Thermally coupled processes in a composite granular mixture (Ni + Al)–(Ti + C)

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Abstract. For the first time combustion of a thermally conjugated granulated mixture consisting of the mixture of Ni + Al and Ti + C granules, differing in burning velocity and temperature has been investigated experimentally in co-current flows of argon and nitrogen. It has been established that in the whole investigated gas flow rates the ignition of Ni + Al granules occurs in the combustion front. The high efficiency of Ti + C donor granules energy usage has been shown, since the time of heat exchange between the granules does not depend on the sample size, but is determined only by the characteristics of internal heat transfer. A strong increase in the burning rate of the composite mixture at low nitrogen flow rates has been explained via interaction of aluminum with nitrogen and effective reduction of heat loss of the donor. The possibility of isolating the target synthesis product was shown even if its melting point is below the adiabatic temperature of combustion of the composite mixture.

1. Introduction
The use of the thermal conjugation method for synthesis in layered powder mixtures, proposed in [1, 2], is complicated when the process is scaled. The problems are concerned, first of all, with ensuring the uniformity of ignition and heating of the charge and removal of impurity gases [3] and with the separation of the products of combustion of different layers. A promising way to solve the problem of scaling can be the use of granulated mixtures instead of powder layers [4–9]. The purpose of this work is to study the regularities and mechanisms of combustion of composite granular mixtures, where a fast burning Ti + C mixture is used as a donor, and a slowly burning Ni + Al mixture is used as an acceptor.

2. Experimental results
The original substances and their characteristics are given in table 1. The method of preparation of the granules, the experimental setup scheme and the experimental technique are described in detail in [4].

First, we determined the burning rates $U$ of each of the granular mixtures of Ti + C and Ni + Al separately and the composite mixture (Ni + Al) + (Ti + C) in the absence of a gas flow (see table 2). The adiabatic temperatures of combustion $T_{ad}$ are calculated using software THERMO (http://www.ism.ac.ru/thermo/). The experiments have shown that the maximum content of the Ti + C donor mixture, which ensures synthesis in the steady-burning mode, was 46 wt %. The data of table 2 show the average burning velocity of the composite charge (12.5 mm/s) to be much higher than that of the acceptor mixture Ni + Al. Therefore, due to the low burning rate of the Ni + Al granules, we assumed they behave as inert in the reaction front. To test this assumption, we replaced them in charge with inert Al$_2$O$_3$ granules of the same size and weight ratio: 54% Al$_2$O$_3$ and 46% (Ti + C). Our experiments have...
shown that such a mixture is incapable of burning, which means that in the studied mixture 54% (Ni + Al)/46% (Ti + C) the ignition of Ni + Al granules occurs in the combustion front.

**Table 1.** Materials and reagents

| Substance   | Grade     | Particle size to 50 wt %, μm | Particle size to 90 wt %, μm |
|-------------|-----------|-------------------------------|------------------------------|
| Titanium    | PTM-1     | < 105                         | < 169                        |
| Soot        | P-803     | < 2.5                         | < 4                          |
| Aluminum    | АСД-4     | < 11                          | < 16                         |
| Nickel      | ПНЭ-1     | < 43                          | < 51                         |
| Argon       | High purity (99.987%) |                        |                              |
| Nitrogen    | High purity (99.987%) |                            |                              |
| Ethanol     | 95%       |                               |                              |
| Polyvinylbutiral | SD-4    |                               |                              |

**Table 2.** Experimental $U$ and theoretical $U_f$ burning velocities of the granular mixtures

|                  | Ni + Al $T_{ad} = 1912$ K | Ti + C $T_{ad} = 3290$ K | 54% (Ni + Al)/46% (Ti + C) $T_{ad} = 2518$ K |
|------------------|---------------------------|---------------------------|---------------------------------------------|
| Q, l/h           | $U$, mm/s | $U_f$, mm/s | Q, l/h | $U$, mm/s | $U_f$, mm/s | Q, l/h | $U$, mm/s | $U_f$, mm/s |
| 0                | 3         | 3           | 0      | 22        | 22         | 0      | 12.5      | 12.5        |
| 630 (argon)      | 4.5       | 3.8         | 750 (argon) | 25       | 24         | 720 (argon) | 16.8      | 15.7        |
| 220 (nitrogen)   | 3         | 3.3         | 200 (nitrogen) | 23       | 22.8      | 200 (nitrogen) | 15.5      | 13          |
| 700 (nitrogen)   | 6.2       | 4.2         | 650 (nitrogen) | 36       | 24.5      | 720 (nitrogen) | 24        | 14.4        |
| 1000 (nitrogen)  | 8         | 4.7         | 1050 (nitrogen) | 45       | 26.1      | 1100 (nitrogen) | 28.5      | 15.43       |

The validity of this conclusion was tested in experiments on the combustion of a granulated mixture of Ti + C, divided in the center of the filling with a layer of Ni + Al granules of a thickness of 2-3 particles (figure 1).

When a layer of Ni + Al granules was reached, the combustion front continued to spread without delay, but its speed and luminosity sharply decreased. After the end of burning, the luminosity of the entire charge became the same after 4-5 s, which is significantly less than the cooling time of the sample. Unlike this experiment, in a uniformly mixed granular mixture, the time taken to equalize the temperature of the donor and acceptor mixture granules should be several times less and, most importantly, this time does not depend on the sample size, but is determined only by the characteristics of internal heat transfer. This indicates the prospects of using a granulated mixture during the combustion of thermally conjugated systems.
Figure 1. The appearance of the granular layered system: (a) the original sample, (b) immediately after the passage of the combustion front, (c) 5 s after the passage of the combustion front.

It is important to note that the combustion products of the compound mixture of 54% (Ni + Al)/46% (Ti + C) did not sinter and the sample was easily divided into individual granules by color manually (figure 2). Perhaps this is the result of the fact that titanium carbide is not wetted by aluminum nickelide.

Next, the combustion parameters of each of the granular mixtures of Ti + C and Ni + Al were determined separately in a co-current stream of argon and nitrogen. The results of measuring the front velocity in a stream of nitrogen are shown in figure 3 (curves 1, 4).

3. Discussion
In accordance with the theory of filtration combustion, the dependence of the burning velocity $U_t$ on the mass flow rate of gas is linear [10]:

$$U_t = U_0 + c_g G_m (c_s \rho_s)$$  \hspace{1cm} (1)

where $U_0$ is the burning velocity in the absence of gas flow, $G_m = \rho_g Q/s$ is the mass flow rate of inflowing gas at volumetric flow rate $Q$ through the cross section of the sample ($s = 2$ cm$^2$), $c_g$ is the specific gas heat capacity, $c_s$ is the specific heat capacity of porous material, $\rho_g$ is the gas density, $\rho_s$ is the bulk density.
mixture density. When calculating, for Ti + C mixture the density was assumed to be 0.8 g/cm³, specific heat capacity is 560 J/(kg K), and for Ni + Al mixture the density is 1.7 g/cm³, specific heat capacity is 590 J/(kg K). As the gas flow increases, the burning velocity growth in the nitrogen flow for the Ti + C mixture is much higher than in the argon flow, and significantly more than theoretical estimates give. This indicates the realization of the convective mode, in which the flow of active gas ignites the granules from the surface and plays a leading role in the mechanism of the combustion front propagation [11]. For the Ni + Al mixture, the calculated increase in the burning velocities agrees well with the experimental data in a flow of argon and nitrogen, which indicates the realization of the conductive mode (see table 2).

When a mixed mixture of 54% (Ni + Al)/46% (Ti + C) was burned in an argon flow, the burning velocity growth was small even at a flow rate of 600–700 l/h in full accordance with the estimates of combustion filtration theory (see table 2). The sample obtained by burning in argon retained the dimensions of the original sample and was fragile. When crushed, it was scattered into individual granules. The latter fact is unusual, since the calculated combustion temperature of the composite mixture ($T_{ad} = 2518$ K) is significantly higher than the melting point of NiAl ($T_{ad} = 1912$ K), while it was previously shown that a large amount of liquid phase causes the sample shrinking when burning the granulated mixture [4, 11].

The results of experiments on the combustion of a granulated mixture of 54% (Ni + Al)/46% (Ti + C) in a co-current flow of nitrogen are shown in figure 3, curve 2. When analyzing the dependence of the burning velocity on the gas flow rate (figure 3, curve 2), a strong increase in the burning velocity at low nitrogen rates (220 l/h) attracts attention. Such an increase in the burning velocity was observed neither for a mixture of Ti + C or for Ni + Al (see figure 4). This result can be explained as follows: at the contact points of the Ni + Al acceptor granules with hot Ti + C donor granules, the aluminum heats up quickly, melts (melting point 933 K) and begins to interact with nitrogen with the release of a large amount of heat. Since the adiabatic temperature of the interaction of nitrogen with aluminum, calculated on the formation of aluminum nitride of AlN composition (2570 K), is significantly higher than that of nickel with aluminum (1912 K), when burning in a stream of nitrogen, the temperature at the contact points of granules of different composition becomes higher, then in the absence of nitrogen. This development of the combustion process leads to a decrease in heat loss from Ti + C granules in the reaction front, an increase in the combustion temperature and, as a consequence, an increase in the burning velocity both by the conductive and convective mechanisms.

In general, the dependence of the burning velocity of the composite mixture on the nitrogen flow rate in the studied range $< 1100$ l/h can be approximated by a linear function (figure 3, curve 2), which is steeper than the calculated dependence on the theory of filtration combustion (figure 3, curve 3). At a high burning velocity corresponding to high gas flow rates, the heat exchange between Ti + C and Ni + Al granules in the combustion wave front could be assumed to have no time to occur, and therefore Ni + Al granules ignite and burn behind the visible combustion front. However, when analyzing the video recording of the combustion process of the granular mixture (Ni + Al)/(Ti + C), no two-front structure was detected, which indicates ignition of the acceptor Ni + Al granules in the combustion front throughout the entire nitrogen flow rate range.

Note that the combustion products of the mixture of 54% (Ni + Al)/46% (Ti + C) in a stream of nitrogen did not sinter and the sample was easily divided into individual granules by hand, as in the absence of a gas flow. This result is a consequence of the convective mode of combustion, when a layer of refractory titanium nitride is formed on the surface of Ti + C granules, which prevents sintering of the granules [6]. Conducted X-ray phase analysis (DRON-3M, Russia) showed that the products consist of phases of TiC and NiAl.

Thus, the experiments confirmed the assumption of the strong influence of the co-current nitrogen flow on the combustion process of the thermally conjugated granular system of 54% (Ni + Al)/46% (Ti + C). The gas flow is a regulating parameter, easily varying in magnitude, duration of exposure and chemical composition. The advantages of carrying out thermally conjugated processes using granulated mixtures are preserved in the co-current gas flow: the heat exchange between donor and acceptor...
mixtures does not depend on the sample size, but is determined only by the size of the granules, the combustion products consist of separate, easily detachable granules.

4. Conclusions

The regularities of the combustion in a co-current gas flow for the thermally conjugated mixture consisting of granules of different composition, taken in the ratio of 54% (Ni + Al) and 46% (Ti + C), are studied.

It is experimentally proven that the ignition of Ni + Al acceptor granules occurs in the combustion front over the entire range of gas flow rate used.

It is shown that in the absence of a gas flow, the time taken to equalize the temperatures of the donor and acceptor mixtures is substantially less than the cooling time of the entire sample, which allows scaling of the process optimized under laboratory conditions, while retaining the characteristics of the target synthesis product.

A high burning velocity growth of the thermally coupled granulated mixture was detected even at low nitrogen rates, exceeding the burning velocity growth of undiluted Ti + C and Ni + Al mixtures separately at the same flow rates, which is explained by the interaction of aluminum with nitrogen and effective reduction of donor heat loss.

Using the 54% (Ni + Al)/46% (Ti + C) mixture as an example, it is shown that the application of granulated mixtures for conducting conjugated thermal reactions makes it possible to obtain combustion products in the form of an easily destructible sample, even if the melting point of the interaction product of the acceptor mixture is less than the adiabatic temperature of combustion. The possibility of isolating the target product from the burnt sample was demonstrated.

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