Study of combustion wave propagation in linear charges from mechanically activated thermite mixtures

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Abstract. The combustion wave propagation in Al–CuO and Al–Bi₂O₃ termite mixtures was experimentally investigated. Waveforms of electric current through the reaction area between electrodes with a given potential difference, chronograms of piezo- and photodiode response, the data of pyrometric measurements, as well as photos of the glowing area were obtained and analyzed. There were revealed the advance filtration of the gas component through pores of mixture, the generation of charges providing considerable electrical conductivity of chemical reaction products, the connection of electrical conductivity dynamics with the optical radiation of the chemical conversion region.

1. Introduction
The high reactivity of nanoenergetic materials can significantly increase the rate of energy release in combustion and detonation processes, which makes it possible to use similar compositions in the development of advanced explosives, propellants, and microenergetic devices. The design of such devices requires the combination of operating conditions and possibility of manufacturing technology, as well as thermophysical characteristics of components. Ensuring required parameters of the device is based on an accurate understanding of a transfer and transformation of energy mechanism in the reaction medium. Schematically the relationship between mixture characteristics and transfer and transformation of energy is shown in figure 1.

The transfer capability is determined by the heat exchange processes by means of radiation, diffusion, convection and thermal conductivity mechanisms at the same time with filtering of hot reaction products through mixture pores [1]. To a large extent, the process and power of transfer are determined by the mixture porosity and the particle size of components.

The power of energy conversion is determined by thermodynamic and kinetic characteristics of the chemical process, thermophysical characteristics of mixture components, as well as contact surface of components [2]. The contact surface of components is related to size and geometry of particles, as well as mixture porosity in the working element. At the same time, the mixture
porosity is the result of a compromise between capabilities of the manufacturing technology and technical requirements.

2. Ideas about the subject of research
The use of thermite mixtures in technology is associated with the exothermic chemical reaction of the thermite mixture. The reaction is characterized by progression time, propagation speed and is accompanied by external manifestations in the form of heat generation, light emission and work [2, 3]. The distribution of reaction energy by types depends on process nuances, associated with chemical and physical characteristics of mixture components. For example, for the reaction $2\text{Al} + 3\text{CuO} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Cu}$ calculated energy release and temperature of emitting products are $4.1 \text{ kJ/g}$ and $2900 \text{ K}$ [4].

Previously we investigated dynamics of outflow from a orifice of two pressed in tablets samples weighing 1 g after shock loading [5]. One tablet was made from a Al–CuO mixture, and the second from an inert LiF–CuO mixture. The layout, loading parameters and mass proportions of components were the same for both tablets. The results were compared based on the proximity of impact characteristics of LiF and Al. It was found that chemical energy release practically does not affect the longitudinal velocity of the tablet material, the kinetic energy of which is determined by the value of $\approx 53 \text{ J}$. Moreover, the transverse expansion energy of reacting
and inert tablets is estimated to be $\approx 6$ J and $\approx 3$ J, respectively. Thus, the excess transverse expansion energy of the reacting material over the inert one is $\approx 3$ J. In our other experiments [6] it was determined that for the burning of a 1 g Al-CuO local sample with a bulk density, placed on a horizontal plane, during a time of $\approx 1000$ $\mu$s, an emitting cloud of products is formed in the form of a hemisphere with a 80 mm radius. For these experiments the kinetic energy of reaction products is estimated at $\approx 3$ J, and the integrated radiation energy is estimated at $\approx 160$ J. These estimates indicate that the main part of chemical interaction energy of Al-CuO mixture components ($\approx 3.9$ kJ, this energy is due to the exothermic nature of Al$_2$O$_3$ molecules formation) is enclosed in their internal energy, i.e., distributed over excited states of the freedom degrees of molecules [7]. The relaxation of excited states of molecules is accompanied by excitation and ionization of copper atoms (ionization potential 7.73 eV), optical radiation during stepwise transitions (transition energy $\leq 0.2$ eV), nucleation of reaction products and formation of large clusters. At the same time the formation of free electrons occurs [8,9], which allows to make an additional diagnostics of reaction zone. Similar processes were observed, for example, in [10]. The present work is devoted to experimental research of displays of a combustion wave of linear charges filled with energy mixtures Al–CuO and Al–Bi$_2$O$_3$.

### 3. Initial components

As a rule, the content of components in experiments corresponds to stoichiometric ratio or with some excess of aluminum. Mixing of components and mechanical activation were carried out in two types of spherical mills [11]: vibration (Aronov’s type with activation power 3.7 W/g) and planetary (“Activator-2sl”, 9.7 W/g, respectively). The preliminary mechanical activation is the significant factor influencing the spread of the reaction [12, 13]. Linear charges were formed filling of thick-walled tubes of different lengths (2–100 mm) and diameters (3–5.5 mm).

The reactions $2\text{Al} + 3\text{CuO} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Cu}$ or $2\text{Al} + \text{Bi}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Bi}$ were initiated by means of a submicrosecond electrospark energy release in a limited volume of the mixture [6]. The porosity of charges from micron particles was 50–60%. At such porosity and volume of air $\approx 1$ mm$^3$ heated in spark, the area of primary reaction initiation does not exceed 2 mm$^3$. Energy output in the initiating spark was $\approx 0.1$ J for a time of 0.5–1 $\mu$s. Presumably, during a spark discharge in pores of the mixture both occur the heating of components and the dissociation of air oxygen molecules and its ionization [14, 15]. Initial oxidation of Al is carried out. The reaction energy of Al oxidation produces vibrationally excited Al$_2$O$_3$ molecules [16]. Owing to their relaxation to equilibrium state, occurs the heating and subsequent thermal decomposition of metal oxide (copper 1000–1100 °C, bismuth 800–900 °C) with the oxygen release [17]. Further, with the appropriate heat balance, the process develops in a self-sufficient manner [18]. Thus, the conversion of the chemical reaction energy in termite mixtures is realized in the form of a combustion wave [19]. Under spark initiation in an oxygen-free gas, the primary energy source for decomposition of metal oxide is atoms of gaseous medium ionized in the spark.

### 4. Electrical conductivity and radiation of the reaction area

The formation of charged particles in a combustion waves is a consequence of the exothermic nature of redox reactions [8, 10, 20, 21].

Thermal ionization of atoms of reduced metal is the most likely source of electric charges in the reaction region due to high temperature of products. In [22] we diagnosed electrical signals generated by the flow of reaction products outside the charge volume in transverse electric and magnetic fields. Due to the uncontrolled particle density in the reaction area, it was not possible to determine the density of charges.

The application of a local electric field in the charge volume across the propagation of the combustion wave causes the transverse motion of electrons, and the current can be diagnosed. In current work we used a simple ohmic two- or three-arm voltage divider circuit in which the
interelectrode gap in the reaction region was the upper arm. Conductivity values were estimated in the framework of Ohm’s law with an uncertainty coefficient of $\approx 2$. This coefficient was due to averaging of current and electric field densities in the interelectrode gap. The value of the lower arm resistance was changed from 0.5 to 610 $\Omega$ depending on the required calibration range. Measuring ranges of conductivity were $1–100$, $100–1000$, $1000–50\,000$ $\Omega^{-1}/m$. Dividers were pre-calibrated with a 10 mF capacitor discharge with a voltage of 10 or 30 V while replacing the interelectrode gap with a known resistance.

In figures 2 and 3 there are experimental schemes in which signals of optical and electrical sensors were simultaneously recorded. Simultaneous control of such signals makes it possible to qualitatively characterize dynamics of thermal ionization of atoms of reduced metal and recombination of charges.

According to the scheme in figure 2(a) a weighed portion of the Al–CuO mixture (0.05 g) was ignited in a cell with a diameter of 4 mm and a depth of 2 mm. It is noteworthy that the optical radiation signal is delayed relative to the electric current signal in the reaction region, see figure 2(b). A subsequent increase in the radiation signal occurs against the background of a decrease in the conductivity signal. That is, the radiation process is associated with a decrease in electric charges.

According to the scheme in figure 3(a) samples of Al–CuO and Al–Bi$_2$O$_3$ mixtures (0.5 g) were ignited in a tube with a diameter of 10 mm and a length of 30 mm. At the end of the tube was an orifice with a diameter of 5 mm for pyrometric measurements of the brightness temperature at four wavelengths (500, 600, 700 and 800 nm). A concomitant measurement of the electrical conductivity of reaction products, see figure 3(b), showed that the maximum of radiation signals practically coincides with the beginning of the decrease in the electrical conductivity signal. Average brightness temperature values are in the range 2800–2900 K for
Figure 3. The brightness temperature of Al–Bi$_2$O$_3$ reaction products at four wavelengths: (a) the experimental scheme; (b) signals of pyrometer for the wavelength (1) 500, (2) 600, (3) 700 and (4) 800 nm as well as (5) of electrical conductivity sensor.

Al–Bi$_2$O$_3$ mixtures, and 3400–3600 K for Al–CuO mixtures. The high temperature of products (Al$_2$O$_3$) contributes to the thermal ionization of atoms of reduced metal and, accordingly, the production of electric charges. Registered optical radiation may indicate the opposite process—the recombination of electric charges. In this case the recombination of charges can occurs both in case of a single or several successive particles collisions. At the same time it should be noted that optical radiation can also occur during stepwise relaxation of vibrationally excited states of Al$_2$O$_3$ molecules [9]. Nevertheless, both radiation mechanisms are realized with the participation of final combustion products—atoms of the reduced metal and Al$_2$O$_3$ molecules.

The through quantitative characteristic of the electrical conductivity of the reaction area is limited by the dynamic range of the recorded equipment: no more than two orders of magnitude (< 40 dB). Therefore, to diagnose the entire spectrum of conductivity in the reaction area, it is necessary to use voltage divider circuits with different division factors. So, for example, to register the maximum electrical conductivity of reaction products, see figure 3(b), a voltage divider of 1 : 12 was connected to electrodes in the measurement zone. Moreover, the maximum value of the electrical conductivity of reaction products in this experiment was estimated at 45 kΩ$^{-1}$/m. The use of such a divider did not allow us to trace the dynamics of the production of electric charges (electrical conductivity) during the formation of a combustion wave.

In figure 4(a) there is a scheme of experiment with Al–Bi$_2$O$_3$, in which signals of optical and electric sensors were simultaneously recorded in case they were located in the middle section of the charge.

The charge was forming by filling the mixture in a closed channel with a diameter of 4.5 mm and a length of 40 mm. In this experiment the lower arm of divider was 0.5 Ω, which allowed us to monitor dynamics of electrical conductivity in the interelectrode gap from the very beginning of its manifestation. The discharge current of capacitor was provided by appearance of electric charges in interelectrode gap at a distance of 20 mm from the initiation point after ≈ 70 µs.
Figure 4. Measurements of the chemical transformation wave front in Al–Bi$_2$O$_3$ mixture: (a) the experimental scheme with ECS of 10–30 V and ORS; (b) signals of sensors.

of spark energy release. Subsequent increase in electric charges in the combustion wave of the Al–Bi$_2$O$_3$ mixture for \( \approx 85 \mu s \) contributed to an increase in the recorded signal, figure 4(b). The high-frequency noise on the electrical conductivity signal can be interpreted as spasmodic generation of charges in reaction points. Then, over a time of \( \approx 13 \mu s \), there is a multiple increase in the conductivity signal. Such a multiple increase in the signal can be associated with explosive fusion of reaction points and is characterized as a flash. The process of combustion wave formation may complete by this event (upon reaching the maximum conductivity). Further, in stationary propagation mode, the maximum temperature of Al$_2$O$_3$ is achieved, which provides the greatest thermal ionization of atoms of the reduced metal and the formation of the maximum number of electric charges. The maximum value of electrical conductivity of \( \approx 1 \) k\( \Omega \)\(^{-1}\)/m is fixed in the middle part of the channel after 280–290 \( \mu s \) from the moment of spark energy release.

The scheme and result of measuring the electrical conductivity of the combustion wave in an Al–CuO mixture are shown in figure 5. In this experiment, a shorter open end channel was used. Oscillograms of changes in the electrical conductivity of both mixtures at the stage of formation of the combustion wave look similar.

Table 1 summarizes values of different parameters characterizing stages of combustion wave formation of Al–CuO and Al–Bi$_2$O$_3$ mixtures; the parameters are estimated based on waveforms of conductivity signals.

The difference in the length of the channel behind electrodes, table 2, affects the duration of the electroconductive state in the region of electrodes, see figures 4(b) and 5(b). A rapid decrease in the electrical conductivity of reaction products in a short open channel, is apparently due to a decrease in the pressure and density of reaction products during their free flow, see figure 5(b).

5. **Strength of reaction area**

In linear charge, the duration of the electrical conductivity signal may indicate the extent of the reaction zone at a known velocity of propagation of the reaction wave over the charge. This can
Figure 5. Measurements of combustion in Al–CuO mixture: (a) the experimental scheme; (b) signals of sensors.

Table 1. Conductivity wave parameters during combustion of Al–CuO and Al–Bi$_2$O$_3$ mixtures in the channel.

| Parameter                                           | Al–Bi$_2$O$_3$ | Al–CuO |
|-----------------------------------------------------|----------------|--------|
| The beginning of the appearance of the conductivity signal (µs) | 186            | 360    |
| Conductivity wave velocity (m/s)                    | 107            | 55     |
| Duration of increase in conductivity (µs)           | 68             | 86     |
| Wavelength (mm)                                     | 7.3            | 4.8    |
| Conductivity before confluence of reaction points (S/m) | 270            | 60     |
| Duration of “fusion of reaction points” (µs)        | 13             | 5.5    |
| Time of reaching the maximum electrical conductivity (µs) | 280            | 455    |
| Maximum value of conductivity (S/m)                 | 1030           | 450    |
| Duration of the “recombination” stage of charges (µs) | 82             | 15     |
| Duration of mixture burning (µs)                    | 1100           | 86     |

also be judged by photographs of the glow region under placing charges in a dense case with transparent walls. A photo of such assembly and x–t diagram of the glow front are presented in figure 6. A dense case in the assembly is the space filled with water between two cylinders of different diameters. The field of the diagram also shows the developmental curve of the reaction space in the luminous manifestation behind the wave front in the Al–Bi$_2$O$_3$ mixture. For an Al–CuO mixture the length of the glowing area behind the wave front is much larger.
Table 2. The geometric parameters of the channel during the combustion of each mixture.

| Parameter                        | Al–Bi$_2$O$_3$ | Al–CuO |
|----------------------------------|----------------|--------|
| The diameter of channel (mm)     | 4.5            | 4.5    |
| The length of channel (mm)       | 40             | 20     |
| The length of charge (mm)        | 40             | 20     |
| The coordinate of electrodes (mm)| 20             | 20     |
| Reaction when channel was closed | Yes            | No     |

Figure 6. Propagation of combustion wave in Al–Bi$_2$O$_3$ mixture: (a) the experimental scheme; (b) $x$–$t$ diagram of the glow front (1—speed of front of glowing area [410 m/s]; 2—size of glowing area).

6. The mechanism of combustion wave propagation
The effect of pressure on the combustion wave propagation immediately after spark initiation was detected experimentally and is shown in figure 7. In these experiments were changed the current in the spark (initiation energy) and the rate of filtration of ionized air into pores of initial mixture. The charge was formed by filling the glass tube with a thermite mixture. The reaction was initiated from the end of the charge. This end of the charge was either left open or covered with a steel plate. By these means, the pressure of the air ionized in the spark was changed and the priority of its filtration direction was regulated. The propagation of the combustion wave was recorded by high-speed photographing with a Cordin 222-4G camera. From photographs it follows that a spark with a small current at the open end of the charge does not initiate the burning of a linear charge, see figure 7(a). An increase in the current three times together with an open end of the charge leads to unstable combustion of the mixture, see figure 7(b). Closing the open end of the charge with a heavy load leads to a stationary burning wave, even with a
9 µs 3250 µs 4000 µs

Figure 7. Photos of experimental assemblies with spark initiation and the combustion process of Al–CuO mixture with different initiation conditions: (a) spark current 44 A, without load; (b) spark current 137 A, without load; (b) spark current 76 A, with load.

1.8 times reduction in the spark current, see figure 7(c). These results confirm the filtration mechanism of the combustion wave propagation in porous thermite charges.

The additional evidence of gas component filtration is a delay in signals of optical and electrical sensors relative to signal of piezoelectric sensor. The piezoelectric sensor reacts on a dynamic pressure under the reaction wave exits at the end of the charge. Experimental scheme and signals of sensors are shown in figure 8.

7. Propagation of reaction along a linear charge
Combination of characteristic signal points allows one to detail the distribution of the reaction along a linear charge. It should be remembered that the electrical conductivity of the medium in the combustion wave is a characteristic of its state, which is not associated with movement
of matter. Therefore, the wave velocity should be determined by measuring the electrical conductivity at several points in the direction of reaction propagation.

Figure 9 shows an assembly, a photograph of the optical radiation of expiring products and $x$–$t$ diagrams based on results of two experiments. The location of charge boundaries and the body end of experimental assembly is indicated by the corresponding lines.

A charge of the mixture with a length of 80 mm was formed in a channel with a diameter of 4.5 mm and a length of 180 mm. The 1.5 mm diameter copper electrodes embedded in pairs along the length of the channel and were introduced into channel walls. A capacitor charged to a voltage of 30 V was connected to electrodes through a voltage divider 1 : 12 (610 Ω). The outflow of glowing reaction products from the channel was photographed with a high-speed camera Cordin 222-4G.

Positions 1 and 2 in the diagram for the Al–CuO, see figure 9(c), show velocities of movement of front of electrical conductivity (99 m/s) and points with the maximum electrical conductivity (80 m/s) within the charge length. Positions 3 and 4 in the same diagram correspond to front velocities (550 and 192 m/s) of two glowing areas with well-different brightness under the reaction products outflow. Bifurcation of the glowing area in brightness is quite well observed in photographs, see positions 1 and 2 in figure 9(b). Under burning the Al–Bi$_2$O$_3$, a similar picture is observed, see figure 9(d). Characterization of the process by two propagation velocity values suggests two causal sources of this fact. Within the initial charge volume, such sources may be the gas-vapor component of products and the reaction in stationary components of the initial mixture. Outside the channel, the expiration of the dense core of reaction products can serve as a second source. In general, results of these experiments are clear evidence of the filtration mechanism of reaction initiation in the initial mixture.

Figure 8. Measurements of combustion in Al–CuO mixture: (a) the experimental scheme with the pressure sensor (PS); (b) signals of sensors.
Figure 9. Spark initiation of mixtures in a dielectric tube with the open end: (a) experimental assembly (1—assembly housing; 2—product outlet channel; 3—mixture charge; 4—potential electrodes; 5—point of spark initiation; 6—spark power cable); (b) expiring combustion products at $t = 2900$ $\mu$s (1—front of expiring gas filtrate; 2—expiring products; 3—assembly); (c) the $x$–$t$ diagram of Al–CuO combustion dynamics (1—conductive front of gas filtrate in pores of charge; 2—conductive front of stationary combustion; 3—front of expiring gas filtrate glowing; 4—front of expiring combustion products glowing; 5—end of assembly body; 6—boundary of charge); (d) the $x$–$t$ diagram of Al–Bi$_2$O$_3$ combustion dynamics (1—conductive front of stationary combustion [127 m/s]; 2—front of expiring gas filtrate glowing [306 m/s]; 3—front of conductivity of combustion products flow within the channel [79 m/s]; 4—end of assembly body; 5—boundary of charge).
8. Conclusions
The bulk of chemical conversion energy is associated with the internal energy of the condensate of reaction products. A smaller part of the energy is emitted through recombination processes in ionized reaction products. A very small part of the energy is associated with the thermal expansion of gaseous reaction products. The analysis of the measurement data allowed to reveal in more details the combustion process sequence in time after the reaction initiation:

- advance filtration of gaseous products through pores of the mixture and the accompanying acceleration of burning particles of the mixture;
- heat release of the chemical reaction in the volume of the charge;
- generation of electrical charges (electrons) during thermal ionization of metal oxide atoms, resulting in electrical conductivity of products;
- intensive optical radiation when the number of hot reaction products increases, resulting in a delay of about 20 µs after the appearance of conductivity signal;
- decrease in electrical conductivity and intensity of optical radiation at reagent production.

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