

Кривая для нанокompозитов в области низких КБ лежит выше зависимости, полученной для механических смесей с Al(7), что связано с усилением влияния структуры заряда на МС при снижении степени окисления Al. Из расчета следует, что преимущество по МС нанокompозита с ТНТ над чистым ТНТ может достигать четырех единиц. Однако даже нанокompозиты на основе ТНТ по МС заметно уступают октогену.

Форма расчетных кривых на рисунке 2б повторяет форму кривых на рисунке 2а. При повышении КБ ВВ сверх нулевого значения кривые устремляются вверх. Это происходит не только благодаря более полному окислению Al, но и за счет высокого теплового эффекта реакции Al со свободным кислородом. Нанокompозиты на основе ВВ с положительным КБ не обладают преимуществом по МС перед составами с Al(7). Причина заключается в том, что гомогенизация системы за счет создания нанокompозита становится малоэффективной в случае, когда за характерные времена процесса даже микроразмерный Al испытывает глубокое окисление.

Таким образом, результаты подтвердили возможность повышения МС ВВ за счет добавления порошкообразного Al. Из экспериментальных и расчетных данных следует, что создание алюминизированного нанокompозита целесообразно лишь в случае, когда взрывчатой основой состава служит ВВ с резко отрицательным КБ (ТНТ, триаминотринитробензол и т.п.). Известно, что именно такие ВВ представляют интерес как возможные компоненты энергетических материалов пониженного риска. Полученные данные могут быть использованы для совершенствования термодинамических программ расчета взрывчатых характеристик ВВ.

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## INFLUENCE OF ALUMINUM ADDITIVES ON ACCELERATION ABILITY OF HIGH EXPLOSIVES

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The acceleration ability (AA) holds a special position among the characteristics of high explosive (HE), because the results of AA measurements allow one not only to determine the important parameter of HE efficiency but to study the process of expansion of detonation products (DP) as well. One of the most extensively used methods of AA investigation in our country is M-40 (analogue of M-60 and M-20) [1]. According to this method, a steel plate, 40 mm in diameter and 4 mm in thickness, is accelerated from the

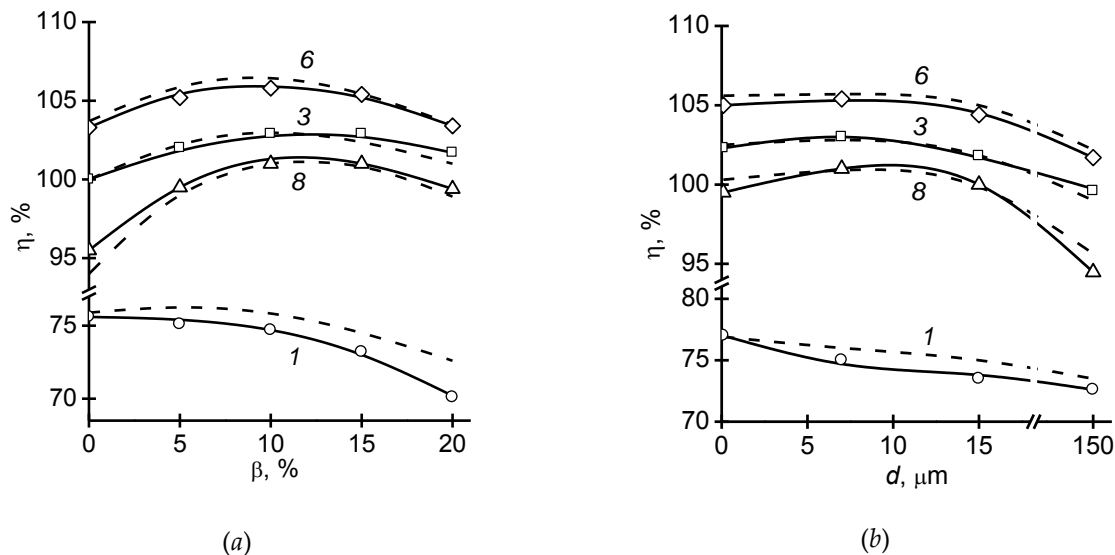
end of a cylindrical charge, 40 mm in height and diameter, in the channel of a thick-walled steel shell. The measure of AA is the plate velocity at a distance of 40 mm from the charge end. The data considered in this report correspond to the M-40 method.

The results of AA investigations, presented in [2–4], suggest that dispersed Al is presently the most promising material for use as a fuel additive in the explosive formulations. In recent years a particular attention of researchers of ICP RAS has been given to the mixtures containing nanosized aluminum (nAl). Specifically, AA of nanostructured composites based on HMX was studied [5]. Contrary to the expectations the nanocomposites representing the systems with uniform distribution of nAl particles in the HMX matrix have no advantages in AA over the mixtures containing Al with the particle size of the order of several microns. However the question of how change-over from a mechanical mixture to a nanocomposite in the case of the other explosive basis, differing from HMX, for example, in oxygen balance (OB), has not been discussed in detail. The work presented is devoted to the study of the dependence of AA of aluminized explosive mixtures on OB of HE as well as on the concentration and particle size of Al (including nAl). The prospects for enhancing AA by creating the aluminized nanocomposites are analyzed using the experimental and calculated data. Both the new results and the data, obtained earlier, are discussed in the report.

The compositions contained HEs: 1 – trinitrotoluene (TNT, -74%), 2 – TNT/RDX = 50/50 (-48%, RDX – cyclotrimethylenetrinitramine), 3 – cyclotetramethylenetetranitramine (HMX, -21.6%), 4 – pentaerythritol tetranitrate (PETN, -10.1%), 5 – trinitroethyltrinitrobutirate (TNETB, -4.1%), 6 – HMX/BTNEN = 50/50 (-2.6%), 7 – dinitroguanidine (DNG, +5.4%), 8 – bis(trinitroethyl)nitramine (BTNEN, +16.5%). HEs are aligned in order of increasing OB, values of which along with the notations of HEs are presented in brackets. The mixtures contained four types of Al, differing in particle size as well as in activity (the concentration of active metal). Al(150), Al(15), Al(7) and Al(0.1) had the activity equal to 99, 98, 98 and 87 % respectively (the mean size of Al particles in micrometers is given in brackets). The nAl powder was produced by the condensation Gen-Miller technique at INEPs CP RAS [5]. The mechanical mixtures were prepared by prolonged mixing of components in the medium of inert liquid in a steel container with roller gears. The particle size of HEs in finished mixtures was 10–40  $\mu\text{m}$ . The charge consisted of pellets, obtained by a cold compression method. The relative charge density was 94–98 % of the maximum possible value. The relative plate velocity was expressed in percent (in relative units). The reference was the HMX charge of the porosity identical to that of the investigated sample. The calculation was carried out using the method developed previously [6].

The data on relative AA of the compositions based on four HEs of different OB are shown in Figure 1 (numbering is presented above). As Figure 1 suggests, the calculation results agree satisfactory with the experimental data. Figure 1a illustrates the influence of Al(7) content on AA of formulations. As it follows from Figure 1a, the Al(7) addition decreases AA of TNT. This effect is caused by the low oxidation degree of Al(7) in reactions with DP of HE depleted in oxygen. According to the calculation method, the effective degree of Al oxidation is evaluated. For example, in the case of the composition TNT/Al(7) = 90/10 this value was found to be  $\sim 0.3$ .

Nonetheless, the usage of Al(7) can lead to the increase in AA, as exemplified by the study of HEs with higher OB than that of TNT (Figure 1a). As the Al content is over the optimal value (10–15 %) AA decreases, because in this case the degree of Al oxidation is not sufficient to compensate for the losses attributable to the presence of condensed phase.



**Figure 1.** (a) – AA of the compositions versus the Al(7) concentration. (b) – AA of the compositions with 15% Al (10% for the system based on TNT) versus the Al particle size. Solid lines with symbols – the experiment for the mechanical mixtures, dashed lines – the calculation.

The greatest increase in AA (of several units) was obtained in the case of BTNEN (HE with positive OB). When estimated with regard to the experimental AA value the effective degree of Al(7) oxidation for the mixture BTNEN/Al(7) = 90/10 approaches 0.9. However the mixture is superior in AA to HMX only slightly. Among the systems considered, the formulations, containing the powerful HMX/BTNEN composition with OB close to zero, have the greatest AA value.

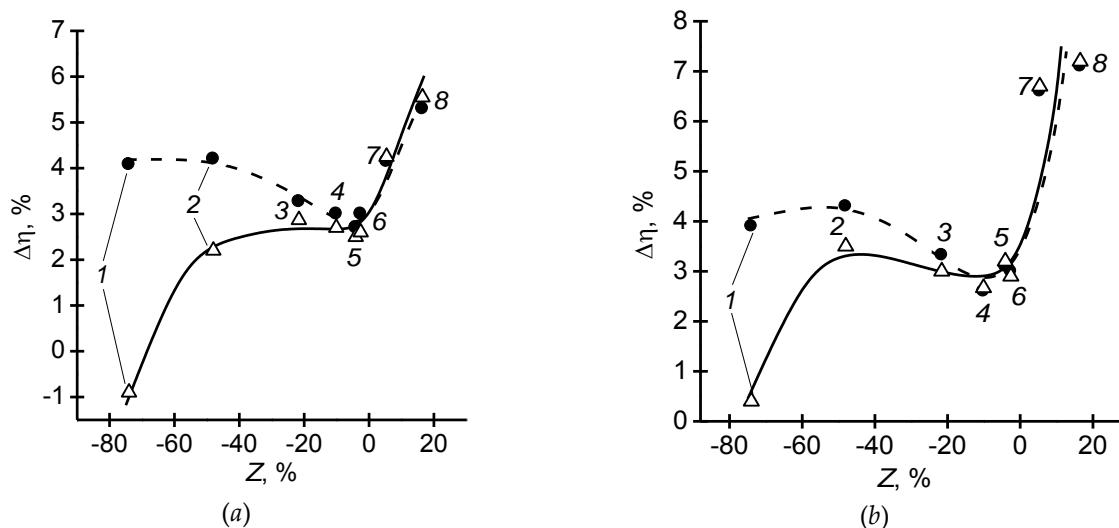
Figure 1b depicts the dependence of AA on the Al particle size. As indicated in Figure 1b, the change-over from Al(7) to Al(0.1) in the mixtures with BTNEN leads even to the slight decline in AA. This result is attributed to the fact that Al(7) undergoes deep oxidation when reacting with DP of BTNEN in a process time frame, and lowering the Al particle size to 0.1  $\mu\text{m}$  doesn't compensate for the losses caused by the increase in oxide film content of Al powder.

The mixtures based on HMX/BTNEN and HMX have a similar nature of the dependence of AA on the Al particle size. However in this case the compositions with Al(7) and Al(0.1) are identical in AA within the limits of experimental error. In the case of the mixtures based on TNT the curve in Figure 1b has an alternative shape. The greatest AA value of TNT/Al = 90/10 corresponds to Al(0.1). The result obtained is attributable to the low degree of Al(7) oxidation during the test. When the degree of active Al oxidation is low the influence of Al particle size on AA grows. As this takes place, replacing Al(7) with Al(0.1) leads to an additional increase in AA. However the gain observed is moderate: AA of the compositions with Al(0.1) exceeds that of TNT by 1.5 units.

As the Al particle size increases from 7 to 150 micrometers, AA of compositions decreases. The most considerable decrease is observed in the case of BTNEN (HE with positive OB). As it follows from the calculation results, for the compositions based on BTNEN the degree of Al oxidation in a process time frame is significantly higher than zero and it is noticeably dissimilar for Al(15) and Al(150). The TNT-based compositions containing Al(15) and Al(150) slightly differ in AA. The calculation performed for the mixtures with TNT has shown the low degree of the oxidation of Al(15) and Al(150) alike.

The results discussed above correspond to the compositions prepared by the way of common mechanical stirring. Creation of aluminized nanocomposites is a scientific and technological challenge in itself. The method for preparing the HMX-based nanocomposites was developed at INEPs CP RAS [5]. This method consists in spray drying of nAl slurry in HMX solution. The curves in Figure 2 express the influence of OB of basic HE on the gain in AA caused by the Al addition. The solid line in Figure 2a has

been constructed using the experimental data. The dashed line in Figure 2a corresponds to the difference between the value calculated for the nanocomposite and the value measured for the basic explosive.



**Рисунок 2.** The gain in AA caused by the addition of 10% Al to HE versus OB of HE: (a) – the solid line with open symbols – the experiment for the mechanical mixtures with Al(7), dashed line with closed symbols – nanocomposites. (b) – the calculation

It is evident from the shape of the solid curve in Figure 2a that in the case of the mechanical mixtures with Al(7) the increase in OB of HE, in general, enhances the gain in AA. However this growth slows down over the certain range of OB. The similar regularity was observed previously at study of the heat of explosion of aluminized compositions [7]. Those data were explained from the viewpoint of the heat effect of reactions of Al with different oxygen-containing products, the concentrations of which in turn depended on the elemental composition of HE. It is not inconceivable that one of reasons for the occurrence of “plateau” on the solid curve in Figure 2a is the distinction in heat effect of reactions of Al with different products.

The curve obtained for the nanocomposites lies above the line constructed for the mechanical mixtures over the area of low OB. This is associated with the growth of influence of a charge structure on AA with decreasing the degree of Al oxidation. From the results of calculations it follows that the advantage of the TNT-based nanocomposite in AA as compared to TNT may run four units. However the TNT-based systems are noticeably inferior in AA to HMX even though the nanocomposites are dealt with.

The curves in Figures 2a and 2b are identical in shape. These curves soar upwards as OB of basic HE increases beyond zero. The increase in the AA gain is caused not only by more complete oxidation of Al, but due to the high heat effect of the reaction of Al with free oxygen. The nanocomposites based on HEs with positive OB have no advantages in AA over the formulations containing Al(7). The reason is that the increase in the degree of homogeneity of explosive system by formation of nanocomposite is not efficient in the case where even micron-sized Al undergoes deep oxidation in a process time frame.

Thus, the results of investigation favour the view that AA of HEs can be enhanced by the addition of Al. As it follows from the analysis of experimental and calculation data, the formation of nanocomposites is reasonable only in the case where basic HE has highly negative OB (TNT, triaminotrinitrobenzene and so on). It is known that such HEs are of interest as possible components of insensitive energetic materials. The data obtained may be used for improving the thermodynamic programs of calculation of HE performance.

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### ВЫБОР МОДЕЛЕЙ ФОРМАЛЬНОЙ КИНЕТИКИ ДЛЯ ОПИСАНИЯ ЭКСПЕРИМЕНТАЛЬНЫХ ДАННЫХ РАЗЛОЖЕНИЯ CL-20

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Большое количество публикаций, посвященных свойствам CL-20, в том числе термической стабильности, свидетельствует об интересе к нему как к мощному энергоемкому соединению, обладающему высокой термической стабильностью [1,4-16].

В работе [1] кинетика распада образцов CL-20 изучалась в изотермическом режиме с использованием метода TGA и FTIR спектрометра в температурном диапазоне 190°C – 204°C в атмосфере воздуха. Экспериментальные данные до 50% разложения удовлетворительно описываются уравнением первого порядка и не подчиняется уравнению Проута-Томпкинса [2,3], на этом основании авторами делается вывод, что разложение CL-20 протекает без автокатализа. Анализ продуктов реакции приводит авторов к выводу, что первичным актом распада является отрыв NO<sub>2</sub>. Константа скорости распада  $k=10^{13.6} \exp(-36300/RT)(1-\eta)$  или  $k=10^{14.1} \exp(-38200/RT)(1-\eta)^2$ .

В работе [4] кинетика разложения изучалась на образцах  $\epsilon$ -CL-20 с размерами частиц 163 мкм и 16 мкм (полученные растиранием крупных кристаллов) массой 5 мг в статических и динамических режимах нагрева. Экспериментальные кривые потери массы при скоростях нагрева 0.5°C/мин, 2°C/мин, 5°C/мин и 10°C/мин для образца размером 163 мкм имеют две четко выраженные стадии разложения, при этом с увеличением скорости разложения величина (в процентном отношении) первой стадии уменьшается (ориентировочно от 55% при скорости 0.5°C/мин до 10% при скорости 10°C/мин). Экспериментальная кривая разложение образца с размерами частиц 16 мкм при скорости нагрева 2°C/мин не имеет таких характерных переходов, как для образца с размерами частиц 163 мкм. В работах [2-3] отмечалось, что в процессе термостатирования образцы распадались на более мелкие и при достижении определенного размера процесс останавливался. При этом мелкие кристаллы оказывались более стойкими, чем крупные.

Экспериментальные данные разложения (до 3%)  $\epsilon$ -CL-20 с размерами частиц 163 мкм в температурном диапазоне 160°C-180°C удовлетворительно подчиняются уравнению автокатализа первого порядка:  $d\eta/dt = 10^{13.81} \exp(-41150/RT)(1-\eta) + 10^{17.99} \exp(-44260/RT)(1-\eta)^2$ .

В качестве первичного акта распада CL-20 авторы также предполагают отрыв NO<sub>2</sub> с последующим раскрытием кольца. В работе [5] изучена кинетика распада  $\epsilon$ -CL-20 в неизотермическом режиме со скоростями 10°C/мин - 25°C/мин. Используя метод Киссинджера,