynamics, in our opinion, allow not only to investigation the peculiarities of the structure formation of binders, but also to pass to adequate problems of control and optimization of the structure formation of building composites.

Reference
[1] Solomatov V, Vyrovoy V, Dorofeyev V, Sirenko A 1991 Composite materials of reduced material consumption *Kiev: Budivelnyk*
[2] Feder E 1988 Fractals *New York: Springer Sience+Business Media*
[3] Dovgan I, Kolesnikov A, Semenova S, Kirilenko G 2011 Description of the geometric properties of dispersed systems using a polynomial *Bulletin of OSACEA* Issue 43 Odessa:Vneshreklamservice pp 115-119
[4] Pokrovsky I 1970 Lectures on the theory of ordinary differential equations *Moscow: Nauka*
[5] Haken G 1984 Synergetics *Berlin: Springer-Verlag*
[6] Gilmore R 1993 Catastrophe Theory for Scientists and Engineers *Dover Publications*
[7] Segalova E, Rebinder P 1962 The appearance of crystallization structures of hardening and conditions for the development of their strength *Moscow: Stroyizdat*

[8] Kolesnikov V 1990 Structure formation in dispersed systems *Odessa: OCEI*

[9] Eigen M, Schuster P 1979 Hypercycle A Principle of Natural Self-Organization *Berlin: Springer-Verlag*

[10] Kuznetsova V, Rakov M 1987 Self-organization in technical systems *Kiev: Naukova dumka*