Shock-wave synthesis in powder mixtures

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Abstract. The work is aimed at studying the features of initiation, reaction, gas generation and final phase formation in the energy condensed “metal-teflon” systems with two types of initiation: local heat pulse and shock-wave loading. Approximate thermodynamic calculations were carried out using THERMO program, which took into account three mixtures and samples of them: (Ni+Al+Teflon), (Ti+B+Teflon), (Hf+B+Teflon). The adiabatic combustion temperatures of mixtures, the composition and the amount of condensed products, and the volume of gaseous products are calculated. Gas formation during combustion of mixtures was measured in a spherical ampoule equipped with temperature and pressure sensors. Shock-wave loading of the samples was carried out in a multi-cell matrix by throwing a flat impactor. The acceleration of the impactor was carried out by the detonation products of the explosive. The design of the recovery fixture provided the same loading conditions in all cells. The investigated compositions are capable of an intense exothermic reaction, both at traditional ignition of a heated spiral, and at shock-wave action.

1. Introduction
The development of new energy condensed systems (reactive materials), based on mixtures of metals and their oxides with inorganic and polymeric oxidants, presents a topical direction of applied research [1, 2].

As a rule, it is necessary to bring a thermal impulse to the local volume of substance on the surface of the sample and to reach the melting point of one of the components to initiate combustion in powder mixtures. The initiating thermal impulse should be powerful enough to heat the charge mixture layer that is comparable in thickness to the width of Michelson zone, which is 0.3 to 1 mm for most SHS compositions [3]. In shock inelastic compression an adiabatic heating of the medium occurs (since heat does not have time to leave the compressible body). This heating, as a rule, is not enough to reach the melting point of the reagents. As a rule, sufficiently high pressures are required to pass the synthesis, or initiation occurs in local volumes [2]. During impact compression, reactive mixtures can undergo exothermic reactions with significant energy release, which in turn can lead to a self-sustaining spread of the chemical reaction in the mixture. If the reaction rate is sufficiently high, conditions can be created for solid-phase or gas-free detonation [4].

The work is aimed at studying the features of initiation, reaction, gas generation and final phase formation in the energy condensed “metal-fluoroplastic” systems at combustion both by a local thermal pulse and by shock wave loading.
2. Materials and experimental methods

In preparation for the experiments the approximate thermodynamic calculations were carried out using THERMO program [5], which took into account three different mixtures and samples from them. The calculation of the equilibrium characteristics is based on the minimizing of the system thermodynamic potential, which accounts for the contributions of the thermodynamic potentials for all the components present in the system, providing their concentrations. The algorithm for minimizing the thermodynamic potential is based on the method of gradient descent [5].

The composition of the mixtures is given in percent by weight: (68% Ni+28% Al+10% Teflon), (70% Ti+20% B+10% Teflon), (75% Hf+15% B+10% Teflon). The adiabatic combustion temperatures of mixtures, the composition and amount of condensed products, and the volume of gaseous products are calculated.

For the preparation of mixtures of metals with Teflon, the following components were used: Teflon powder F-4NTD-2 (particle size \( d < 5 \mu m \)), Al – ASD-1 with \( d < 10 \mu m \), Ti – PTM with \( d < 40 \mu m \), Hf – GF-N with \( d < 5 \mu m \), Ni – PNE-1 with \( d < 70 \mu m \), and amorphous black boron V99-A. The powders were mixed for one hour in “Turbula” type mixer to make the samples. For the preparation of Ni-Al-Teflon mixture, a mixture of Ni and Al powders was mechanically pre-activated in a planetary ball mill AGO-2 for 5 minutes. The portable rotational speed of the drum was 2220 rpm at a mixing ratio of the mass of the mixture to the mass of the balls of 1:20. From the obtained mixtures the tablets of diameter 5 mm and mass of about 0.5 g and length of 7-10 mm were pressed to determine the burning rate and gas evolution. The extrusion pressure of the samples ranged from 20 to 130 MPa.

Determining the gas evolution, a spherical glass bulb with a volume \( V = 620 \text{ cm}^3 \) was used (figure 1a). The bulb is equipped with an initiating tungsten spiral, thermocouples for determining the burning time and a 24PC gas pressure sensor with a time resolution of 1 ms and a range of measured pressures of 13÷200 kPa. The time of the beginning and the end of the sample combustion was determined from the indications of thermocouples \( T_1 \) and \( T_2 \). In the experiments the bulb was pumped out and filled with argon. The initial argon pressure in the bulb was about 75-80 kPa.

For solving the problem of initiating the reactive materials combustion by shock-wave impact, a scheme was used with a flat storage multi-cell ampoule (figure 1b). In the steel matrix the blind holes (cells) with a diameter of 10 mm are made equidistant from the center to place initial samples in the form of pre-compressed tablets. Shock-wave loading was carried out by throwing a steel flyer on the
surface of the matrix and samples by the explosive charging. The initiation of detonation was preceded by an electric detonator located in the center along the assembly axis. Thus, the design of the recovery fixture provided the same loading conditions in all cells.

After the experiments on combustion and shock wave initiation the reaction products were crushed and subjected to X-ray phase analysis. X-ray diffraction was recorded on a DRON-3M diffractometer (radiation CuKα) with step of 0.02° angle and 1 second exposure time. X-ray phase analysis (XPA) was carried out in the program “Crystallographica Search-Match”. The quantitative analysis was carried out by the method of corundum numbers.

3. Results and discussion

All calculated and experimental results are summarized in table 1.

Table 1 shows the used compositions calculated according to “Thermo” program, the adiabatic combustion temperature of $T_{ad}$ mixtures, the calculated composition of the condensed phases, the ratio of the mass of liquid products to solid $L/S$, the ratio of the liquid products to the gaseous $L/G$, the content of the products after the explosive initiation, the combustion products content, the content of gaseous products, the calculated volume of released gases, reduced to normal conditions and the volume of released gases $V_{Gnc}$, measured in experiments $V_{Gr}$.

| № Mixture  | $T_{ad}$ (K) | The condensed products (wt. %) | $L/S$ (calc.) | $L/G$ (calc.) | Products expl. (exp.) | Products comb. (exp.) | Gas (wt.%) | $V_{Gnc}$ (calc.) | $V_{Gr}$ (exp.) |
|------------|--------------|-------------------------------|--------------|---------------|-----------------------|-----------------------|------------|----------------|----------------|
| 1 Ni–Al–Teflon | 2018 72.5 NiAl (L) 2.4 C(S) 2.4 Ni(L) 12 | NiAl, Ni$_2$Al$_3$, AlF$_3$ | 35.2 | 6.45 | NiAl, Ni$_3$Al, AlF$_3$ | 13.1 | 52$^a$ | 31-39 |
| 2 Ti-B-Teflon | 3192 TiB$_2$(L) 24 TiB(S) 18 TiB$_2$(S) 29 TiC(S) 12 | TiC, TiB$_2$ | 0.41 | 1.41 | TiC, TiB$_2$, TiB | 17 | 56 | 62 |
| 3 Hf-B-Teflon | 2727 HfB$_2$(S) 84 HfB$_2$(S) 2 B(L) 2.7 C(S) 2.4 | HfB$_2$, HfC | 0.03 | 0.25 | HfB$_2$, HfC | 10.9 | 76 | 56$^b$ |

$^a$ Excluding condensation AlF$_3$.

$^b$ The volume of released gases obtained by burning the compressed samples.

The actual contents of the products obtained in the experiments on combustion and shock-wave initiation in Table 1 differ from the calculated ones. As can be seen from Table 1, a chemical reaction was successfully initiated in all compositions exposed to shock-wave processing by throwing a steel flyer. Differences in the composition of products can be associated with a different mechanism (stage) of the reaction under different conditions and a high rate of hardening of products formed during the explosive loading of samples. In addition, the calculation gives the composition of the products at an adiabatic combustion temperature at which, for example, aluminum fluoride is in a gaseous state. Upon cooling AlF$_3$ condenses and is found in reaction products. As the calculation by program gives the volume of gases $V_t$ at $T_{ad}$, it is recalculated according to the equation (1).
\[ V_{Gnc} = \frac{295 V_g}{T_{ad}} \]  

\( V_{Gnc} \) is the volume and the average value of the extracted gas volume reduced to room temperature. Here, the measured values of the volumes of \( V_{Gr} \) separated gases are averaged from the results of 10–13 experiments.

After the sample is burned, the gassing is stopped and the temperature is cooled to room temperature, the pressure in the reactor drops to \( P_f \) final value. The volume of the separated gas \( V_{Gr} \), reduced to atmospheric pressure of \( P_{atm} \) and room temperature \( T_0 \), is calculated by the equation (2).

\[ V_{Gr} = \frac{V(p_f-p_0)}{P_{atm}} \]  

\( P_{atm} = 100 \) kPa – atmospheric pressure during the experiments.

At the same concentration of Teflon (10 wt.%) in the studied mixtures the average volume of released gases in Ni-Al-Teflon system is nearly 2 times lower than in Ti-B-Teflon and Hf-B-Teflon systems. This is due to the fact that the resulting aluminum trifluoride (its share in the combustion products is about 7 wt%) has a sublimation temperature of 1272°C (\( T_{melt} \)=1290°C) and, accordingly, rapidly condenses upon cooling. In addition, titanium and hafnium, which are part of other mixtures, contain significant concentrations of hydrogen released during combustion.

A typical picture of the change in pressure during the combustion of the studied systems is shown in figure 2. For systems of Ni-Al-Teflon (figure 2a) and Hf-B-Teflon (figure 2c) the gas evolution continues for some time after the burning ends. Therefore, the combustion time \( t_c \) is less than the gas release time \( t_{gr} \). In Ti-B-Teflon system the gas release end time coincides with the burning end time (figure 2b).

**Figure 2.** Change in pressure and thermocouple readings during combustion of systems: a – Ni-Al-Teflon; b – Ti-B-Teflon; c – Hf-B-Teflon.
The samples from Ni-Al-Teflon mixture during combustion are completely destroyed, despite the fact that the gas release is minimal from the studied systems, and the calculated concentration of products in the molten state is maximal. The samples from Ti-B-Teflon mixture retain a shape close to the original and their surface is melted. At shock-wave initiation all samples lose shape, and most of the reaction products are sprayed.

For Hf-B-Teflon and Ti-B-Teflon compositions the combustion rate is directly proportional to the density, for Ni-Al-Teflon the velocity decreases monotonically with the compaction of the initial samples (figure 3).

4. Conclusion
Based on the experiments and studies of the samples produced by combustion and shock-wave-loading, the following conclusions can be drawn:

1. The studied reactive materials have a sufficiently high adiabatic combustion temperature: 2018 K, 3192 K, and 2727 K for Ni-Al-Teflon, Ti-B-Teflon, and Hf-B-Teflon systems, respectively.
2. For Ni-Al-Teflon and Hf-B-Teflon systems the gas evolution continues for some time after the burning ends. In Ti-B-Teflon system the end of gas release coincides with the end of combustion time.
3. The dependence of the combustion rate of samples on their density is not universal. For Hf-B-Teflon and Ti-B-Teflon compositions the combustion rate is directly proportional to the density, for Ni-Al-Teflon the velocity decreases monotonically with the compaction of the initial samples.
4. The studied mixtures are capable of an intense exothermic reaction both with the traditional ignition of heated spiral and with shock-wave action. Thus, they are promising for use in engineering as reactive materials.

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