METHOD OF DETONATION NANODIAMONDS CALORIMETRY

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To study the possibility of determining the energy content of detonation nanodiamonds (DND), it is proposed to use the method of reaction calorimetry using the method of self-propagating high-temperature synthesis (SHS). The SHS reactions occur at temperatures no less than at 1500 - 1700 ° C, which limits the possibilities of using standard instrumental methods to study the mechanism and thermodynamics of these processes. In this regard, to study the classical high-temperature gas-free processes of SHS, a special method of electrothermal explosion was developed [1]. To study the mechanism of low-temperature reactions, standard methods of thermal analysis were used. Thus, the study of the heat release of the reaction of titanium with organic substances was carried out by the calorimetry method [2]. However, carrying out the reaction at atmospheric pressure did not ensure the completeness of the reaction, which showed the limitations of this method. The study of the nitriding mechanism of ferrosilicon in the combustion mode was studied under conditions of dynamic heating to a temperature of 1100 °C on a DTA / TG analyzer [3]. DSC [4] and TGA [5] methods were used to study SHS processes involving hydrogen occurring at a temperature of 600 °C. To study the combustion of mixtures of nitrates and nitrites of alkali and alkaline earth metals with coal, an MOM derivatograph was used when heating the samples to 900 °C [6].

Object of research and experimental technique

Detonation nanodiamonds are reactive — they enter into oxidation, substitution, addition, and carbidation reactions [7]. However, at present, reactions with DNA in the self-propagating mode are not described. The purpose of this work is to study the possibility of studying the SHS reaction with the participation of DND.

Experimental part. The SHS reaction for the formation of sodium carbonate was chosen as a model reaction [8]. The choice was justified by the fact that sodium carbonate melts without decomposition at 851 ° C [9], and the mixture of

$$2NaNO_2 + C + 1/3 \, (NH_2)_2CO \rightarrow Na_2CO_3 + 4/3 \, N_2 + 1/3CO_2 \tag{1}$$
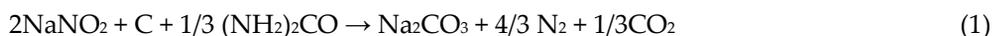
with a zero oxygen balance, it burns steadily at atmospheric pressure with a quantitative yield of sodium carbonate. The calculated combustion temperature of this mixture is 1840 °C, and the calculated specific heat release is 3.28 kJ / g [8], and the boiling point of sodium carbonate is estimated at 2200 °C. This, taken together, makes it possible to rely on the use of this reaction for analytical purposes, comparing the process with DND and carbon. For the preparation of mixtures used $NaNO_2$ "hch" GOST 4197-74 (basic substance content not less than 99%), activated carbon brand BAU-2 GOST 6217-74 (AU), urea GOST 2081-2010 grade B (basic substance content 99.7 %), detonation nano-diamond is a product of the brand UDA GO (TU 84-1124-87), dried to constant weight at a temperature of 110 °C (the content of the diamond phase is not less than 99%).

Before burning, the initial components were ground to a dispersion of less than 50 microns and mixed in a given mass ratio. A powder mixture weighing about 1 mg was placed in an aluminum cup and, in open form, placed in a cell of the device. The interaction of the components with each other was studied under conditions of dynamic heating at a rate of 10 °C / min to a temperature of 600 ° C on a Shimadzu-60 DTA-TGA analyzer in a nitrogen atmosphere at atmospheric pressure. Nitrogen of 99.9% purity was used and passed at a rate of ~ 40 cm3 / min. The instrument was calibrated in India (melting point 156.6 ° C, heat of fusion 28.45 J / g). To process the received data, standard instrument software was used.

Results

A comparison of the DTA / TGA curves of the samples is presented in Figure 1.
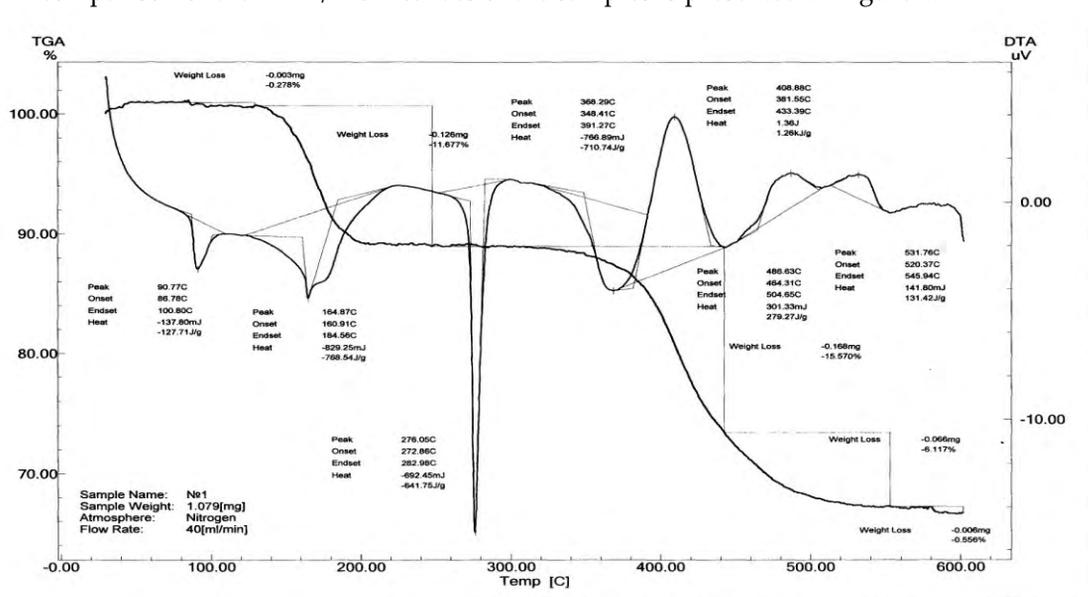
a) DTA / TGA curves of a mixture of sodium nitrite, AC and urea
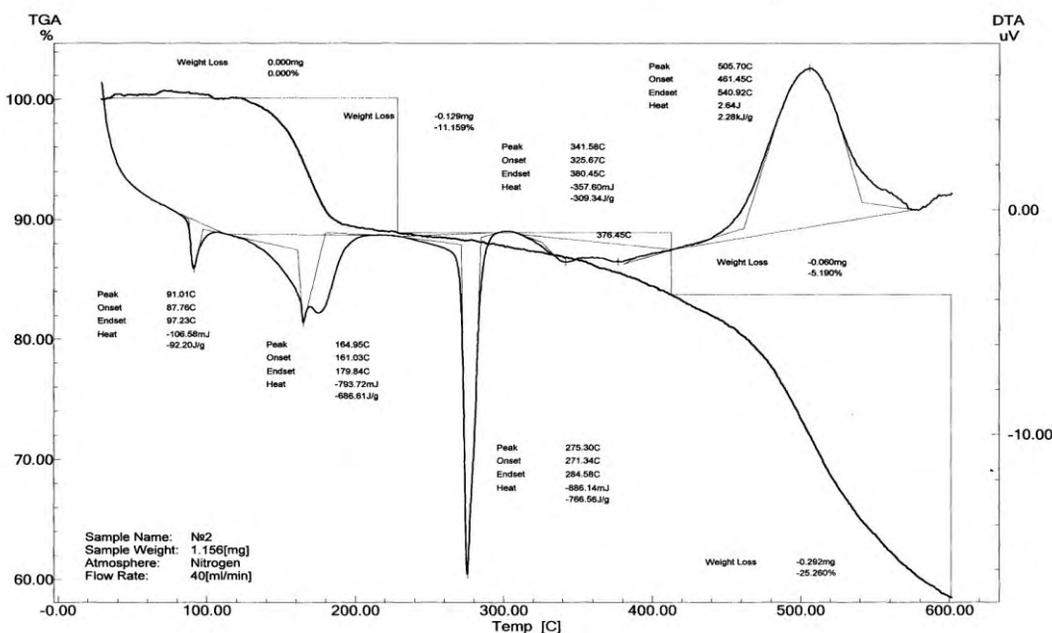
b) DTA / TGA curves of a mixture of sodium nitrite, DND and urea

Figure 1. DTA / TGA curves for heating mixtures of sodium carbonate synthesis

When carrying out these experiments, the reaction was assumed to be based on equation (1), the calculated mass loss at 100% yield of sodium carbonate is 41.1%. In the case of a mixture with AU, the mass loss was 33.4%, and in the case of DND it was 41.6%. On the basis of these data, it can be assumed that according to a formal characteristic, the reaction in the case of a mixture with DND was quantitative, and in the case of AU - by 80%. It should be noted that the combustion conditions (atmospheric pressure) and the mass of the mixture of 1 mg a priori does not imply 100% yield due to heat losses.

When inspecting aluminum crucibles, where the combustion reaction proceeded, it was discovered - Figure 2 - differences in their color and the nature of the process.

Figure 2. The appearance of aluminum crucibles after the experience:
left - experience with AU; on the right - with the DNA

From the comparison of images it follows that the reaction in the case of DND was more (white products) and with the dispersion of liquid combustion products. This nature of combustion can be explained by the release of additional amounts of gases inside the DND at elevated pressure [7]. In the process of DND oxidation, the thickness of their compressive outer crystalline shell decreases, reaching a critical value, and as a result, a nanophysical explosion of DND occurs, leading to dispersion of the reaction mass, which is illustrated in Figure 2. The possibility of such a process was reported in a previous work [10].

As follows from the data presented above, the behavior of the samples differs at temperatures above 300 ° C. To identify the origin of the observed thermal effects of the reaction mixture, a thermal analysis of the DTA / TGA of individual components and binary mixtures of sodium nitrite oxidant with combustible components, urea and coal, was carried out with the same ratios as in the original mixture. Analyzing the data we can come to the following conclusions. Sodium nitrite is characterized by endo-effect without mass loss at a temperature of 165 ° C and a value of 118 J / g (phase transition). At a temperature of 283.5 ° C, sodium nitrite melts (the heat of fusion is 775 J / g), and at a temperature above 320 ° C it begins to decompose.

The process of urea heating is characterized by endoeffects in the range of 20–200 ° C, which is associated with melting and subsequent thermolysis [11] with the formation of biuret and the subsequent chain of transformations.

The behavior of a mixture of urea and sodium nitrite when heated indicates a stabilizing interaction of sodium nitrite after a phase transition with urea to a temperature of 417 ° C, with the intensive decomposition of the mixture at 508 ° C. A possible mechanism of stabilization of the urea-nitrite mixture is associated with the well-known use of urea derivatives to stabilize the powders, for example [12].

Sodium nitrite and AC begin to interact after the melting of sodium nitrite with the products of its decomposition, starting with a temperature of 410 °C. Moreover, the decomposition proceeds in two stages. Perhaps this is due to the fact that the hydrophobic surface of the coal prevents the homogenization of the mixture components in the melt, and the subsequent oxidation occurs after an increase in the activity of the alkaline medium of the melt.

Thus, from the analysis of the data presented in Figure 2, it follows that liquid sodium nitrite begins to decompose reacts with AC — the onset temperature of oxidation is 348 ° C, three stages) and the DND is 481 °C, one stage). Moreover, no other processes are superimposed on the stage of carbon oxidation, which makes it possible to use it for analytical purposes. Also, molten sodium nitrite does not react with an aluminum crucible. Note that the temperature of the onset of the oxidation of DND in air is 430 °C [7]. The difference in the nature of the oxidation is probably due to the fact that the surface of the AC is

hydrophobic, and the density of the DND (3.1 g / cm^3) is higher than the density of sodium nitrite (2.1 g / cm^3), and its density is higher than the density of AC (0.4 -1.0 g / cm^3) [13]. As a result, the DND reaction with the oxidizing agent should proceed in the condensed phase, and the AC should occur at the boundary of the liquid and gas phases.

Thermal effects of the oxidation of DND and AU by the decomposition products of nitrite from these curves Fig. 1, a (three stages) and DND (one stage) are respectively 1.67 and 2.28 kJ / g of the mixture (the calculated heat release is 3.28 kJ / g for the reaction with carbon), which can be attributed to the non-equilibrium nature of the process. The increase in the mass of the sample to reduce heat loss when conducting experience on this equipment is impractical because of the dispersion of the reaction products. The difference in the heat of oxidation could be attributed (ceteris paribus) to the difference in the enthalpies of formation of the allotropic modifications of carbon studied. However, the conditions of the experiment do not ensure the completeness of the reaction and it is not yet possible to evaluate the enthalpy of formation of DND from the difference in the heat of reaction with molten sodium nitrite. For this purpose, it seems appropriate to study the process at elevated pressure and with a device operating in the temperature range up to 1100 °C. Nevertheless, the obtained data reliably indicate a higher value of the standard enthalpy of formation of DND compared with AU. Based on these data, it can be assumed that the following reaction can be used for analytical purposes

$$2NaNO_2 \text{ (liquid)} + C \text{ (solid)} \tag{2}$$

between molten sodium nitrite and the carbon phase. The staging of the oxidation process has been established, which can also be used for analytical purposes to describe the reactivity of carbon phases.

Thus, as a result of the study, it was established that during combustion of a composition with DND in the SHS formation of sodium carbonate, DND is oxidized with dispersion of the reaction mass, which can be explained by their physical explosion with decreasing thickness of the compressive crystalline phase due to its oxidation and burning in the gas phase.

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ЗАВИСИМОСТЬ ВЕЛИЧИНЫ ПРЕДДЕТОНАЦИОННОГО УЧАСТКА В ОБРАЗЦАХ ИЗ ФЛЕГМАТИЗИРОВАННОГО ОКТОГЕНА ОТ СКОРОСТИ И РАЗМЕРА СФЕРИЧЕСКОГО УДАРНИКА

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Для прогнозирования параметров взрыва деталей из ВВ в условиях ударного воздействия важно иметь информацию о динамике развития взрывчатого превращения, которая характеризуется, в первую очередь, возможностью возбуждения детонационного режима взрыва и размером участка ВВ на котором этот режим устанавливается (преддетонационный участок). Такая информация может быть получена путем численного моделирования условий конкретной задачи с использованием адекватной модели инициирования. Для создания и верификации модели инициирования необходим набор экспериментальных данных для представительного диапазона начальных и граничных условий. Большинство таких данных, например [1], [2], получены в условиях плоского ударноволнового нагружения образцов ВВ. В то же время, согласно [3], на динамику развития взрывчатого превращения влияние оказывает и геометрия фронта входящей в образец ударной волны (УВ). Масштаб этого влияния выявлен недостаточно. Поэтому целью данной работы являлось получение экспериментальной зависимости длины преддетонационного участка в образцах из флегматизированного октогена от скорости и размера сферического ударника вблизи пороговых условий инициирования детонации.

1 Постановка экспериментов

Схема проведения экспериментов представлена на рисунке 1.

Исследуемые образцы из флегматизированного октогена представляли собой цилиндры диаметром 120 мм и высотой 60 мм.

Нагружение образцов ВВ осуществлялось стальными ударниками двух типов:

1) сферической формы (диаметр 14,3 мм);

2) имитатором сферического ударника диаметром 30 мм (рисунок 2).