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Development of pyrotechnic delay mixtures based on a composite material hardened with carbon nanotubes

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This work is devoted to the development of pyrotechnic delay mixtures from a titanium matrix reinforced with carbon nanotubes using a combination of preliminary mechanical activation and thermal explosion. The phase and structural transformations of the Ti-CNTs mixtures were analyzed by microscopy and X-ray diffraction. The combustion temperature is practically independent of pressure, it remains constant over the entire range of argon pressure. These delay compositions are not sensitive to different mechanical influences. It is proved that certain amount of CNTs added to delay composition can increase delay precision and further doing so achieved less temperature dependence. The retardant compositions $BaCrO_4$ + Ti / CNT containing carbon nanotubes have the improved characteristics of the retardant composition, such as delay accuracy, combustion stability. The developed retarding compositions are safe in production and at all stages of circulation.

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1. Introduction

In recent years, much attention has been paid to the development of new modified energy-intensive compositions that can be used to solve practical problems. Energy-intensive compositions are widely used in the mining industry, in the military, in the field of pyroautomatics, as well as in the national economy (in agriculture, industry, etc.) [1-7]. Among the variety of energy-intensive compositions, delay pyrotechnic compositions are of great interest, which serves to create time delays of the required duration [8-12]. The need to ensure a time delay in the operation of pyrotechnic products arose with the appearance of black powder and the first powder bombs, hand grenades and rockets. The delay was necessary to have time to move away to a safe distance, to detonate the charge at the right moment. Pyrotechnic retarding compositions are thermal sources and are widely used as a heat source during welding and soldering, to maintain the required elevated temperature for a given interval and as a means to increase the safety of industrial explosions. The greatest practical interest is represented by small-gas delay compositions, which provide a lower dependence of the burning rate on external pressure because very few gaseous combustion products are released during the combustion of these compositions and an accurate time delay [13-15].

The unique properties of carbon nanotubes make it possible to use them in various branches of science and technology [16]. Modification of materials with carbon nanotubes opens up new areas of their application. With the introduction of carbon nanomaterials, the properties of substances and products made from them change significantly. These properties allow them to be used in various industries, including pyrotechnics [17]. To date, there is little research on the use of carbon nanotubes in pyrotechnic mixtures [18]. At present, the efforts of scientists are mainly

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directed to the development of composite materials hardened with carbon nanotubes. Of great interest is the introduction of carbon nanotubes (CNTs) into metal matrices [19-23].

One of the most promising materials of the metal matrix is Ti and its alloys. The high specific strength of Ti and its alloys allows them to be used as technical materials with low weight and high strength in the industry. To improve the mechanical and physical properties of Ti and obtain new promising composite materials based on it, carbon nanotubes are added to the titanium matrix.

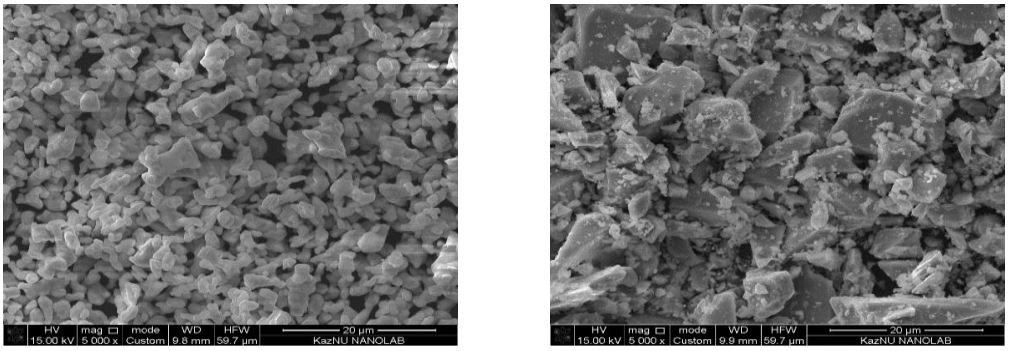
The use of a composite material made of Ti matrices hardened with carbon nanotubes in retarding compositions is still unknown. High mechanical and anticorrosive properties, as well as a significant strength, make titanium a very valuable structural metal, thanks to which it quickly gained great importance in modern technology. The bulk of titanium is consumed by the military industry. Pyrotechnics use the ability of titanium to ignite [24].

The aim of this work was creation of new low-gas delay compositions, the combustion of which does not depend on pressure and temperature; development of $BaCrO_4$ + Ti / CNT delay compositions containing carbon nanotubes that have been added to improve the performance of retardant mixtures.

2. Experimental

The following substances were used to prepare the initial reaction mixtures and perform the experimental study: barium chromate (TC 4211-75, 99.2% $BaCrO_4$); titanium (marks PTOM-2, 98.50% Ti), and carbon nanotubes of the MCNT-3 mark.

Figure 1 (a, b) shows micrographs of the initial powders of barium chromate and titanium diboride.



(a) *(b)*

Fig. 1. SEM images of the initial components: a– $BaCrO_4$; b – TiB_2.

Carbon nanotubes of the MCNT-3 mark with an average diameter of 19 nm and purity greater than 95.0 %, a specific surface area of 115 m^2/g, and the length of the nanotubes varies between 5-25 microns were used.

The method of preparation of incineration samples and investigation of the macrokinetic characteristics of the compositions consisted of the following operations: 1) weighing; 2) dry mixing of the oxidizer and fuel manually; 3) mixing with the binder component; 4) pressing in a hydraulic mold; 5) drying. Electronic scales "Sartogosm" MV 210-A were used for weighing.

Mechanical activation of the reaction mixtures was carried out in a water – cooled planetary ball mill AGO-2, with a volume of each of the two steel drums of the mill of 160 cm^3. The mass of the balls in each drum is 200 grams, the diameter of the balls is 8 mm, the mass of the sample is 10 g. The centrifugal acceleration of the balls is 400 m/s^{-2} (40 g). To prevent oxidation during mechanical activation, the sample drums were filled with an inert argon gas. After mechanical activation, the mechanically activated samples were unloaded from the drums in a box with an argon atmosphere. The time of mechanical activation varied within 1-11 minutes.

The method of preparation of initial mixtures of CNT with titanium was as follows: carbon nanotubes were treated in alcohol for 10 minutes in an ultrasonic low-frequency dispersant UZDN-1U4.2. A specified amount of titanium powder was added to the resulting alcohol suspension, and then the sample was dried in an oven at 40ºC for 1 h. After that, to increase the homogeneity of the mixture, the sample was ground in a porcelain mortar. The resulting mixture of initial reagents underwent mechanical activation. The resulting mechanically activated Ti / CNT mixture was used as a fuel of a pyrotechnic delay composition and was mixed with a certain amount of $BaCrO_4$. The developed Ti/CNT/$BaCrO_4$ delay compound was prepared by the traditional method of making pyrotechnic compositions, which includes weighing, mixing, pressing, etc.

Scanning electron microscopy TM-1000, S-3400 N (Hitachi), Carl Zeiss EVO50 XVP (X-Act) were used for research. X-ray diffraction patterns were obtained using a DRON-4.0 diffractometer and D 8 ADVANCE (Bruker) using CuKα radiation and a Lynx – Eye single-axis detector with a nickel filter.

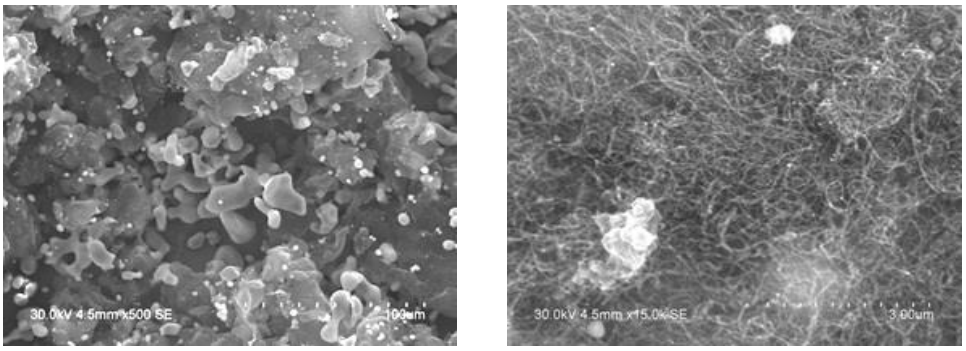
Experiments to study the combustion process of samples were carried out in a 3.3 L constant pressure bomb in an argon atmosphere. Pressed samples were used for research. The experiments were carried out in the pressure range of 1-4 atm. For determination of the burning rate, the samples were pressed in a cylindrical mold with a diameter of 10 mm and a height of 8-10 mm using a hydraulic press tool YES Series Compression Testing Machine in several pressings to achieve a uniform charge density. The samples were initiated using a nichrome spiral. The burning temperature was measured with a Raytek 3i1m pyrometer.

3. Results and discussion

3.1. Determination of the physicochemical properties of mixtures

It is known that during machining in planetary mills, the microstructure and morphology of the initial reagents significantly change. In mixtures of brittle substances, grinding occurs, and in mixtures of plastic metals, or mixtures with amorphous carbon or boron, the formation of mechanocomposites occurs. These are, as a rule, rather large formations with sizes from tens to hundreds of microns, and in some compositions even larger, up to millimeter sizes. However, the grain size of the initial components in these composites decreases to nanometer values.

Figure 2 shows micrographs of a mixture of the initial components of titanium powder and carbon nanotubes, obtained by the above-described method. In the initial mixture, the particles have different shapes and sizes (Fig.2a), on the surface, we can see round-shaped titanium crystals and lamellar structures, carbon nanotubes after pre-mixing cover the titanium powder particles (Fig.2b).

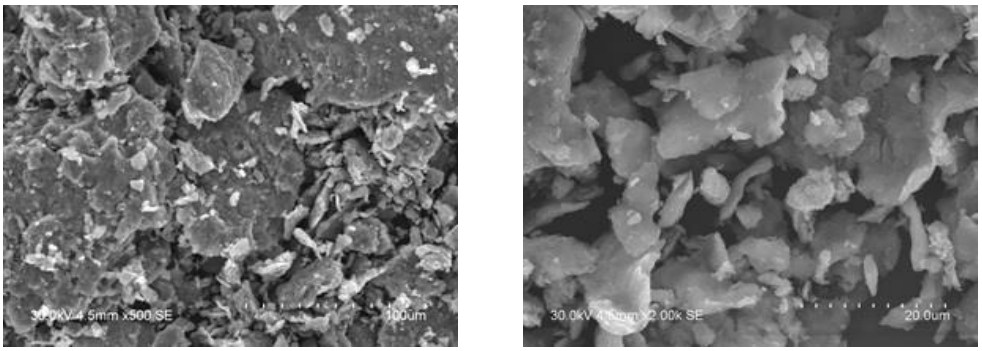


(a) *(b)*

Fig. 2. Micrographs of the initial mixture: a – Ti + 4% CNT; b – the surface of an individual titanium particle.

As a result of studying the changes in the morphology of samples after mechanical activation (MA), it was found that already after 2 min. MA, mechanocomposites of various sizes

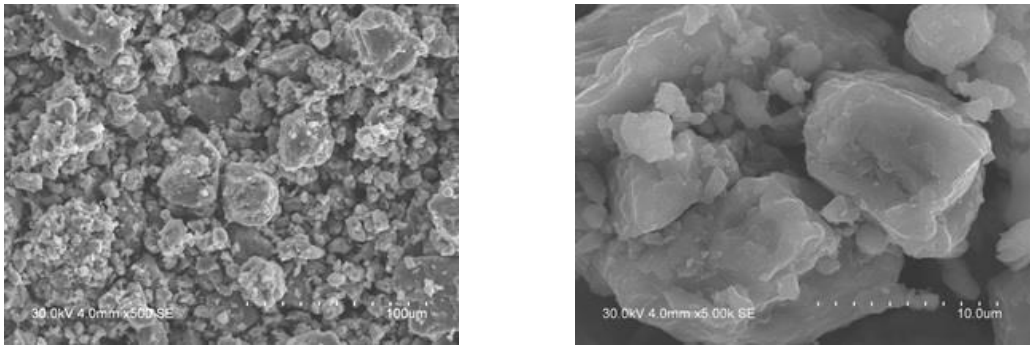
of irregular shapes are formed (Fig.3 a), some of which have a plate shape. After 2 min. MA, there are no carbon nanotubes on the surface of titanium particles, which confirms their integration into the titanium matrix (Fig.3 b).



(a) *(b)*

Fig. 3. Micrographs of a Ti + 4% CNT sample after 2 min. MA: a – Ti + 4% CNT; b – the surface of an individual titanium particle.

As the duration of mechanical activation increases, larger mechanocomposites acquire a rounded shape, and at 4-5 min. MA, the formation of loose agglomerates begins from smaller ones. Subsequently, the number of such agglomerates increases, and their density increases. Figure 4 shows photographs of mechanocomposites formed after 8 min MA.



(a) *(b)*

Fig. 4. Micrographs of a Ti + 4% CNT sample after 8 min. MA: a – Ti + 4% CNT; b – the surface of an individual titanium particle.

Using X-Ray phase analysis, the phase composition of the mechanically activated mixture was determined (Fig.5-7).

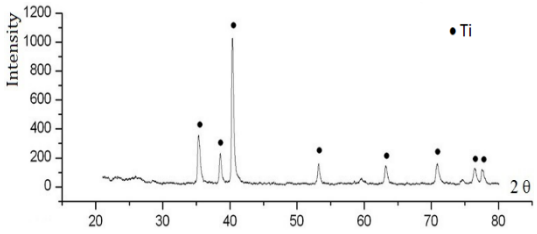


Fig. 5. X-ray diffraction pattern of the initial mixture without MA.

The results of X-ray phase analysis showed that after 2 min. of MA, in addition to titanium lines, the X-ray diffraction pattern also contains weak TiC lines (Fig.6). This indicates that the process of partial formation of the primary products of the interaction of CNTs with titanium begins already in the drums of the mill. With a further increase in the MA time, the intensity and width of the TiC lines also increase. As the duration of the MA increases, the intensity and width of these lines increases. It is seen that, after 4 min. MA, more intense TiC lines appear on the X-ray diffraction pattern. After 8 min. MA, X-ray diffraction patterns show abnormally wide lines of titanium and TiC (Fig.7).

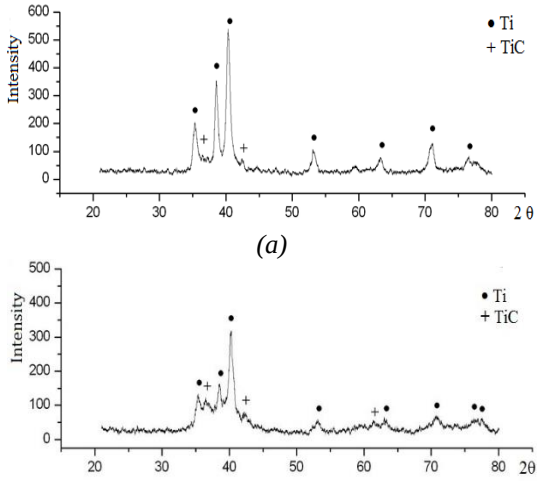


Figure 6. X-ray diffraction pattern of the mixture of Ti/ CNT after MA of different duration: 2 min (a), 4 min. (b).

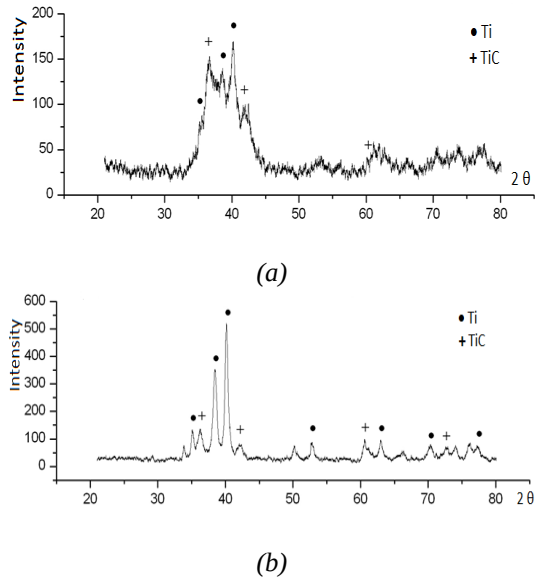


Fig. 7. X-ray diffraction pattern of a sample of the composition Ti + 4 wt. % CNTs after 8 min. MA.

So microscopic and X-ray phase studies have made it possible to establish that during MA activation, carbon nanotubes are evenly dispersed inside the titanium powder and titanium carbide is partially formed.

To illustrate the rate of dispersion of titanium during MA, Fig. 8 shows a graph of the dependence of the sizes of the coherent scattering regions (OCR) of titanium on the time of MA in the samples of the studied composition. It can be seen that the greatest decrease in CSR values is observed already at the earliest stages of activation (at 1 - 3 min. MA). With an increase in the activation time to 9 min, the CSR values of titanium decrease to ≈ 15 nm.

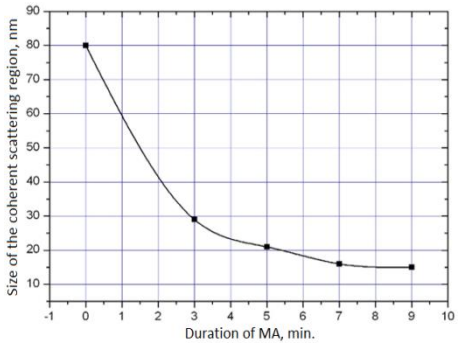


Fig. 8. Dependence of the value of the coherent scattering region of titanium on the MA duration of the Ti / CNT mixture.

3.2. Development of pyrotechnic delay compositions

At the next stage of our work, we developed a delay compound based on Ti / CNT and $BaCrO_4$. As a promising fuel in slow-burning pyrotechnic compositions, the powders of refractory metals and their compounds [25-29] were added in the composites. Such components can interact with the melt of oxidizing agents at high temperatures and do not form gaseous products during oxidation. Thus to improve the precision of delay, reliability, and stability of combustion of the carbon nanotubes titanium was added to the delay composition. When carbon nanotubes with high thermal conductivity are added to the delay compound, the delay accuracy increases, so the delay accuracy will be higher than that of the delay mixture without carbon nanotubes.

Four experimental samples were made, and the ratio of oxidizer and fuel was varied (Table 1).

Table 1. The ratio of the components of the delay composition $BaCrO_4$ - TiB_2 - $C_6H_8N_2O_9$.

Components	Mass., %			
	I	II	III	IV
$BaCrO_4$	50.00	60.00	65.00	70.00
TiB_2	46.00	36.00	31.00	26.00
$C_6H_8N_2O_9$	4.00	4.00	4.00	4.00

Thermogravimetric analysis was used to study the mechanism of thermal degradation of $BaCrO_4$-Ti / CNT (Fig. 9).

As can be seen from the Fig. 9, the phase transformation curve assumes the destruction of the binder at 100ºC. Further $T_{max.}$ = 500 ºC, it is known that the maximum of the differential mass loss curve corresponds to the maximum speed of any process occurring under the influence of temperature, and is equal to 50% wt. loss.

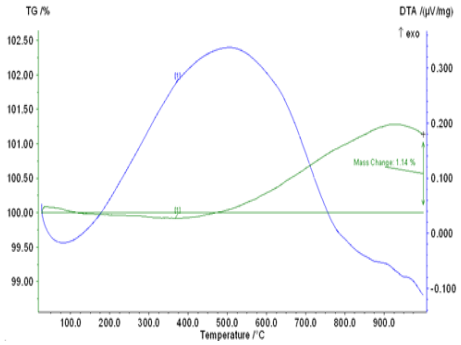


Fig. 9. Thermal analysis of the delay composition $BaCrO_4$-Ti/CNT.

With an increase in temperature to 500ºC, an exothermic reaction is observed, characterized by the occurrence of surface chemical reactions, at a temperature of 540ºC, barium chromate decomposes with an endothermic effect:

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

Mass loss is observed in the $BaCrO_4$-Ti / CNT composition; when heated to 1000ºC, the sample weight increases. The change in mass by 1.14% is possibly associated with the oxidation of combustible elements with oxygen released during the decomposition of barium chromate:

$$Ti+O_2 = TiO_2 \quad (2)$$

When titanium carbide is heated to 600ºC, it becomes incandescent and burns to form titanium and carbon dioxides [30]:

$$TiC+ 2O_2 = TiO_2 + CO_2 + 275.05 \text{ kcal} \quad (3)$$

The oxidation of titanium carbide has been extensively studied. Mainly powdered samples were subjected to oxidation. Various considerations were expressed about the mechanism of the interaction of TiC with oxygen, both in the scale composition and its protective properties [31-33].

Based on the above analysis, we present the total reaction of the combustion of the delay composition:

$$4BaCrO_4+Ti+TiC = 4BaO+2Cr_2O_3+2TiO_2+CO_2 \quad (4)$$

From the above calculation, the stoichiometric mixture of $BaCrO_4$ and Ti / CNT is the ratio of 90.3% of the mass. barium chromate and 9.7% of the mass. respectively Ti / CNT mixtures.

It was calculated the mass loss coefficient: $k_m = 0.07$. It was found that the changes in the crystal structures of reagents due to high temperatures lead to a loss of sample mass. The sample burned in argon almost does not change its shape.

The sensitivity of a mixture is a measure of the response of a mixture to external influences and is used to determine the energy required to initiate a delay mixture.

We have carried out experimental work to study the sensitivity of the developed delay compositions to mechanical influences, to impact with sliding on the failing weight apparatus.

Based on experimental results, it is shown that the developed delay compositions based on $BaCrO_4$+Ti/CNTs are not sensitive to mechanical influences: to friction on the pendulum, to impact, to impact with sliding. An important factor in the development of a delay mixture is their stability, which is a measure of the stability of the substance at elevated temperatures. Table 2 shows the results of the experimental work.

Table 2. Stability of the moderating composition $BaCrO_4$ + Ti / CNT.

Parameter	Before storage	After storage in during		
		1 week	2 week	4 week
Rated burning time, s				
Average value	4.82	4.98	4.88	4.70
Maximum value	5.26	5.91	5.88	5.20
Minimum value	4.48	4.89	4.60	4.79
Number of failures for 8 tests	0	0	0	0

Preliminary tests were carried out for one, two, and four weeks at a temperature of 65ºC. After storage, no noticeable change in the composition of the mixture was detected, and the change in the combustion time after storage was very insignificant, which indicates the stability of mixtures based on barium chromate and a composite material based on a titanium matrix hardened with carbon nanotubes.

One of the main requirements for slow-burning low-gas delay compositions is a small dependence of temperature and burning rate on pressure. Figure 10 shows the pressure dependence of the temperature and burning rate of the sample.

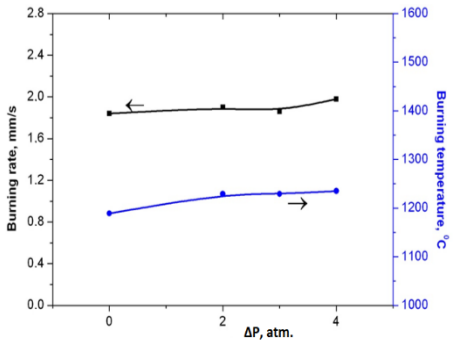


Fig. 10. Dependence of the temperature and combustion rate of the delay composition on the inert gas pressure.

As can be seen from Fig.10, the combustion temperature is practically independent of pressure; for the $BaCrO_4$-TiC system, the combustion temperature remains constant over the entire range of argon pressure. Under these conditions, the ignition of the mixture causes the propagation of the flame front and the beginning of the combustion process of the mixture in a stationary mode. Also it's clear from the Fig. 10, that when argon pressure changes in the range of 1–4 atm., the burning rate changes slightly, from 1.86 mm / s to 1.98 mm /s. This suggests that the combustion reaction is in many cases occur in the solid phase until reaching a solid mixture the ignition temperature. The maximum value of the burning rate is observed at a pressure of 4 atm., the minimum value - at 3 atm. These processes can be explained by the fact that during the ignition of the pyrotechnic retardant mixture, an intense exothermic redox reaction occurs, mainly in the condensed phase without the formation of gaseous products.

4. Conclusions

Thus, as a result of the research, a delay mixtures containing carbon nanotubes was developed, the composition of which can be varied and subsequently determine the combustion stability. It is found that carbon nanotubes increase the delay accuracy and reliability of combustion because the thermal conductivity of carbon nanotubes is a one-dimensional property

that leads to a large amount of heat passing along the direction of the sample length. The role of heat exchange is played by the cavities between carbon nanotubes and their layers.

The linear dependence of the burning rate on the pressure of the inert gas observed in this work and insignificant weight losses allow us to assume that the combustion of the composition proceeds according to the "gas-free" mechanism and the composition can be used in sealed delay devices. The composition is not sensitive to mechanical stress, is safe in production, and at all stages of use, has high physical stability, and does not require special storage.

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