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Ignition of inhomogeneous nanothermite mixtures

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To assess the reactivity of nanothermites, the mathematical model of ignition of a nanothermite tablet by a hot body or radiation flux is expanded to take into account the incomplete homogeneity of the mixture. An approximation expression is given for the ignition time depending on the conditions and degree of homogeneity.

Keywords: nanothermite, degree of homogeneity, ignition, reactivity.

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Nanothermites are composite materials in which metal particles ranging in size from a few nanometers to several micrometers are mixed with metal oxides. They are distinguished by high energy density, which makes them efficient in various applications, including pyrotechnics, explosives engineering, and welding [1]. Owing to the small particle size, nanothermites are easy to integrate into various products (specifically, via additive techniques). However, the use of these promising materials faces challenges related to safety and manufacturing difficulties. Specifically, it is problematic to produce homogeneous mixtures for precise control of the ignition time and combustion rate of such materials [2]. The smallness of particles and their tendency to aggregate make it hard to achieve homogeneity in a mixture of nanopowders. Special techniques (ultrasonic treatment and chemical reagents for microencapsulation) are used to improve the mixing quality.

A method for assessing the homogeneity of a nanothermite mixture based on the analysis of scanning electron microscopy (SEM) images was proposed in [3]. A mathematical model of ignition of a homogeneous nanothermite mixture by a hot body was presented. The mathematical model allows one to predict the ignition time and specifies critical conditions.

The aim of the present study is to extend this mathematical model of nanothermite ignition to the case of incomplete mixture homogeneity.

The problem of ignition of an explosive tablet by a hot body and a heat flux is considered in the general formulation. Interpolation expressions for the dimensionless ignition time, which generalize the results of numerical calculations, are obtained. In the case of tablet ignition by a hot body with temperature T_s [4],

$$\tau_i \approx 1.18|\theta_n|^{1.5}. \quad (1)$$

In the case of ignition by a heat flux (convective or luminous flux q_s),

$$\tau_i \approx 1 + 2\beta + 0.5|\theta_n|,$$
$$|\theta_n| = \frac{2q^2}{\pi}. \quad (2)$$

Here, parameter $\beta = \frac{RT_s}{E}$ characterizes the degree of dependence of the rate of a chemical reaction on temperature; the dimensionless initial temperature is defined as $\theta_n = \frac{E}{RT_s^2}(T_n - T_s)$, where T_n is the initial temperature. In the case of ignition by a heat flux, heating temperature T_s is specified by heat flux density q_s; q is the dimensionless heat flux, $q = q_s \frac{E\sqrt{at_a}}{\lambda RT_s^2}$. In dimensional variables, the ignition time is determined through the adiabatic induction time: $\tau_i = t_i/t_a$, $t_a = \frac{cRT_s^2}{EQz}\exp\left(\frac{E}{RT_s}\right)$. The notation is as follows: a is the temperature conductivity, Q is the specific heat of the thermite decomposition reaction, z is the pre-exponential factor, λ is the thermal conductivity, c is the specific heat capacity, E is the activation energy, and R is the universal gas constant.

Depending on the conditions and under the assumption of mixture homogeneity, the ignition theory allows one to determine the ignition time using formulae (1) or (2). The initial data for calculations for copper–aluminum nanothermite were as follows [5,6]:
$\rho = 5.6 \cdot 10^3$ kg/m^3, $E = 3.03 \cdot 10^5$ J/mol,
$\lambda = 48.5\,\mathrm{W/(m \cdot K)}$, $c = 0.61 \cdot 10^3\,\mathrm{J/(kg \cdot K)}$,
$Qz = 9.39 \cdot 10^{42}\,\mathrm{J/(kg \cdot s)}$,
while the data for iron–aluminum nanothermite were [5,7]
$\rho = 1.71 \cdot 10^3$ kg/m^3, $E = 4.42 \cdot 10^4$ J/mol,
$\lambda = 0.293\,\mathrm{J/(m \cdot s \cdot K)}$, $c = 1.22 \cdot 10^3\,\mathrm{J/(kg \cdot K)}$,
$Qz = 4.39 \cdot 10^{13}\,\mathrm{J/(kg \cdot s)}$.

Thermite mixtures consisting of electro-explosive nanoaluminum powder and iron oxide powder (first mixture) or copper oxide powder (second mixture) in a stoichiometric

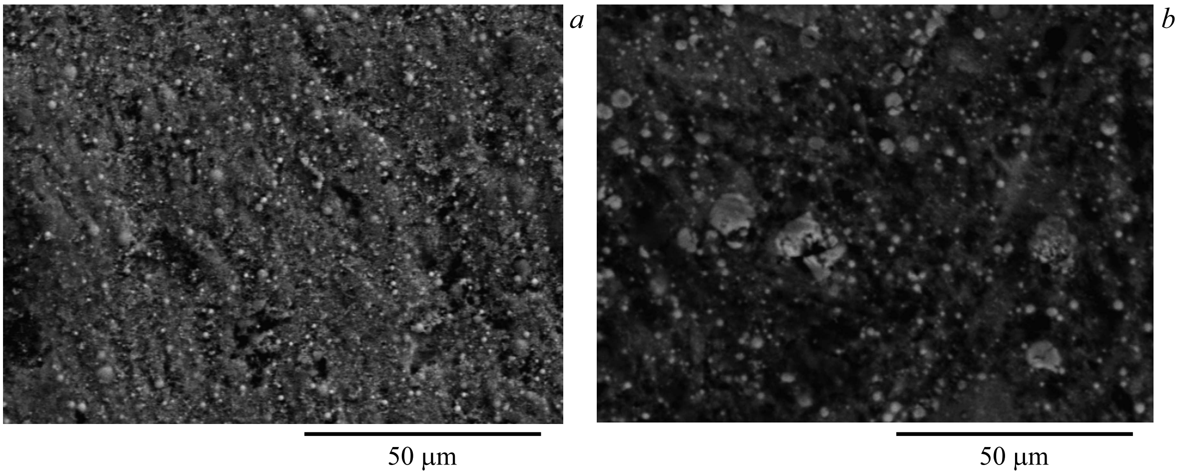

Figure 1. SEM images of $Al-Fe_2O_3$ nanothermite mixtures. *a* — Aluminum particles coated with fluororubber; *b* — without the chemical agent.

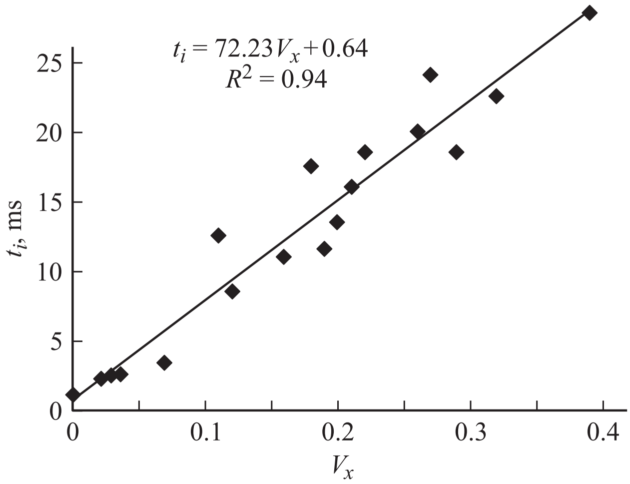

Figure 2. Ignition time of Al–CuO (ultrasonic homogenization) and $Al-Fe_2O_3$ (ultrasonic + chemical particle treatment) nanothermite mixtures as function of the coefficient of variation (common approximation).

ratio were used in the experiment. The mixture homogeneity was improved in two ways. Copper–aluminum powders were subjected to ultrasonic treatment in an inert medium (hexane, isopropanol); the intensity varied from 50 to 150 W, and the treatment time was 5–30 min.

In addition to 10 min of ultrasonic treatment at 50 W, aluminum particles in iron–aluminum thermites were treated with chemical agents (pyrocatechol, acetylacetone, ethyl salicylate together with triethanolamine, fluororubber). These substances promote dispersion of particle agglomerates and increase their reactivity. In the control series of experiments, chemical agents and ultrasonic treatment were not used.

The prepared mixture of powders weighing 1 g was pressed into a tablet under a pressure of 10 kgf/cm^2. This tablet had an area of 0.89 cm^2 and a height of 0.43 mm. It was heated from the end with an ignition wire ($T_s = 190°C$). Ignition time t_i was determined according to the condition of reaching the temperature maximum. A laser monitor was used to visualize the combustion process [8].

The following procedure for assessment of the degree of homogeneity was adopted. A SEM image of the distribution of components was obtained (an example image is shown in Fig. 1), and the image area was divided into ten subregions. The ratio of areas of the fields corresponding to components was calculated in each subregion, and the coefficient of variation of this ratio was found. The higher the coefficient of variation is, the greater is the deviation of the ratio of components in a subregion from the one averaged over the entire surface. Average coefficient of variation V_x was chosen as a measure of mixture homogeneity.

As should be expected, coefficient of variation V_x decreases (the uniformity of distribution of components throughout the volume of the mixture increases) and the average particle size decreases with increasing time and intensity of ultrasonic treatment coupled with the use of chemical agents.

Figure 2 presents the dependence of ignition time on coefficient of variation V_x. The points corresponding to $V_x = 0$ (complete homogeneity of the mixture) were calculated theoretically, while the remaining points were obtained experimentally. The dependencies are approximated by a linear function (CL 0.94)

$$t_i = AV_x + t_0, \quad (3)$$

where coefficient $A = 72.23$ ms and t_0 corresponds to the time of ignition of a homogeneous mixture, $t_0 = 0.64$ ms (under conditions corresponding to the experimental ones).

Experiments reveal a significant dependence of the ignition time of nanothermites on the degree of homogeneity of the mixture. The longest ignition time (20–30 ms) corresponds to thermite mixture tablets that have not been subjected to homogenization treatment. This implies that the components were not mixed well enough and particle aggregates were not broken up. It is important to note that a common approximation was obtained for two nanothermites and two homogenization methods. This suggests that the degree of homogeneity remains an important parameter in assessment of reactivity regardless of the method used to achieve it. The ignition time may be regarded as a measure of nanothermite reactivity, while the proposed coefficient of variation of the ratio of the areas of SEM image fields corresponding to the mixture components may be considered a measure of homogeneity.

Thus, a mathematical model of nanothermite ignition in two versions with boundary conditions of the first kind (ignition by a hot body) and the second kind (ignition by a heat flux) was proposed. Having processed experimental data on the ignition of iron–aluminum and copper–aluminum nanothermite tablets, we extended this mathematical model to the case of ignition with incomplete homogeneity of mixtures. Expressions for the ignition time as function of the conditions (temperature difference), properties of the explosive material (activation energy, reaction heat), and the degree of mixture homogeneity were provided.

The obtained results should be of interest to engineers and researchers working in the field of advanced energy materials and products. They provide an opportunity to perform a preliminary assessment of reactivity of the nanostructured materials being developed with the degree of homogeneity of mixtures and other physical and chemical properties taken into account.

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Conflict of interest

The authors declare that they have no conflict of interest.

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