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Combustion rate and response time of porous silicon-based ignition compositions

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The results of experimental studies to determine the combustion rate of ignition compositions based on two types of doped (boron or arsenic) porous silicon as a propellant with perchlorate oxidizers are presented.

Keywords: porous silicon, perchlorates, combustion rate, energy-saturated composite.

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The manufacturers of cartridges for civilian (hunting and sporting) firearms are faced with the task of engineering and introducing new environmentally friendly and efficient energy materials into their products. The first element of any firearm cartridge is a primer, which consists of a shell (cap) and an ignition composition (IC). Both in Russia and abroad, civilian primers are unified to the maximum extent with military models [1].

The formulation of an ignition composition, which is a mechanical mixture, normally includes a primary explosive (PE) and a pyrotechnic composition. The latter consists of an oxidizer, propellant, various inert additives, binders, and explosive additives (tetrazene, pentaerythritol tetranitrate) that enhance the sensitivity to impact and impression [1]. Mercury fulminate; lead styphnate; lead, cadmium, and silver azides; and other substances are used as PEs. The use of PEs is driven by one of the main requirements for ignition compositions: the need to maintain a response time within $20-40\,\mu$s [1]. The issue of enhancing the reliability (depending mainly on the sensitivity of the composition) and reducing the response time of a primer is also worth noting here. It has been proposed to solve this problem by improving the design of the primer itself [2].

It can be seen from the presented list of PEs that most of them are salts of heavy metals (mercury, lead, cadmium), which violate environmental safety requirements for production and operation, since these metals accumulate in ecosystems and living organisms and exert adverse effects on them. Moreover, the addition of a PE or pseudo-PE (lead styphnate) to the formulation of an ignition composition makes the process of production of a primer more complicated and reduces its safety.

A solution to these problems is the use of environmentally friendly compounds that do not contain or form toxic substances in the course of production and operation and provide a sensitivity on par with regular ICs. In addition, the response time of such environmentally friendly compositions should not exceed the response time of regular ICs. Note that two parallel research trends are pursued in the United States: the first is associated with the development of fundamentally new pyrotechnic compositions that do not require a PE, while the second involves the substitution of PEs with compounds intermediate between primary and high explosives that are free of the shortcomings inherent in a classical PE [3].

In the present case, the use of porous silicon powders, which are doped heavily with boron (KDB) or arsenic (KEM) to a concentration of $10^{19}\,\mathrm{cm}^{-3}$, as propellants with various oxidizers filling the nanosized propellant pores appears promising. The pore size and the wall thickness of porous silicon (*por*-Si) are such that the resulting energy-saturated composite (ESC) (*por*-Si + oxidizer) is similar to an individual energy-saturated material in which the propellant and oxidizer reside in the same molecule.

Since the response time of an IC (with the geometric parameters and the primer cap material being the same) is specified by its combustion rate, it appears relevant to determine this parameter for the most common *por*-Si + oxidizer compositions. This is exactly the aim of the present study.

The combustion rate was determined for the following energy-saturated composites: (1) KDB + sodium perchlorate (SPC) ($NaClO_4$), component masses: KDB — 10 mg, $NaClO_4$ — 10 mg; (2) KEM + calcium perchlorate (CPC) ($Ca(ClO_4)_2$), component masses: KEM — 10 mg, $Ca(ClO_4)_2$ — 5 mg; (3) KDB + barium perchlorate (BPC) ($Ba(ClO_4)_2$): KDB — 10 mg, BPC — 10 mg; and (4) KDB + ammonium dinitramide (ADN) ($NH_4N(NO_2)_2$): KDB — 10 mg, ADN — 10 mg. Thus, the propellant mass was equal to the mass of the oxidizer. The exception is the KEM+CPC composition, where the propellant mass is 2 times greater than the oxidizer mass (i.e., the composition is deficient in oxidizer). In most cases, an excess amount of oxidizer is used [4].

The method for producing porous silicon powders and their characteristics were detailed in [5], while the method

Values of the parameters of an explosive ESC transformation

№	Energy-saturated composite	*por*-Si/oxidizer, mg/mg	Response time, μs	Combustion rate, m/s
1	KDB+SPC	10/10	13.4	75
2		10/10	11.0	90
3		10/10	12.0	83
4	KEM+CPC	10/5	8 ± 2	120 ± 30
5	KDB+ADN	10/10	6.4	156
6	KDB+BPC	10/10	14 ± 3	70 ± 20

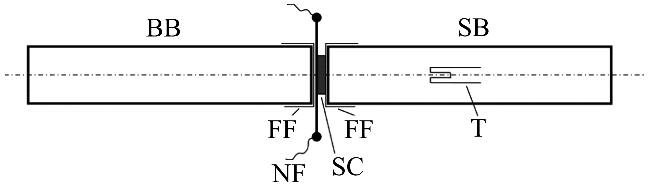

Figure 1. Schematic image of the sample secured between two measuring bars of the tension sensor. SB — measuring bar with tension sensor T ($d = 8$ mm), BB — bearing bar ($d = 8$ mm), SC — sample, FF — fluoropolymer film with a thickness of $100\,\mu$m, and NF — nickel-chromium foil (thermal initiator).

for ESC (*por*-Si + oxidizer) production was discussed in [6].

The obtained ignition compositions were pressed under a pressure of 100 MPa to a height of 1.0 mm (the height of pressed regular ICs in a primer is $\leqslant 1$ mm) into aluminum caps 8 mm in diameter and 1.5 mm in height.

Tests were carried out using an experimental setup that implements the Kolsky method with a split Hopkinson bar [7]. The experimental setup is a system of two bars made of high-strength steel. A tension sensor is glued to one of them, and data on the bar deformation is read out from this sensor (Fig. 1). These data allow one to determine the pressure of an explosive ESC transformation (in the present case, combustion) products and the response time. The pressure amplitude ($p_{\max}$) was calculated based on the amplitude of mechanical stresses accompanying the deformation wave in the bar induced by an explosive transformation:

$$p_{\max} = \sigma = \frac{\Delta U E S_1}{I R_0 k S_0},$$

where ΔU is the voltage pulse in the oscilloscope record, $I = 15$ mA is the current in tension sensors, $R_0 = 200\,\Omega$ is the resistance of tension meters, $E = 200$ GPa is the Young's modulus of the material of measuring and bearing bars (soft steels), $k = 2$ is the coefficient of tensosensitivity, S_1 is the cross-section area of the measuring bar, and S_0 is the area of the end sample surface.

The response time of the energy composition in the cap was determined using the oscilloscope time base. The combustion rate was calculated as the IC height divided by the response time.

Typical (processed) signals from the tension sensor visualized by the oscilloscope are shown in Fig. 2. The table presents the data obtained by processing the oscilloscope records.

Having analyzed these data, we determined the following.

1. The response times of all the investigated ignition compositions with a sample thickness of 1 mm are significantly shorter than those of regular ignition compositions (20–40 μs) (see above). The KDB+ADN composition has the shortest response time (and, consequently, the highest combustion rate): it is almost 2 times shorter than that of the other studied compositions.

2. The obtained combustion rates of the studied ICs are several orders of magnitude higher than the combustion rates of fast-burning PEs ($\sim$ tens and hundreds of mm/s) [8].

3. Although the KEM+CPC composition is deficient in oxidizer, it has a low response time (at the level of the KDB+ADN composition) and a high combustion rate, which may be indicative of fine oxidizing characteristics of calcium perchlorate and higher energy parameters of porous silicon doped with arsenic.

Thus, it may be concluded that porous silicon-based ignition compositions have a clear potential for application in modern and advanced firearms.

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Conflict of interest

The authors declare that they have no conflict of interest.

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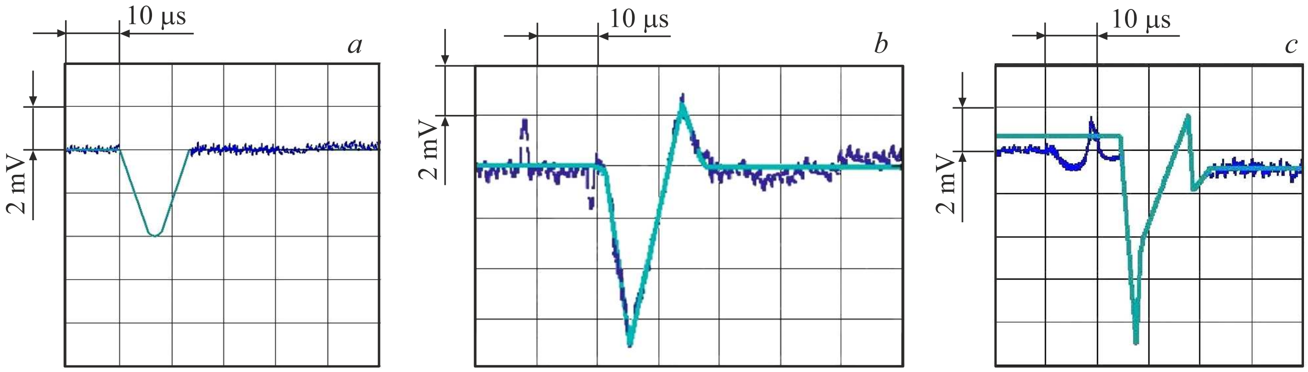

Figure 2. Processed oscilloscope records of deformation pulses in measuring bars. *a* — KDB+$NaClO_4$, *b* — KEM + $Ca(ClO_4)_2$, and *c* — KDB+$NH_4N(NO_2)_2$.

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