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STRUCTURE FORMATION IN POWDER SYSTEMS WITH CAPILLARY SPREADING

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Structure formation in a powder mixture with capillary spreading of one of its components is considered. The spreading processes are described by a diffusion-type equation derived and homogenization equations, with fractal representations employed to characterize the spatial structures of a melt in a powder medium. Experimental studies with a model system show satisfactory agreement between the model and experimental data.

Introduction. Capillary spreading plays a significant role in many technological processes, in particular, in such phenomena as self-propagating high-temperature synthesis (SHTS) in systems with a melting reagent or product. When a reagent spreads, a primary layer of the product is formed, which determines the final spatial and chemical structures of the end product. In spreading, the processes of heat release are most intense, which determines the temperature regime of formation of the phase composition of a sample. Therefore, investigation of processes of structure formation in the case of capillary spreading is, in our opinion, of great importance.

The majority of works along this line, e.g., [1], have been devoted to impregnation of a chemically homogeneous medium by either an inert liquid or a reagent. In this, it has, as a rule, been assumed that the skeleton was sufficiently rigid and not deformed upon impregnation. It is pertinent to note that structure formation of composite materials with capillary spreading of one of the components of the latter is insufficiently studied. The filtration models used allow determination of the characteristics of a powder medium after capillary spreading, but they were obtained, firstly, under the assumption of a rigid skeleton, which is not always, as experiments have shown, justified. Secondly, for quantitative evaluation it is necessary to know the physical properties of the melt and the wetting angle. But these quantities depend greatly on the state of the skeleton surface (the presence of oxide films, adsorbed gases), and the melt viscosity is also dependent of the content of impurities. These characteristics are rather difficult to control. Moreover, it is impossible to carry out experiments on individual particles. Also, it does not seem correct to characterize the structure of the skeleton or pore space by a single parameter, i.e., porosity (or by the crookedness of the pores). Therefore, penetration determination is so approximate that use of this or any other model becomes equally possible and impossible.

Proceeding from the above reasoning we should seek a model that corresponds to the observed picture and at the same time provides a quantitative description of the structure without complicated experiments to determine the physical properties of the mixture components and the initial structure of the medium.

Formulation of the Problem and Its Solution. We have undertaken some theoretical and experimental studies of the processes of structure formation of composite materials involving spreading of one of their components. As a model system, we selected an iron-bronze pair, which is convenient in many respects: the great difference in melting points, the low melting point of the low-melting component, and relatively good moldability. This pair is also convenient for microscopic structure studies. It should be noted that for some filtration problems [1] solutions have been obtained that depend on the x^2/t combination, which suggests the possibility of describing our problem by equations of the diffusion type. In [2], an assumption is also made about the possibility of reducing the problem of viscous fingers in porous media to the diffusion problem. Therefore, it seems reasonable to formulate our problem in the following way.

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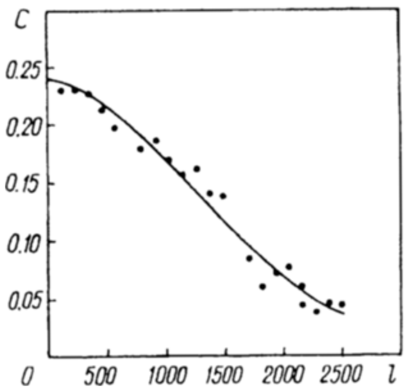

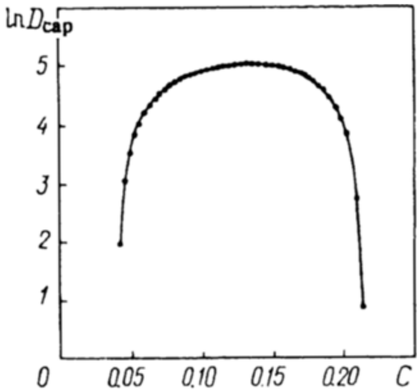

Fig. 1. Depth distribution of bronze. C, %; l, μm.

Fig. 2. Concentration dependence of the natural logarithm of the capillary mass transfer coefficient of bronze in compressed iron powder. Compression pressure is 6 ton/cm^2. D_{cap}, μm^2/sec.

We use the law of mass conservation in differential form:

$$\partial m/\partial t = \operatorname{div}(\rho v)\,. \tag{1}$$

We assume that $m = C\rho$. Now we write the Darcy equation

$$V = -K\nabla p\,, \tag{2}$$

where it is assumed that pressure is a function of concentration, $f(C)$. Substituting (2) into (1), we arrive at

$$\partial c/\partial t = -\operatorname{div}(D_{cap}\nabla C)\,, \tag{3}$$

where $D_{cap} = K(\partial p/\partial C)$. Using Eq. (3), we can propose an experiment scheme similar to a diffusion scheme according to the definition of $D_{cap}(C)$.

An experiment was conducted following the method of diffusion pairs: the melt was situated below, while the high-melting skeleton was compressed from above. Heating was carried out for 20 min at up to 1000°C; heat treatment was accomplished in a hydrogen atmosphere. The volume concentration of bronze was measured on a "Neophot-31" unit with automatic image processing. As a result, we obtained the depth distribution of the bronze in the sample (Fig. 1). The concentration dependence of the capillary mass transfer was calculated by the Matano method [3], whose disadvantage is low accuracy at the ends of a concentration profile. The results obtained are shown in Fig. 2, where the form of the curve allows the coefficient of capillary mass transfer to be constant in the entire concentration range measured (the end effects are neglected). Then the mean value of the capillary mass transfer coefficient is $D_{cap} = 1.06^{+} - 0.05 \cdot 10^{-4}$ cm^2/sec.

Measurement of depth distribution of the melt in a "diffusional" pair can be based on either metallographic methods [4] or X-ray microspectroscopic methods.

We assume that D_{cap} = const in the experiment conducted. Then for this case it can be shown [5] that the concentration distribution is of the lognormal.

To check this assumption experimentally, we measured the copper-concentration distribution in the powder mixture (iron-bronze) after heat treatment. A histogram of the copper concentration distribution is given in Table 1 and shows fair agreement with theory. Thus, the diffusional approach formulated above has proved to be fruitful and can be used to describe processes of capillary spreading of a low-melting component in a powder medium. It also has the advantage that methods which have proven to be successful are available for determining the diffusion characteristics of the materials.

We now consider the possibility of obtaining the geometric characteristics of the spatial distribution of a melt in a powder medium. From the following considerations we will try to establish a relationship between the

TABLE 1. Histogram of Copper Concentration Distribution

C, % wt.	Experiment	Calculation	Variance	Probability density function
0.000254–0.0749	200	223	0.182	0.77
0.0749–0.15	46	37.3	0.0109	0.129
0.15–0.224	16	16.1	0.539	0.554
0.224–0.229	9	8.87	0.0853	0.0306
0.229–0.373	9	5.57	0.162	0.0192
0.373–0.448	2	3.78	0.064	0.013
0.448–0.523	3	2.71	0.123	0.00936
0.523–0.597	5	2.02	0.319	0.00698

parameters characterizing homogenization ($V = \delta/\langle C\rangle$ is the coefficient of concentration variation, which is a numerical characteristic of the distribution function, and δ is the variance) and the geometric characteristics of a power medium by employing fractal representations. For this we use the expression for V derived in [5]

$$V = V_0 \exp\left\{bD_0 t \exp\left(-Q/RT\right)\right\}, \tag{4}$$

where b has a dimension that is the reciprocal of the square of length and characterizes the spatial inhomogeneity. Following [5] we rewrite (4) as

$$V = V_0 \exp\left\{\beta \langle C\rangle^{2/3}\, t \exp\left(-Q/RT\right)\right\}, \tag{5}$$

Thus, we have an expression for the capillary homogenization of the powder medium. It is clear that during spreading the inhomogeneity decreases from V_0 to V_t in time t, while the microspace containing, e.g., 99% of the mass of the low-melting component increases from $\Delta\nu_0$ to $\Delta\nu_t$. Then we can write

$$V_t/V_0 \sim \left\{\Delta\nu_0/\Delta\nu_t\right\}^{1/2}. \tag{6}$$

Now we pass from spaces to their characteristic dimensions. At the initial moment of time before spreading, $\Delta\nu_0 \sim R_0^3$. Some time t after the beginning of spreading, the structure of the melt, as experiment shows, becomes fractal. Then the space occupied by the melt can be represented as $\Delta\nu_t \sim R_t^{D_f}$, where D_f characterizes the spatial position of the considered component, and R_0 and R_t are the dimensions of microspaces at the initial moment and at time t. Substituting the obtained expressions into (6) and taking into account (5), we obtain after some logarithmic operations an expression for D_f:

$$D_f \approx 3\,\frac{\ln R_0}{\ln R_t} - 2\left\{\beta \langle C\rangle^{2/3}\, t \exp\left(-Q/RT\right)\right\}/\ln R_t. \tag{7}$$

Expression (7) can be rewritten in terms of the coefficient of concentration variation as

$$D_f \approx 3\,\frac{\ln R_0}{\ln R_t} + \ln\left(V_0/V_t\right)/2\ln R_t. \tag{8}$$

It is clear that R_t is a function of time, and this dependence can be found by solution of the diffusion problem for a grain of powder in a matrix with the corresponding boundary conditions. But to a first approximation we can assume that

$$R_t \approx R_0 + \sqrt{D_{\text{cap}} t}\,. \tag{9}$$

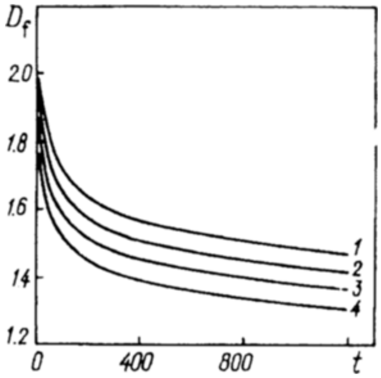

Fig. 3. Fractal dimension versus sintering time at different capillary mass transfer coefficients: 1) 1 cm^2/sec, 2) 2, 3) 3, 4) 4 for particles sized to 100 μm. t, sec; D_f, dimensionless quantity.

Then for small times when (9) is valid we can rewrite (8) in the form

$$D_f \approx 3 \bigg/ \left(1 - \left(\frac{\sqrt{D_{cap}}}{R_0}\right)\right) - 2 \left\{\beta \langle C\rangle^{2/3} t \exp\left(-Q/RT\right)\right\} \bigg/ \ln R_0 \left(1 - \left(\frac{\sqrt{D_{cap} t}}{R_0}\right)\right). \tag{10}$$

Thus, an expression is obtained that relates the initial structural characteristics of a powder medium (the capillary mass transfer coefficient, the mean concentration of the low-melting component, the size of its particles) with the structure of the end product D_f, knowledge of which allows determination of the melt surface S, which depends on the fractal dimension $S \sim R_f^{D_f - 1}$. The final porosity, the portion of the melt that has penetrated into pores, etc. can be found from simple geometric considerations; therefore, it makes no sense to discuss them.

Let us take the ratio of the fractal dimensions of samples with the same diffusion characteristics but different mean concentrations of bronze. Then, for the values used we obtain

$$\frac{D_{fC_1}}{D_{fC_2}} = \frac{3 - 2C_1^{2/3}/\ln(R_0)}{3 - 2C_2^{2/3}/\ln(R_0)} \approx \frac{3 - 2\cdot 0.1^{0.67}/\ln(100)}{3 - 2\cdot 0.5^{0.67}/\ln(100)} \approx 1.2\,.$$

The experimental values give ~1.1, which corresponds to the calculated data (within the experimental error); therefore, we can assume that the obtained expressions describe the observed picture adequately and that the assumptions made are valid.

It should be noted that the expressions for the fractal dimension and the coefficient of concentration variation were obtained under the assumption of "unlimited solubility," but it is clear that microspaces with a zero melt concentration (i.e., containing a skeleton) exist. Therefore, "unlimited solubility" can be spoken of only when the scale of spatial averaging is sufficiently great, i.e., insufficiently detailed. Then (5) must be rewritten in the form

$$V = V_{fin} + V_* \exp\left\{\beta \langle C\rangle^{2/3} t \exp\left(-Q/RT\right)\right\}, \tag{11}$$

where V_{fin} is the final coefficient of concentration variation: $V_* = V_0 - V_{fin}$. The quantity V_{fin} can be written [5] as:

$$V_{fin} = \left\{(1 - \langle C\rangle)\, C_v\right\}^{1/2}/\langle C\rangle\,. \tag{12}$$

With the aforesaid taken into consideration, the expression for the fractal dimension changes as well.

It is noteworthy that the obtained expressions make it possible to trace the evolution with time of a structure for various characteristics of the medium, which are to be determined in a separate experiment. It is clear that with prolonged impregnation, the melt structure strives to reproduce the structure of the pore space by forming pores at the initial sites of particles of the low-melt component, thus tending to some equilibrium structure. This conclusion follows from the proposed model. Figure 3 shows the evolution of the fractal dimension of a melt for various coefficients D_{cap}. As follows from the equations derived, the coefficient of capillary mass transfer is also a structural characteristic of the initial medium, provided that it interacts with the melt. Therefore, it can be stated that the final structure of a powder medium is determined by the coefficient D_{cap}.

The dependence of the coefficient D_{cap} on the structural characteristics of a powder medium requires a separate study that can be accomplished by both full-scale and computer-aided experiments.

The proposed approach can be extended to the case in which diffusion and chemical reactions proceed simultaneously. For this it is sufficient to supplement Eq. (3) with equations of the corresponding processes and include terms to describe sinks. It is also noteworthy that the proposed approach makes it possible to avoid an analysis of the shapes and sizes of the pores and particles of the high-melting skeleton. Moreover, the approach is not restricted to the case of a rigid skeleton.

Concluding Remarks

1. A scheme is proposed to describe spreading of a low-melting component in a powder medium. The obtained solution, taking into account the concentration of the components and the structural characteristics of the pore space, allows quantitative experimental verification. Moreover, it can be used to determine optimum characteristics of a powder medium.

2. The influence of the structural characteristics of the medium on the formation of the final microstructure is studied experimentally.

3. The method proposed to describe capillary spreading is compared with experiment and satisfactory agreement is obtained.

4. It is shown that traditional "diffusional" procedures can be successfully used for investigation of the processes under consideration.

5. The proposed approach can be extended to the case of chemical reactions accompaning capillary spreading.

NOTATION

t, time; m, mass; ρ, density; v, velocity; C, concentration; $\langle C \rangle$, mean concentration; indices 1 and 2 pertain to the samples with different concentrations of the low-melt component; K, penetration coefficient; D_{cap}, capillary mass transfer coefficient; V, coefficient of concentration variation; subscripts fin and 0, indicate final and initial value; Q, activation energy; R, gas constant; T, absolute temperature; Δv, volume element; b and β, m^{-2}-dimension and dimensionless constants, respectively; C_v, volume portion of the component; D_f, fractal dimension; R_0, R_t, microspace dimensions at the initial moment and at moment t.

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