

HEAT AND MASS TRANSFER IN DISPERSE MEDIA

ON THE COMPETITION OF DIFFERENT MECHANISMS OF SINTERING UNDER SHS-DISINTEGRATION

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Theoretical estimates of changes in the strength of SHS products that take place during their sintering and cooling are proposed. The possibility of passing from the mechanism of diffusion sintering to the mechanism of sintering by compaction of the material under the action of external mechanical loads has been taken into account. It has been shown that the competition between these mechanisms of sintering under cooling of products is responsible for the nonmonotonic character of the dependence of the strength of product on the delay time.

Introduction. The use of the process of self-propagating high-temperature synthesis (SHS) in combination with the shearing of the initial components and products formed in the course of synthesis opens up wide possibilities for developing new heat- and corrosion-resistant structural materials. Mechanical action leads to a mixing of the incipient highly dispersed structure and depresses the development of the crystallization and recrystallization processes. Preliminary experiments permit the conclusion that the deformation parameters and, first of all, the deformation rate have a strong effect on the combustion and structure-formation processes: the change in the grain size and form and the relative positions of grains [1]. Varying these parameters over a wide range, it is possible to change the quality of the powder obtained and its morphology. However, the different aspects of the influence of mechanical actions on the SHS process have been little studied up to now.

One specific example of conducting the SHS process under mechanical actions is the new technological method for obtaining powders of refractory oxygen-free compounds proposed in [2–4] and named the SHS-disintegration. This method (Fig. 1) relies on the disintegration of the material obtained in the combustion wave under the conditions of shearing and the external pressure applied. The realization of the method is based on the macroscopic deformability of the hot mass of the synthesized product; therefore, the key to the understanding of this process is knowledge of the rheological behavior of SHS products in the high-temperature region. In performing experiments on the SHS-disintegration, we have revealed many interesting phenomena. It turned out that it is not always possible to completely disintegrate the material obtained by the SHS method. Upon completion of the chemical reaction in the SHS product various physicochemical postprocesses proceed. The hot porous material is compacted under the action of the external pressure, individual particles form a structural frame, and in the material intensive sintering and solidification of combustion products due to the cooling down occur. Concurrently, the processes of structure and phase formation, crystallization, and recrystallization proceed in the material. Contacting grains of the crystalline substance upon sufficient heating form, as a rule, a common boundary. The intergranular contact expands; in other words, the process of grain intergrowth develops. The development of this process depends on the presence of the liquid separating adjacent grains and the action of the internal and external forces. Under the experimental conditions different sintering mechanisms can be realized: sintering under the action of the internal forces alone (works before an external pressure begins to be applied) and under the conditions of the applied external pressure (from the beginning of disintegration to the end of the process). It has been shown experimentally in [4] (Fig. 1) that the competition between these sinter-

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ing mechanisms against the background of the cooling down of combustion products determines the nonmonotonic character of the dependence of the disintegrated mass of products M on the time of application of mechanical actions. This means that under optimal conditions the proceeding of the postprocesses (sintering, compaction, cooling, etc.) should provide a minimum strength of the material favorable for its disintegration. With increasing delay time t_d (the time interval between the initiation of combustion and the beginning of the application of a load) the material can acquire such a strength that complete disintegration will turn out to be impossible. Thus, one of the crucial points in conducting the SHS process under mechanical actions is the choice of the optimal delay time at which, all other things being equal, there is a maximal yield of disintegrated powder. The physical meaning of the optimal delay time is the time at which the rheological properties of the material become optimal for shearing.

The aim of the present work is to endorse the simple ideas expressed on the basis of a phenomenological description of the change of the possible sintering and heat transfer mechanisms with account for the temperature dependence of viscosity coefficients and diffusion of the material. On the basis of the mathematical SHS-disintegration model the time dependence of the product strength has been calculated for different mechanisms of the sintering process.

Theory. Let us introduce a geometric characteristic x — the intergranular contact. Qualitatively, it may be assumed that it also defines the contact strength between particles in sintering (x is directly proportional to the strength). The formation and development of a contact between individual particles can occur by different sintering mechanisms. In particular, detailed theoretical and experimental studies of the features of the sintering of spherical particles (diffusion-viscous flow, bulk, surface, and boundary diffusion, evaporation–condensation and dislocation mechanisms) have been made [5]. For each of these sintering mechanisms the kinetic equations defining the $x(t)$ dependences are known. In the literature, it is noted that one should use particular care in formulating qualitative laws and a specific kind of kinetic equations, since they are empirical and describe only a certain set of experimental data, and are not dictated by the general laws of mechanics and thermodynamics [6]. Under real conditions, interparticle contacts can grow under the action of several sintering mechanisms whose occurrence in time is not always sequential (one after another). However, for the purpose of the present estimate, let us make the simplifying assumptions that the sintering process has two stages: at the first stage the diffusion mechanism of sintering due to the internal forces acts, and at the second stage the motive force of sintering is the external mechanical action leading to a compaction of the material due to the viscous flow. Let us consider each mechanism separately.

1. *Mechanism of bulk diffusion in sintering due to internal forces.* The kinetics of this process can be described by an equation of the form [5]

$$\frac{dx}{dt} = \frac{\alpha\omega D \nabla K}{kT}, \quad K = \frac{1}{x} - \frac{1}{r}, \quad r = \frac{x \cos(\varphi)}{1 - \cos(\varphi)}. \quad (1)$$

Substituting the values of K and r into (1), we obtain

$$x^2 \frac{dx}{dt} = \frac{\alpha\omega D (1 - 2 \cos(\varphi))}{kT \cos(\varphi)}. \quad (2)$$

Here the diffusion coefficient is temperature-dependent $D = D(T)$. For clarity and simplicity of the calculation of the total strength $x(t)$, let us write the temperature dependence of the viscosity and the diffusion coefficient in the following form:

$$\mu = \mu_0 \sqrt{\frac{T_0}{T}}, \quad D = D_0 \sqrt{\frac{T}{T_0}}.$$

Let us assume instantaneous heating of the reactive mixture to the combustion temperature (T_c) followed by a smooth cooling as $T = T_c \exp\left(-\frac{t}{t_{th}}\right)$. Integrating (2) and taking into account that the process proceeds from 0 to t_d , we can write

$$\int_{x_{01}}^{x_1} d\frac{x^3}{3} = \int_0^{t_d} \frac{D_0 \exp\left(\frac{t}{2t_{th}}\right) \alpha \omega \psi}{kT} dt, \quad \psi = \frac{1 - 2 \cos(\varphi)}{\cos(\varphi)}.$$

Assuming that $x_{01} \ll x_1$, we obtain the expression for the intergranular contact at the instant of time t_d — termination of the sintering process by the first mechanism

$$x_1 = \left[\frac{6D_0 \alpha \omega \psi t_{th} \left(\exp\left(\frac{t_d}{2t_{th}}\right) - 1 \right)}{kT} \right]^{1/3}. \quad (3)$$

2. *Mechanism of sintering under compaction conditions.* The kinetics of the sintering process under compaction conditions can be described by an equation of the form

$$\frac{dx^2}{2} = \frac{4\alpha R}{3\mu} dt. \quad (4)$$

This process proceeds in the time interval from t_d to $t_d + t_{dis}$ (time of termination of disintegration); therefore, we can write

$$\int_{x_1}^{x_2} \frac{dx^2}{2} = \int_{t_d}^{t_d+t_{dis}} \frac{4}{3} \frac{\alpha R}{\mu} dt.$$

Usually, it is assumed that viscosity is a quantity inverse to the diffusion coefficient: $\mu(T) = 1/D(T)$. Then

$$\mu(T) = \mu_0 \sqrt{\frac{T_0}{T}}.$$

Choosing the same law of cooling as in case 1 and taking into account that the process proceeds from t_d to $t_d + t_{dis}$, we obtain

$$\int_{x_1}^{x_2} \frac{dx^2}{2} = \int_{t_d}^{t_d+t_{dis}} \frac{4}{3} \frac{\alpha R \exp\left(-\frac{t}{2t_{th}}\right)}{\mu_0} dt.$$

Hence the value of the quantity of intergranular contact at the instant of time $t_d + t_{dis}$ is the termination of the process of sintering by the second mechanism

$$x_2 = \left[\frac{16}{3} \frac{\alpha R}{\mu_0} t_{th} \left(1 - \exp\left(-\frac{t_{dis}}{2t_{th}}\right) \right) \right]^{1/2} \exp\left(-\frac{t_d}{4t_{th}}\right) + x_1. \quad (5)$$

According to the assumption made, the sintering processes proceed sequentially one after another. Therefore, the initial condition for the intergranular contact by the second mechanism is the finite quantity of intergranular contact by the first mechanism. Thus, the total quantity of the intergranular contact x is defined as a result of the proceeding of the sintering processes (1) and (2) and $x = x_2$. In view of (3) and (5) we have

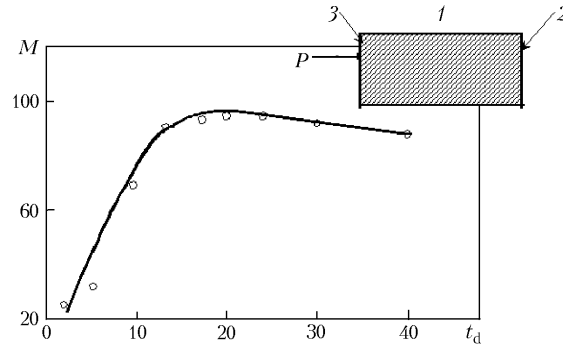


Fig. 1. Experimental dependence of the relative mass M of the disintegrated product on the delay time t_d ; in the inset — scheme of the SHS-disintegration process: 1) mould; 2) disintegration boundary; 3) mobile boundary to which pressure P is applied. M , %; t_d , sec.

$$x_2 = \left[\frac{16}{3} \frac{\alpha R}{\mu_0} t_{th} \left(1 - \exp\left(-\frac{t_{dis}}{2t_{th}}\right) \right) \right]^{1/2} \exp\left(-\frac{t_d}{4t_{th}}\right) + \left[\frac{6D_0\alpha\omega\psi t_{th} \left(\exp\left(\frac{t_d}{2t_{th}}\right) - 1 \right)}{kT} \right]^{1/3}. \quad (6)$$

To determine the value of the delay time corresponding to the maximum product yield, one should find the minimum point of the function $x_2(t_d)$. As a result of the differentiation of expression (6) and adequating it to zero, we obtain

$$\frac{dx_2}{dt_d} = \left[\frac{16}{3} \frac{\alpha R}{\mu_0} t_{th} \left(1 - \exp\left(-\frac{t_{dis}}{2t_{th}}\right) \right) \right]^{1/2} \left[-\frac{1}{4t_{th}} \exp\left(-\frac{t_d}{4t_{th}}\right) \right] + \left[\frac{6D_0\alpha\omega\psi t_{th}}{kT} \right]^{1/3} \frac{\exp\left(\frac{t_d}{2t_{th}}\right)}{6t_{th} \left(\exp\left(\frac{t_d}{2t_{th}}\right) - 1 \right)^{2/3}} = 0.$$

To simplify the form of this expression, let us make the following substitutions:

$$\tau = \frac{t_d}{2t_{th}}, \quad h = \frac{3 \left[\frac{16}{3} \frac{\alpha R}{\mu_0} t_{th} \left(1 - \exp\left(-\frac{t_{dis}}{2t_{th}}\right) \right) \right]^{1/2}}{\left(\frac{6\alpha\omega D_0\psi t_{th}}{kT_0} \right)^{1/3}}.$$

Then it can be given as

$$\frac{\exp(\tau)}{(\exp(\tau) - 1)^{2/3}} - h \exp\left(-\frac{\tau}{2}\right) = 0. \quad (7)$$

Results of Numerical Calculations. From the transcendental equation (7) we can get the optimal value of the delay time corresponding to the minimal quantity of the intergranular contact (minimal strength) acquired by the specimen in the course of the process of SHS-disintegration, i.e., to the maximal quantity of disintegrated powder. The calculation scheme should be as follows. For given disintegration time, properties of the material, and characteristics of the process, we calculate the initial parameter h . From (7) we determine its corresponding value of τ . The value obtained establishes the relation between the delay time and the characteristic cooling time at which the function $x(t_d)$

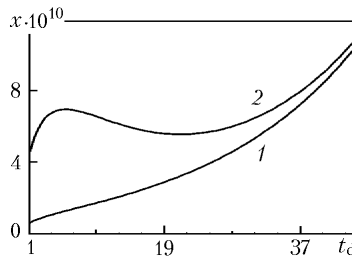


Fig. 2. Value of the intergranular contact x versus the delay time t_d for different methods of sintering: 1) sintering due to internal forces; 2) total strength due to the action of both forces. t_d , sec; x , m.

has a maximum. For example, for the disintegration time $t_{\text{dis}} = 2$ sec and $h = 3$ the delay time corresponding to the minimal strength $t_d = 20$ sec, which is in agreement with the experimental results (Fig. 1).

Let us make numerical calculations of the dependences of the quantities of the intergranular contact $x(t)$ and $x(t_d)$ for the sintering process provided by both mechanisms. For the calculations, we took the data for the Ni-Ti intermetallide powder: $D_0 = 1.4 \cdot 10^{-2} \text{ m}^2/\text{sec}$, $\omega = 1.5 \cdot 10^{-29} \text{ m}^3$, $\alpha = 0.1 \text{ J/m}^2$, $k = 1.38 \cdot 10^{-23} \text{ J/K}$, $R = 5 \cdot 10^{-6} \text{ m}$, $\mu_0 = 10^{11} \text{ Pa}\cdot\text{sec}$, $r_0 = 15 \cdot 10^{-3} \text{ m}$, $c = 522.16 \text{ J/(kg}\cdot\text{K)}$, $\lambda = 22 \text{ W/(m}\cdot\text{K)}$.

Figure 2 shows the dependence $x(t_d)$ of the contact strength on the delay time by the mechanism of sintering due to the internal forces (curve 1) and the dependence of the total quantity of the intergranular contact on the delay time (curve 2). Curve 1 is rising, and curve 2 is monotonic and has a maximum. This feature of sintering with a change of its mechanisms can be interpreted qualitatively as a consequence of the different rate of change in the contact strength depending on the temperature.

Indeed, according to the kinetic equation (1), the sintering rate is directly proportional to the self-diffusion coefficient $D(T)$, and according to Eq. (4), it is inversely proportional to the coefficient of viscosity $\mu(T)$. One should differentiate between the dependences of the quantity of the intergranular contact, or the contact strength, on the current time and on the delay time. Under the experimental conditions of [4] the disintegration time remains constant. Since the total time of the experiment $t = t_d + t_{\text{dis}}$, then with increasing delay time the total time of the experiment also increases. If only one sintering mechanism acted, then the contact strength would increase with time. In our consideration, under sequential actions of the two sintering mechanisms an increase in the delay time leads to a widening of the time interval of sintering due to the first mechanism (from 0 to t_d), which causes an increase in the contact strength (curve 1). In so doing, the time of sintering due to the second mechanism equal to the disintegration time t_{dis} remains constant (such are the experimental conditions in [4]), and the total time of the experiment $t = t_d + t_{\text{dis}}$ increases. However, the influence of the total sintering time on the total contact strength may turn out to be weaker than the influence of the rate of growth of this strength with cooling combustion products. As a result, the total strength turned out to depend nonmonotonically on the delay time (curve 2). The physical meaning of this result is exactly the fact that there exists an optimal time of application of mechanical actions on the SHS-processes providing the minimal strength of the material sintered against the background of the cooling of combustion products.

Conclusions. Under the action of external forces compaction of the material occurs and the sintering process intensifies, which leads to an increase in the strength of the structural frame of the material formed. Sintering and cooling of combustion products decrease the capacity of the material for plastic deformation. The experiments and theoretical studies described in this paper point to the existence of an optimal temperature-time interval in which mechanical actions on the SHS-products are the most effective. Its boundaries depend not only on the temperature and the depth of completion of gross-postprocesses, but also on the deformation rate and pressure. For practice of the SHS-processes, of great interest is the question on the effect of deformation on the stage of the incipient highly dispersed structure. It is known that the deformation parameters, primarily the deformation rate, strongly influence the effect of hardening of the initial morphology at which fine grains do not intergrow to form a single crystal. It is difficult to determine from the above considerations the influence of such parameters as the external pressure and the rotation velocity of the rotor. For a theoretical description of the influence of these parameters, it is expedient to develop models proceeding from the general consideration of the material flow.

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NOTATION

c , heat capacity, J/(kg·K); D , bulk self-diffusion coefficient, m²/sec; D_0 , bulk self-diffusion coefficient at ambient temperature, m²/sec; K , curvature, m⁻¹; k , Boltzmann constant; M , relative mass of the disintegrated product, %; R , particle radius, m; r , radius of surface curvature of the near-contact isthmus, m; r_0 , characteristic size, m; T , temperature, K; T_0 , ambient temperature, K; T_c , combustion temperature, K; t , process time, sec; t_d , delay time, sec; t_{dis} , disintegration time, sec; $t_d + t_{dis}$, time of termination of disintegration, sec; t_{th} , characteristic time of cooling determined by the relation $t_{th} = c\rho r_0^2/\lambda$, sec; x , value of intergranular contact, m; x_1 , value of intergranular contact in the first mechanism (bulk diffusion mechanism), m; x_2 , value of intergranular contact in the second mechanism (mechanism of sintering under the conditions of compaction), m; α , surface energy at the interface, J/m²; λ , heat conductivity coefficient, W/(m·K); μ , viscosity, Pa·sec; μ_0 , viscosity at ambient temperature, Pa·sec; ρ , density, kg/m³; φ , central angle of the contact isthmus arc, rad; ω , atomic volume, m³. Subscripts: c, combustion; d, delay; dis, disintegration; th, thermal relaxation; 1, the first method of sintering (due to diffusion); 2, the second mechanism of sintering (due to compaction); 0, initial value of a parameter at ambient temperature.

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