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Effect of random internal structure on combustion of binary powder mixtures

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Combustion of a mixture of two solid reactants is considered. A combined geometrical and physicochemical model of mixing of these reactants is proposed. The model takes into account random distribution of reactants and voids over the system. This allows description of incomplete burning of reactants. The model is used for studying the combustion wave propagation in a binary heterogeneous mixture. The obtained results are compared with those calculated from the perfect-mixing model, which implies that the deficient (with respect to the stoichiometry) component burns completely. It is shown that micrononuniformity of mixing not only reduces the combustion wave temperature and velocity but also can lead to a shift of the maximal wave velocity away from the stoichiometric composition of the mixture. The results of this study allow us to suggest that one of the main reasons for such a shift, which was observed in a number of experimental works, is structural disorder of binary mixtures.

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I. INTRODUCTION

The self-propagating high-temperature synthesis (SHS), or synthesis in the self-sustaining combustion wave, is one of the most energy-saving and cost-effective methods for producing inorganic compounds, in particular, intermetallics and ceramics [1]. This synthesis proceeds in a heterogeneous condensed system, i.e., a mixture of powders. The structure of heterogeneous condensed mixtures is one of the major factors affecting the combustion wave characteristics as well as the properties of synthesized products. An important role of the charge structure in SHS processes became especially evident after experimental studies using *in situ* high-resolution microscopic video recording [2–5]. Most of solid combustible systems are characterized by random (disordered) spatial distribution of different-kind particles. There were only a few attempts in the literature to take into account this randomness and its influence on the combustion of heterogeneous condensed systems.

One aspect of combustion in disordered heterogeneous systems is the loss of smoothness and continuity of the combustion front when its characteristic scale becomes comparable with the size of combustible particles. It is well known that in such systems the propagation of combustion process can bear a percolation nature (like forest fires) [6–9]. A number of works on percolation combustion (for the forest-fires problem) have merely a formal character due to the use of formal cellular automaton rules. First attempts to relate the percolation characteristics and critical exponents with a set of structural, thermophysical, and kinetic properties of a forest-fire system were made in Ref. [7]. But basically, a problem of determining the conditions for a transition from frontal to percolation regimes in SHS, where random structure of the charge plays a key role, is still an open issue.

Another aspect of the effect of randomness on combustion relates to a wide class of binary (or multicomponent) systems, even if the spatial scale of combustion front much exceeds the scale of structural disorder of the system. In such systems, the affecting factor is nonuniform mixing of components. In this case, the interfacial area of reactants plays an important role. In Ref. [10], the interfacial area of a binary heterogeneous system was studied using a statistical model and its effect on SHS was discussed qualitatively.

The present work is aimed at the development of a model accounting quantitatively for the influence of disordered structure of a binary heterogeneous solid mixture on combustion. The concept of the study lies in the following: to apply a statistical approach to the description of the system structure and then incorporate the determined structural characteristics into a conventional model of combustion wave propagation (the continuum description).

The key point of our consideration is the "contact point" model which implies that (i) the surface area of an exothermic chemical reaction is proportional to the number of contacts between partiles of the first and second reactant, and the combustion rate is proportional to this surface area, (ii) each particle of any reactant is distributed in equal proportion between all its nearest neighbors of the opposite kind during the reaction. Before proceeding to the detailed development of the model it is necessary to justify its applicability to the description of combustion waves propagation in a certain class of heterogeneous media.

There are a number of examples when the propagation of combustion wave over a heterogeneous medium is accompanied by complete melting of a lower-melting-point reactant and its spreading over the porous space. Therefore such a situation is not described by the contact point model. However, there are certain SHS systems where a purely solid-state interaction (i.e., via solid-state diffusion) mechanism works. We can mention here the system Ta/C as an example. The adiabatic temperature of the TaC formation in SHS wave, $T_{\mathrm{ad}}=2700$ K, is below the tantalum melting point, $T_m(\mathrm{Ta})=3270$ K (see Ref. [11]). Similarly, SHS temperature of molybdenum boride in the Mo/B system is lower than the Mo melting temperature [12]. For such systems our model is valid.

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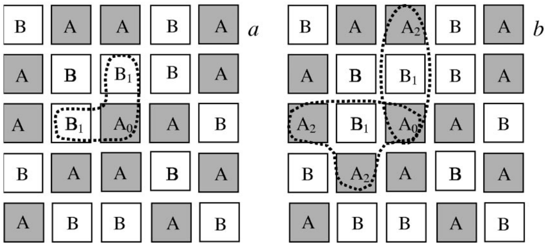

FIG. 1. Determination of the burnt fraction of particle A_0 (explanations in text).

Besides, known are systems with quasi-solid-state interaction. Those are systems where the SHS temperature T_{ad} exceeds the melting temperature of a metallic reactant T_m. But during heating from the ambient temperature to T_m in the preheat zone of the SHS wave, a shell of a primary refractory product forms on the particle surface. At attaining T_m, the particle core melts but the outer shell does not permit the melt to spread. In this case, solid-state diffusion through this spherical layer is the rate-limiting stage of interaction. This situation is analyzed in detail on the example of a metal-gas (viz., Ti/N) system in paper [13]. A similar phenomenon is possible in metal-carbon systems (e.g., Ti/C [14]) as well for small-sized metal particles. In such situations, the number of contacts between different-kind particles plays an important role. In the next part of the paper, on the basis of contact point model we examine two characteristics of the random mixture, viz. the interfacial area and the mean degree of conversion, which are important for the combustion problem.

II. STRUCTURAL MODELS

A. Two-component system without porosity

A heterogeneous disordered system composed of particles of two-kind reactants, A and B (A particles and B particles) is considered. All the particles are of the same density ρ, shape, and size and are placed in the sites of a regular lattice (e.g., square, Fig. 1). Particles A and B are randomly distributed over the system and their numerical fractions are p and $1-p$, respectively. Since absolutely random distribution is assumed, the properties of an arbitrary particle are not correlated with the properties of its neighbors, and hence the probability that the particle is of A or B kind is equal to the fraction of such particles in the system: $P_A=p, P_B=1-p$. It is also supposed that for product formation one volume unit of the A particle should react with ν_{st} volume units of the B particle. Parameter ν_{st} is an analog of chemical stoichiometric coefficient. The volumetric stoichiometric concentration of particles A is expressed through parameter ν_{st} as $p_{\mathrm{st}}=1/(\nu_{\mathrm{st}}+1)$.

The first parameter required to construct the model is the total number of contacts between particles of different kind per one particle. This value can be found using the percolation theory methods. As shown in Ref. [10], the number of contacts between different-kind particles per one particle of the system is determined by expression

$$E_{\mathrm{tot}} = zp(1-p). \tag{1}$$

Here z is the coordination number of the lattice, i.e., the number of nearest neighbors per site. Parameter E_{tot} is known in the percolation theory as "energy" [15], but in the considered situation its meaning differs from the conventional use of this term in physics. Because of this, hereinafter this term is written in quotes. It should be noted that "energy" has its maximal value for a random system at point $p=0.5$, and $E_{\mathrm{tot}}^{(\max)}=z/4$. Particularly, in the case of square lattice $(z=4)E_{\mathrm{tot}}^{(\max)}=1$, but for a regular configuration (for example, chess packing) $E_{\mathrm{tot}}^{(\max)}=4$. In the latter case, each particle has four contacts with particles of the other kind. So, taking into account the disorder in the system we came to the four-time decrease of the interfacial area for the case of a two-dimensional square lattice.

The second parameter, which is important for the combustion wave propagation in a disordered system, is the mean reacted part (mean final conversion degree) of one of the reactants $\varpi(p)$ for given parameters of the system. Henceforward, reactant A will be considered as a basic one for calculating $\varpi(p)$:

$$\varpi(p) = 1 - \frac{\rho_A^f}{\rho_A^0} = 1 - \frac{\rho_A^f}{p\rho}. \tag{2}$$

Here ρ_A^0 and ρ_A^f are the mean initial density of reactant A and its density after the reaction completion, respectively.

We suppose that a necessary condition for reaction between two particles is their immediate contact. Unlike ordered structures where the existence of such contact is always assumed for each particle, in a random mixture some particles can have no contacts with the other reactant due to imperfect mixing. This results in incomplete burning of reactants.

The calculation of the value of $\varpi(p)$ is based on the use of the second assumption of contact point model about equal distribution of reacting particle between its opposite kind neighbors.

Let us consider an arbitrary particle A, which is denoted by subscript "0" (Fig. 1). Using the example presented in Fig. 1, we calculate the mean final conversion degree (within the frame of the considered model) for particle A_0. Let particle A_0 have two B particles in its neighborhood (the latter are denoted by subscript "1"). Then the fraction of particle A_0, which can react with B particles, is $\alpha_2=G(2/\nu_{\mathrm{st}})$. Here function $G(x)$ with the argument x is determined as

$$G(x) = \begin{cases} x, x < 1; \\ 1, x \geqslant 1. \end{cases} \tag{3}$$

Hence, if $\nu_{\mathrm{st}}=3$, the reacted part of particle A_0 is equal to $2/3$; if $\nu_{\mathrm{st}}=2$ then the whole particle A_0 will be burnt; at last if $\nu_{\mathrm{st}}=1$ then the whole particle A_0 will react but on the average one B_1 particle does not react at all. It should be noted that each of the particles A (including particle A_0) can have 0 to z neighbors with a different probability (the concentration of A particles, p, is given). Then, taking into account that these are pairwise incompatible events and using the formula for total probability, it is possible to write for $\varpi(p)$:

$$\varpi(p) \approx \sum_{i=0}^{z} \left[\alpha_i \binom{z}{i} P_A^{z-i} P_B^{i} \right] = \sum_{i=0}^{z} \left[G\left(\frac{i}{\nu_{\mathrm{st}}} \right) \binom{z}{i} p^{z-i} (1-p)^{i} \right]. \tag{4}$$

Here $(1-p)^i$ is the probability that particle A_0 has any i B neighbors; p^{z-i} is the probability that the rest $(z-i)$ neighbors of particle A_0 are A particles; α_i is the reacted part of particle A_0 under the condition that it has i B-particle neighbors.

Expression (4) is a rather rough approximation yet. It follows from a simple qualitative consideration that for a system with $\nu_{\mathrm{st}}=1$ there is a definite symmetry between components A and B, i.e., their formal transposition will not lead to changes in the reactant concentration giving the maximal combustion wave velocity. However, this symmetry disappears when using expression (4).

For a more accurate determination of $\varpi(p)$ value, it should be taken into account that particles B_1 can react not only with particle A_0 but with other A particles as well (in Fig. 1 these particles are denoted by subscript "2"). Let particle A_0 has i B neighbors. Each of these B_1 particles can neighbor, aside from particle A_0, with 0 to $z-1$ other A particles (they are marked as A_2 in Fig. 1). If i B_1 particles have respectively $\{j_1, j_2, \ldots, j_i\}$ A_2 neighbors, then in first approximation the probability of occurrence of such combination on the lattice is determined as

$$\prod_{k=1}^{i} \binom{z-1}{j_k} p^{j_k} (1-p)^{z-1-j_k},$$

and the fraction of reacted particle A_0 in this case is expressed by the formula

$$G\left(\frac{1}{\nu_{\mathrm{st}}} \sum_{k=1}^{i} \frac{1}{j_k+1} \right),$$

where function G is defined by Eq. (3) and the value in parentheses is its argument.

By summing over all possible combinations $\{j_1, j_2, \ldots, j_i\}$, one can arrive to a corrected expression for the reacted part α_i of particle A_0:

$$\alpha_i \approx \sum_{j_1=1}^{z-1} \cdots \sum_{j_i=1}^{z-1} G\left(\frac{1}{\nu_{\mathrm{st}}} \sum_{k=1}^{i} \frac{1}{j_k+1} \right) \times \left[\prod_{k=1}^{i} \binom{z-1}{j_k} p^{j_k} (1-p)^{z-1-j_k} \right]. \tag{5}$$

Then the mean final conversion of A particles over the system, $\varpi(p)$, can be determined by the following expression:

$$\varpi(p) \approx \sum_{i=1}^{z} \left\{ \sum_{j_1=1}^{z-1} \cdots \sum_{j_i=1}^{z-1} G\left(\frac{1}{\nu_{\mathrm{st}}} \sum_{k=1}^{i} \frac{1}{j_k+1} \right) \times \left[\prod_{k=1}^{i} \binom{z-1}{j_k} p^{j_k} (1-p)^{z-1-j_k} \right] \binom{z}{i} p^{z-i} (1-p)^{i} \right\}. \tag{6}$$

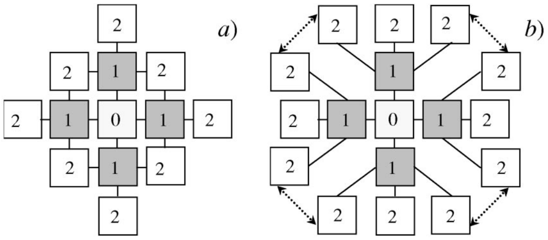

FIG. 2. Explanatory scheme for derivation of Eqs. (4)–(6); *a* is a fragment of regular square lattice $(z=4)$; *b* is a fragment of a Bethe lattice $(z=4)$.

Approximations made during derivation of Eqs. (4)–(6) need a more detailed explanation, which will be made by giving an example of a square lattice (Fig. 2). According to the proposed computational scheme an arbitrary particle of the system is considered (it is labeled by number 0). The first two layers of the nearest neighbors of this particle are labeled in Fig. 2 by numbers 1 and 2. As already noted above, it is not sufficient to consider only one layer of nearest particles (label 1) for a correct description of conversion of reactants. The second layer of the nearest particles (label 2) should also be taken into account. Those particles, which can immediately "interact" during chemical reaction, are connected by bonds in Fig. 2. It is difficult to describe analytically the fact that the properties of a particle in the second layer of a regular lattice affect simultaneously the reaction behavior of two particles in the first layer (Fig. 2). Therefore the structure pattern corresponding to the regular lattice (Fig. 2) was replaced by a more simplified one [Fig. 2(b)]. Such a pattern is known in physics as a Bethe lattice. In this case, properties of a particle in the second layer influence the conditions of reaction in only one particle of the first layer. It is important that the total number of nearest neighbors z (Fig. 2) and the probability to find particle of the first or the second kind are not changed. For a simplified case of a Bethe lattice it is possible to obtain an analytical expression for a mean degree of reactant conversion [Eq. (6)]. The substitution of structure patterns implies that from the mathematical viewpoint, we have neglected some correlations between properties of particles in the second layer [they are connected by arrows in Fig. 2(b)]. Two such particles in a Bethe lattice correspond to one and the same particle in the regular lattice. To estimate inaccuracy introduced by the above mentioned substitution, statistical Monte Carlo simulation was performed. Results of this simulation have shown that within the frame of the proposed model, Eq. (6) has an inaccuracy below 2%. This small value of inaccuracy is explained by the fact that the Bethe lattice was actually used to take into account the properties of particles belonging only to the second layer of nearest neighbors.

Theoretically, the procedure for more accurate determination of α_i values [Eq. (5)] can be continued by taking into account the fact that A_2 particles react not only with B_1 particles but are shared between other nearest B particles (Fig. 1). As noted above, numerical simulation has shown that taking into account the properties of neighbors in the second layer allows us to describe the mean degree of reactant conversion with a good accuracy. On the other hand, expression

(6) permits meeting the above mentioned symmetry condition (at $\nu_{\mathrm{st}}=1$) with the inaccuracy of 0.01 with respect to relative concentration. The presented estimations of the error allow us to restrict our consideration to the use of Eq. (6) because its accuracy corresponds to the general accuracy level of the model itself. The developed model can be generalized to take into account the porosity of the system.

B. Two-component system with porosity

Let ε is the porosity of a binary powder mixture, i.e., the fraction of volume occupied by voids. Voids can be treated as the third component (along with particles A and B). It is implied that "void" particles are of the same size and shape as particles A and B. Since the distribution of particles over the system is absolutely random, a probability to find the void in an arbitrary cell of the system is $P_{\varepsilon}=\varepsilon$. If p, as previously, is the fraction of A particles in the system, then the probability of finding a particle A or B in a cell is $P_A=p$ and $P_B=1-p-\varepsilon$, correspondingly. In a system with porosity the stoichiometric coefficient ν_{st} should be expressed as follows:

$$\nu_{\mathrm{st}}=\frac{1-p_{\mathrm{st}}-\varepsilon}{p_{\mathrm{st}}}. \tag{7}$$

Based on the computational method described in Ref. [10], for the "energy" of the whole system we obtain

$$E_{\mathrm{tot}}(p,\varepsilon)=(1-p-\varepsilon)\sum_{j=1}^{z} j\binom{z}{j}p^{j} \times\sum_{m=0}^{z-j}\binom{z-j}{m}\varepsilon^{m}(1-p-\varepsilon)^{z-j-m}. \tag{8}$$

The second sum in Eq. (8) can easily be calculated:

$$(1-p)^{z-j}=(1-p-\varepsilon+\varepsilon)^{z-j}=\sum_{m=0}^{z-j}\binom{z-j}{m}\varepsilon^{m}(1-p-\varepsilon)^{z-j-m}. \tag{9}$$

Hence upon summation in Eq. (8) we obtain

$$E_{\mathrm{tot}}(p,\varepsilon)=zp(1-p-\varepsilon). \tag{10}$$

As expected, expression (10) grades into expression (1) at $\varepsilon=0$.

Similarly, for the mean conversion degree of the system we arrive at the following expression:

$$\varpi(p,\varepsilon)\approx\sum_{i=1}^{z}\left\{\sum_{j_1=1}^{z-1}\cdots\sum_{j_i=1}^{z-1}G\left(\frac{1}{\nu_{\mathrm{st}}}\sum_{k=1}^{i}\frac{1}{j_k+1}\right)\times\left[\prod_{k=1}^{i}\binom{z-1}{j_k}p^{j_k}\sum_{m=0}^{z-1-j_k}\binom{z-1-j_k}{m}\times\varepsilon^{m}(1-p)^{z-1-j_k-m}\right]\binom{z}{i}(1-p-\varepsilon)^{i}\times\sum_{n=0}^{z-i}\binom{z-i}{n}\varepsilon^{n}p^{z-i-n}\right\}. \tag{11}$$

It can be shown in the way it was done for expression (9) that $\sum_{n=0}^{z-i}\binom{z-i}{n}\varepsilon^{n}p^{z-i-n}=(p+\varepsilon)^{z-i}$. Then, taking into account this expression and Eq. (9), one can obtain from Eq. (11)

$$\varpi(p,\varepsilon)\approx\sum_{i=1}^{z}\left\{\sum_{j_1=1}^{z-1}\cdots\sum_{j_i=1}^{z-1}G\left(\frac{1}{\nu_{\mathrm{st}}}\sum_{k=1}^{i}\frac{1}{j_k+1}\right)\times\left[\prod_{k=1}^{i}\binom{z-1}{j_k}p^{j_k}(1-p)^{z-1-j_k}\right]\times\binom{z}{i}(1-p-\varepsilon)^{i}(p+\varepsilon)^{z-i}\right\}. \tag{12}$$

For function $\varpi(p,\varepsilon)$, in the limit $\varepsilon\to 0$, expression (12) grades into Eq. (6). It should be noted that for $\varepsilon\to 1$ $\varpi(p,\varepsilon)\to 0$.

The derived expressions (1), (6), (10), and (12) will be used in further modeling of the combustion wave propagation in a binary disordered heterogeneous system.

III. PROPAGATION OF COMBUSTION WAVE IN A BINARY DISORDERED MIXTURE OF REACTANTS

A. Governing equations

To reveal the basic effects of the micrononuniformity of a two-component mixture on combustion we consider a simple model of a continuous combustible medium where the spatial scale of the combustion wave much exceeds the particle scale of the mixture. On the microlevel, the above-described structural model is used. The unavoidable imperfect mixing on the microlevel in disordered systems results in incomplete conversion of reactants. Thus if the initial mean density of component A is $\rho_A^0=\rho p$, then the instantaneous relative conversion degree of this component is determined as

$$\eta=\frac{\rho_A^0-\rho_A}{\rho_A^0-\rho_A^f}=\frac{\rho_A^0-\rho_A}{\rho_A^0\varpi(p,\varepsilon)}. \tag{13}$$

Here ρ_A is the instantaneous mean density of the A component.

A kinetic model of chemical conversion in the system is described by a global Arrhenius-type reaction with initiation temperature T_{in}, and we imply that the reaction rate, i.e., the mass of component A consumed in a unit volume per unit time is proportional to the number of interphase contacts per lattice site:

$$W(T,\eta)=\rho k E_{\mathrm{tot}}(p)\exp\left[-\frac{E'}{RT}\right]H(T-T_{\mathrm{in}})f(\eta). \tag{14}$$

Here T is temperature of particle [K]; k is the pre-exponential factor [$1/s$]; E' is the activation energy of the reaction (J/mol); R is the universal gas constant; $f(\eta)$ is the reaction retardation function due to solid-product formation. In the simplest case we use Heaviside function for $f(\eta)$ as well: $f(\eta)=H(1-\eta)$.

Within the frame of this model we arrive at the system of energy and mass conversion equations in the reference frame connected to the combustion front moving with velocity U:

$$-\rho c_p(1-\varepsilon)U\frac{dT}{dx}=\lambda\frac{d^2T}{dx^2}+QW(T,\eta), \tag{15}$$

$$-\rho p\varpi(p,\varepsilon)U\frac{d\eta}{dx}=W(T,\eta). \tag{16}$$

Here Q is the reaction heat (J/kg); λ is the thermal conductivity of particles (Wt/m K); c_p is the heat capacity of particles (J/kg K). Boundary conditions to Eqs. (15) and (16) are formulated as follows:

$$x\to-\infty: T=T_b, \quad \eta=1, \quad \frac{dT}{dx}=\frac{d\eta}{dx}=0; \tag{17}$$

$$x\to+\infty: T=T_0, \quad \eta=0, \quad \frac{dT}{dx}=\frac{d\eta}{dx}=0. \tag{18}$$

Equations (15) and (16) are readily integrated over interval $[-\infty,+\infty]$ with the use of boundary conditions (17) and (18) to give the following expression for the adiabatic combustion temperature T_b (maximal temperature of the combustion front):

$$T_b=T_0+\frac{Qp\varpi(p,\varepsilon)}{(1-\varepsilon)c_p}. \tag{19}$$

The structure of a disordered mixture is characterized by two values: porosity ε concentration of A particles p. But since the heat capacity of empty sites (pores) is negligible, the adiabatic combustion temperature in the case of perfect mixing depends only on the equivalence ratio of components A and B. This conventional for the combustion theory parameter [16] is defined as the ratio of volume of component A to the volume of component B divided by the same ratio for the stoichiometric mixture:

$$\phi=\left(\frac{p}{1-\varepsilon-p}\right)\Big/\left(\frac{p_{\text{st}}}{1-p_{\text{st}}-\varepsilon}\right). \tag{20}$$

If $\phi<1$ then component A is deficient; in the opposite case $(\phi>1)$ this component is in excess. Then, using Eqs. (7) and (20) the adiabatic combustion temperature for a random system can be expressed as follows:

$$T_b=T_0+\frac{Q\varpi(p,\varepsilon)\phi}{(\nu_{\text{st}}+\phi)c_p}. \tag{21}$$

B. Dimensionless variables and equations

The characteristic temperature for transition to dimensionless variables can be determined as the adiabatic combustion temperature attained after complete burning of a stoichiometric mixture of A and B components with perfect mixing (i.e., at $p=p_{\text{st}},\phi=1$, and $\varpi=1$): $T_*=T_0+Q/(\nu_{\text{st}}+1)c_p=T_0+\Delta T_{\text{ad}}^{\text{st}}$. The characteristic temperature scale is $\Delta T_*=RT_*^2/E'$. Thus this scale is the same for all systems with a given value of ν_{st} but different porosity ε. The characteristic time scale is more specific because the time of mixture burning depends on the porosity at fixed ϕ. In the considered problem, the characteristic time scale is chosen equal to the reaction time for the stoichiometric mixture at the characteristic temperature and given porosity: $t_*=p_{\text{st}}[kE_{\text{tot}}(p_{\text{st}})\exp\times(-E'/RT_*)]^{-1}$. Thus the time scale varies with changing ε because p_{st} and E_{tot} depend on porosity. On one hand, this choice of t_* permits simplifying the final dimensionless equations. On the other hand, below we consider only the ratio of the combustion wave velocity to its maximal value at given porosity and this choice of t_* does not influence the final results. It should be noted that by using porosity-specific scaling factors for proceeding to dimensionless variables we exclude from consideration the effect of thermal conductivity on the combustion wave velocity which can mask the role of nonuniform mixing and, strictly speaking, deserves a separate consideration.

Definitions of dimensionless variables are close to those conventionally used in the combustion theory: $\xi=x/x_*$ is a dimensionless spatial coordinate; $\theta=(T-T_*)/\Delta T_*$ is dimensionless temperature; $u=U/u_*$ is a dimensionless combustion wave velocity. The other scaling factors are $x_*=\sqrt{a\gamma t_*}$ (characteristic width of the reaction zone), where a is the thermal diffusivity of particles (m^2/s); $u_*=x_*/t_*$ and the dimensionless parameters of the system are $\gamma=\Delta T_*/\Delta T_{\text{ad}}^{\text{st}}=RT_*^2(\nu_{\text{st}}+1)c_p/E'Q;\beta=\Delta T_*/T_*=RT_*/E'$.

Then the dimensionless initial temperature of the system is $\theta_0=-1/\gamma$ and dimensionless combustion temperature is

$$\theta_b=\frac{1}{\gamma}\left(\varpi\frac{p}{p_{\text{st}}}-1\right)=\frac{1}{\gamma}\left(\varpi\phi\frac{\nu_{\text{st}}+1}{\nu_{\text{st}}+\phi}-1\right). \tag{22}$$

Master equations (15) and (16) are reshaped in the dimensionless form as follows:

$$-\gamma u\frac{d\theta}{d\xi}=\frac{1}{1-\varepsilon}\frac{d^2\theta}{d\xi^2}+\sigma(\phi)\Phi(\theta,\eta), \tag{23}$$

$$-\pi(\phi)\varpi(\varepsilon,\phi)u\frac{d\eta}{d\xi}=\sigma(\phi)\Phi(\theta,\eta), \tag{24}$$

where

$$\Phi(\theta,\eta)=\varphi(\theta)\psi(\eta), \quad \varphi(\theta)=H(\theta-\theta_{\text{in}})\exp\left(-\frac{\theta}{1+\beta\theta}\right),$$

$$\psi(\eta)=H(1-\eta), \quad \pi(\phi)=\frac{p}{p_{\text{st}}}=\phi\frac{\nu_{\text{st}}+1}{\nu_{\text{st}}+\phi},$$

$$\sigma(\phi)=\phi\left(\frac{\nu_{\text{st}}+1}{\nu_{\text{st}}+\phi}\right)^2=\frac{\pi^2(\phi)}{\phi}.$$

Reshaping of the boundary conditions is trivial and is not presented here.

After conventional transformations (substituting the right-hand side of Eq. (24) into Eq. (23), integrating the latter over interval $[\xi,+\infty]$, and using θ as an independent variable) we arrive at the final differential equation in the space of variables η and θ:

$$\frac{d\eta}{d\theta} = \frac{\sigma(\phi)\Phi(\theta,\eta)}{\pi(\phi)\varpi(\varepsilon,\phi)(1-\varepsilon)u^2[\gamma(\theta-\theta_0)-\pi(\phi)\varpi(\varepsilon,\phi)\eta]}. \tag{25}$$

This equation was used for numerical calculation of parameter u by the shooting method: the equation was integrated from $\theta=\theta_{\text{in}}$ to $\theta=\theta_b$ and the parameter u was fitted to meet the boundary conditions $\eta=0$ at $\theta=\theta_{\text{in}}$ and $\eta=1$ at $\theta=\theta_b$.

Equation (25) is close to conventional equations used in the theory of gasless combustion. The difference from the conventional form lies in functions $\sigma(\phi), \varpi(\varepsilon,\phi)$, and $\pi(\phi)$ which reflect the dependencies of the interfacial area, final conversion degree, and heat release on the structural parameters of the mixture.

IV. RESULTS AND DISCUSSION

A three-dimensional (3D) simple cubic lattice ($z=6$) was used to model the structure of binary mixture. The following values of dimensionless parameters characterizing the combustion process were used in numerical modeling: $\gamma=1/6, \beta=1/8, \theta_{\text{in}}=-0.8/\gamma$. These values of parameters γ and β correspond to stable combustion. The approach described in Sec. II of this paper permits calculating the mean final conversion [Eq. (12)] and maximal temperature in the adiabatic combustion wave [Eqs. (21) and (22)] for different stoichiometry and porosity. It is important that due to imperfect mixing on the microscopic scale (the scale of structural elements of the mixture) the maximal conversion degree $\varpi(\varepsilon,\phi)$ appears to be substantially lower than 1 and the maximal heating at complete burning of the stoichiometric mixture is not achieved (Table I). It can be seen that maximal adiabatic heating $\Delta T_{\text{ad}}^{\max}$ is attained at the equivalence ratio ϕ_* greater than 1 for a mixture with stoichiometric coefficient $\nu_{\text{st}}>1$: at larger ν_{st} and ε the deviation of ϕ_* from unity increases. At the same time, the conversion at point $\phi=\phi_*$, where the temperature of the wave is maximal, is lower that at $\phi=1$ (stoichiometric mixture) which is attributed to the fact that maximal heating is attained at the maximum of function $\varpi(\phi)p(\phi)$.

Since the combustion wave velocity u strongly depends on temperature, the calculations of u reflect the above-discussed effects of nonuniform mixing on the heat release (Fig. 3). In Fig. 3, the velocities are shown as relative values with respect to the maximal velocity $u_{\max}$ attained at the given stoichiometry, porosity, and perfect mixing. Thus all the curves on charts a,b, and c in Fig. 3 refer to different velocity scales. For each combination of stoichiometry and porosity, imperfect mixing lowers the combustion velocity and shifts its maximal value to higher equivalence ratios if $\nu_{\text{st}}>1$. For mixtures with volumetric stoichiometric ratio 1 : 1 this shift is absent.

TABLE I. Mean final conversion ϖ and dimensionless adiabatic heating $\Delta T_{\text{ad}}^{\max}/\Delta T_{\text{ad}}^{\text{st}}$ for systems with different stoichiometry and porosity.[a]

Stoichiometry	Porosity	ϕ_*	$\Delta T_{\text{ad}}^{\max}/\Delta T_{\text{ad}}^{\text{st}}$	$\varpi\vert_{\phi=1}$	$\varpi\vert_{\phi=\phi_*}$
1:1	0.0	1.0	0.80	0.80	0.80
($\nu_{\text{st}}=1$)	0.05	1.0	0.75	0.78	0.78
	0.10	1.0	0.70	0.77	0.77
	0.20	1.0	0.60	0.75	0.75
	0.40	1.0	0.41	0.68	0.68
1:2	0.0	1.18	0.82	0.82	0.74
($\nu_{\text{st}}=2$)	0.05	1.22	0.77	0.81	0.71
	0.10	1.22	0.72	0.78	0.70
	0.20	1.27	0.61	0.76	0.66
	0.40	1.33	0.41	0.66	0.57
1:3	0.0	1.35	0.81	0.78	0.65
($\nu_{\text{st}}=3$)	0.05	1.39	0.75	0.76	0.63
	0.10	1.43	0.70	0.73	0.60
	0.20	1.45	0.59	0.70	0.57
	0.40	1.62	0.39	0.60	0.46

[a] ϕ_* is equivalence ratio at which adiabatic heating is maximal; $\Delta T_{\text{ad}}^{\text{st}}$ is adiabatic heating in stoichiometric mixture at perfect mixing; $\Delta T_{\text{ad}}^{\max}$ is maximal adiabatic heating in disordered mixture.

Note that within the frame of the above model (the number of interfacial contacts per lattice site does not change during the reaction) the dependence of the velocity u on the equivalence ratio ϕ has a sharp peak at perfect mixing of reactants. The use of different model retardation functions $f(\eta)$ does not remove this peak (curves 1 in Fig. 3) because this is a peculiarity of the perfect mixing model. From this standpoint, combustion in solid heterogeneous mixtures differs essentially from gas-phase combustion: in gases mixing proceeds continuously during reacting whereas in solid flames only *premixing* determines the system structure and interphase reaction area.

The combustion of solid heterogeneous mixtures is a complex process and the proposed model does not include such factors as phase transitions (melting), dependences of thermal properties on the mixture composition, porosity, and temperature. The main goal of this work is to take into account in the simplest way the effect of structure randomness on the combustion of binary solid mixtures. Therefore the comparison of the obtained results with experimental data in this case may be performed on the qualitative or semiquantitative level only. Most suitable systems for comparison with our model are monodisperse mixtures used for solid-flame combustion. Unfortunately, data for such systems are scanty in literature. Here we use data from Ref. [17] where combustion of the Al/NiO system was studied as a function of the mixture composition. One of those results which is important for comparison with our model is presented in Fig. 4. As can be seen, the shift of the maximum combustion wave velocity to Al-richer mixtures ($\phi>1$) in this system really exists. A similar shift of the maximal combustion wave velocity was observed in Ref. [18] for systems $\text{Al}/\text{Ni}_2\text{O}_3$ and $\text{Al}/\text{Fe}_2\text{O}_3$. According to data from Ref. [17], the volumetric stoichiometric coefficient for mixture Al/NiO is $\nu_{\text{st}}=1.72$ (the mass fraction of Al $\zeta_{\text{Al}}=0.19$) while the maximal velocity is attained at $\phi_*\approx 1.8$ ($\zeta_{\text{Al}}=0.30$). We can compare this shift with that obtained in our model for $\nu_{\text{st}}=1.72$ and porosity $\varepsilon=0.4$, which corresponds to the experimental packing

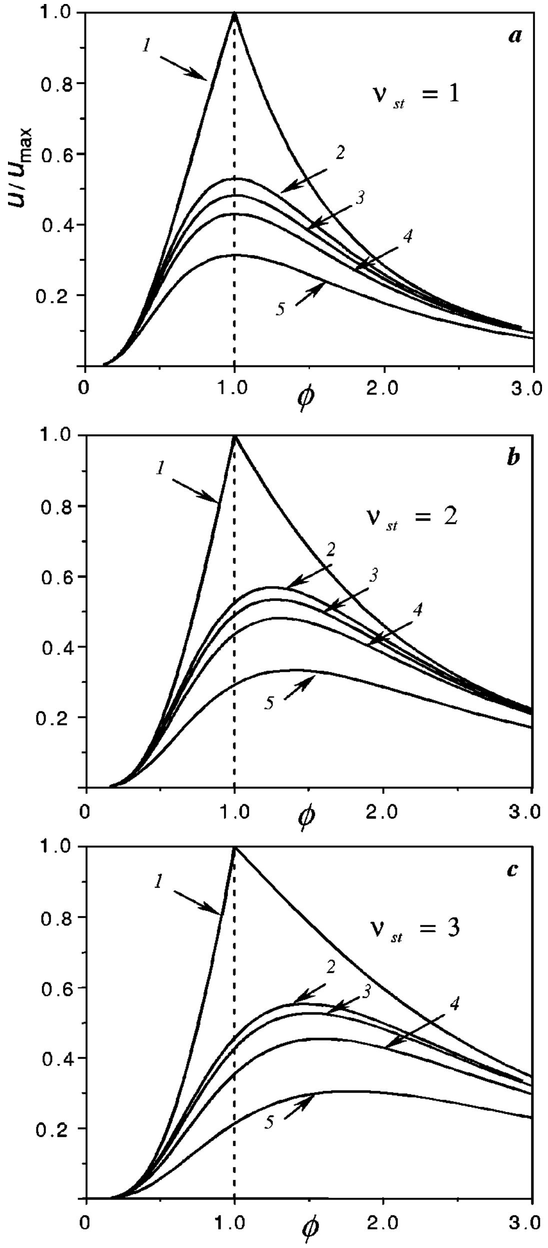

FIG. 3. Relative velocity of the combustion wave in the structurally disordered binary heterogeneous mixture. Curves: 1 for the model of perfect mixing (arbitrary ε); 2–5 for disordered systems ($\varepsilon = 0$, 0.1, 0.2, 0.4, respectively).

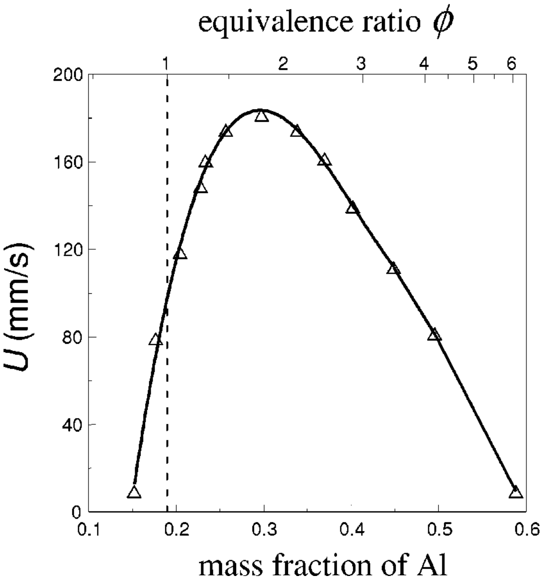

FIG. 4. Combustion wave velocity vs mass fraction of aluminum and equivalence ratio ϕ according to Ref. [17].

density in Ref. [17]. Our calculations give the value $\phi_* \approx 1.3$. Considering all the above discussed limitations of the model, this correlation between the theoretical and experimental data can be regarded as satisfactory. Along with the aforesaid thermophysical limitations, there is a structural reason for a discrepancy between the experiments and theory: the proposed model does not take into account the polydispersity of a mixture (particles *A* and *B* have equal size). At the same time, it is known that the velocity of combustion depends on a particle size distribution (this fact is outlined in Ref. [17], too). It can be expected that a correlation between experiment and the model will become better when the polydispersity is taken into account. But simultaneous consideration of random internal structure and polydispersity of a mixture is a complex statistical and geometrical problem and would be the subject of future investigation.

V. CONCLUSION

A combined geometrical and physicochemical model is proposed which includes the effect of structural disorder of solid binary reactant mixtures on the combustion process. The results of modeling permit describing such known experimental facts as incomplete conversion of the reactants, a decrease of adiabatic heating, and a shift of the maximum combustion velocity away from the stoichiometric ratio. Since the effect of nonuniform mixing is important for both the combustion wave characteristics and the properties of final SHS products, this model should be integrated into more complete models of solid-flame combustion.

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