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Research of the combustion of gas-generating compositions with additives of carbon powders

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ABSTRACT

Carbon materials obtained from secondary plant raw materials are widely used in various industries, where they are applied as catalysts, adsorbents and in pyrotechnics for creating gas-forming systems. In this work, activated carbon of two types– obtained from the walnut shell and as a product of utilization of gas adsorbents was used. The combustion of a three-component mixture of sodium nitrate, magnesium, and carbon obtained by carbonization of a walnut shell or by grinding gas mask elements was studied. It was found that at a low carbon content, the combustion of the mixture occurs at a high rate in a convective mode. As the working composition, a mixture with a component ratio of 60% – $NaNO_3$, 20% – Mg, 20% – C was chosen, which is characterized by rather high values of gas productivity. The burning rate of a composition based on carbon from walnut is about two times higher than in the case of carbon from a gas mask, and the flame temperature is higher by about 500 K. X-ray phase analysis of solid combustion products showed that the main products are magnesium oxide and sodium carbonate. The presence of a partially unreacted initial oxidant of sodium nitrate has also been found, and its content in combustion products of a carbon-based incendiary composition from a gas mask is higher than in the case of combustion of a mixture based on carbon obtained from a walnut shell. This can probably be explained by the fact that gaseous products are released during combustion, and this leads to partial dispersion of the initial components in the combustion wave, which is more pronounced when using carbon obtained from a gas mask. As a result of the research the prospect of using such a mixture in gas generator cartridges is shown.

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1. Introduction

In order to reduce the high-explosive impact during blasting, various methods and means are used, such as loosening charges with a low specific consumption of explosives, designs of soft loading charges with air, water gaps and gaps filled with compact media. In the process of extracting piece stone and destroying concrete and brick buildings in dense urban development, the issue of safety and efficiency of work is very important. An increase in the destruction efficiency for obtaining transportable pieces is accompanied by an increase in the number and range of small fragments, as well as an increase in the intensity of seismic and explosive waves and air shock waves [1–4].

Currently, when extracting block stone, substances that can create pressure in the hole due to the combustion reaction in deflagration mode are used [5–11]. Nonex gas-generating cartridges are known as non-detonating pyrotechnic devices for destroying rocks and artificial barriers. In these compositions, ammonium nitrate is used as an oxidizer in a mixture with smokeless gunpowder. Such charges operate in deflagration mode, do not create shock waves and crushing. One requirement for gasifier compositions is a high

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combustion rate. Nitrocellulose powder as well as high nitrogen explosives such as ammonium nitrate, guanidine nitrate and nitroguanidine is often used to generate gases. The predominant use of ammonium nitrate in gas-generating compositions is due, in particular, to the fact that it is a cheap and non-deficit product and does not give solid substances during combustion [12–19]. Traditional pyrotechnic compositions containing compounds of lead, mercury, barium and cadmium are sources of pollution [20–29]. In the early 60 s, gas-generating compositions based on ammonium perchlorate were developed in the USA. In addition to NH_4ClO_4, they contained dihydroxylglyoxime $C_2H_4O_4N_2$, polyester resins and polymerization catalysts. A mixture containing 74% $NHClO_4$ and 26% organic matter had a density of 1.63 g/cm^3 and a combustion temperature of 1,230 °C. At 70 kgf/cm^2, it burned at a speed of 2.7 mm/s. Dihydroxylglyoxime $(C(OH) = NO–H)_2$ has a heat of formation of 136 kcal/mol (570 kJ/mol), it is slightly soluble in water and not hygroscopic. One of the main ways to make pyrotechnics more environmentally friendly is to exclude the components of heavy metals present in traditional pyrotechnic compositions. It is believed that green pyrotechnics for military or civilian use should avoid the use of heavy metals and perchlorates [30–34].

The method of activation of charcoal was developed in 1916 by the Russian scientist T. E. Lovitz. In the same year, a gas mask based on activated carbon was developed. Activated carbon as an adsorbent is used not only in gas masks, but also for air purification at industrial enterprises, for clarification of various solutions. The high adsorption capacity of activated carbon is explained by a highly developed surface. The total surface of the pores present in 1 g of such coal is from 300 to 1000 m2. Such a huge area causes the appearance of a large excess of surface energy at the coal-gas interface. Due to free surface energy, gas adsorption occurs, i.e. increasing its concentration in the surface layer of coal while reducing the concentration of impurity gas in the surrounding space [35–45].

Due to some shortcomings of activated carbon, the Kazakhstan Emergency Committee is forced to utilize up to 30 thousand tons of carbon from gas masks every year. The products of this disposal in the form of carbon granules can be used to create gas-generating compositions [37].

Starting from the last century, for use as a gas-generating composition, a two-component $NaNO_3$/Mg mixture was studied in detail experimentally in different ratios of components and conditions. However, studies on the combustion of the ternary composition of $NaNO_3$/Mg/C are practically absent in the literature.

Currently, carbon materials derived from recycled plant materials are widely used in various industries where they are used as catalysts and adsorbents. These materials can find application in pyrotechnics when creating gas-generating systems [36–38,44]. To obtain carbon, the walnut shell is crushed and sieved from a sieve crushed by a working fraction with a diameter of 2–4 mm. The chemical activation of the samples of Greek walnut was impregnated with 80% phosphoric acid of walnut in various proportions and dried at 160 °C for 12 h in a muffle furnace. The resulting mixture was subjected to pyrolysis in a beaker placed in a muffle furnace at 500 °C. Charred walnuts are washed by boiling in distilled water to a neutral pH. At the carbonization stage, the framework of the future active carbon is formed – primary porosity and strength. Walnut carbon preparation techniques are described in detail in [40].

This research aims to investigate the effect of carbon powders of different nature on the combustion of sodium nitrate and magnesium nitrate-based gasifier compositions. Thermodynamic analysis of gasification processes of multicomponent compositions using universal program of calculation of heterogeneous TERRA systems [8,36] used for high-temperature processes was carried out beforehand.

2. Materials and methods

To prepare the initial mixtures of $NaNO_3$ + Mg + C, technical sodium nitrate powder (State Standard 19906–74), magnesium (Mg) powders and carbon particles from a gas mask and walnut shell were used. Granulometric analysis of fractions was performed using a projection microscope and a semi-automatic 24-channel counting device. Either the entire fraction or a sample taken by quartering was used as the preparation.

In this research, activated carbon of two types was used – obtained from the walnut shell and in the form of a product for the utilization of gas mask adsorbents. Samples of carbon were crushed and scattered on sieves; fraction 100–200 μm was mainly used in experiments. Ready-to-burn mixtures were placed in paper tubes. The mass of the sample was 4.0 g; the bulk density of the samples was in the range 0.8–0.9 g/cm^3. The combustion process was recorded by a video camera with a frequency of 300 frames/sec. For processing the video-file the program Virtual Dub was used.

Samples for burning in air were prepared from powdered components. The components were weighed on an Sartogosm MV 210-A electronic balance and manually mixed in a porcelain mortar. The cumulative particle size distribution function of the starting components in the size range from 10 μm to the maximum was constructed using an original computer program developed at the Institute of Chemical Kinetics and Combustion of the Siberian Branch of the Russian Academy of Sciences. The results of processing measurements for particles of magnesium, sodium nitrate and carbon from a gas mask are shown in Fig. 1.

The burning rate of the compositions was measured by the method of blown wires. To measure the burning rate of the compositions, samples were prepared with a diameter of 13 mm and a height of 25 mm. The components were thoroughly mixed and poured into a paper sleeve. The minimum compaction was ensured by tapping the liner, while the relative density of the mixture equal to 0.55 was achieved. The experiments were carried out at atmospheric pressure in the open air.

Combustion was initiated by the flame of a gas burner from the upper open end of the paper sleeve onto which a pyrotechnic spread consisting of ammonium perchlorate and a combustible bundle of hydroxyl terminated polybutadiene was placed. To measure the temperature in the combustion wave, tungsten-rhenium thermocouples (BP5/BP20) with a diameter of 100 μm, fixed in the sample at a fixed distance from each other, were used, which provided additional information on the burning rate. Thermocouple signals were fed to the LA-2USB-14 analog-to-digital converter and then to a computer.

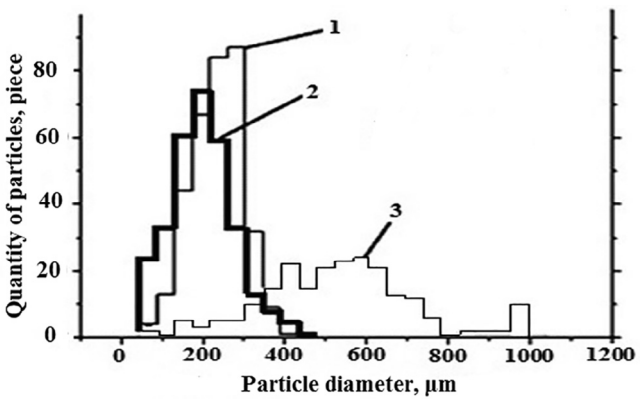

Fig. 1. Estimated histograms of particle size distribution; 1-carbon from a gas mask, 2-magnesium, 3 – sodium nitrate.

The composition of the reaction mixtures and combustion products was investigated using XRD. X-ray diffraction patterns were recorded on a DRON-4.0 diffractometer in CuK_{α} radiation.

Thermodynamic calculations were performed at a pressure of 0.1 MPa using the TERRA program, which was improved and designed for computer operation. The TERRA program is based on the principle of maximum entropy, has an extensive database of thermodynamic properties of substances and allows you to get complete information of thermodynamic analysis. The program is characterized by high speed and ease of use. To enter the TERRA program, the initial composition of raw materials in molar fractions, the pressure P = 0.1 MPa and the enthalpy of initial formation are set.

3. Results and discussion

To find the optimal ratio between the oxidizer ($NaNO_3$) and the fuel (Mg + C), comparative calculations of the equilibrium thermodynamic characteristics of this composition were performed. The results of thermodynamic calculation of parameters of different compositions are given in Table 1. The adiabatic temperature T, the gas constant R, the gas-productivity V and the efficiency of the combustion products RT are given.

Preliminary experiments showed that, at a low carbon content, the mixture burns at a high rate in the convective mode. Uniform flame propagation was recorded in a 60/20/20 combustion wave. Accordingly, a composition with a ratio of components of 60%-$NaNO_3$, 20%-Mg, and 20%-C was selected as the working composition. It differs in rather high values of gas productivity and parameter RT, which is proportional to the working capacity of the mixture.

The investigated compounds:

Composition No. 1: 60% $NaNO_3$ technical, 20% Mg MPF-3, 20% C from gas mask.

Composition No. 2: 60% $NaNO_3$ technical, 20% Mg MPF-3, 20% C walnut.

By the method of blown wires, the burning rates of gas-generating compositions No. 1 and No. 2 were determined (Table 2).

As can be seen from Table 2, the burning rate of the composition based on carbon from walnut is approximately twice as high as in the case of carbon from a gas mask. This fact can be explained by the large specific surface area and higher reactivity of walnut carbon.

Temperature measurements in the gas phase above the sample surface were carried out using a tungsten – rhenium thermocouple installed at a height of 1 cm from the sample; the experiment was repeated 3–4 times.

Figs. 2 and 3 show temperature records in a flame of 60% -$NaNO_3$, 20% – Mg, 20% – C with a variable carbon type.

The initial segment in the thermograms corresponds to ignition and combustion of the igniter composition. In the case of mixtures with carbon from a gas mask, the temperature in the flame reaches ~1400 K. This is approximately 500 K below the thermodynamic calculation. In the case of carbon from walnut, the temperature in the flame is close to thermodynamically calculated. Apparently, in the latter case, the completeness of combustion in the gas phase is higher and this is due to the larger specific surface area and higher reactivity of walnut carbon. The unevenness of the temperature curve can be explained by the fact that the mixture was coarse-grained and bulk density.

The results of the X-ray phase analysis of the condensed combustion products of mixtures 60% – $NaNO_3$, 20% – Mg, 20% – C, containing carbon from a gas mask and walnut, are shown in Figs. 4 and 5, respectively.

Table 2
Burning rate of gas-generating compositions.

Compositions	h_{sleeve}, mm	d_{sleeve}, mm	$V_{burning}$, mm/sec.
Composition No. 1	10.0	13.0	1.7 – 2.1
Composition No. 2	10.0	13.0	4.0 – 5.0

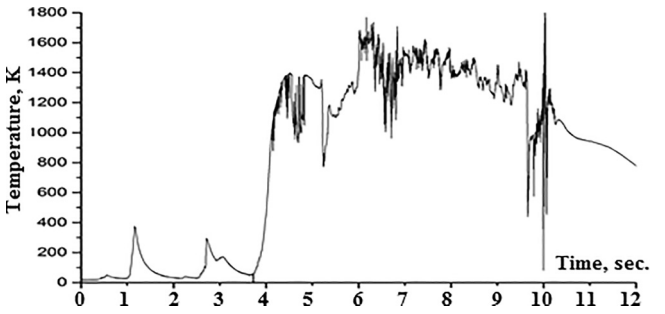

Fig. 2. The temperature in the flame of the composition 60% -NaNO3, 20% – Mg, 20% – C, carbon 100–200 μm from the gas mask.

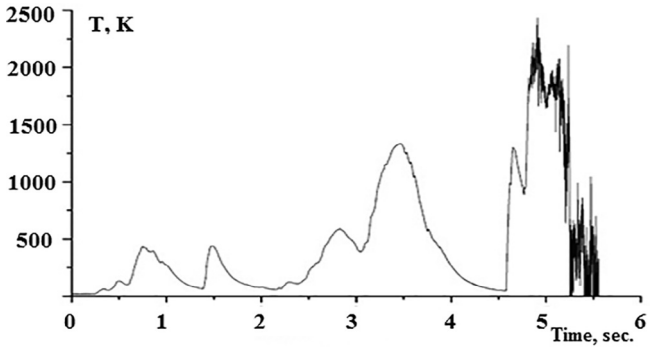

Fig. 3. The temperature in the flame of the composition 60% -$NaNO_3$, 20% – Mg, 20% – C, carbon 100–200 μm from walnut.

According to XRD data, the main phases in the combustion products of the test mixture are magnesium oxide and sodium carbonate. However, partially unreacted initial oxidizing agent sodium nitrate is also recorded, and its content in the combustion products of a carbon-based composition from a gas mask is higher than in the case of a carbon-based composition from walnut. This is because gaseous products are released during the combustion process, which leads to partial dispersion of the starting components in the combustion wave, most pronounced in the case of carbon from a gas mask.

4. Conclusion

The aim of this work was to study the effect of carbon powders of various nature on the combustion of gas-generating compositions based on sodium and magnesium nitrate. Tests for the flammability of mixtures and thermodynamic calculations of the combustion parameters to determine the optimal ratio of the starting components in case of three components mixture ($NaNO_3$/Mg/C) were performed. Carbon was produced from the walnut shell or by grinding gas mask. Thermodynamic calculations of the combustion of the mixture with different contents of the components were carried out. Sufficiently high performance and uniformity of combustion are observed when the ratio of the starting components is 60% – $NaNO_3$, 20% – Mg, 20% – C. It is characteristic that the

Table 1
Thermodynamic calculation of the composition at different ratios of the components ($NaNO_3$ /Mg/C).

Parameters	90/10 without carbon	85/10/5	80/10/10	75/10/15	70/15/15	65/20/15	60/20/20
T, K	1634	2033	2254	2682	2857	2924	1954
V, m^3/kg	2.27	3.62	4.9	5.96	6.22	6.3	4.8
R, J/ (kg·K)	268.59	276.55	260.8	265.6	281.07	294.04	314.43
RT, J/kg	438 874	562 232	587,843	712,339	803,020	859,987	614,705

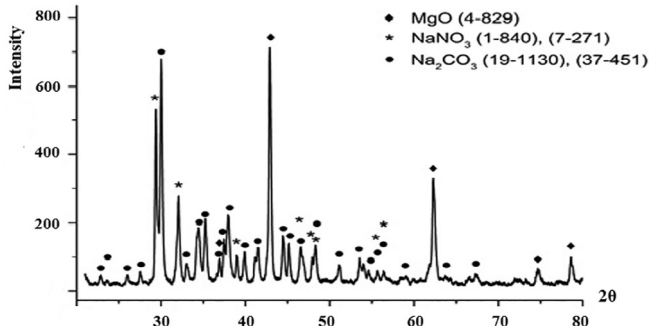

Fig. 4. The results of the XRD of combustion products with composition 60/20/20 (carbon from gas mask).

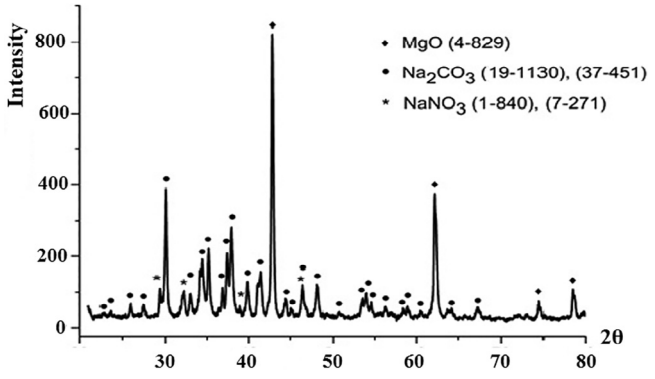

Fig. 5. The results of XRD of the products of combustion with the composition 60/20/20 (carbon from walnut).

burning rate of a composition based on carbon from a walnut is approximately twice as high as in the case of carbon from a gas mask, and the flame temperature is higher by approximately 500 K. According to X-ray phase analysis of solid combustion products the main products are magnesium oxide and sodium carbonate. It was concluded that the developed gas-generating compositions based on sodium, magnesium and carbon nitrate can be recommended for use in open-pit mining for cracking block stone in a gentle mode or for breaking hard mineral rocks.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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