PREPARATION AND TEST OF SLOWLY BURNING ENERGY-INTENSIVE MATERIALS WITH TIME-DELAY COMPOSITION

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ABSTRACT

The time-delay compounds serve to create the necessary time delays that ensure a given duration of work. These compounds consist of low-level oxidants and combustible, so their energy and combustion temperature are relatively low. Today an increased interest in slowly burning mixtures with delay composition is noticed. It is associated with an obvious tendency towards miniaturization of the slowing elements of various devices. The article describes development of a delay composition based on chromium barium and titanium diboride burning slowly at a burning rate of 1.26 mm/s. For researching the combustion process, the samples were burned in a bomb with a constant pressure in an argon medium. Regularities of burning of the mixture $BaCrO_4/TiB_2$ in the medium of inert gas have been investigated. At combustion of the slow-burning $BaCrO_4/TiB_2$ spinel-shaped crystalline structures are formed. The prepared slow-burning composition, not sensitive to mechanical influences and possessing high physico-chemical stability, can be used in the pressure-sealed delay devices.

Keywords: gas-free combustion, energy-intensive material, pyrotechnic delay composition, barium chromate, titanium diboride.

INTRODUCTION

The slow-down compositions (or "delay compositions") are pyrotechnic mixtures intended for equipping remote tubes, fuses, fire cords. Such mixtures, burning at a constant speed, provide a temporary delay in the operation of ammunitions, pyrotechnic products or some elements of automation. The reliability and the accuracy in respect to time are the characteristics of greatest importance in all cases of application of retarders. The anticipation or the delay of the functioning of the device leads to a significant decrease in the system's efficiency. From year to year, the requirements to pyrotechnic retarding compounds become more diverse and much more stringent, especially in the field of pyroautomatics equipment. Therefore researchers and developers of pyrotechnic systems to meet qualifying standards, continue to apply and test new pyrotechnic compositions and to investigate their performance data. But even in the development of new formulations, the dependency of the combustion characteristics of the composition on pressure and temperature, as well as reproducibility and reliable ignition, remain unresolved problems [1-6]. The pressurized pyrotechnic delay devices are of the greatest practical interest. The sealing eliminates the effect of the external pressure upon the rate and the time of burning of the delay mechanism and protects it from effects of atmospheric humidity that is necessary for a possibility of long storage of these devices. The sealed pyro-delay mechanisms can be equipped only with low-pressure retardant compounds, the combustion of which takes place without the formation of gaseous

products [7 - 12]. One of the main tasks of the development of slow-burning compounds that are able to burn sustainably under conditions excluding the outflow of the gaseous products formed refers to the minimization of the amount of gases released during the combustion. For this, zirconium, titanium and borides of these metals are most suitable as combustibles, because gaseous products are not formed during their oxidation. These combustibles can interact at elevated temperatures with the melt of oxidants [13, 14]. Alloys of refractory metals or mixtures on their basis, carbides and borides attract great interest [15 - 19] as fuels in the corresponding delay compositions.

The aim of this work was preparation of a slow-burning composition based on titanium diboride and barium chromate and investigation of the patterns of combustion of a mixture in an inert gas environment.

EXPERIMENTAL

Barium chromate (Technical Requirements 4211-75, 99.2 % $BaCrO_4$) and titanium diboride (Technical Requirements 113-07-11.040-89, 98 % TiB_2) were used as oxidizers. Dinitrocellulose (State Standard 4976-83) was used as a binder in small quantities.

The ratio of the components of the delay composition, wt. %, referred to: $BaCrO_4$ - TiB_2: dinitrocellulose: 50:46:4.

The procedure for preparing $BaCrO_4/TiB_2$ delay composition was as follows:

weighing → dry mixing of the oxidizer and the fuel → mixing with the binder component → pressing in a hydraulic mold → drying.

For researching the combustion process, the samples were burned in a bomb of constant pressure in an argon medium. The samples were initiated by a nichrome spiral. The combustion temperature was measured with a pyrometer, and a stopwatch was used to determine the burning time. To determine the burning rate, the samples were pressed in a cylindrical mold with a diameter of 10 mm and a height of 8 mm - 10 mm by means of a hydraulic tool press. Several pressings were applied to achieve a uniform charge density at a maximum stress of 6 MPa.

The semi-quantitative elemental composition of the burned samples was determined by the method of energy-dispersive X-ray microanalysis on QUANTA 3D 200i electron microscope equipped with an energy dispersive X-ray spectrometer (EDAX Co).

RESULTS AND DISCUSSION

The initial sample and the final product (burnt sample) are shown in Fig. 1. It shows that the sample burned in argon almost does not change its shape. It is found that when the sample is burned, spiral combustion is observed (Fig. 2). It can be explained by the fact that when a cylindrical sample burns on a lateral surface, two foci of energy release are formed that propagate in opposite directions along the circumference. It can be seen from Fig.1(b) that the burnt out sample has a spiral pattern and a corresponding structure on its outside surface. Spiral waves arise from discontinuities in the wave front in a two-dimensional medium. The nature of the formation depends essentially on the intensity of the heat released in the combustion zone. If the heat dissipation is sufficiently high, the free end of the wave

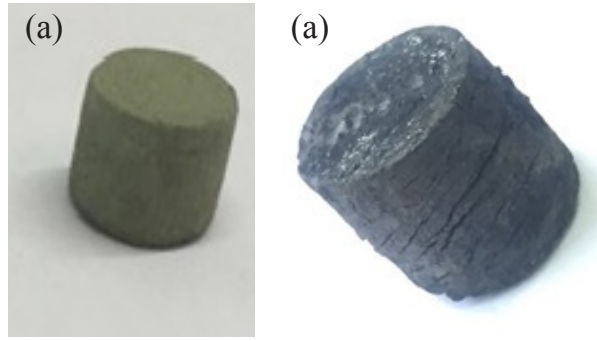

Fig.1. Images of an initial sample (a) and a final product (b).

Fig. 2. Process of combustion.

"sprouts", lags behind and twists into a spiral [20, 21].

An intense exothermic oxidation-reduction reaction occurs upon ignition of a pyrotechnic delay mixture. One of the main requirements for slow-burning delaying compositions is a small temperature dependence and the burning rate on pressure.

It was found that the combustion temperature is practically independent of the pressure. For $BaCrO_4/TiB_2$ system the combustion temperature remains constant over the entire argon pressure range. Under these conditions, the ignition of the mixture causes the spread of the flame front, and the beginning of the burning process of the mixture in the steady-state regime.

The rate of oxidation of fuel and the decomposition rate of the oxidant are the important criteria in the development of delay compounds. Such indicators must be almost identical. If the rate of decomposition of the oxidant is very fast, the fuel does not have time to interact with all the oxidant that is released, and as a result, some of the oxidant will not react. In the reverse case, at a very slow rate of the decomposition reaction of the oxidizer, the reaction rate can be too small to ensure the propagation of the flame front. The oxidative properties of the fuel play also an important role, since the oxide surface forms a protective coating. Furthermore, oxygen diffusion through the oxide film is required to oxidize the fuel, while the rate of the entire process depends on that of the diffusion. The fuel will immediately oxidize if the surface is not covered with an oxide film.

When the argon pressure is varied in the interval 1 atm - 4 atm, the burning rate varies slightly (Fig. 3), from 1.26 mm/s to 1.37 mm/s. The maximum value of the burning rate is observed at a pressure of 2 atm, while the minimum value - at 3 atm. The thermal analysis illustrated in Fig. 3 demonstrates that the reactions occur in many cases on the solid phase before the solid mixture reaches the ignition temperature.

When the delaying mixture burns, the temperature and the rate should be high enough to ensure that the heat dissipation rate exceeds the heat loss intensity. If the heat losses become higher than the heat release, the propagation of the flame front can stop. Fig. 4 presents the kinetic characteristics of the combustion of $BaCrO_4/TiB_2$ system and shows temperature increase in the initial section. There, the reaction proceeds in the condensed phase. The temperature rise in the reaction zone in the condensed phase occurs both due to the heat transferred from the reaction zone in the gas phase, and due to the reaction passing in the condensed phase itself. There, decomposition of barium chromate occurs, and as a result of this process oxides of barium and chromium (III) are formed and oxygen is released. Then there is a transition through the maximum. This maximum is the reaction zone of the gas and condensed phase, where occurs the oxidation of titanium diboride oxygen released in the decomposition of barium chromate. The subsequent decrease of the reaction rate indicates the formation of combustion products. The maximum

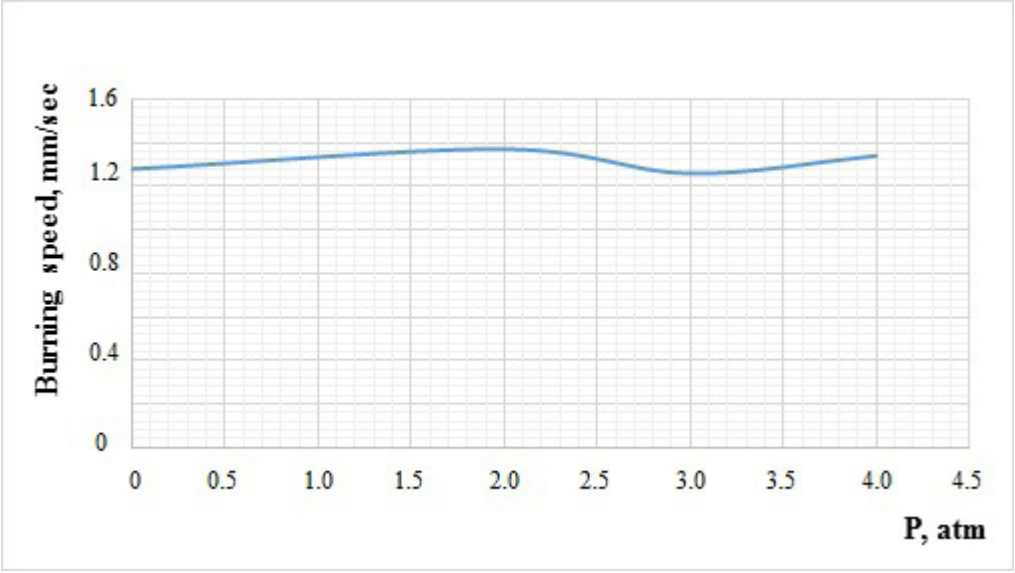

Fig. 3. Effect of pressure on the combustion rate of the $BaCrO_4/TiB_2$ system.

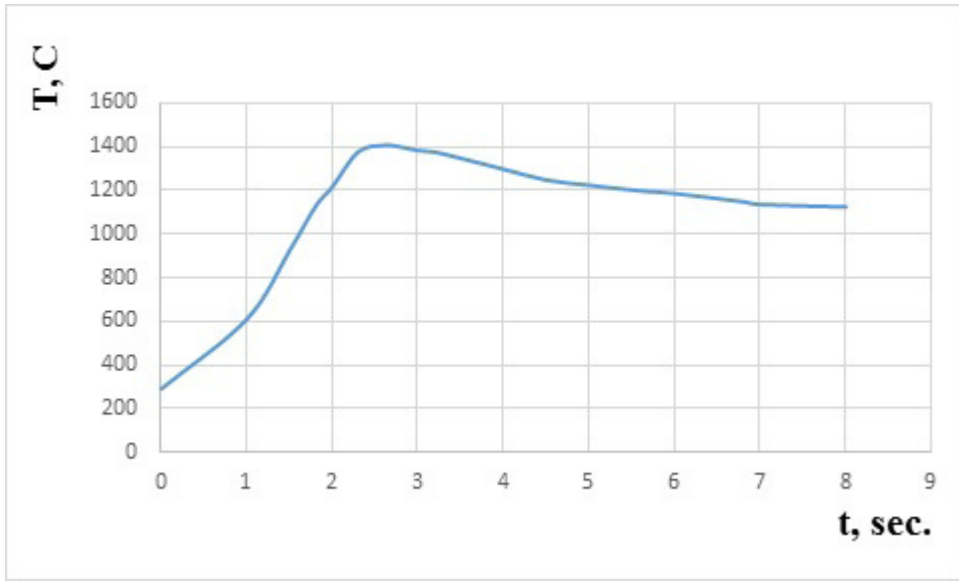

Fig. 4. Influence of the burning time of a slowly burning mixture of the $BaCrO_4/TiB_2$ system on the temperature.

value of the combustion temperature, T_{max} = 1,410°C, is reached at $t_{burning}$ = 2.6 s.

The mass loss coefficient, k_m = 0.04, is calculated from the difference between the masses of the initial and the burnt sample. Since the mixtures have the highest combustion temperatures, it can be assumed that the weight loss is associated with the volatilization during the combustion of a small amount of boric anhydride B_2O_3, which is formed during the oxidation of titanium diboride by oxygen, released during barium chromate decomposition. Also, the change of the crystal structures of the reagents due to high temperatures leads to mass loss of the samples. It is known that during combustion an oxidation-reduction reaction takes place: a decomposition of the oxidant and an oxidation of the fuel. According to the literature [22 - 24], as a result of the decomposition of barium chromate at a temperature above 1,300°C, oxides of barium and chromium (III) are formed and oxygen is released:

$$4BaCrO_4 \rightarrow 4BaO+2Cr_2O_3+3O_2 \quad (1)$$

Further oxidation of titanium diboride with oxygen, released by the decomposition of barium chromate proceeds, and thermodynamically possible is the following reaction [23]:

$$2TiB_2 + 5O_2 \rightarrow 2TiO_2 + 2B_2O_3 \quad (2)$$

Theoretically, it can be assumed that oxides of barium, chromium and titanium are the combustion products of the delaying mixture of barium chromate/titanium diboride.

The combustion products have been investigated by electron microscopy and energy dispersive X-ray microanalysis, as well as X-ray phase analysis. The morphology of the combustion product was studied by electron microscopy (Fig. 5). It can be seen that the sample is melted and fibrous and spinel-like solid crystalline

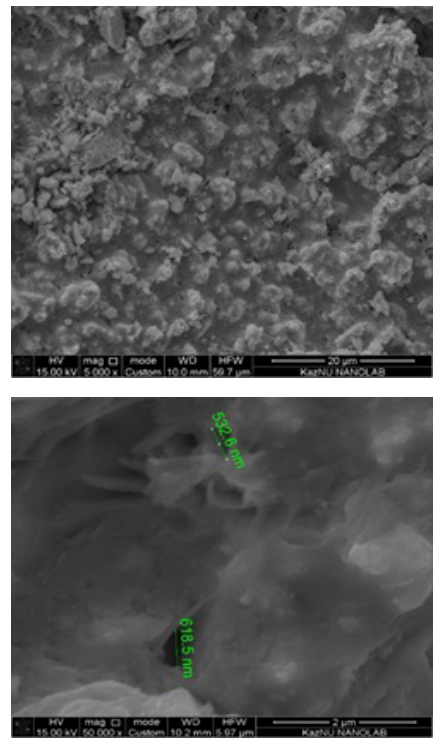

Fig. 5. SEM-images of the combustion products of the $BaCrO_4/TiB_2$ system

Element	Wt%	At%
CK	1.80	4.41
OK	33.23	61.17
SiK	0.48	0.51
BaL	11.43	2.45
TiK	33.08	20.34
VK	3.27	1.89
CrK	10.89	6.17
FeK	5.81	3.07

Fig. 6. Data on the semi-quantitative elemental composition of the burned samples.

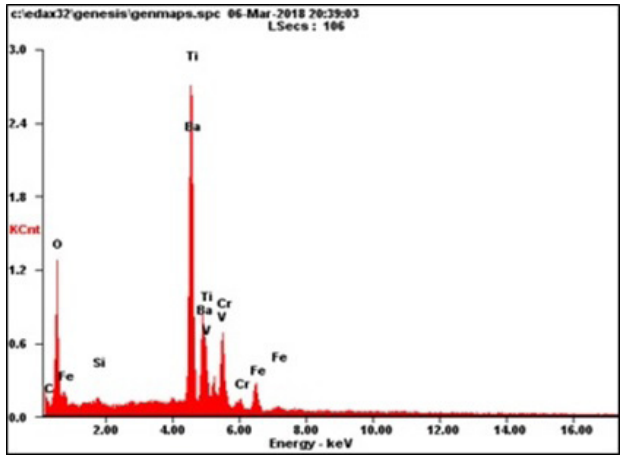

Fig.7. EDX analysis of products of the $BaCrO_4/TiB_2$ system combustion.

structures are formed because of the phase transformation [25, 26]. When the samples are burned, a micro-mesoporous structure is developed and the surface of the burned sample is characterized by roughness which can be explained by the appearance of pores and cracks.

Figs. 6 - 8 show data of the physico-chemical researches of the burnt samples. According to the EDX-microanalysis results, the combustion products consist mainly of oxygen (18.1 %), titanium (24.1 %), barium (21.8 %), chromium (6.2 %). They contain also some impurities (V - 3.27 %, Fe - 5.81 %, C - 1.80 %, Si - 0.48 %). According to the results of the X-ray phase analysis (Fig. 8), the combustion products of $BaCrO_4/TiB_2$ sample refer to TiB_2 - 40.3 %, $Ba_2(Cr_2Ti_4)O_{13}$ - 27.7 %, $Ba(TiO_3)$ - 22.1 %, $Ba(B_2O_4)$ - 6.7 %, SiO_2 - 3.1 %. Under the influence of the high temperatures, spinels are formed as products of the combustion process. Based on the presented analysis data, as a result of combustion of a slowly burning $BaCrO_4/TiB_2$ mixture, spinel-shaped crystalline structures are formed, sufficiently hard and difficult to grind.

CONCLUSIONS

A slow burning composition based on chromium, barium and titanium diboride with a burning rate of 1.26 mm/s has been developed. A linear dependence of the combustion rate on the inert gas pressure is observed. The insignificant weight loss allow us to assume that the combustion of the composition proceeds according

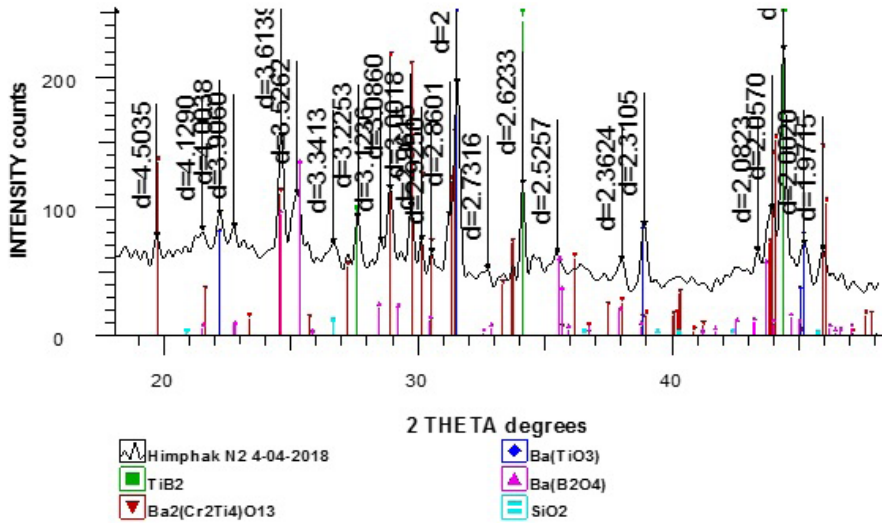

Fig. 8. The XRD pattern of the combustion products of the $BaCrO_4/TiB_2$ system.

to the "gas-free" mechanism and the composition can be used in sealed moderating devices. The composition can be used in sealed moderating devices. The developed composition is not sensitive to mechanical effects, it is safe in production and at all stages of circulation, has high physico-chemical stability and does not require special storage facilities.

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