Voltaic effect in burning high-caloric (Zr+CuO+LiF)/(Zr+BaCrO$_4$+LiF) sandwich structures

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Abstract. This experimental study is devoted to the electric and optical phenomena, that becomes apparent during the combustion of the two-layer heterogeneous energetically-condensed solid-phase systems with the (Zr+CuO+LiF)/(Zr+BaCrO$_4$+LiF) structure. It was found that such systems combustion is accompanied by an electric pulse signal generation with duration ~ 1.0 s at half-width and the maximal amplitude 1.2–1.5 V. The signal arises at the combustion beginning and is continuing to the reaction completion. For the mentioned systems it was firstly registered a flame optical emission from the reaction zone within the visible spectral region ($\lambda \sim 300$–700 nm). The initial (green) mixtures and combustion products were explored by x-ray diffraction and scanning electron microscopy. The combustion experiments were carried out by using a home-made experimental mounting, allowing in on-line regime to record the physical parameters of the energetically-condensed systems during a combustion process.
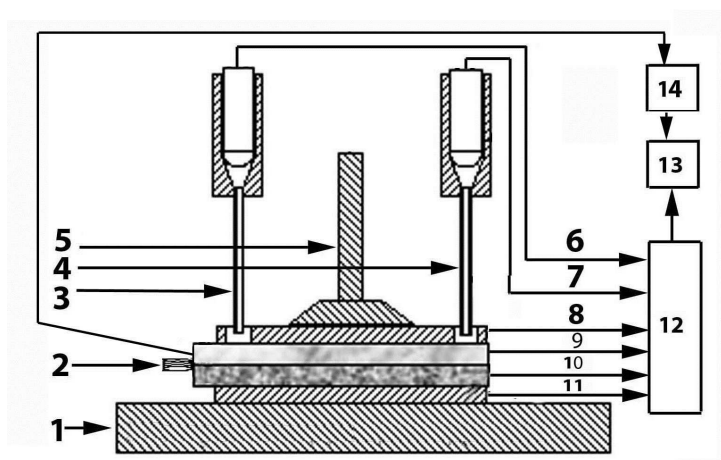
1. Introduction

The direct transformation of the energetically-condensed solid-phase systems (ECS) chemical energy into an electric one due to a combustion process is very important and actual problem of modern science. Therefore, there is a need to carry out some experimental and theoretical investigations of the physical processes, going on during the ECS combustion. One of such model processes is self-propagating high-temperature synthesis (SHS) used in the work. As is known from many literature data [1], during SHS process into different heterogeneous materials there are arising some electrical signals. At present work, the results of electrical and optical phenomena studies are presented for the combustion of the complex energetically condensed systems.

2. The experimental methods

In figure 1 the scheme of an experimental installation is shown, being especially developed for the (Zr+CuO+LiF)/(Zr+BaCrO$_4$+LiF)-type energetically-condensed solid-phase systems (ECS) combustion studies [2]. The samples had a form of an assembly of two disks from the ECS of different chemical composition: the heterogeneous system 1 has composition (Zr+CuO+LiF) (5), the system 2—(Zr+BaCrO$_4$+LiF) (6). The disk cathode and anode elements have diameter ~ 14 mm and thickness ~ 0.5 mm (these elements are described in details below). Such complex heterogenic systems and their components were selected for our studies, starting from the next reasoning: Zr is ensuring a high-temperature combustion of the finely dispersed systems at
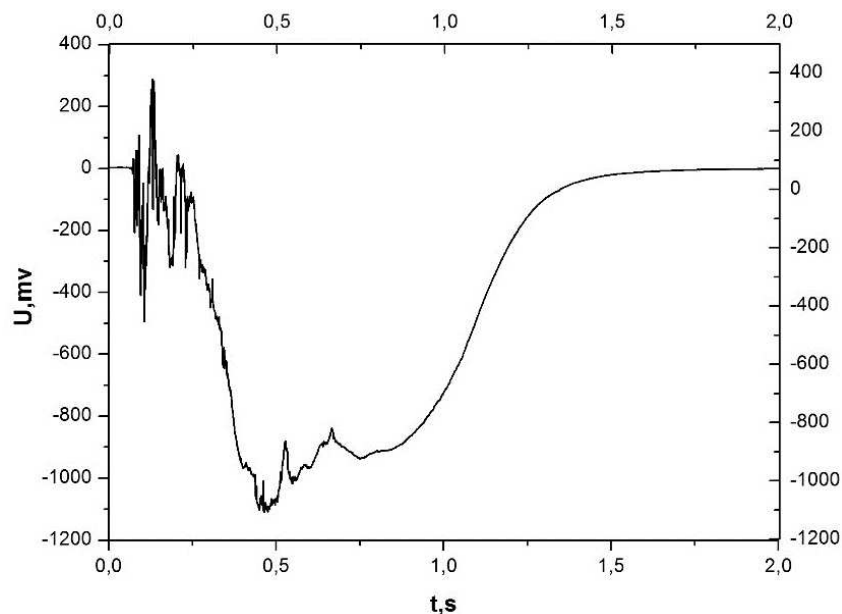
Figure 1. The experimental installation scheme: 1—mounting; 2—inflammation band; 3, 4—collimators; 5—loading; 6—photo-diode PhD1; 7—PhD2; 8—upper electrode; 9—energetically-condensed system (Zr+BaCrO$_4$+LiF); 10—energetically-condensed system (Zr+CuO+LiF); 11—lower electrode; 12—ACP 17–U8 device; 13—PC; 14—CCS 100M spectrometer.

sufficient heat removal; CuO is one of the most active cathode oxidizer, used in the storage batteries; BaCrO$_4$ is a fine dispersed oxidizer with low gas content; LiF is the widely used as the electrolyte in accumulators. The experiments were carried out in air at pressure 1 atm. As is shown in figure 1, the 8-channel device ACP A17–U8 allows synchronously record the signals from photodetectors FD1 and FD2 (to which the light emission of the burning ECS is coming through collimators), indicate the electric signals (generated under this combustion process) and fix the time of this combustion front development from detector PhD1 to PhD2 (for the given distance between the detector collimators). The detection of these signals gives an information about the combustion stage, when an electrical potential originates, and for to study of the combustion rate for the given (Zr+CuO+LiF)/(Zr+BaCrO$_4$+LiF) energetically-condensed solid-phase system. For these purposes at the electrode 8 edge there were drilled some openings, through which the light of the burning films achieves to the detectors through collimators 3 and 4. The collimators have a form of the nickel capillary with the inner diameter 0.4 mm and length 40 mm. The electrodes under an action of the load F are compressing the films with pressure 6.5 kPa. For the film combustion temperature measuring we used (instead of photodetectors) the thermopiles with thickness 100 μm from 5/20 alloys, and for a measurements accuracy increase the thermopile was dipped into 3–4 ECS layer films. This installation allow also detect the flame optical emission from the reaction zone within the visible spectral region during a combustion process.

3. The results obtained
Our experimental studies had revealed, that under the (Zr+CuO+LiF)/(Zr+BaCrO$_4$+LiF) combustion there is generated a pulse electric signal. As it is shown in figure 2 this signal arises at the combustion process beginning ($t = 0.1$ s).

Its amplitude maximum is achieved at $t = 0.46$ s and equals ~ -1.1 V with the pulse duration at half-width ~ 1.0 s. It must be marked also that the signal polarity is defined with the system connection with the ACP 17–U8 device, but not with process physics itself. The experiment, carried out with the installation shown in figure 2, had demonstrated that the signal begins with a combustion process and continues to a final sample cooling off. The photo-diodes allow
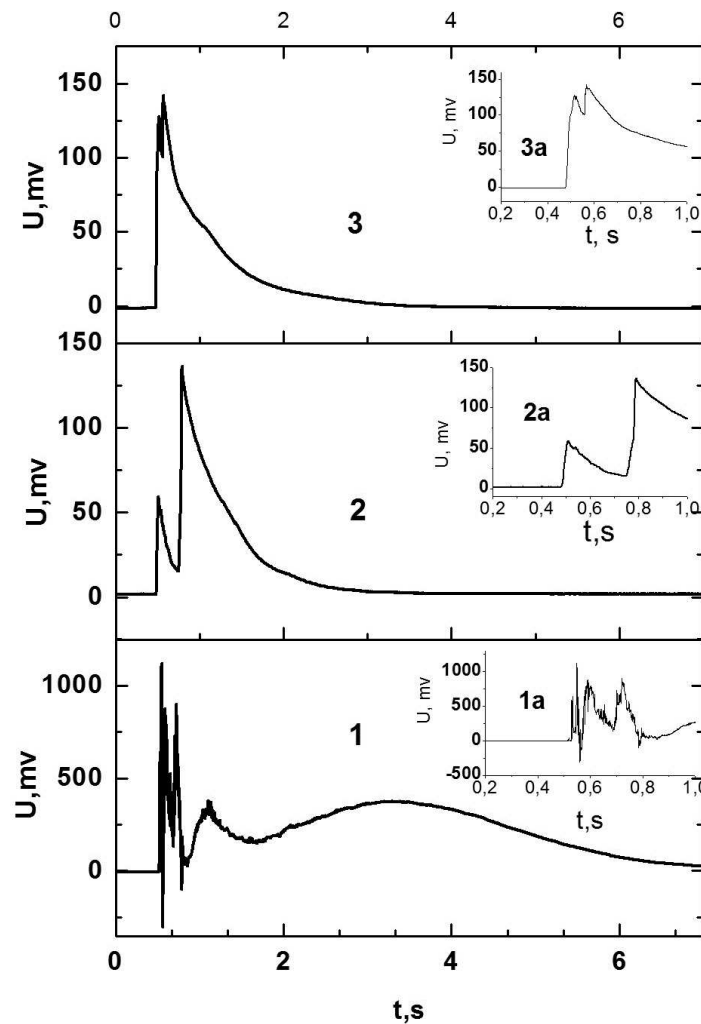
Figure 2. The electric signal amplitude on the time during a combustion process of the (Zr +CuO+LiF)/(Zr+BaCrO$_4$+LiF)-type ECS.

determine the time and combustion rate of the given two-layer energetically-condensed. In figure 3, shown are the dependencies on time for the electric signals from photo–diodes PhD1, PhD2 and total electric signal.

The studies had shown that mean combustion time is $\sim$ 0.25 s (it is corresponding to a combustion rate $\sim$ 4–5 cm/s). As is shown in figure 3, the electric signal during the combustion process directly start (during $\sim$ 0.25 sec) has a harmonic oscillating character with an amplitude range (positive and negative polarity) about 800 mV. During the combustion products cooling (crystallization) a signal amplitude is increasing (up to $\sim$ -1.1 V), but we did not see any high harmonics at this reaction stage, thus it can be proposed that the signal size and forms at different reaction stage are defined by the various physical processes. On the base of the results obtained we can suppose that directly during a combustion process of the studied (Zr+CuO+LiF)/(Zr+BaCrO$_4$+LiF)-type system can be present as a voltage (electro-motive) source with a little internal resistance. In fact the temperature into such systems is achieving $\sim$ 1200–1500°C, i.e. some system components are in a melted state and its internal resistance is very low.

At the same time the ACP 17–U8 device internal resistance is $\sim$ 100 kΩ, and the harmonic vibrations will most likely connected with a double electric layers (of ions, cations, electrons and holes) into a melt, arising in the combustion front [3]. A process macro-kinetic mechanism can be described in the next way: a sample consists of the asbestos cloth strips, impregnated by some compounds, well dried and clamped by two metallic plates, stand duty as the electric contacts. Since asbestos is an isolator, the assembly in a hole before the inflammation has a great electric resistance. At the ignition and during the combustion front propagation there arise a conductive zone and an electric current is generated. At this process stage, the electric resistance is decreasing both for the electrolyte (lithium fluoride) melting and for the burned conductive surface area rise. The voltage at this region is variable and when the combustion front is achieving the sample end, its resistance becomes maximal for both mentioned factors
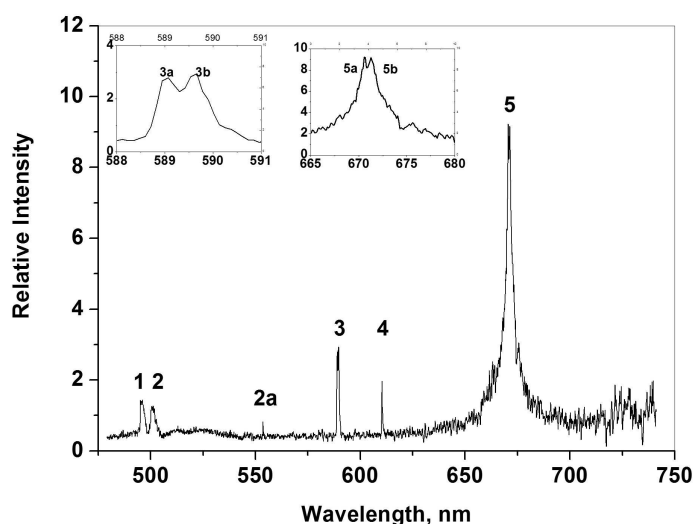
Figure 3. The dependencies on time for the electric signals from the photo-diodes PhD1, PhD2 and total system electric signal during combustion: 1—electric signal of photo-diode PhD1, registering an ECS combustion; 2—electric signal of photo-diode PhD2, registering the system combustion process finishing; 3—signal of photo-diode PhD1, registering a combustion process start; 1, 2, 3—the insertions, showing the signals at the combustion regions.

(electrolyte melting and the burned conductive surface area rise), and at this region the sample can be presented as a current source. Due to the great heat removal through the massive electric contacts (the total sample thickness is near these electric contacts width) the sample is cooling and thus the charge carriers diffusion and the current generation itself are terminating. Thus during the source active stage work is characterized by action of the opposite processes. In the strict sense, the regime of the voltage and current generation can be (only by convention) divided to the two modes, one of which is prevailing at the combustion stage and second at the cooling stage.

It is known from literature [3] that under the SHS-products cooling there can run the processes of the combustion products after-reaction (crystallization). It is obvious that at this stage the system internal resistance is growing and we can suppose, that at this stage into the combustion

Table 1. The results of the combustion rate measurements at the various experiment conditions.
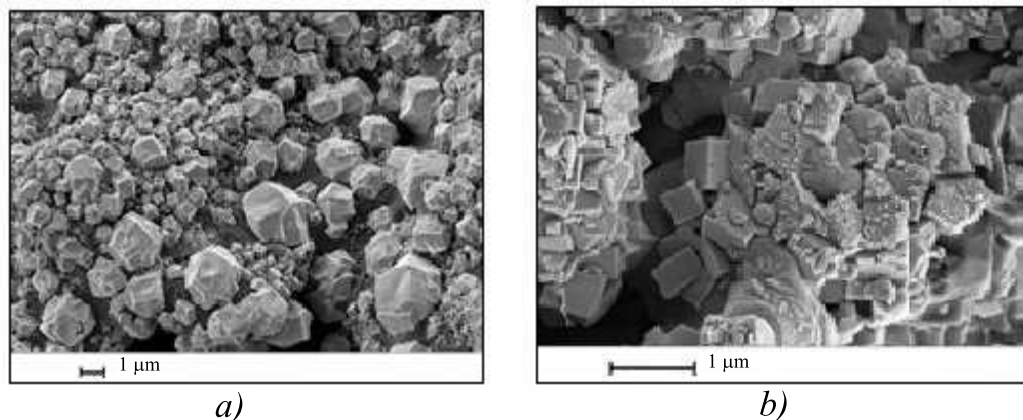
U, cm/s	Notes
4.1	ECS Zr+BaCrO$_4$+LiF placed assembly upward
3.1	ECS Zr+BaCrO$_4$+LiF placed assembly upward
3.7	ECS Zr+CuO+LiF placed assembly upward
3.0	ECS Zr+CuO+LiF placed assembly upward
4.1	ECS Zr+BaCrO$_4$+LiF placed assembly upward
5.2	ECS Zr+CuO+LiF unitary
4.4	ECS Zr+BaCrO$_4$+LiF unitary

Figure 4. The emission spectrum of two-layer system: (Zr+CuO+LiF)/(Zr+BaCrO4+LiF).

products (during their crystallization) some electrochemical reactions can proceed and generate the electric signals with amplitude above 1 V. It can be supposed also that at this after-reaction stage the combustion products itself represent some electrolytic components of a current source, having a sufficiently high internal resistance and for a low-ohm loading such system can produce a sufficiently high electric current.

The results obtained needs the following theoretical and experimental investigations, particularly connected with the loading characteristic measurements for these systems during the combustion process. In our studies, using the photodiode signals, we had calculated the combustion rates for the separate components of the (Zr+CuO+LiF) and (Zr+BaCrO$_4$+LiF) systems, as well for the two-layer energetic condensed (Zr+CuO+LiF)/(Zr+BaCrO$_4$+LiF). The results of the combustion rate measurements at the various experiment conditions are presented in table 1.

The experimental equipment, shown in figure 1, had allowed record the flame optical emission spectrum from the reaction zone within the visible spectral region ($\lambda \sim 300$–700 nm) for the systems under study.

a)   *b)*

Figure 5. The variants of ECS combustion products crystallization.

A typical ECS emission spectrum is presented in figure 4.

After several experiments with ECS combustion we have carried out the spectra averaging and "sewing" by intensity, using a licence program, supplied with CCS-spectrometer. Next, we have identified the emission lines during combustion by the Zaidel spectral tables. The observed emission lines were identified by following way:

Blue emission: $l_1 = 495.9$ nm (doublet) can be identified as Ba, the doublet second line $l_2 = 501.1$ nm corresponds to Zr $= 501.146$ nm emission line, the emission green line $l_{2a} = 553.5$ nm (also by Zaidel spectral tables) corresponds to Ba emission 553.548 nm. Red line l_3—doublet from two lines: $l_{3a} = 589.0$ nm can be identified as Zr emission, the doublet second line $l_{3b} = 589.7$ nm corresponds apparently to Ba or Li, because after reaction is formed $l_4 = 610.4$. The line with the emission biggest intensity is uniquely identified as Li emission 670.684 nm, the doublet second line $l_{5b} = 671.3$ nm is identified as Zr emission line.

From the emission optical spectra, obtained during the combustion reaction process it may be conclude that into the air atmosphere during the reaction an intensive emission is mainly observed for zirconium and lithium. There are also the emission lines of Ba and Li with lesser intensity. It can be concluded that the optical emission spectrum from the reaction zone within the visible spectral region give an additional important information, concerning the processes of the energetic condensed (Zr+CuO+LiF)/(Zr+BaCrO$_4$+LiF) system combustion.

The electron microscopic analysis of ECS combustion products had shown that after final cooling there are the various crystallographic structures in these products. One of these results is shown in figure 5 and it demonstrated that the ECS combustion products can be crystallized in the different modifications. The crystallographic structure in figure 5a can be tentatively described as a hexagonal one, and the structure in figure 5b can be related to the cubical clusters.

4. Conclusions

It is found that during the combustion of the energetically–condensed system (Zr+CuO+LiF) /(Zr+BaCrO$_4$+LiF) the electric signals are generated ith amplitude up to ~ 1.1 V and duration at half-width is ~ 1.0 s.

During the combustion process in this electric signals some harmonic oscillations arise with deviation range ~ 0.8 V.

After combustion wave propagation in the combustion products the signal amplitude is rising

and achieves ~ 1.1 V, the harmonic oscillations are absent.

During the ECS combustion process the flame optical emission spectrum was recorded within the visible spectral region. It was found also that in the combustion spectrum mainly the power emission of Zr and Li is presented.

The experimental installation is developed for to study the electric and optical phenomena, arising under the energetically-condensed system combustion.

Acknowledgments

References

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