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MATHEMATICAL MODEL OF THE EVOLUTION OF THE MESOSTRUCTURE IN POWDER COMPOSITE

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At the level of hierarchic representation of a powder medium intermediate between the macrostructure and the submesostructure (by the submesolevel within the framework of which the medium is approximated by a homogeneous mixture of particles differing from each other by coordination), we represent the powder composite as an association of mesoelements distributed in space in the form of an aggregate of contiguous random polyhedra [1]. As representative element of the mesostructural level of the hierarchic structure of powder composites we have to take the reference element whose characteristic parameters are the averaged values of the parameters for the real mesoelements of which the medium is composed.

The reference mesoelement is a powder cluster of polyhedral shape (in fact it is a Voronoi polyhedron [2]) whose structure is formed by a core consisting of particles with high values of coordination, and a shell characterized by low coordination numbers. It should be emphasized, in particular, that in a real powder composite there may be realized mesoelements of any magnitude, from the size of the body of the composite (which is improbable) to the size of several powder particles. The size of the reference mesoelement depends functionally on the dimensions of the composite itself and of the particles of which it is composed, and on the mean relative density.

Thus the compaction of the powder composite during its technological processing can be approximated in terms of the evolution of the reference mesoelement. This process is connected with the increase of the mean relative density of the mesoelement which is identically equal (by definition) to the mean relative density of the composite.

The following remark is of interest. A special trait of the structure of the mesoelement is that it is in fact a fractal object since obviously the density of the number of particles in it ρ_N decreases with the radius r, i.e. [3]

$$\rho_N \sim r^{-(E-D)}$$

where E is the Euclidean dimension of space; D is the fractal dimension of the mesoelement. We may therefore say that the compaction of the powder medium can be identified with the process of increasing the fractal dimension of the reference mesoelement. Here we take into account the limit condition:

$$\lim_{\langle\rho\rangle\to\langle\rho\rangle_{max}} D = E.$$

The evolution of the mesostructure can consequently be described in terms of the theory of fractals. However, particular attention has to be given to the circumstance that from the point of view of its submeso- and macrostructure the powder composite is not a fractal.

The increase of the mean relative density of the reference mesoelement during compaction of the composite is due to the mutual displacement of particles between the shell and the core. This entails, compaction, firstly of the core in consequence of the increased coordination of its particles; secondly as a result of exchange of particles between the shell and the core (some particles of the shell become part of the core, and conversely particles of the core become part of the shell); thirdly, it is possible that particles of the shell become part of the core beyond their boundary (such a situation arises as a result of fluctuational increase of coordination of particles inside the shell with their subsequent capture by the core when its volume increases).

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For the quantitative description of the presented scenario we introduce the characteristics of the core A and of the shell B whose correlation we represent as

$$A+B=1 \tag{1}$$

(as such characteristics we may regard, e.g., the corresponding concentrations of particles or the relative volumes taken up by the core and the shell). Then the above-named processes can be represented within the framework of the formalism of generalized reactions [4]. The processes of transition of particles on the boundary of the core and shell from the shell into the core and conversely from th core into the shell can be written as A + B → 2A and 2A → A + B, respectively; the transition of shell particles into the core outside their boundary as B + B → A + B (or B → A, which is the same); and the process of increased coordination of core particles as A + A → 2A. Thus we can write the system of generalized reactions:

$$\begin{cases} A+B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2A\,, \\ B \xrightarrow{k_2} A\,, \end{cases} \tag{2}$$

where k_1, k_{-1}, k_2 are the speeds of the corresponding generalized reactions (in system (2) transitions type A → A are not taken into account since they are insubstantial in the given context).

The processes described by system (2) are represented by the differential equation describing the evolution of the parameter:

$$\frac{dA}{dt} = k_1AB - k_{-1}A^2 + k_2B\,, \tag{3}$$

where the minus sign in the second term on the right-hand side indicates that the parameter A decreases since the corresponding stage of the process occurs. With (1) taken into account, the right-hand side of (3) assumes the form $k_1AB - k_{-1}A^2 + k_2B = k_1A(1 - A) - k_{-1}A^2 + k_2(1 - A) = -(k_1 + k_{-1})A^2 + (k_1 - k_2)A + k_2$.

Thus processes described by system (2) are represented by the differential equation describing the evolution of the parameter:

$$\frac{dA}{d\left[\left(k_1 + k_{-1}\right) t\right]} = -A^2 + \frac{k_1 - k_2}{k_1 + k_{-1}} A + \frac{k_2}{k_1 + k_{-1}}\,, \tag{3}$$

which in view of the changed designations

$$\left(k_1 + k_{-1}\right) t \equiv t^*\,, \quad \frac{k_1 - k_2}{k_1 + k_{-1}} \equiv \alpha\,, \quad \frac{k_2}{k_1 + k_{-1}} \equiv \beta \tag{5}$$

assumes the form

$$\frac{dA}{dt^*} = -A^2 + \alpha A + \beta\,. \tag{6}$$

Model (3), describing a real physical process, has to be structurally stable. Let us carry out the respective investigations.

The steady states $S_{1,2}$ of the system described by Eq. (6) are determined from the condition dA/dt* = 0, i.e.,

$$A^2 - \alpha A - \beta = 0\,,$$

hence

$$S_{1,2} = \alpha/2 \pm \sqrt{\alpha^2/4 + \beta}\,. \tag{7}$$

The second steady state of the system is nonphysical ($S_2 < 0$); to solve the problem of the stability of the state S_1 we rewrite (6) with a view to (7) in the form

$$-\frac{dA}{dt^*} = \left(A - S_1\right)\left(A - S_2\right) \tag{8}$$

and we examine the fluctuation $\sigma(t^*)$ of the steady state S_1. Then

$$A(t^*) = S_1 + \sigma(t^*) \ . \tag{9}$$

Substituting (9) into (8) we write

$$\frac{d}{dt^*}[S_1 + \sigma] = [S_1 + \sigma - S_1]\,[S_1 + \sigma - S_2]$$

or

$$\frac{d\sigma}{dt^*} = \sigma\left[\sigma - (S_1 - S_2)\right] \ . \tag{10}$$

Integration of Eq. (10) yields the time dependence for the fluctuation:

$$\sigma\,(t^*) = \frac{C(S_1 - S_2)\exp\left[-(S_1 - S_2)\,t^*\right]}{1 - C\exp\left[-(S_1 - S_2)\,t^*\right]} \tag{11}$$

(C is the integration constant), and an analysis of the asymptotics of expression (11)

$$\lim_{t^*\to\infty} \sigma(t^*) = 0 \tag{12}$$

leads to the conclusion that the steady state S_1 of the model system is asymptotically stable, and that consequently the corresponding model is structurally stable.

We note now that the differential equation (8) is autonomous, and the nature of the steady-state solution S_1 (7) can be investigated from the point of view of the evolution of the affix on the phase line [5]. The general form of the equation is as follows:

$$\frac{dA}{dt^*} = F(A) \ ,$$

where

$$F(A) = -(A - S_1)\,(A - S_2) \ . \tag{13}$$

When the parameter A deviates from the steady state S_1 to the right by some value $\delta > 0$, expression (13) becomes negative:

$$F(A \equiv S_1 + \delta) = -(S_1 + \delta - S_1)\,(S_1 + \delta - S_2) < 0 \ ,$$

and when it deviates to the left, the expression becomes positive:

$$F\,(A \equiv S_1 - \delta) = -(S_1 - \delta - S_1)\,(S_1 - \delta - S_2) > 0 \ .$$

Consequently, the steady state of Eq. (8) is an attractor of the investigated system.

We rewrite (8) in the form

$$\frac{dA}{(A - S_1)\,(A - S_2)} = -dt^* . \tag{14}$$

Integration of (14) leads to the time dependence of the characteristic parameter of the mesostructure:

$$A\,(t^*) = \frac{S_1 - S_2(A_0 - S_1)\,(A_0 - S_2)^{-1}\exp\left[-(S_1 - S_2)\,t^*\right]}{1 - (A_0 - S_1)\,(A_0 - S_2)^{-1}\exp\left[-(S_1 - S_2)\,t^*\right]} \ , \tag{15}$$

where $A_0 \equiv (t^* = 0)$. For solving (15) with a view to Eq. (8) the following asymptotic relation is correct:

$$\lim_{t^*\to\infty} A(t^*) = S_1 \ . \tag{16}$$

That the investigated system contains the attractor (16), of which $S_1 \neq 1$ is characteristic, shows that it is impossible to compact the material to a state in which the difference between the core and the shell of the reference mesoelement would disappear (this does not apply to the vicinity of the point corresponding to the mean relative density at which all the topological phases are equiprobable). In other words, we have to assume that the mesostructure is inherited in the material at all stages of the technological process, and consequently it gives rise to sources of pores (sutural porosity) which have a direct effect on the behavior of the material, both during its technological processing and in its subsequent operation.

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