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Thermal analysis of high-temperature fast reactions in energetic materials

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Abstract To get round two main difficulties of the kinetic study of fast reactions of high-temperature decomposition of energetic materials (EM) (spatial non-isothermality and self-inflammation) two new methods for sample preparation called "mechanical dilution" and "thermal dilution" were applied. In the first part of the presentation, some experimental and theoretical data on kinetics of fast high-temperature decomposition of some typical homogeneous and heterogeneous energetic materials (including pyroxylin, ammonia copper chromate, ammonium perchlorate, solid rocket propellants, and others) are given. In a number of cases, kinetic constants of fast reactions dominating at high temperatures were shown to significantly differ from those of low-temperature reactions. The second part of the presentation deals with a new method of thermal analysis—electrothermal analysis (ETA). By using a multi-channel high-speed optical pyrometer, variation of the temperature field in an electrically heated sample of conductive energetic material (or its mixture with metal powder) during its heating followed by thermal explosion is registered. Due to application of this method in the ETA-100 (allowing one to measure kinetic data at the temperature up to 3800 K with a time step as short as 0.1 ms, i.e., for full conversion times as short as 10^{-3} s) some important patterns of mechanisms of gasless combustion and explosion in SHS-mixtures (Si + C, Ni + Al, and Ti + C) were identified. More details regarding these and some additional important aspects can be found in [1, 2].

Keywords Kinetics · Ignition · Combustion · Explosives · Propellants

Information about patterns, mechanisms, and kinetic parameters of high-temperature decomposition of EM (that includes all explosives, pyrotechnic compositions, gun powders, and modern solid, liquid, and hybrid rocket propellants) is of large importance for scientifically founded solution of many practical tasks associated with their production and application. For theoretical analysis by using main expressions of the theory of stationary and non-stationary combustion of solid propellants as well as for practical applications, kinetic constants of fast high-temperature decomposition of components and compositions of solid and hybrid propellants are of special importance. Extrapolation of low-temperature kinetic data into a high-temperature region gives the values for the burning surface temperature which drastically disagree with experimental data obtained by thermocouple measurements. Classical isothermal methods of chemical kinetics absolutely cannot be used for solution of the mentioned tasks. Commercially available thermal analysis devises are not designed to study reaction kinetics. So in the general case, one cannot clearly identify the heat exchange conditions between the environment and the experimental cell based on its design. This complicated the quantitative analysis of the experimental data and markedly decreases the accuracy of the estimated kinetic parameters. To ensure low coefficient of heat exchange between the sample and the thermostat and to equalize the temperature and at the same time to decrease the self-heating an approach based on significant ballasting

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("dilution") of the reactant was proposed. Two methods of dilution were developed: "mechanical" and "thermal". The basic experimental scheme and cells used in experiments with "mechanical" and "thermal dilution" of reactive EM with heat-conducting inert material are shown in Fig. 1.

The "mechanical dilution" is used for the study of decomposition kinetics for homogeneous EM. In this case, a sample is blended with highly heat-conducting inert material in the ratio $M/m \approx 100$, where m and M are weights of the sample and the diluent. In the "thermal dilution" method developed for the study of heterogeneous energetic materials, *s* solid sample (about 0.5 mm thick) is pressed between the ends of two aluminum cylinders placed into a cell with the shape of a cartridge case. Due to the efficient heat removal into the aluminum cylinders, sample self-ignition at high rates of specific heat emission in the sample accompanying its high-temperature decomposition does not take place.

This method allows one, on the one hand, to ensure spatial uniformity of heating of the compound and, on the other hand, to exclude possibility of the sample self-ignition. Also (that is extremely important), due to this method the interval of the temperatures at which behavior of energetic materials can be studied significantly widened to the region of high temperatures characteristic for their combustion and explosion. An approach for the calculation of the kinetic constants is given in [1, 2]. Here just the resultant expressions are presented:

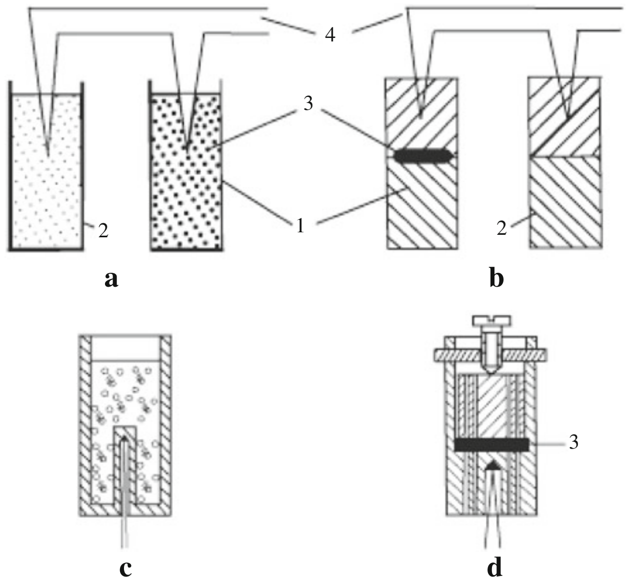


Fig. 1 Experimental approach scheme and cells for DTA, TGA, and DSC; **a**, **c** "mechanical dilution", **b**, **d** "thermal dilution"; *1* experimental cells, *2* reference cells, *3* sample, *4* differential thermocouples

$$Q = \frac{1}{m}\int_0^{\infty} K(T)S\Delta T\mathrm{d}t, \qquad (1)$$

$$\alpha = \alpha(\beta, t) = \frac{1}{Qm}\left[m_{\mathrm{cell}}C\Delta T + \int_0^{t} K(T)S\Delta T\mathrm{d}t\right], \qquad (2)$$

$$\mathrm{d}\alpha/\mathrm{dt} = \dot{\alpha}(\beta, t) = \frac{1}{Qm}\left[m_{\mathrm{cell}}C(\Delta\dot{T}) + K(T)S\Delta T\right], \qquad (3)$$

where Q is the reaction thermal effect, m is the sample weight, K, the coefficient of heat exchange between the cell and the furnace walls, S, the external surface of the cell, ΔT, the DTA-signal, $\Delta\dot{T} = \frac{\mathrm{d}(\Delta T)}{\mathrm{d}t}$, the rate of self-warming, m_{cell}, the cell weight, C, heat capacity of the cell material, α, the conversion degree, $\dot{\alpha}$ the reaction rate, β, the heating rate.

This approach was used for the study of irreversible decomposition of ammonium perchlorate (AP). The reaction was found to occur via two stages characterized by the same value of the activation energy (125 kJ/mol) and pre-exponential factors different by a factor of 100. The first (fast) stage described by the first-order process finishes when the conversion degree attains approximately 15%. Kinetics of the second (slow) stage occurring in the temperature range of 280–500 °C can be described by equation

$$\mathrm{d}\alpha/\mathrm{d}t = k_2(1-\alpha)^{0.5} \qquad (4)$$

where $k_2 = 5.9 \cdot 10^6 \exp(-129000/RT)\ \mathrm{s}^{-1}$.

Decomposition patterns for heterogeneous materials were studied by the "thermal dilution" method in a wide range of the conversion degree. The original thermograms for the ammonium perchlorate–polystyrene mixture (AP–PS) obtained under thermal dilution are shown in Fig. 2. From the thermograms and the results of their analysis (Figs. 3, 4, 5), one can conclude that the decomposition of the AP–PS system occurs via two stages with total thermal effect of 2.5 ± 0.2 kJ g^{-1}. This conclusion is based on the monotonous change in the effective activation energy as the conversion degree grows (Fig. 5).

The rate constants and the effective activation energy ($E_{\mathrm{a1}} = 133$ kJ mol^{-1}) of the decomposition first stage ($\alpha < 0.15$) are close to those of AP decomposition. The second-stage reaction rate depends weakly on the conversion degree ($0.4 < \alpha < 0.8$), which is characteristic of pseudo-zero order reactions.In this case, the expression for the rate constant is

$$k_2 = 10^{18.8 \pm 0.7}\exp\left(-\frac{263000 \pm 9600}{RT}\right)\left[s^{-1}\right]. \qquad (5)$$

Decomposition of mixtures of AP with almost all studied polymers (rubber resin, polyurethane, polystyrene, and others) was found to occur via two stages.

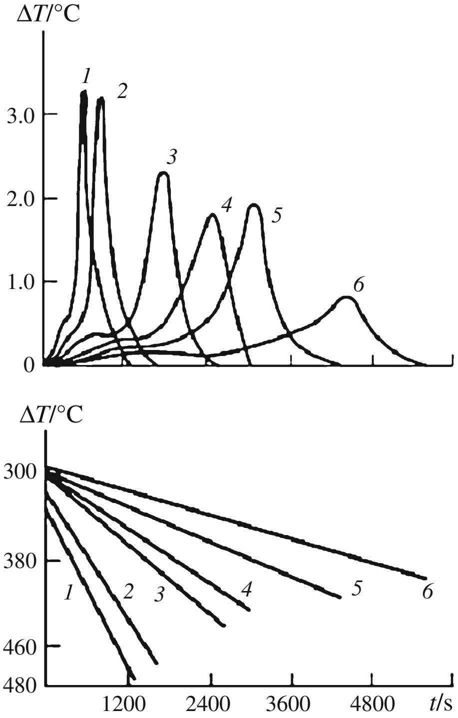


Fig. 2 Thermograms of AP–PS decomposition at $\beta = 7.6$ (*1*), 6.1 (*2*), 3.0 (*3*), 2.6 (*4*), 1.6 (*5*), and 1.1 (*6*) °C min^{-1}

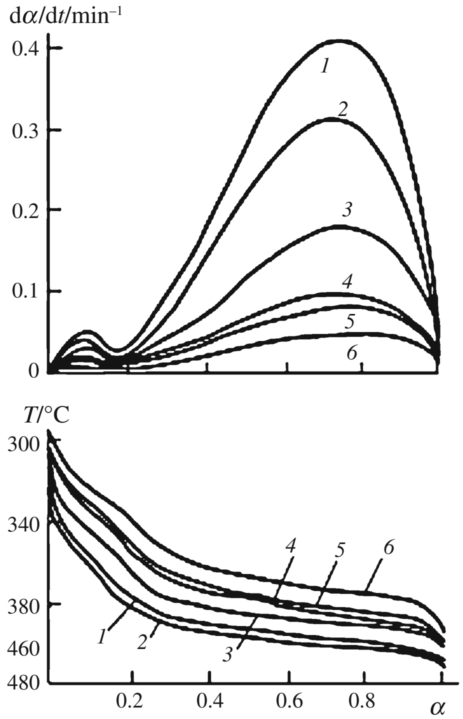


Fig. 3 Nonisothermal rate of AP–PS decomposition at $\beta = 7.6$ (*1*), 6.1 (*2*), 3.0 (*3*), 2.6 (*4*), 1.6 (*5*), and 1.1 (*6*) °C min^{-1}

In the first stage, polymer is oxidized by products of irreversible decomposition of AP. At $\alpha < 15\%$, the kinetics of the reaction taking place in the mixture is similar to that of the first (fast) stage of AP decomposition. In the second (slow) stage of decomposition of the AP–polymer mixtures, the overall reaction rate is determined by the process of a complex gas (product of irreversible decomposition of AP saturated with chloric acid vapors) formation. The vapor pressure increases with increasing temperature. As a result, the activation energy of the gross-process of high-temperature decomposition of AP-based solid propellant can be expressed as a sum of the AP decomposition activation energy (E_{aAP}) and a half of the AP dissociative sublimation heat (ΔH):

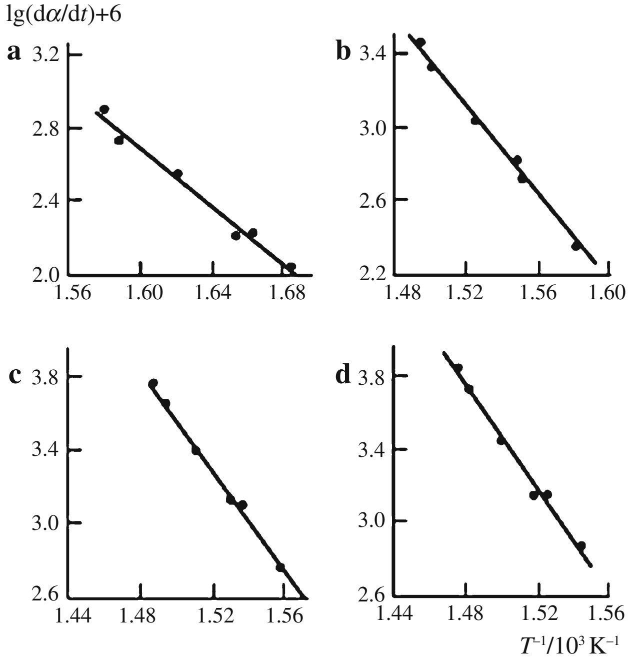


Fig. 4 Temperature dependence of the rate of AP–PS decomposition at $\alpha = 0.1$ (**a**), 0.3 (**b**), 0.5 (**c**), and 0.7 (**d**)

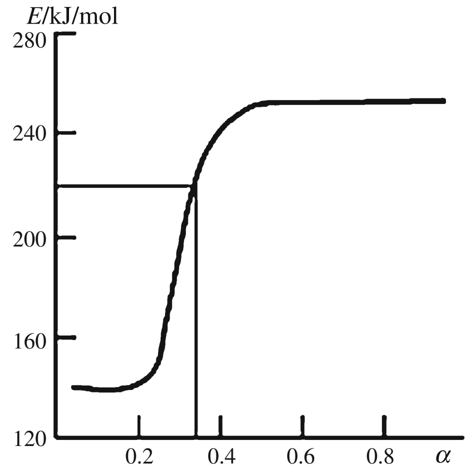


Fig. 5 Effective activation energy of AP–PS decomposition vs the conversion degree

$$E_{a\Sigma} = E_{a\mathrm{AP}} + \Delta H/2 = 129 + 21 = 250\,\mathrm{kJ/mol}. \quad (6)$$

Some aspects of high-temperature decomposition of so-called volatile EM including liquid nitrates, highly concentrated H_2O_2, hydrazine and AP were thoroughly studied. Simultaneously occurring volumetric irreversible reactions and phase transformations under conditions of dynamic equilibrium at the interface (evaporation, in case of liquids, and dissociative sublimation, in case of AP) are characteristic for macrokinetics of high-temperature reactions in these EM. Processes of gas formation accompanying decomposition of the volatile EM and their thermal explosion are shown to have different character than those of nonvolatile EM. Some instruments for determination of kinetic parameters and critical conditions of thermal explosion of volatile EM are described in this work. Kinetic parameters for homogeneous and heterogeneous (on surfaces of commonly used constructional materials) decomposition of highly concentrated H_2O_2 and hydrazine are determined for a wide range of temperature and reaction rate. Experimental results on thermal explosion of highly concentrated H_2O_2 quantitatively confirmed the correctness of the theory of thermal explosion of volatile EM developed by Shteinberg [1].

The second part of the presentation is devoted to electrothermal explosion (ETE) of condensed EM [3–7] belonging to a class of gasless combustion systems (including various mixtures used in self-propagating high-temperature synthesis/combustion synthesis and thermite). Experiments on ETE are performed by using samples pressed from EM powders and characterized by high electric conductivity. The fast electrical heating of the samples is characterized by relative uniformity.

The design of an ETE experiment is schematically given in Fig. 6.

As soon as the heat-evolution rate due to high-temperature reaction in the reaction mixture becomes comparable with the Joule heat generation rate the current is switched off. Due to a high reaction rate, further warming up of the sample occurs under adiabatic conditions. This feature of ETE significantly facilitates calculation of effective kinetic constants for super-fast high-temperature reaction responsible for combustion and explosion parameters of corresponding composite EM.

Progress in theory and practice of ETE in various SHS-systems resulted in development of a specialty instrument called electro-thermoanalyzer ETA-100 manufactured by ALOFT, Berkeley (Fig. 7). Today this instrument allows one to measure kinetic parameters of gasless reactions for a wide range of working temperatures (900–3600 K) at reaction times as short as 100 µs. Typical thermograms obtained by using ETA-100 for ETE of a sample pressed from mechanically treated mixture of Al and Ni powders are shown in Fig. 8a [7]. A 3D temperature profile taking place as combustion waves propagate from the sample central part (with the maximum temperature caused by local thermal explosion) towards its ends is shown in Fig. 8b. The numbers of 16 autonomous electron-optic channels are indicated on the X-axis.

The distance between the adjacent channels corresponds to a 500 µm vertical shift along the surface of a cylindrical sample. Thus, in this experiment the temperature profile as a function of time was scanned every 1 ms for a sample surface section 8-mm long.

The switching off of the sample electrical heating is programmed, and a corresponding mark appears on the thermogram. In the experiments illustrated by Fig. 8a, b the heating was switched off as soon as the average temperature in the sample cross-section (channel 9) reached $T = 1250$ K. Data on kinetics of very fast high-temperature reactions occurring in the gasless combustion mode in the Ti + C (up to $T = 3300$ K), Ti + B (up to

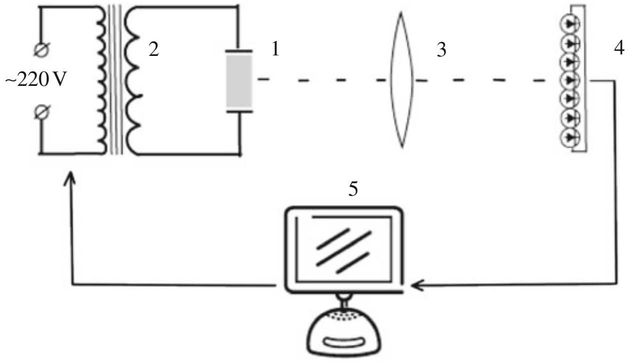


Fig. 6 Experimental setup for the study of kinetics of EM high-temperature reactions by the ETE method: *1* sample, *2* power transformer, *3* optical system, *4* Hamamatsu photodiode set, *5* PC

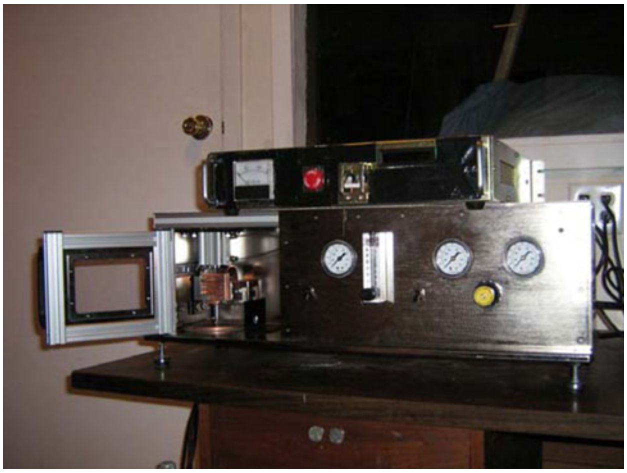
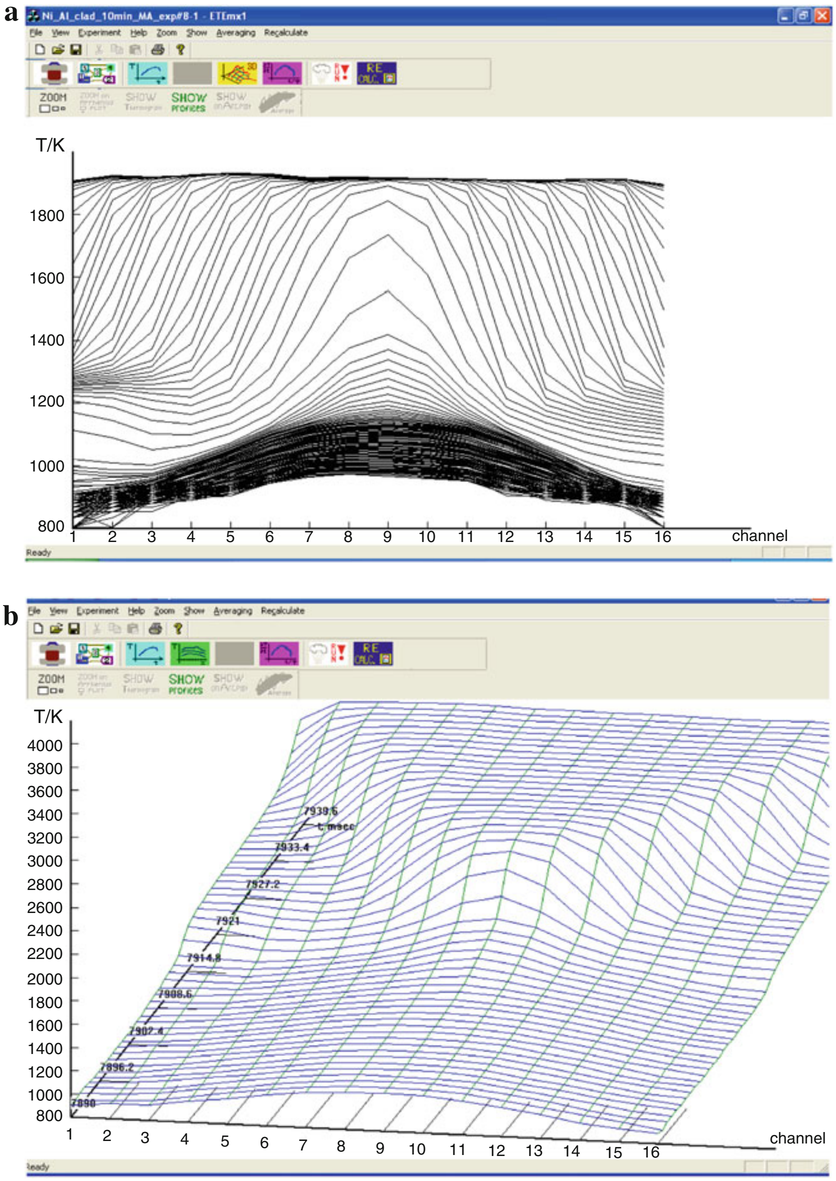


Fig. 7 Electron-optic unit of electro-thermoanalyzer ETA-100 (ALOFT, Berkeley, CA)

Fig. 8 ETE of a sample prepared from the powder mixture Ni–Ni-clad Al performed in ETA-100; distance between the channels 500 µm, time step 1 ms, the temperature of joule heating switch-off $T = 1250$ K; **a** 2D thermogram, **b** 3D thermogram [7]



$T = 3100$ K) and some other systems obtained by ETE are given in [3–7].

Data on kinetics of heat emission during high-temperature reaction in the Si + C system (up to $T = 2400$ K) are presented in Fig. 9 as an Arrhenius plot.

The dependences correspond to two systems consisting of Si with the particle size 5–16 µm and C with the particle size 63 µm (system 1) and 63–90 µm (system 2). The activation energy of the silicon carbide synthesis for both systems was found to be $E_a = 230$ kJ/mol. This value is close to $\Delta H = 245$ kJ/mol characterizing the exponential growth of the C solubility in liquid Si with increasing the temperature. Therefore, it was concluded that under these conditions the overall process rate is determined by the rate of C dissolution in Si melt. Due to extremely high reaction rate at the temperatures exceeding the Si melting point, ETE is the only method that can be used for determination of macrokinetic parameters of SiC synthesis in this temperature region. Data on kinetic constants for this reaction at high temperatures is of practical interest since this information can be used for development of ETE-based techniques for fast synthesis of this valuable material.

The quantitative data on kinetics of fast high-temperature reactions in condensed EM obtained by the ETE method provided new information about mechanism of gasless SHS. For example, the limiting stage in macrokinetics of reactions in the Ni + Al and Ti + C systems responsible for the rate of their SHS was found to be dissolution of refractory component particles in the liquid phase of the low-melting component (but not reaction diffusion).

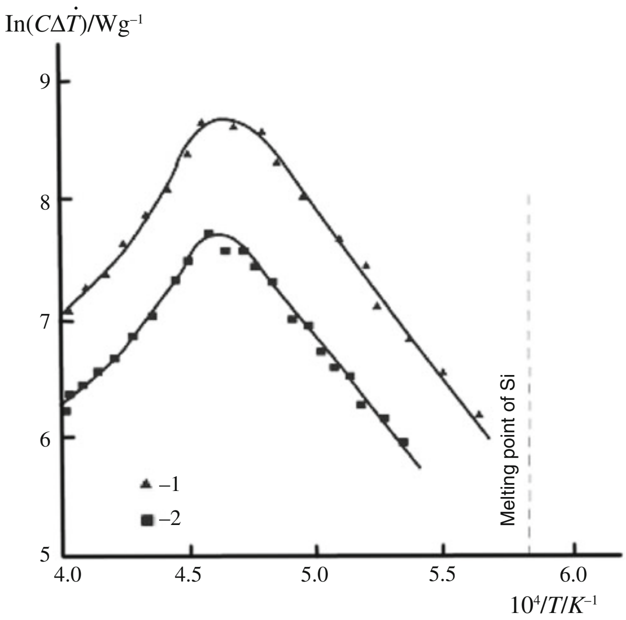


Fig. 9 Kinetics of heat emission at high-temperature interaction between Si melt and graphite powders with different particle size values; *1* system 1; *2* system 2

Kinetics of the Ni + Al system was studied by using samples pressed from powders as well as multilayer cylindrical samples tightly rolled from two-layer Ni/Al foil bands (Fig. 10a) [3]. At gasless combustion of the cylindrical samples the combustion rates were measures and combustion wave temperature profiles were recorded by using a standard experimental setup (Fig. 10b) [8].

The rate of gasless combustion wave propagation (SHS) was found to be determined not by thermally activated solid-phase diffusion but by dissolution of the refractory reagent particles in the second component melt weakly dependent on the temperature. In this case, the combustion rate can be expressed as

$$U = (\xi D)^{0.5} d^{-1}, \tag{7}$$

where ξ is the mixture thermal diffusivity, D, the diffusion coefficient in the melt, d, the particle size (thickness of the layers) of the refractory component. Data on gasless combustion of Ni + Al samples pressed from the powders as well as multilayer (laminated) foil samples and ultrathin layers deposited in vacuum are summarized in Fig. 11. Almost all points fall on a straight line with the slope giving the diffusion coefficient value. The obtained $D = 10^{-9}$ m^{2}s^{-1} clearly indicates that liquid-phase diffusion rate determines the system combustion rate. Similar studies for the Ti + C system [4, 15] brought out clearly that this conclusion is valid for the most systems characterized by melting of one of the components in the gasless combustion front.

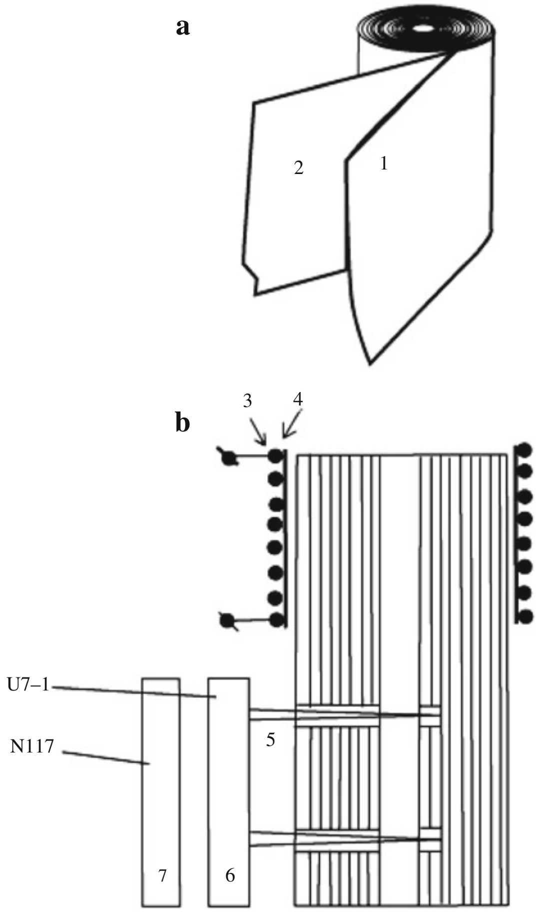


Fig. 10 Multilayer sample (**a**; *1* Al, *2* Ni) and the experimental setup scheme (**b**; *3* nichrome heater, *4* mica, *5* thermocouples, *6* electronic amplifier, *7* oscillograph

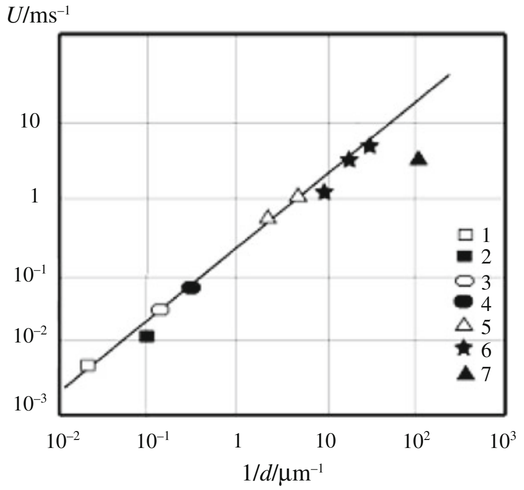


Fig. 11 The effects of the particle size and refractory components layer thickness on the combustion rate for powder and multilayer Ni + Al samples (*1* [8], *2* [9], *3* [10], *4* [11], *5* [12], *6* [13], *7* [14])

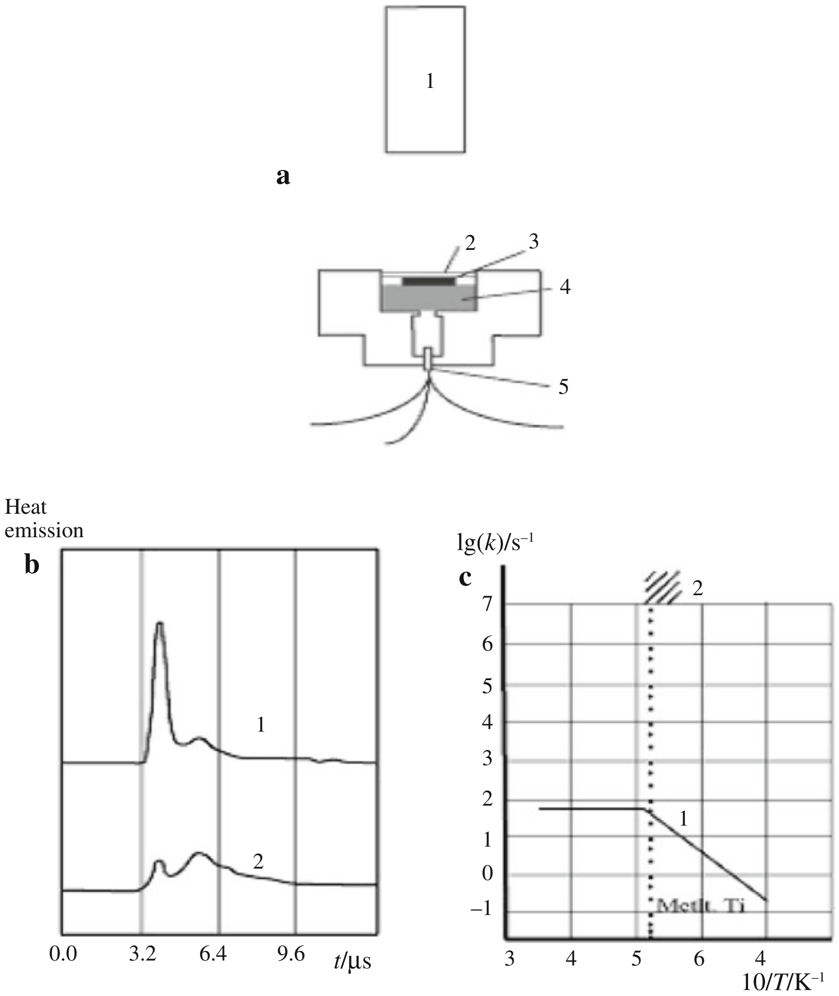


Fig. 12 The study of the fast reaction in the Ti + C system under conditions of high-speed impact; **a** experimental setup, **b** the sample heat emission as a function of time (*1* Ti/C black, *2* inert Ni/C black); **c** kinetics of the Ti + C reaction under static (1) and high-speed impact (2) conditions

This provides a simple explanation for paradoxically equal rates of gasless combustion in the systems characterized by tremendous difference in parameters of reaction (i.e., solid-phase) diffusion of the components.

Availability of information obtained by ETE allowed one to compare data on kinetics of fast high-temperature reaction in the Ti + C system occurring under static conditions (ETA-100) and under high-speed impact. Fast self-heating of the sample at high deformation rates was studied. The ignition process was experimentally studied by using a ballistic system of 14 mm in caliber [16, 17]. The sample temperature was measured by using an optical system. The experimental setup is shown in Fig. 12a. Duraluminum bullet 1 ($\approx$15 g) was brought up to speed of 1150–1300 m/s to hit then an ampoule containing sample 3 placed in between 5.45 mm thick single-crystal sapphire glass 4 and 1 mm duraluminum disk 2. The side surface of the sample was covered with a steel band. Radiation from the sample surface was received by three optical fibers 5 calibrated with a standard light source. Optical signals were transmitted through interfilters to photomultiplier tubes and then transformed into electrical signals and detected by digital oscilloscopes. The time resolution of the detection system determined by the clock rate of the oscilloscopes was 50 ns. The minimum reliably detected temperature was about 1700 K. The measurement accuracy at temperatures above 2300 K was not less than 2%. The samples (2 mm thick pressed pellets, the density of 2700 kg/m^3) were prepared from a stoichiometric mixture of Ti powder (for 70% of the particles are of size d_{Ti} = 20–100 μm) and C black (particle size < 1 μm). To evaluate the effect of the chemical reaction on the sample self-heating some of the experiments were carried out in the inert mixture of C black and Ni powder, Fig. 12b. The bullet rate was determined by the time of its flight between two contact pickups with an accuracy higher than 0.1%. The chemical reaction rate in this (dynamic) mode was found to be several orders of magnitude higher than that under static conditions, Fig. 12c.

Some obtained data allow one to assume that the reaction kinetics under high-speed impact is determined by absolutely different patterns and characterized by parameters which differ from those of reaction occurring under static conditions. For the Ti + C system the characteristic reaction time t_r is close to $t_r = d_{Ti}/u$, where u is the average rate of the mixture deformation by high-speed impact [18].

The results of the direct comparison of kinetic parameters for fast EM reactions under dynamic and static conditions allow one to assume a significant difference in the corresponding mechanisms. Under normal (i.e., static) conditions even at very fast heating characteristic for thermal explosion, ignition, and combustion, kinetics of solid EM decomposition is determined exceptionally by the temperature. On the contrary, at the sample significant deformation (especially under high-speed impact) macrokinetics of the overall process and kinetics of single stages of the chemical reaction are determined mainly by mechano-chemical phenomena. In this case, the temperature does not play the main role.

Despite a long-term interest in this area, the studies of kinetics of fast reactions in solid EM under conditions of high-speed impact have just begun.

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