Pseudoideal detonation of mechanoactivated mixtures of ammonium perchlorate with nanoaluminum

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Abstract. Detonation properties of mechanochemical activated ammonium perchlorate with aluminum (AP–Al) mixtures with increased detonation velocity was studied. For compositions with nanoscale aluminum was obtained nonmonotonic dependence of the detonation velocity vs reciprocal diameter. The results generally showed that the combined usage of mechanical activation and nanoscale components of explosive mixtures can significantly increase the detonation ability and reduce the critical diameter to $d_{cr} = 7$ mm.

1. Introduction
For most of high explosives (HE), including ammonium perchlorate (AP) \cite{1}, detonation velocity grows monotonically with charge diameter increase, so the dependence of detonation velocity vs reciprocal charge diameters $D(1/d)$ is close to linear. In so doing, the velocity achieves the constant value called infinite detonation velocity at $d = d_{inf}$.

However, for a number of explosive compositions the dependence $D(1/d)$ is of non-motonous character including the areas with a constant value of detonation velocity at the charge diameter change. Earlier, such detonation mode obtained for a number of composite explosives, including AP–wax (90/10) \cite{2}, was named “pseudoideal detonation”. Pseudoideal detonation was observed in the compositions containing non-explosive fuel and base explosive, the decomposition products of which serve as oxidant. The authors \cite{2} suggested that the detonation velocity at the constant areas is controlled by the energy release of the oxidizer decomposition, while further increase of the detonation velocity can be explained by fuel reaction in a detonation zone.

Pseudoideal detonation was also observed in the compositions, in which all components are explosives. So, such process occurs in the mixture of coarse RDX crystals (1–4 mm) with tetranitromethane while it was not found in the mixes of tetranitromethane and fine RDX (0.1 mm) \cite{2}. Also pseudoideal mode was found for ammonium nitrate mixed with RDX \cite{3}.

A possible explanation was given in \cite{3}. The authors assumed the change in leading mechanism of explosive decomposition with increase in diameter from the decomposition in
local hot spots to decomposition in the volume. So, the growth of the detonation velocity with charge diameter increase does not occur continuously due to the different times of the decomposition reaction of explosive components. Constant values of detonation velocity at pseudoideal detonation mode correspond to the completion of the intermediate stages of the decomposition.

In [4], we found pseudoideal detonation for mechanically activated AP-based mixtures with nanosized aluminum Alex. In this paper we present the results of our further investigations in this field suggesting some possible explanation of pseudoideal detonation mode in AP-based mixtures with nano-Al.

2. Materials

The mixture components were the following AP powder (20–50 $\mu$m) and different Al powders: Al(8) with specific area of 8 m$^2$/g consisting of two fractions 3–5 $\mu$m and 100–300 nm, Alex (150–200 nm), and more uniform nAl (100 nm). All the mixtures were activated in planetary mill “Activator-2SL”. The procedure of the mechanochemical activation, the found optimum AP–Al mass ratio and the technique of the manufacturing of high density charges are described in [5]. To reduce the mechanical sensitivity of the compositions fluoroplastic F-42 also added in an amount of 3%.

Images from scanning electron microscope (SEM) of activated AP-based mixtures with different Al powders (Al(8), nAl) are shown in figure 1.

In AP–Al(8) mixture, the characteristic particles size is 1–50 $\mu$m, as can be seen from these images. SEM-images obtained with higher resolution allow one to see the presence of conglomerates of the particles with the sizes of up to 5–6 $\mu$m, at which surfaces it is seen the inclusions with linear dimensions about 300–500 nm. It’s difficult to distinguish the AP particles and Al(8) ones from each other because of their shape and characteristic sizes are very much alike. Both completely deformed particles Al(8) rolled in flakes and slightly deformed ones can be seen in the pictures.

In compositions containing nAl (50–700 nm), spherical Al particles located at surfaces of the AP particles are clearly distinguished. For the composition with nAl, in contrast to the mixtures with Al(8), AP particles are partially crushed up to 2–6 $\mu$m, and partially the particles remain their original size of 50 $\mu$m. Within mechanoactivation, fluoroplastic F-42 forms threads coating the particles of AP and Al.

Comparison of compositions with nAl and Al(8) shows the presence of ultrafine aluminum at the surface of larger AP particles, this is able to increase significantly the contact surface area of the fuel with the oxidizer.
3. Results and discussion

Detonation propagation in high pressed charges was studied at charge diameters varied from 7 to 50 mm. The pellets were manufactured with a relative density $\Delta = 0.6–0.95$. The experimental set-up is described in [4]. The obtained values of detonation velocity $D$ were ascribed to the middles of the measurement bases; the length of the test charge ($L$) was measured from the end of the intermediate charge.

Experimental data on detonation velocity vs. reciprocal diameter are presented in figure 2 (the mode of steady-state detonation is shown by solid lines, damping detonation—by dashed lines, and dash-dot line represents the extrapolation of the experimental data previously obtained for AP–Al(PP-2) with micron-sized Al.

Analysing the whole body of the experimental data given in figure 2, one can see that pseudoideal detonation is observed in compositions with nanoaluminum (curves 1, 3–6) only. The increase in relative density from 0.6 to 0.9 leads, on the one hand, to the narrowing of the field of diameter values, in which this mode is observed, and, on the other hand, to the “blurring” of the boundary between the area at which the velocity would grow with $1/d$ decrease and the area at which the velocity would be almost constant with $1/d$ decrease. This is seen by comparing the curves 1 ($\delta = 0.6$) and 5 ($\delta = 0.91$). Two parts in the curve 1, one of which ($d$ varied from 10 to 40 mm) can be described as pseudoidel detonation, actually have no sharp differences in detonation velocity gradient.

Analyzing the whole volume of the data for $\Delta = 0.75$, one can see that the mode of the pseudoideal detonation in AP–nAl (curve 4) is characterized by the same velocities as was previously obtained for AP–Alex. The curves 3 and 4 are practically coincide within the limits of the error, which is not more than 150 m/s.

For AP–Alex, the dependence $D(1/d)$ (curve 5, $\delta = 0.91$) is of linear character, and critical diameter was found to be 25 mm, while charge diameter decrease to 20 mm resulted in a sharp detonation failure at the second measurement base.

At slightly less relative charge density, the replacement of Alex by ultrafine nAl (curve 6, $\delta = 0.89$) showed the steady state detonation up to $d = 17$ mm. In the curve 6, one can distinguish two detonation areas. In the first area ($d = 17–20$ mm), it is seen an increment in detonation velocity about 700 m/s. At $d = 15$ mm detonation slow decreased along the charge.
length (damping detonation), and at the last measurement base the velocity was 3920 m/s. So, for AP–nAl, critical diameter can be estimated as $d_{cr} \geq d = 15$ mm, at $\delta = 0.89$. In the second area ($d = 20–50$ mm), 2.5 fold diameter growth resulted in detonation velocity increase no more than $\approx 150$ m/s, it is observed pseudoideal detonation.

Comparing the curves 5 and 6, we can only assume the existence of very narrow area ($d = 40–50$ mm) of pseudoideal detonation for AP–Alex at $\Delta = 0.91$, but this should be verified experimentally. We can see, that in any way, pseudoideal detonation mode is explained by the existence of several stages in energy release in the reaction zone, which differ in characteristic time. At the detonation of AP–Al compositions, it is reasonable to assume first stage to be the decomposition of AP particles, and the second one would be oxidation of Al particles by AP decomposition products. Drawing the qualitative picture of the pseudoideal detonation mode, one should take into account several experimental facts found in the frame of present study. First, pseudoideal detonation is observed only for mechnoactivated compositions with nanoaluminum, and is not observed in a similar composition with a micron-sized aluminum PP-2. Second, both type of the compositions (containing micron- or nanosized Al) demonstrate the same detonation velocities at $d \geq 40$ mm (curve 3 matches the curve 2, see figure 2). Both facts can be explained on the basis of the obtained SEM-images of mechnoactivated mixtures. In the compositions with micron- and nano-sized Al there were found large particles of AP up to $10–20 \mu m$. In the compositions with nAl an appreciable fraction of AP particles is of size of a few microns. Thus, the characteristic size, by which the composition with micron-sized Al can be described, is tens of microns, and the composition with nAl has two characteristic sizes: micron size and sub-submicron one. It is possible to assume, that this difference by an order is the reason for the existence of the abovementioned two stages in energy release. The fraction of fine AP particles increases the detonability of the compositions with na-noscale aluminum nearby critical diameters. The larger particles demand larger time to decompose and react with Al, so they mainly contribute to detonation propagation at larger diameters.

The charge porosity is an important factor which determines denotation limits in composite explosives, so one can assume that the mentioned above effect of AP decomposition of both coarse particles and fine ones is less prominent at larger charge porosity. This is a possible explanation of “blurring” of the boundary of pseudoideal detonation.

The presence of pseudoideal detonation mode on the dependences $D(1/d)$ in compositions based on nano-sized Al indicates staging of the detonation process. At charge diameter $d < 40$ mm velocity of detonation process caused by the fastest reaction of well mixed nanoscale and submicron part of the composition, and for $d > 40$ mm in the reaction zone of the detonation wave front contributes reacting of the rest composition of AP particles with sizes in microns and tens of micron. Matching of the dependencies $D(1/d)$ at $d > 40$ mm for compositions with activated micron (curve 2) and nanoscale (curve 3) aluminum is evidence in favor of such a representation.

4. Conclusion
Overall results showed that the usage of nano-sized aluminum in conjunction with mechano-chemical activation allows increasing detonation ability, reducing the critical diameter and having a record of detonation velocity for AP-based composition.

References
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