Limit of inert functional admixtures depending on the dispersion in the combustion synthesis of nickel aluminides

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Abstract. The aim of this study is to report a new experimental possibility of determining the thermal stability limit in the combustion synthesis of nickel aluminides, when the reaction mixture is diluted with inert additives. The paper presents the results of measuring the temperature and velocity in the propagation of a combustion wave, obtained using a special television micro-pyrometer (1200 x 800 pixels) with high spatial (5.85 µm / pixel) and resolution time (1000 fps). High accuracy of temperature measurement was provided by using a new method of spectrally-bright pyrometry from 800 to 2000 ºC with an error of less than 1%. This paper shows the experimental procedure and statistical data on the hysteretic dependence of velocity on temperature. Experimental results are given of the measurement of the dependence of the velocity and temperature of the combustion wave in the Ni-Al system for different proportions of inert additives in the range from 2.5 to 30% with a change in the dispersion from 80 to 220 µm. It is shown that for a small size of an inert additive, the thermal stability of the combustion wave is lost faster, and the limit of the inert addition decreases from 22.5 to 17.5%.

1. Introduction

The main problem with the introduction of functional additives is the determination of the maximum permissible mass fraction of an inert, at which a loss of thermal stability of the combustion wave occurs. The theoretical possibility of loss of diffusion-thermal stability of laminar combustion was studied in [1]. The main result is that if the diffusion coefficient of fuel D is greater than the thermal diffusivity of mixture α, then for D>α the flame proves to be unstable.

The phenomenon of self-propagating high-temperature synthesis of materials (SHS), discovered in 1967 by Academician A.G. Merzhanov is the process of gasless combustion of a solid powder localized in a narrow reaction zone and propagating at the same speed throughout the initial volume of products [2]. Traditionally, SHS was considered as an autowave process in a quasihomogeneous medium with heat sources, described by a system of heat conduction and reaction diffusion equations [3]. Modern ideas about such a model contradict the experimental data on the discrete nature of SHS [4], but can be explained by the hysteresis dependence of the reaction rate on temperature [5]. For the first time with the development and application of new methods of high-speed micro-pyrometry [6-8], and then special electron-optical complexes with synchronous scanning of streak-cameras with nanosecond time resolution [9-11]. Particular attention is paid to recording the velocity and
temperature in local foci of discrete combustion, which makes it possible to distinguish between the quasihomogeneous and microheterogeneous regimes of such processes [12-15]. It should be noted that the nonlinear hysteresis effect of diffusion combustion, explaining the effect of "heat localization" and the appearance of metastable thermal structures of finite, so-called "fundamental" thickness, is now little studied and therefore rarely used in theoretical models of discrete combustion of SHS.

It was previously believed that the effect of heat localization is not feasible in solids due to a small change in the thermal conductivity and the linearity of the internal heat sources of the burning medium. As we showed earlier [15], in the SHS processes considered by us this restriction does not exist. The purpose of this study is to establish the experimental dependences of the local combustion wave velocity of SHS on the local adiabatic temperature of the discrete focus, depending on the amount and size of the inert additive in the form of a powder from the final product of synthesis [16].

2. Experimental procedure
To record the high-speed propagation of the SHS combustion wave, an optoelectronic micro-pyrometric complex was used [10], based on the nanosecond video resolution system "Video Sprint NanoGate" (Vidoscan, Russia) with the image analysis and image processing program Fiji-ImageJ (NIH, USA) [11]. At the combustion of reacting mixture, we observed a rapid propagating of high temperature along the tablet after its ignition. Figure 1 shows an example of recording successive frames of high-speed (1000 frames per second) shooting of the combustion wave.

Figure 1. Example of video recording of a combustion wave: serial frames of the solid state combustion synthesis of nickel aluminides (top) and the characteristic thermal structure of the SHS combustion wave (bottom).

Figure 1 (top) demonstrates serial frames of records of the solid state burning process. The basic stages of the process can be observed figure 1 (bottom). The warming up of the lowest cold layer is presented in zone 1. Here we do not observe any chemical reactions. In zone 2 the rapid ignition and exothermic combustion reaction as local thermal explosion take place. The effective thermal width $X_T$ varies from 0.15 to 1 mm. However the necessary structural and phase changes of the crystal lattice still do not have time to occur. Zone 3 presents the disintegration process of high-temperature site to the small ones due to internal heat outflow. New sites form a vast "heat cloud", where the temperature approaches the adiabatic value and promotes complete burn-out of the initial products. The next step is presented in zone 4, where the heat sink reduces the temperature of the final product and the diffusion slowly sets the required stoichiometric proportion.
The micro-pyrometry measurements are presented in figure 1 of the heat monitoring photo-matrix. As shown in figure 2b, thermal emission time in zone 2, the time of heat induction in zone 3 and the constant of the heat outflow time in zone 4 can be easily measured.

As a result of the statistical processing of all the chronograms - in our case, their number is equal to the number of columns of the photodetector array (N = 1200), we can obtain the temperature distribution density when registering the wave front, shown in figure 3.

With the calculation of the velocity distribution, the situation is slightly more complicated, because the speed is the result of an indirect measurement, and in our case it was decided to take the average velocity in the form of approximating the time derivatives, that is, the averaged slope of the chronogram in figure 2a. In this way, each value of the temperature was associated with a velocity value calculated using the Euler difference scheme. As a result of the analysis of all scanning lines, the distribution shown in figure 4 was obtained.

An analysis of the correlation dependence of velocity on temperature can be performed by constructing a phase space \{V_x, T\} mapping the points \([V_x (i), T (i)]\) for all \(i\) from 1 to \(N = 1200\), as shown in figure 5. Obviously this dependence has a nonlinear character and a pronounced hysteresis. This behavior of the wave, as is known [1-5], can be explained by a number of physical mechanisms that require additional study. The hysteresis form obtained experimentally clearly indicates a competition between thermal diffusivity (\(\alpha\)) and diffusion (D).

The experimental procedure consisted in determining the average velocity V and the temperature T of the combustion front for SHS synthesis of an equimolar mixture of nickel powders (PNC-UT3) and aluminum (PA-4) with an inert powder addition from the final Ni_1Al_1 synthesis products, whose mass...
fraction $\Delta$ varied from 0 to 30% in increments of 2.5%. The choice of the additive is due to the fact that the same heat capacity of the inert and the synthesis products makes it possible to estimate the efficiency of the internal heat sink when the dispersion of the additive varies under conditions of equal mass fractions of the powders.

Figure 5. Example of the experimental dependence of the combustion wave velocity of SHS on the temperature of the wave front, with a large mass fraction of the inert additive.

3. Results and Discussions

The results of measurements of the instantaneous velocity $V$ and the temperature $T$ in the combustion wave front were obtained by examining 37 samples, one of which was a standard (without an inert additive), and the rest consisted of three series of samples of 12 pieces each with an inert powder addition with particle sizes 220, 120 and less than 80 $\mu$m. The experimental diagrams of the macro-kinetic parameters of the state $V$ and $T$ in the combustion wave are shown in figures 6-8 for three series of samples. Three different combustion modes can be seen in the diagrams, the areas of existence of which are indicated by the figures 1, 2 and 3. Conditionally, we can name mode 1 - "quasi-stationary", mode 2 - "controlled", mode 3 - "restriction".

Figure 6. Macro-kinetic parameters of the combustion wave in the Ni-Al system with the particle size of the inert additive 220 $\mu$m
Figure 7. Macro-kinetic parameters of the combustion wave in the Ni-Al system with the particle size of the inert additive 120 µm.

Figure 8. Macro-kinetic parameters of the combustion wave in the Ni-Al system with the particle size of the inert additive < 80 µm.

The region of the diagram corresponding to mode 1 is well known in combustion theory [1-3] and arises under the condition of diffusion or hydrodynamic instability of the combustion wave ($D > \alpha$). The combustion rate in mode 1 is almost constant, even with a decrease in the reaction temperature due to the internal heat removal in the powder particles of the inert additive. Such a regime should be considered stationary and suitable for the synthesis of nickel aluminate with functional inert additives [16]. The decrease in the size of the inert additive particles results in the fusion of the "controlled" mode 2 and the "quasi-stationary" mode 1. In this case, the increase in the contact surface and heat transfer in the inert filler leads to a hysteresis dependence of the synthesis wave velocity on temperature, with the transition of combustion to the unstable regime 3. The authors showed that to recognize non-stationary phenomena that arise as a result of the loss of thermal stability of the wave and the rupture of the reaction front to several high-temperature foci, it is convenient to apply methods
of differential chronoscopy followed by Fourier or Trace-analysis [15]. This approach allows us to formulate the problem of analyzing the thermal diffusion instability of the SHS combustion wave in the classical formulation of the question of the spatial and temporal coherence of the wave front.

4. Conclusions
1. For solid state combustion synthesis in the Ni-Al system, the fact of stability of the chemical reaction during dilution to 15-17% is experimentally confirmed, which corresponds to the region of thermostimulated diffusion 1, where \( D > \alpha \).
2. For the first time, a "controlled combustion" mode is detected in the macro-kinetic parameters diagram, where the combustion wave velocity is directly proportional to temperature, and for a large dispersion the inertia depends linearly on its mass fraction, which corresponds to the condition \( D \approx \alpha \).
3. The limiting value of the inert additive (\( \Delta > 20-30\% \)) is limited by the region of thermal instability with the characteristic effect of temperature hysteresis due to an increase in the heat transfer of the combustion wave to the cold inert at \( D < \alpha \).

Acknowledgments
The reported study was funded by RFBR according to the research projects No. 18-08-01475, 18-47-860018, 18-41-220004 and No. 13-01-20/28 Leading Scientific School of Yugra State University.

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