

INFLUENCE OF THE RANDOM STRUCTURE OF AN INITIAL MATERIAL ON THE PROCESSES OF SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS IN THIN FILMS

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UDC 536.46

Numerical simulation of the process of self-propagating high-temperature synthesis in two-dimensional systems, the physical prototypes of which are thin films, has been performed. The emphasis has been on consideration of the heterogeneity of the system and randomness in the spatial arrangement of its different components. It has been found that taking into account the randomness factor, all other things being the same, leads to a substantial change in the basic characteristics of both the combustion process (for example, of the wave velocity) and the end product of synthesis. It has been demonstrated that, first, the critical level of external heat loss decreases significantly as compared to the case of a uniform distribution of the reagents and, second, this characteristic undergoes an abrupt increase in the vicinity of the reagent concentration corresponding to the percolation threshold for the lattice used in simulation. A qualitative comparison of the simulation results with experimental works has been carried out.

Self-propagating high-temperature synthesis (SHS) is one of the most high-technology and efficient methods of synthesis of new materials. The basis for this process is the propagation of a combustion wave in a heterogeneous system. SHS-technology is very profitable in energy terms due to the utilization of the chemical energy of the initial components for attainment of the synthesis temperature. At the same time, this technology enables one to obtain a number of high-melting materials (metal nitrides, borides, and silicides and various intermetallides) that have unique properties different from the properties of the same materials produced by traditional methods (for example, by melting in furnaces).

In SHS-technology, growing recent attention has been given to the synthesis of materials consisting of progressively smaller structural elements. In particular, this refers to the SHS of nanostructural materials and nanofilms [1–3]. One characteristic property of nanosized objects is that their heterogeneity, discreteness, and random structure play a decisive role on such scales. Neglect of these characteristics often leads to errors or even to a qualitatively incorrect description of the process. This work is devoted to the simulation of SHS in thin films to establish the peculiarities caused by their heterogeneity and structural disorder.

Powder mixtures with a particle size of $\sim 100 \mu\text{m}$ are the object of investigation of the present work. When one reagent is gaseous, it is assumed to be in excess at all points of the system. It is also suggested that the occurrence of interlayers of a liquid phase in the combustion process does not lead to a substantial change in the geometric connectivity of solid fuel particles in the system. At the same time, it is necessary to note that the laws of combustion of a random heterogeneous medium in the vicinity of the limit values of the concentration or the heat loss that have been established in the work are apparently common to a wider class of systems, for example, to aerosols [4].

In cases where the spatial scale that characterizes the process of combustion of a heterogeneous system is found to be comparable to the sizes of the elements of the heterogeneous medium, the random nature of the medium is brought to the fore. This manifests itself primarily in the randomness of the geometric structure of the system, which can give rise to a percolation (geometric) phase transition [5–7]. At present, one successfully uses percolation theory for description of structurally disordered systems and geometric phase transitions. Therefore, a natural step in

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further investigation of the influence of the structure of a heterogeneous medium on the propagation of combustion in it is the use of the methods of percolation theory [5] as a component part of a more complicated model of the combustion process in a heterogeneous system.

Macrokinetic Model of a Reacting Structurally Disordered Heterogeneous Medium. The combustion of heterogeneous condensed systems as a complicated macrokinetic phenomenon includes several simultaneously occurring elementary processes: chemical interaction, heat transfer, diffusive reagent transfer to the reaction zone, etc. We briefly dwell on the model of chemical kinetics used in description of the combustion of heterogeneous condensed media.

Model of Chemical Kinetics. Chemical interaction is governed by the supply of reagents to the reaction zone and depends on the temperature, the concentrations of the initial reagents, and the reaction products. The specific form of the rate of chemical transformation is determined by the reactions that can take place in an actual system and by the structure of the medium. As a first approximation, it is possible to introduce the bulk-average reaction rate. In this work, the rate of a one-stage exothermic reaction in the systems is described by the following general dependence:

$$W(T, \eta) = k_0 f(\eta) F(T), \quad (1)$$

where the temperature part $F(T)$ can be represented in the form of the product of the Heaviside function and the Arrhenius factor:

$$F(T) = H(T - T_{in}) \exp\left(-\frac{E}{RT}\right). \quad (2)$$

The parameter T_{in} is the reaction-initiation temperature associated with the melting of one reagent [8]. The Arrhenius kinetics best describes gas-phase systems where quick mixing of the components at a molecular level takes place. However, if one or both components involved in the binary reaction are in the condensed state, a pure Arrhenius model, which does not allow for a change in the reaction mechanism, does not always adequately reflect the physical picture of the phenomenon. Examples of non-Arrhenius behavior are provided by systems in which a sharp change in the reaction mechanism due to the phase transition takes place, in particular, in melting of one reagent. This leads to the fact that the reaction rate increases sharply with temperature transition through the melting point due to the increase in the area of contact of the reagents (because of the so-called effect of capillary spreading [9]) and due to the acceleration of mass-transfer processes as a result of the transition from solid-phase diffusion to liquid-phase diffusion.

It should be noted that the rate of binary reactions generally depends on the concentrations of both components. However, in this work, consideration has been given to heterogeneous processes in which one component is always present in the system in excess. Then the concentration dependence of the reaction rate is expressed by the function of the degree of conversion $f(\eta)$ of the condensed reagent, which is insufficient. Simultaneously, this function characterizes the macrokinetics of the process, i.e., the diffusion of the component that is present in excess through the product layer into the reaction zone.

In accordance with what has been said above, in this work we have used the following dependence of the reaction rate on the degree of conversion:

$$f(\eta) = H(1 - \eta) \exp(-m\eta). \quad (3)$$

It is necessary to note that in simulation of combustion in heterogeneous systems, the selection of such parameters as the initiation temperature and the index of deceleration of the reaction plays an important role. It is known that for the Arrhenius kinetics without deceleration, selection of the initiation temperature for homogeneous mixtures affects the results of calculations of the combustion rate only slightly if this temperature is lower than half the temperature of adiabatic warmup of the system [10]. For heterogeneous systems this statement is generally incorrect. Our numerical calculations for a regular heterogeneous system have shown (Fig. 1) that the value of the initiation temperature increasingly affects the combustion-wave velocity with decrease in the dimensionless criterion Bi determined below and characterizing the degree of heterogeneity of the system.^{*)} At a sufficiently high (limit) initiation temperature, combustion in the system becomes completely impossible, even in the adiabatic case [6]. In simulation of the

^{*)} The system becomes substantially heterogeneous for $Bi \lesssim 10^{-2} - 10^{-1}$.

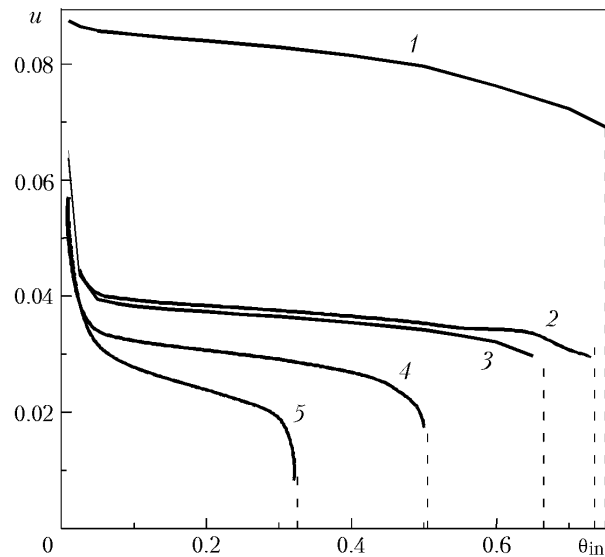


Fig. 1. Dependence of the combustion-wave velocity u in a regular heterogeneous system on the dimensionless initiation temperature θ_{in} for $S = 0.005$: 1) $Bi = 10$, $m = 0$, and $p = 1$; 2) 10, 4, and 1; 3) 0.1, 4, and 1; 4) 0.015, 4, and 1; 5) 0.015, 0, and 0.6.

combustion of heterogeneous random systems with heat loss, we have selected the value $\theta_{in} = 1/6$ (in the units of adiabatic warmup of the system), taking into account that the initiation temperature in the systems considered in the present investigation is physically the melting temperature of one component. The value of the index describing deceleration of the reaction by the product was selected to be $m = 4$ (this value of m was used in a number of works, for example, in [11]). On the one hand, such values of the kinetic parameters correspond to systems that occur in practice [12]. At the same time, the initiation temperature used for simulation falls in the range of a weak dependence of the combustion-wave velocity on θ_{in} (see Fig. 1); whence it follows that in a fairly wide vicinity of the selected value of θ_{in} , the results of calculations will be characterized by similar qualitative dependences. As far as the parameter m is concerned, its value $m = 4$, among other things, enables us to carry out calculations with a wide reaction zone, i.e., on a larger-scale grid. The latter circumstance is important in scale statistical simulation of combustion in multidimensional systems.

Two-Dimensional Model of Heat and Mass Transfer with Combustion in Random Heterogeneous Media. Before passing to the derivation of a mathematical model of the process, it is necessary to make some remarks relative to the existence of percolation combustion regimes due to the structural disorder of the system. In combustion of heterogeneous systems, the percolation regime is possible when any burning particle can ignite just its nearest neighbors. Such a regime is realized only when the local width of the combustion front is smaller than the particle size. In this case it is unnecessary to warm up a particle completely to ignite it. For example, in forest fires, the ignition of a tree can be caused by just a single spark. If the front width is fairly large, the role of each particle by itself is counterbalanced and the ignition of a new particle will be determined by the collective influence of a large number of its neighbors. From what has been said above, it follows that for investigation of percolation combustion, which is one of the main objectives of this work, it is necessary in the general case to consider the structural element of a heterogeneous medium as nonisothermal (unlike the standard models of heterogeneous combustion [13, 14]). A model of combustion of a two-dimensional random heterogeneous system with account for the above-stated peculiarities of the process is proposed below.

A unit cell is the basic element of the model proposed. This cell includes both the solid phase (effective particle) and chemically inert gas interlayers (Fig. 2). All the cells of the system have the same physical (thermal conductivity, density, etc.) and geometric properties (shape and size). They differ only in the initial chemical composition of the solid phase: a particle contains either a mixture of reacting components in a fixed proportion or just one component. The cell is considered in the first case as reactive (combustible) and in the second case as inert. The local

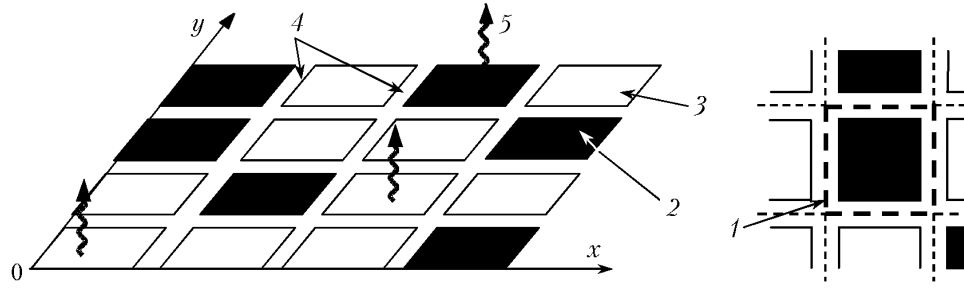


Fig. 2. Geometric scheme of a two-dimensional heterogeneous reaction medium: 1) unit cell; 2) combustible particles (black squares); 3) inert particles (white squares); 4) gas interlayers; 5) heat loss.

chemical composition of the cell that is characterized by the degree of conversion $\eta(x, y)$ changes during the reaction of the cell components. The system's geometry is simulated by a two-dimensional square grid, at the nodes of which either combustible or inert particles are randomly located (Fig. 2). An arbitrary cell is either reactive with an assigned probability p (which is one parameter of the problem) or inert with a probability $(1 - p)$. Due to the fact that the property that enables a particle to be combustible is independent of the properties of its neighbors, the value of p is equal to the volumetric fraction of combustible particles in the system ($0 \leq p \leq 1$).

As has been noted above, each unit cell is considered as an object with an internal distribution of the temperature and the degree of conversion and not as a point. Heat transfer within a particle is determined by the conductive mechanism with a certain thermal conductivity. Estimations have shown that radiative heat exchange between particles of size of the order of $100 \mu\text{m}$ was negligibly small as compared to the heat conduction through interparticle contacts and gas interlayers. In what follows, the latter two mechanisms of heat transfer between the particles will be characterized by a certain effective heat-transfer coefficient α_{eff} .

One peculiarity of the percolation model proposed is the fact that the system includes the external heat loss characterized by the effective coefficient of external heat exchange $\alpha_{\text{eff,ext}}$ and the concentration limit of combustion related to this heat loss.

The model proposed is described by the following system of equations:
the energy equation

$$\rho c_p \frac{\partial T}{\partial t} = \lambda_s \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + p_{ij} \rho Q W(T, \eta) - \alpha_{\text{eff,ext}} (T - T_0), \quad (4)$$

the equation of chemical kinetics

$$\frac{d\eta}{dt} = W(T, \eta). \quad (5)$$

The kinetics of chemical transformations was described by a gross reaction and their rate was described by Eq. (1)–(3). It should be noted that the initial concentration is $p_{ij}|_{t=0} = 1$ if a fuel is present in the particle and $p_{ij}|_{t=0} = 0$ if it is absent; the average initial concentration of the fuel in the system (fraction of fuel particles) is equal to p . In what follows, the dimensionless temperature is determined as $\theta = (T - T_*)/\Delta T_*$, where $T_* = T_0 + \Delta T_{\text{ad}}/2$. By going to the dimensionless temperature, which is traditional for combustion theory, this temperature changes in the limits $-1/(2\gamma) \leq \theta \leq 1/(2\gamma)$, where $\gamma = \Delta T_*/T_{\text{ad}}$. Then the dimensionless system of equations has the following form:

$$\frac{\partial \theta_{ij}}{\partial \tau} = S \left(\frac{\partial^2 \theta_{ij}}{\partial \xi^2} + \frac{\partial^2 \theta_{ij}}{\partial \psi^2} \right) + p_{ij} \Phi(\theta_{ij}, \eta_{ij}) - \chi(\theta_{ij}, \theta_0), \quad (6)$$

$$\frac{d\eta_{ij}}{d\tau} = \gamma \Phi(\theta_{ij}, \eta_{ij}), \quad (7)$$

$$\Phi(\theta_{ij}, \eta_{ij}) = H(1 - \eta_{ij}) H(\theta_{ij} - \theta_{in}) \exp\left(\frac{\theta_{ij}}{1 + \beta\theta_{ij}}\right) \exp(-m\eta_{ij}). \quad (8)$$

Here $\beta = \Delta T_*/T_*$, $S = x_r^2/d^2$, $x_r = \sqrt{\alpha\gamma t_r}$, $t_r = \left[k_0 \exp\left(-\frac{E}{RT_*}\right)\right]^{-1}$, and $\chi = (\alpha_{\text{eff,ext}}\gamma t_r)/(\rho c_p)$.

It should be noted that the special properties of combustion in the heterogeneous medium manifest themselves in the fact that a new similarity criterion S appears, representing dimensionless thermal diffusivity. There is another interpretation: the criterion S is equal to the squared ratio of the reaction-zone size to the particle size. In anticipation, we emphasize that heterogeneity and randomness in combustion processes play an important role for small S ($S \ll \gamma$).

The system of equations should be supplemented with boundary conditions that describe heat exchange between particles at each of the four boundaries of a cell:

$$\text{Bi}(\theta_{i,j}|_{\text{lf}} - \theta_{i-1,j}|_{\text{rt}}) = -\frac{\partial\theta_{ij}}{\partial\xi}\Big|_{\text{lf}}, \quad (9)$$

$$\text{Bi}(\theta_{i+1,j}|_{\text{lf}} - \theta_{i,j}|_{\text{rt}}) = \frac{\partial\theta_{ij}}{\partial\xi}\Big|_{\text{lf}}, \quad (10)$$

$$\text{Bi}(\theta_{i,j}|_{\text{b}} - \theta_{i,j-1}|_{\text{u}}) = -\frac{\partial\theta_{ij}}{\partial\psi}\Big|_{\text{b}}, \quad (11)$$

$$\text{Bi}(\theta_{i,j+1}|_{\text{b}} - \theta_{i,j}|_{\text{u}}) = \frac{\partial\theta_{ij}}{\partial\psi}\Big|_{\text{b}}. \quad (12)$$

In this case, the Biot number is determined in the following way: $\text{Bi} = \alpha_{\text{eff}}d/\lambda_s$.

At the boundaries $\psi = 0$ and $\psi = L$, periodic boundary conditions were specified [15] to decrease the influence of the system's size on the results of simulation:

$$\text{Bi}(\theta_{i,1}|_{\text{b}} - \theta_{i,L}|_{\text{u}}) = \frac{\partial\theta_{i,1}}{\partial\psi}\Big|_{\text{b}} = \frac{\partial\theta_{i,L}}{\partial\psi}\Big|_{\text{u}}. \quad (13)$$

At the right-hand boundary of the system, conditions of the third kind were specified. The coefficient of heat exchange with the surrounding medium was selected so that when the combustion of the particle layer adjacent to the boundary takes place, superadiabatic temperatures and "reflection" of the combustion wave do not arise, whereas burning of the particles in the layer can be complete.

Combustion was initiated by the assignment of a fairly high temperature at the left-hand boundary of the system. After the complete burning of at least one particle in the first layer, the boundary condition at the considered boundary was replaced by the adiabatic one.

Estimations of the values used in simulation of the dimensionless parameters, as applied to a mechano-activated Al–Ni powder mixture (which is one standard SHS system), were performed in [6]. The size of the Al–Ni agglomerates was assumed to be in the interval of 100–300 μm . According to the estimations, we had $\text{Bi} \approx 0.01\text{--}0.1$ and $S \approx 0.001\text{--}0.1$. The values of the parameters γ and β were fixed during all the calculations: $\gamma = 1/6$ and $\beta = 0.001$. Such a selection of the parameters, among other things, allowed us to avoid the appearance of vibrational regimes of combustion within the particle.

Numerical Experiment. In this investigation, the emphasis has been on the role of external heat loss in combustion of heterogeneous condensed systems and on the search for relations between the level of heat loss, the

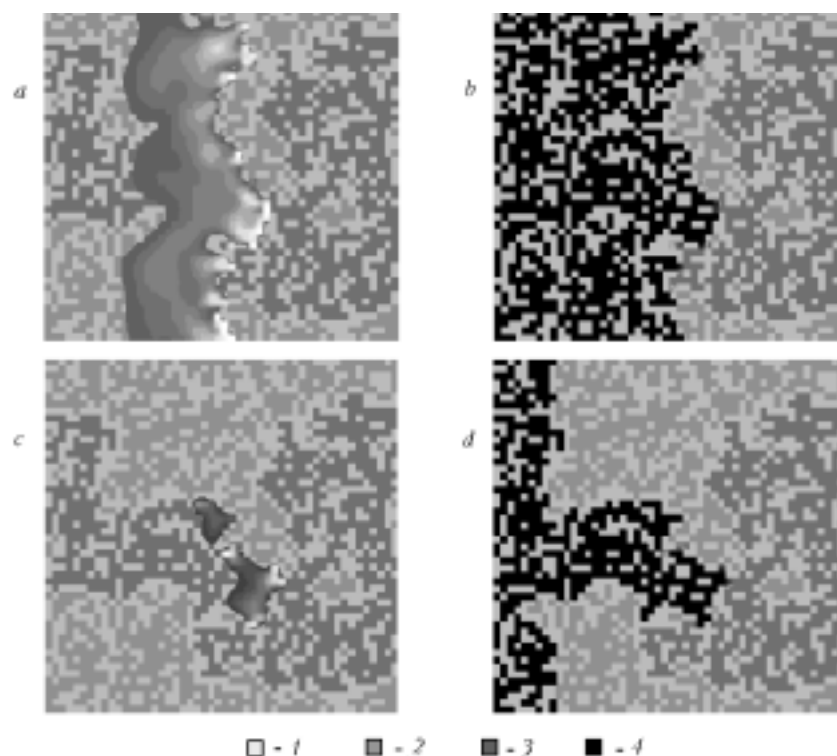


Fig. 3. Frontal (a and b) and percolation (c and d) regimes of propagation of the combustion wave in a random heterogeneous system: 1) inert particles; 2) combustible particles belonging to finite clusters; 3) combustible particles belonging to a percolation cluster; 4) burnt particles (*a* and *c*, temperature fields (change in the cell color from dark to light corresponds to a temperature increase; the temperature of cold regions is not presented); *b* and *d*, fields of degrees of conversion (change in the cell color from light gray to black corresponds to an increase in the degree of conversion from zero to unity)).

combustion-wave characteristics, and the scale of inhomogeneity of a random system for which disorder is of primary importance.

The external heat loss, shortening the zone of cooling of products, localizes the combustion wave. As a consequence, the geometric structure of the system begins to play a more important role. Indeed, in the percolation regime of combustion, the "fracture" of a percolation cluster formed by combustible particles must lead to an extinction of the combustion wave. However, in the absence of heat loss, a zone of warmed-up reaction products arises behind the combustion front and, if the "fracture" is much narrower than the indicated zone noted and the activation energy of the reaction is moderately high, the thermal energy stored in the wave is sufficient to overcome an obstacle. Thus, in a large (as compared to the combustion-zone width) adiabatic heterogeneous system, the percolation regimes of combustion are not realized (with the Arrhenius kinetics), and the propagation of the reaction front is possible with any nonzero concentration of combustible particles. When the heat loss is fairly high, it can be impossible for the combustion wave to overcome inert obstacles, and the geometric connectivity of the reactive elements, i.e., the presence of a percolation cluster, will be of decisive importance for the evolution of the process.

Stimulation of combustion in random heterogeneous two-dimensional systems was carried out on the basis of the system of equations (6)–(13), which was solved numerically. Here, the number of grid points in a cell in each direction was equal to seven for the majority of variants of calculations, which was sufficiently exact for $S > 0.005$. The temperature within the particles was calculated using an explicit finite-difference scheme, and calculation at the particle boundaries was carried out by solution of a system of implicit equations for points of the opposite boundaries of neighboring particles. In the work, we have investigated two-dimensional systems with dimensions of 12×12 , 25×25 , and 50×50 particles. For each combination of the parameters (L , S , p , χ , and Bi), 100–200 histories of propaga-

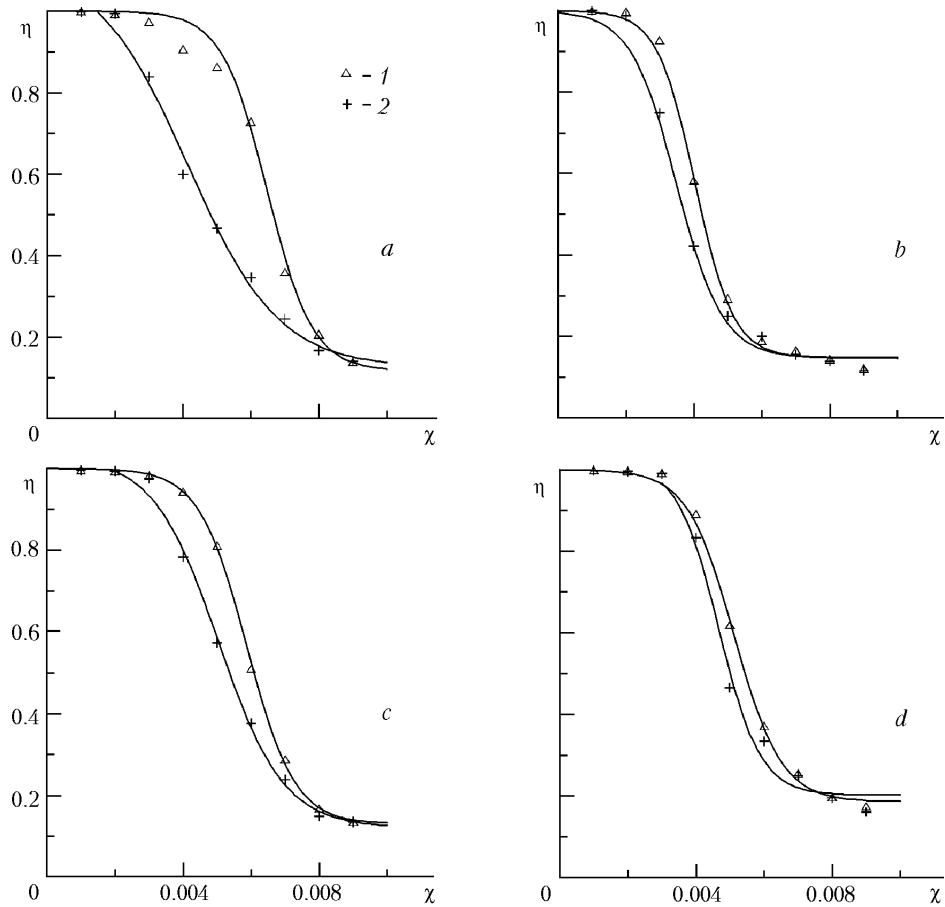


Fig. 4. Dependence of the mean degree of conversion in the 25×25 system on the external heat loss at $p = 0.60$: a) $Bi = 0.015$ and $S = 0.005$; b) 0.015 and 0.05 ; c) 0.1 and 0.005 ; d) 0.1 and 0.05 (1 and 2 correspond to the presence and absence of a percolation cluster).

TABLE 1. Extinction Threshold $\chi_{cr} \cdot 10^5$ for a 25×25 Heterogeneous Condensed System for Different Parameters S and Bi ($p = 0.60$)

S		Bi		
		0.015	0.05	0.1
0.005	1	648	598	587
	2	414	488	504
0.01	1	533	530	553
	2	432	474	475
0.05	1	405	477	513
	2	350	448	468

Note: 1 and 2 correspond to the presence and absence of a percolation cluster.

tion of the combustion wave over the sample were processed; it took hundreds of hours of computer time to generate the histories in a number of cases. The time expended in simulating (on a Pentium III PC, 2×800 MHz) was longer than 7000 h.

Numerical simulation of gasless combustion in random heterogeneous two-dimensional systems made it possible to reveal the existence of two different regimes of propagation of the flame. For high values of the parameter S ($S > 0.05$) and a low heat loss χ , the combustion wave propagates as a continuous front that consists of numerous in-

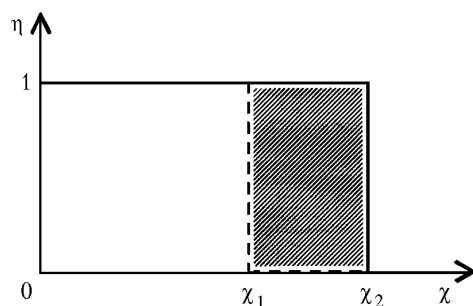


Fig. 5. Scheme of the dependence of the degree of conversion on the heat loss for an infinite system (χ_1 and χ_2 are the extinction thresholds for the systems with and without a percolation cluster respectively).

interacting hot spots (Fig. 3a). During the development, the hot spots exchange energy, as a result of which we have a complete conversion of the reacting components (Fig. 3b).

As the heat loss increases, the zone of cooling of the products is constructed, and hot spots of combustion can interact with each other only when they are situated on a percolation cluster (Fig. 3c and d). Thus, as has been indicated above, the geometric connectivity of reactive particles is brought to the fore.

The above-described qualitative transition in combustion regimes can be illustrated at a more rigorous quantitative level. We have already noted that transition to the percolation regime of combustion occurs with a high heat loss. Indeed, as is seen from Fig. 4, for a high heat loss, all other things being the same, the mean degree of conversion over the entire system is much higher for the samples containing a percolation cluster than that for those without such a cluster. We note that for random heterogeneous systems of finite size the inflection point on these plots is an analog of the extinction threshold for infinite systems [6]. The value of the extinction threshold (based on the heat loss) is one substantial characteristic of the process considered. Its values for different combinations of S and Bi are presented in Table 1.

In the limit of infinitely large systems, we must have an abrupt decrease in the degree of conversion to zero as the heat loss goes beyond the critical level and not a smooth decrease (Fig. 5). It is significant that the threshold heat loss is different for the systems with a percolation cluster and without it. It is in the range of heat loss between the thresholds indicated (respectively χ_1 and χ_2 in Fig. 5) that the percolation regime of combustion may be realized: the combustion wave propagates just over the percolation cluster.

The above difference of the critical levels of heat loss in the vicinity of the percolation threshold has an important practical result — the dependence of the critical level of heat loss on the fuel concentration for infinite systems must undergo a jump in the percolation threshold. When systems of finite size are used in numerical experiment, this dependence exhibits a smoother transition between two asymptotic forms corresponding to systems with and without a percolation cluster and has no discontinuity. The numerical simulation performed has shown that such a situation does occur. Figure 6 presents results of calculation of the critical level of heat loss for systems with uniform and random distributions of fuel. Here, the dashed lines correspond to the rates of change of the critical level of heat loss as a function of the fuel concentration. The transition between the indicated asymptotic forms for the system with a random fuel distribution is particularly clearly illustrated by the sharp peak of the derivative $d\chi_{cr}/dp$. At the same time, this derivative changes monotonically for a regular system. We note that the value of the discussed jump of the critical heat loss in the percolation threshold can be determined for different parameters S and Bi from the data of Table 1.

As is seen from Fig. 6, a random internal organization of the system has one more result of practical importance — the critical level of heat loss in the system turns out to be substantially lower than that for the regular system with the same quantity of fuel. It can be assumed that such a difference is due to the much higher instability of the combustion wave in the random system as compared to the regular one.

It should be noted that the role of a percolation cluster is counterbalanced with increase in the parameter S , as has been pointed out at the stage of preliminary analysis. As is seen from Fig. 4, the difference in the degrees of conversion for the systems with and without a percolation cluster noticeably decreases with increase in S . The same tendency also occurs in growth of interparticle heat exchange (of the parameter Bi). Here, just as with increase in S , an inert particle is an obstacle of less importance in the path of the combustion wave.

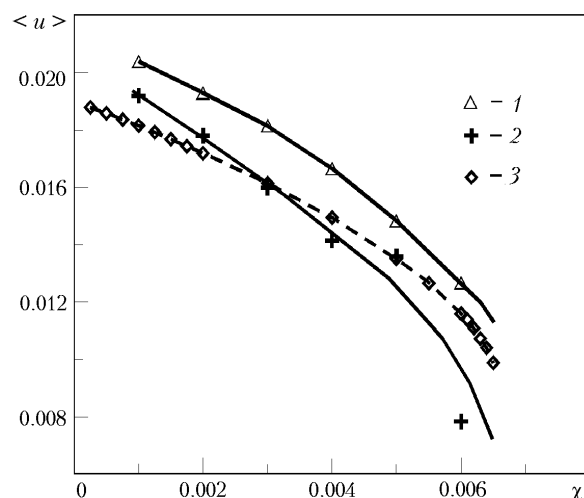
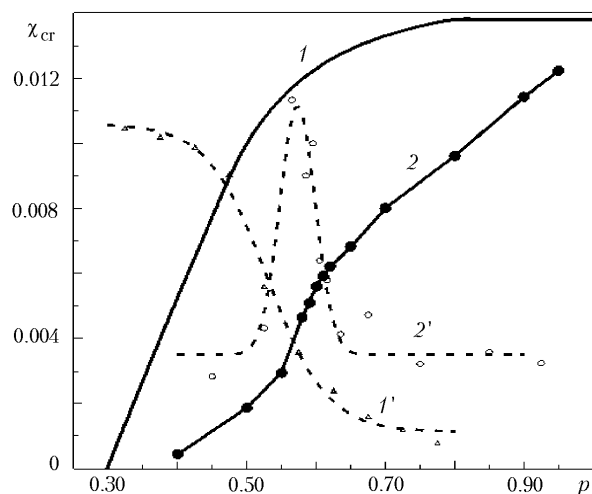


Fig. 6. Dependence of the critical level of heat loss χ_{cr} on the fuel concentration in a heterogeneous system for $Bi = 0.015$ and $S = 0.005$: 1) uniform fuel distribution over the system; 2) random fuel distribution; 1') rate of change of the critical heat loss ($d\chi_{cr}/dp$) for the uniform fuel distribution; 2') the same for the random fuel distribution.

Fig. 7. Dependence of the mean velocity of the combustion wave on the external heat loss in the 25×25 system at $p = 0.60$, $Bi = 0.015$, and $S = 0.005$: 1) the percolation cluster is present; 2) the cluster is absent; 3) regular heterogeneous system with the same quantity of fuel.

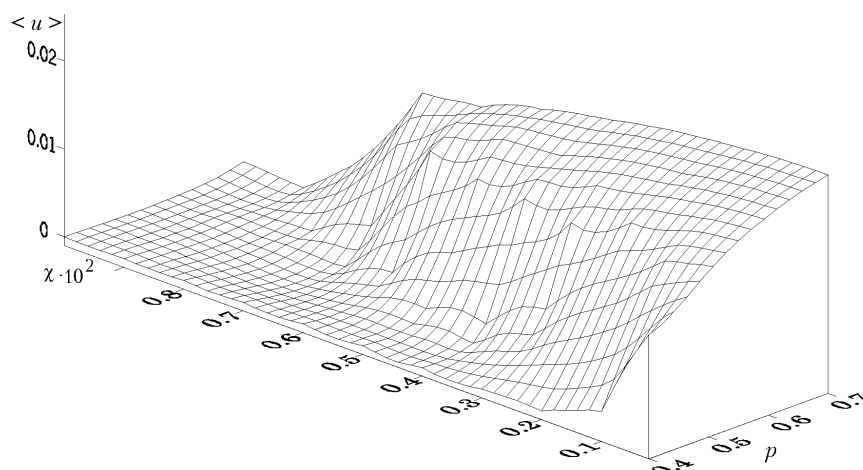


Fig. 8. Dependence of the mean velocity of the combustion wave $\langle u \rangle$ in a random heterogeneous system on the fuel concentration p and the level of external heat loss χ for $Bi = 0.015$ and $S = 0.005$.

Apart from the degrees of conversion it is of interest to study the dependence of the mean velocity $\langle u \rangle$ of the combustion wave on the parameters of the system. This velocity was determined as the ratio of the sample length to the time it takes for the combustion wave to reach the right-hand boundary of the sample. When the wave does not reach this boundary, the time and velocity were assumed to be equal to infinity and zero respectively. The plots presented in Fig. 7 show that the combustion rate also strongly depends on the presence of a percolation cluster in the system. The slower propagation of the wave over the system without a percolation cluster is related to the additional time required for warming up inert particles that inevitably arise in the path of the wave in this case. Just as for the degree of conversion, the difference in the combustion-wave velocities for the two considered cases is counterbalanced with increase in S and Bi .

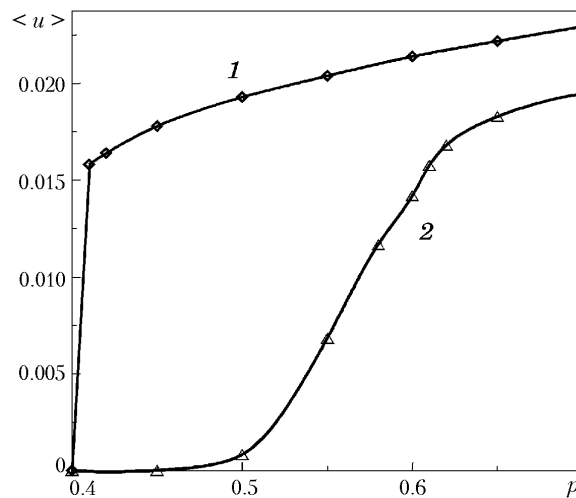


Fig. 9. Dependence of the mean velocity of the combustion wave $\langle u \rangle$ on the fuel concentration p for $\chi = 0.005$, $Bi = 0.015$, and $S = 0.005$: 1) regular heterogeneous system; 2) random system.

TABLE 2. Fraction of the Samples (%) in Which the Combustion Wave has Reached the Opposite Edge ($p = 0.60$)

χ	S											
	0.005		0.01		0.05		0.005		0.01		0.05	
	1	2	1	2	1	2	1	2	1	2	1	2
	$Bi = 0.015$						$Bi = 0.1$					
0.001	100	100	100	100	100	100	100	100	100	100	100	100
0.002	100	100	100	100	96	92	100	100	100	100	100	100
0.003	96	77	—	—	75	50	100	100	100	97	88	94
0.004	91	26	88	53	18	2	100	70	94	71	50	23
0.005	81	16	61	14	3	0	77	26	33	10	4	2
0.006	51	2	13	0	0	0	5	0	3	0	0	0
0.007	10	0	0	0	0	0	0	0	0	0	0	0

Note: 1 and 2 correspond to the presence and absence of a percolation cluster.

Figure 8 presents the dependence of the mean combustion rate on the fuel concentration and the level of external heat loss. A characteristic of this dependence is a sharp increase in the combustion-wave velocity not only in going beyond the critical level of heat loss (for a fixed concentration) but also in going beyond the critical concentration (for a fixed heat loss). Such behavior of the velocity is illustrated more clearly in Fig. 9, where the external heat loss is fixed. We note that a monotonous change in the combustion-wave velocity with increase in the concentration is observed for the system with a uniform fuel distribution; the value of the velocity is substantially higher than the corresponding value for the random system.

Apart from the degree of conversion and the combustion-wave velocity, the process considered may be characterized by the fraction of samples in which the combustion wave has reached the right-hand boundary. These data are presented in Table 2, from which it is clear that the above characteristic also strongly depends on the presence of a percolation cluster in the system and points to the predominant burning of the samples in which the reactive particles form a geometrically connected system.

We dwell once again on the question of the influence of the system's size on the characteristics of the process investigated. As has been noted above, in the limits of large systems, a sharp change in the degree of conversion down to zero must occur as the heat loss goes beyond the critical level. This implies that, when the system's size increases, we must observe a sharper transition of the degree of conversion upon the attainment of the critical level of heat loss. It is such behavior that has been observed in numerical experiment.

Experimental Evidence of the Existence of Percolation Combustion Regimes. Among the experimental studies on the combustion of heterogeneous systems, we primarily note [16], where the combustion of a mixture of Ti and SiC fibers for different packing densities ω has been investigated. The packing density changed from unity (total absence of the pore space) to values approaching zero (very loose structures). Grigoryan et al. [16] observed a pattern of the combustion-wave front qualitatively similar to that observed by us in numerical equipment (Fig. 3). It follows from the results of [16] that for dense systems ($\omega = 0.60$ and 0.40) the frontal regime of propagation of the combustion process takes place. When the system becomes looser, i.e., more heterogeneous ($\omega = 0.30$ and 0.20), the front is subdivided into separate hot spots, which presumably correspond to the combustion of the cluster formed from the reactive compositions of the fibers.

Indirect experimental confirmation of our results is also available in [17], where a study has been made of the propagation of the wave of the Belousov–Zhabotinskii reaction catalyzed by a photosensitive complex of ruthenium bipyridyl. In this experiment a random distribution of light and darkened squares was generated by a computer and then transferred to a transparent film. Next, the obtained filter was imposed on the reacting medium and the entire system was irradiated with visible light. The excitation of the medium decreased by several orders of magnitude in the regions situated below the transparent areas of the filter as a result of irradiation. Then a wave of chemical reaction was initiated which propagated only over the percolation cluster consisting of darkened regions. An important point was that the size of the squares was much larger than the characteristic width of the reaction front. The described system differs from that investigated in the present work in the mechanism that ensures wave propagation; however, in either case the disorder of the geometric structure leads to the same qualitative behavior of the system.

Among the number of experimental works, we should also note [18], where the combustion of powder mixtures (Al/Ni, Al/Zr, and Al/Fe₂O₃) has been investigated. One factor revealed in this work is a sharp increase in the heat release (from zero to a maximum) in such systems upon the attainment of the threshold concentration (15–22 percent by volume) by one component (which is insufficient). At the same time, the Scher–Zallen invariant corresponding to the fraction of space occupied by the particles of a certain substance, for which they form a percolation cluster, is approximately equal to 16 percent by volume for three-dimensional systems. The latter circumstance allows us to infer that the combustion in the mixtures studied in [18] begins with concentrations corresponding to the formation of a percolation cluster consisting of particles of the same kind. In other words, the combustion of such systems in the vicinity of the threshold concentration represents a typical example of percolation combustion.

Unfortunately, the evidence presented is indirect; therefore, direct experimental proof of the existence of percolation regimes of combustion in the systems considered must be the subject of further investigation. We assume that experimental detection of an abrupt increase in the critical heat loss for a certain concentration of fuel in the system could be taken to be such a proof.

CONCLUSIONS

Investigation of the combustion of structurally disordered heterogeneous condensed mixtures has enabled us to reveal the existence of a new percolation regime of propagation of the combustion wave. In this regime, the internal organization of a medium (geometric connectivity of reactive particles) contributes to the propagation of the combustion wave. A new dimensionless parameter S has been presented which is equal to the ratio of the reaction-zone width squared to the particle size squared and the value of which is one determining factor of transition from the frontal to percolation regime of combustion. The conditions of existence of the percolation regime of combustion have been determined:

- 1) the width of the combustion zone (reaction zone plus warmup zone) is smaller than the characteristic dimension of particles, i.e., the condition $S \lesssim \gamma$ must be fulfilled ($S \lesssim 0.05$ and $x_r/d \lesssim 0.2$ at $\gamma = 1/6$);
- 2) weak interparticle heat exchange ($Bi \lesssim 0.1$);
- 3) the highest external heat loss ($\chi \rightarrow \chi_{cr}$);
- 4) the volume concentration of combustible particles is close to the percolation threshold.

It has been demonstrated that the critical heat loss of the system undergoes a sharp increase (threshold increase in the limit of an infinite system) in going beyond the threshold concentration corresponding to the formation of a per-

colation cluster. The peculiarities of the combustion process in two-dimensional structurally disordered systems that have been revealed in numerical experiment are expected to manifest themselves in SHS in thin films.

This work was carried out within the framework of the State Sectoral Program of Scientific Investigations "Nanostructural Materials and Nanotechnologies" (Nanotekh 5.10).

NOTATION

a , thermal diffusivity of the particle, m^2/sec ; Bi , Biot number; c_p , specific heat of the particles, $\text{J}/(\text{kg}\cdot\text{K})$; d , size of a particle, m ; E , activation energy of the reaction, J/mole ; $f(\eta)$, concentration dependence of the reaction rate on the degree of conversion of the condensed reagent; $H(x)$, Heaviside function; k_0 , kinetic reaction constant, $1/\text{sec}$; L , size of the system (number of cells in one direction); m , index characterizing reaction deceleration as the product layer is formed; p , volumetric fraction of the combustible particles in the system; p_{ij} , relative volume concentration of the fuel in the particle with numbers i and j along the abscissa and ordinate axes respectively; Q , thermal effect of the reaction, J/kg ; R , gas constant ($R = 8.31 \text{ J}/(\text{mole}\cdot\text{K})$); S , dimensionless thermal diffusivity; T , temperature averaged over a local volume, K ; t , time, sec ; t_r , characteristic reaction time, sec ; u and $\langle u \rangle$, dimensionless velocity of the combustion wave and its mean value; W , reaction rate, $1/\text{sec}$; x, y , space coordinates, m ; x_r , reaction zone width, m ; α_{eff} , effective coefficient of heat transfer between the particles, $\text{J}/(\text{m}^2\cdot\text{K}\cdot\text{sec})$; $\alpha_{\text{eff,ext}}$, effective coefficient of external heat exchange, $\text{J}/(\text{m}^3\cdot\text{K}\cdot\text{sec})$; $\Delta T_* = RT_*^2/E$, characteristic temperature interval, K ; $\Delta T_{\text{ad}} = Q/c_p$, adiabatic warmup of the system as the result of reaction, K ; η , degree of conversion of the product; θ , dimensionless temperature; ρ , density of the particles, kg/m^3 ; λ_s , thermal conductivity of the particles, $\text{J}/(\text{m}\cdot\text{K}\cdot\text{sec})$; $\tau = t/t_r$, dimensionless time; $\xi = x/d$, $\psi = y/d$, dimensionless space coordinates; χ , dimensionless coefficient of heat loss; ω , density of the fiber packing. Subscripts: ad, adiabatic; cr, critical; eff, effective; ext, external; in, initiation; i and j , numbers of particles along x and y axes, respectively ($i = 1 \dots L, j = 1 \dots L$); lf, rt, u, and b, left-hand, right-hand, upper, and bottom boundaries of a cell, respectively; p, pressure; r, reaction; s, solid; 0, initial.

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