Shock initiation of exothermic reactions in mechanically activated mixtures

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Abstract. Experiments on initiation of chemical transformation in mechanically activated thermit mixtures are described. The initiation was produced by shock loading of compact porous thermit specimens in a semi-enclosed volume by explosion of an HE charge. Energy losses for shock wave passing through the thermit specimens and expansion rate of the field of chemical transformations in a free space were estimated.

1. Introduction
Recently, considerable attention has been paid to studies of mixtures of solid oxidizers and combustibles. The interest is caused by the prospect of using pulsed sources of chemical energy. In this work, we conducted research to select promising compositions capable of fast energy release at times of 100–1000 \(\mu\text{s}\).

The initiation of any chemical transformations (CTs) occurs due to the energy deposition into a reactive mixture. The form (kind) of energy can be arbitrary because the initiation of CTs is based on a thermal mechanism. Therefore, of importance for energy deposition is the amount of energy and the efficiency of its conversion into heat. In this work, CTs were initiated by the high energy density shock-wave method. In addition, we studied the dynamics of exothermic reactions.

2. Materials
We studied mixtures reacting with high exothermic effect (thermit mixtures of Al+metal oxide, metals+polytetrafluoroethylene and Ni+Al). As initial metals and oxidizers we used commercial-grade metal powders (having a particle size of 20–100 \(\mu\text{m}\)) and nanosized MoO\(_3\) powder. Mechanical activation and mixing were carried out in a vibration mill by a special technique described in [1]. The specimens were made in the form of pellets having a diameter of 8 mm.

Mixtures, powders, activation times, densities \(\rho\) and porosities \(\varepsilon\) are given in table 1. Also given are the calculated values of the maximum reaction heat \(E_{\text{max}}\) without considering possible secondary reactions.
| No. | Components | Comp., wt. % | $t_o$, min | $\rho$, g/cm$^3$ | $\varepsilon$, % | $E_{\text{max}}$, J/g |
|-----|------------|--------------|------------|----------------|----------------|------------------|
| 1   | Al-PP-2    | Al-PNK-1     | 31.5       | 7              | 3.26           | 17.5             | 1380             |
| 2   | Al-PAP-2   | Ni-PNK-1     | 31.5       | 12             | 2.84           | 11.4             | 4590             |
|     | MoO$_3$-nano|              | 65         |                |                |                  |                  |
|     |            | (C$_2$F$_4$)$_n$-F4 | 3.5     |                |                |                  |                  |
| 3   | Hf-GFM-1   |              | 80         | 15             | 6.02           | 8.5              | 2240             |
|     | (C$_2$F$_4$)$_n$-F4 |          |            |                |                |                  |                  |
| 4   | Zr-PCtZ1   |              | 50         | 15             | 3.75           | 7                | 5500             |
|     | (C$_2$F$_4$)$_n$-F4 |          |            |                |                |                  |                  |
| 5   | Al-PP-2    |              | 35         | 12             | 2.72           | 19.8             | 4175             |
|     | MoO$_3$-nano|              | 65         |                |                |                  |                  |
| 6   | Al-PP-2l   | CuO$_3$-cc   | 19.7       | 15             | 3.83           | 22               | 4000             |
|     | CuO$_3$-cc |              | 80.3       |                |                |                  |                  |
| 7   | Al-PP-2l   | CuO$_3$-cc   | 25         | 15             | 3.97           | 21.5             | 2750             |
|     | CuO$_3$-cc |              | 80.3       |                |                |                  |                  |
| 8   | Al-PP-2l   | Bi$_2$O$_3$-cc| 15        | 15             | 5.07           | 23.5             | 1990             |
|     | Bi$_2$O$_3$-cc |            |            |                |                |                  |                  |
| 9   | AlCuO (Mix 7) |              | 50         | 15             | 4.99           | 8.8              | 3120             |
|     | HfC$_2$F$_4$ (Mix 4) |          |            |                |                |                  |                  |
| 10  | AlCuO (Mix 7) |              | 30         | 15             | 5.34           | 6.1              | 2770             |
|     | HfC$_2$F$_4$ (Mix 4) |          |            |                |                |                  |                  |

3. The experimental assembly and the scheme of shock-wave loading
The shock loading of specimen 1 (figure 1a) was carried out in a steel cylindrical sheath 4 through a nonreactive spacer 2 by detonation products of the HE charge 3. The nonreactive spacer, made from Rose’s alloy, protected the specimens from the influence of hot detonation products. The mass ratio of the charge, the spacer and the specimen was 1:1:1. The sheath was placed on a steel barrier 5 resting on a sand base 7 on restrictive support rings 6. As a result of the HE charge detonation, assembly elements are affected by a frontal shock wave. Deformation of the steel barrier occurs due to the kinetic energy of assembly elements. The deformation of barrier (figure 1b) looks like a conical deflection 2 within the internal part of the restrictive ring and as a pressed spherical segment 1 in the center.

4. Evaluation of the energy absorption in specimens
The evaluation of energy losses is based on the measurement of plastic deformation of the barrier. The reason for choosing this way was the assumption that the sums of energy losses for different specimens, including the losses in the nonreactive spacer, in the specimen and in the barrier, are equal:

\[
(W_s + W_t + A_{\text{def}})_i = \text{const},
\]
Figure 1. (a) Experimental assembly: 1—specimen, 2—nonreactive spacer, 3—HE charge, 4—steel sheath, 5—steel barrier, 6—restrictive ring, 7—sand base. (b) The diametrical section of the steel barrier in combination with the schematic layout of experimental assembly: 1—the area of spherical deformation, 2—the area of conical deflection.

where $W_s$ are the losses in the inert spacer, $W_t$ are the losses in the specimen (absorbed energy), and $A_{def}$ are the losses in the steel barrier. The deformation energy was found based on the empirical ratio for steel [2]:

$$A_{def} = 471\pi R_0^2 H_0 (1.33(h/R_0)^2)^{1.23}, \quad (2)$$

where $R_0$ is the the radius of the thermit specimen, $H_0$ is the thickness of the steel barrier, and $h$ is the depth of the spherical segment. These data were used to estimate the energy losses in the specimens (see table 2).

5. Estimation of pressure at the thermit specimen–steel barrier interface

The pressure at materials interfaces is usually estimated by the grapho-analytical method with construction of Hugoniots in pressure–particle velocity coordinates. Such data were not available for thermit mixtures. Therefore, a special series of experiments was carried out, in which dense specimens from a nonreactive material with known Hugoniots were used instead of thermit specimens with the same weight (sand, paraffin, aluminum, titanium, copper and steel). As a spacer material (2, figure 1a) we used Sn.

The results of finding shock wave parameters at the interface between the steel barrier and inert specimens from paraffin, Al, Cu, Fe, and Ti are presented in table 3 and in figure 2a in pressure–particle velocity coordinates ($P$–$U$). The Hugoniots of the nonreactive spacer (Sn) and the steel barrier are denoted by numbers 1 and 2, respectively. Dashed line 3 shows the pressure level in the spacer (Sn) upon interaction with the detonation wave. Dotted line 4 represents the unloading isentrope of detonation products.

Based on these data one can establish an empirical correlation between the steel barrier deformation and the shock loading parameters. It is necessary to combine data of experimental deformation $C_i$ and pressure on the steel barrier $P_{def}$ (red points in figure 2b). As a result, such an empirical correlation can be described by the dependence:

$$P_{def} = 28.89 - 12.57 \ln(C/D_0), \quad (3)$$
Table 2. The results of data processing for measurements of steel barrier deformation.

| No. | Mixtures                  | Stress energy absorbed (sphere) $A_{def}$, J | Energy absorbed $W_t$, J | Density absorbed energy $\omega_t$, J/cm$^3$ | Specific energy losses $\eta$, %/mm | Deform. pressure $P$, GPa |
|-----|---------------------------|---------------------------------------------|--------------------------|---------------------------------------------|---------------------------------|-------------------------|
| 1   | Al+Ni (table 1 row 1)    | 2.7                                         | 13.4                     | 46.6                                        | 13.1                            | 24.7                    |
| 2   | Al+MoO$_3$+(C$_2$F$_4$)$_n$ (table 1 row 2) | 1.7                                         | 14.3                     | 44.2                                        | 9.1                             | 22.0                    |
| 3   | Hf+(C$_2$F$_4$)$_n$ (table 1 row 3) | 2.0                                         | 14.1                     | 85.1                                        | 25.1                            | 22.7                    |
| 4   | Zr+(C$_2$F$_4$)$_n$ (table 1 row 4) | 5.0                                         | 11.0                     | 31.4                                        | 14.7                            | 26.5                    |
| 5   | Al+MoO$_3$ (table 1 row 5) | 2.6                                         | 13.5                     | 50.8                                        | 11.8                            | 24.0                    |
| 6   | Al+CuO+HfC$_2$F$_4$ (table 1 row 9) | 12.4                                        | 10.7                     | 53.4                                        | 15.7                            | 25.3                    |
| 7   | Al+CuO+HfC$_2$F$_4$ (table 1 row 10) | 1.7                                         | 11.4                     | 61.0                                        | 19.8                            | 26.5                    |

Table 3. The results of data processing for measurements of steel barrier deformation (for dense nonreactive spacers).

| No. | Spacer material | Density $\rho_0$, g/cm$^3$ | Stress energy absorbed $A_{def}$, J | Deform. pressure $P$, GPa | Energy absorbed $W_t$, J | Density of absorbed energy $\omega_t$, J/cm$^3$ | Specific energy losses $\eta$, %/mm |
|-----|-----------------|-----------------------------|------------------------------------|--------------------------|--------------------------|---------------------------------|---------------------------------|
| 1   | Paraffin        | 0.91                        | 0.3                                | 14.3                     | 12.8                     | 13.9                            | 4.4                             |
| 2   | Aluminum        | 2.71                        | 1.7                                | 24.0                     | 11.5                     | 31.1                            | 11.4                            |
| 3   | Titanium        | 4.32                        | 3.0                                | 25.7                     | 10.1                     | 43.8                            | 14.8                            |
| 4   | Copper          | 8.9                         | 2.9                                | 26.0                     | 10.2                     | 90.9                            | 23.7                            |
| 5   | Steel           | 7.85                        | 2.8                                | 26.5                     | 10.3                     | 80.9                            | 24.5                            |
| 6   | Sand            | 1.9                         | 3.2                                | 25.1                     | 10.0                     | 18.9                            | 7.1                             |

where $P_{def}$ is the pressure, $D_0$ is the spacer diameter, and $C$ is the arch of the spherical segment. The correlation coefficient in the approximation was equal to 0.96.

The pressure at the thermit specimen–steel barrier interface was determined using the experimental values of deformation and equation (3). The same values of pressure can be obtained through graphic expression of equation (3), figure 3. Pressure values are given in the last column of table 2. In figure 3, these values (dark markers) are combined with the Hugoniot of the steel barrier. The red dashed line represents the pressure level in the nonreactive spacer.
during interaction with the detonation wave. One can see that the pressure at the specimen outlet is higher than at the input. The difference is up to 4 GPa. At the same time, the breakdown at the interface of the spacer and the porous thermit specimen should occur with decreasing pressure, because the acoustic stiffness ($\rho c$) of the porous material is lower.

In table 3 the estimations of energy losses in dense materials are made by neglecting the losses in the nonreactive spacer (Sn). The estimates were made based on the measurements of barrier deformation.

From the results of experiments it follows that in terms of force transmission to the barrier impact loading of the investigated porous thermit specimens almost does not differ from impact loading of the nonreactive materials. At the same time, the shock wave movement through a thermit specimen is accompanied by high energy dissipation. The difference on average is 2.5–3.0 J. Despite the small value of this quantity, its density can be sufficient for activation of an exothermic CT in a thin interphase layer of thermit mixture components.

6. Kinetics of chemical transformations in thermit mixtures sprayed in free space

CTs manifest themselves through visible light emission on shock breakout from thermit specimens in the absence of a barrier (figure 4a). The light emission was registered using the high-speed camera Cordin 222-16 in a special experiment (figure 4b). Six cylindrical sheaths with different thermit specimens were placed in an arc at the same distances from each other. On the left there was a cylindrical sheath with a nonreactive material (Rose’s alloy) instead of a thermit specimen. Shock loading of the specimens was carried out synchronously by one detonator. In four mixtures, the light emission had sufficient intensity. The weak light emission behind Rose’s alloy (left) in the absence of CT is indicative of a weak shock wave. There is no light emission behind Al-Ni (right) etc. This is indicative of a very weak shock wave in the air, and lack of visible CT. Dynamics in the light emission area (chemical transformation) was studied during dispersion of the thermit material through holes in the barrier. The hole diameter varied in the range of (0.35–1.00)$d^2$, where $d$ is the diameter of the cylindrical channel. The length of the hole was equal to the thickness of the cylindrical sheath wall.

**Figure 2.** (a) The calculated parameters for the steel barrier loading through various materials: 1—Hugoniot of nonreactive spacer, 2—Hugoniot of steel barrier, dashed line 3—pressure level in the nonreactive spacer at interaction with detonation wave, dotted line 4—unloading isentrope of detonation products. (b) The analytical approximation of the calculated ($Y$ axis) and experimental data ($X$ axis): dark badges represent the superimposition of the values of the barrier deformation on the analytical curve by equation (3) for different thermit specimens.
Figure 3. Combination of the Hugoniot of the barrier with the values of deformation pressure for different thermit specimens: 1—Hugoniot of the nonreactive spacer, 2—Hugoniot of the steel barrier. Dashed line 3 is pressure level in the nonreactive spacer during interaction with the detonation wave. Dotted line 4 is the unloading isentrope of detonation products.

Figure 4. Photos: (a) Light emission on shock breakout from the material of thermit specimens in the absence of a steel barrier, (b) Experimental assembly with six cylindrical sheaths and detonation scheme.

High-speed photography allowed us to record the rate of displacement and expansion of the light emission area behind the barrier. The photographing was made by the Cordin 222-16 camera with an exposure time of 50–100 ns for up to 1600 µs. The initial geometry of the light
emission area has a jet kernel with a “skirt” extending behind. Then the jet kernel blurs, and the rear boundary of the area breaks free from the hole. The light emission area extends with time and transforms as it moves away from the hole. The brightness of light emission in the pictures varies from specimen to specimen and changes in time, but it is comparable to the brightness of the air shock wave from an electrodetonator (3.8 km/s) captured in the same mode. Time and brightness of light emission also depend on the hole diameter. The brightest and longest light emission is obtained when the ratio of the hole to the specimen area is about 0.5. The light emission in the zone behind the barrier is related to the chemical transformation of the thermit mixture and afterburning of the products. In case of nonreactive spacers in control experiments, we only observed a weak shock wave glowing behind the hole within 6–7 μs.

Processing of the streak camera images allowed us to plot $x$–$t$ diagrams of the central part of the light emission area (figure 5a) and to track the expansion dynamics of its cross-sectional area (figure 5b). The rate of light emission area displacement was 260–450 m/s. The rate of area expansion was 3.5–35 mm$^2$/μs.

The brightest light emission (brightness temperature about 4000 K) was obtained for activated compositions of AlCuO, but the duration of light emission did not exceed 250 μs. The maximum time of light emission was obtained for the combined mixture of Al+CuO+Hf+(C$_2$F$_4$)$_n$ which is apparently associated with rapid initiation of the AlCuO mixture and subsequent active afterburning of hafnium in the air.

### 7. Resume

- Shock loading of investigated porous thermit specimens was found to be practically the same as that of dense nonreactive materials in terms of power action on the barrier.
- Shock propagation in a thermit specimen is accompanied by higher energy dissipation in comparison with its propagation in dense nonreactive spacers.
- Shock loading with a pressure of $\sim$ 20 GPa leads to the initiation of exothermic chemical reactions inside thermit materials with different components.
- Mixtures of AlCuO–HfC$_2$F$_4$ were recognized to be the most promising compositions for use as pulsed power sources.
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