Influence of Mechanoactivation on Detonation Parameters of Perchlorate Based Mixtures

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1 Introduction

One of the ways to increase the rate of energy release during combustion and detonation of mixtures of solid oxidizers and fuels is to use the method of preliminary mechanical activation (MA). Previously obtained results on activation of Me/Ox mixtures (Me = Al, Mg, Si; Ox = S, MoO_3, Teflon, etc.) showed the perspectives of this method [1-3]. During MA both grinding of the initial components with partial components diffusion and producing of the defects in crystal structure take place and as result mechanoactivated energetic composites (MAECs) with increased reaction ability are produced. The conditions for MAECs production are selected to ensure the maximum degree of particle crushing, their uniform mixing, and activation but avoiding possible chemical interaction between components. In this report the new data on Al-containing MAECs based on ammonium perchlorate are presented.

2 Materials and Activation

For preparation of mixtures as initial materials there were used powders of chemically pure ammonium perchlorate (AP) with average particle size 20 ÷ 50 μm and Al powders: PP-2 with flaked particles of 50 ÷ 200 μm × 2÷5 μm, and spherical Al(8) with particles of 280 nm in diameter. Al mass content was varied from 10% to 30% nearby stoichiometric ratio which is 27.7/72.3 for Al/AP mixture. Also for the mixture samples intended for further pressing the fluoropolymer F-42 was added up to 3% of the mass ratio. The additive of F-42 was necessary for simplification of pressing of charges and to decrease in sensitivity as the mechanoactivated mixes in pure form possess mechanical sensitivity at the level of the initiating explosives.

The mixing of the components accompanied by activation was performed in stainless steel drums of a planetary ball mill "Activator 2SL" (JSC "Activator ", Novosibirsk, Russia). The mass ratio of the mixture to the stainless steel balls was 10 g to 300 g. In order to prevent any possibility of an explosion to be caused by friction heating-up in the course of mixing it is necessary to provide liquid layer in-between solid particles and balls. So, 60-80 g hexane was added into the mixtures which were treated in the cycle mode using water cooling of the drums. The time duration of the cycle was 60 s, while total operating time, considered as the time of activation (t_{act}) was varied from 0.5 min to 60 min. Activated mixture being dried consists of relatively large conglomerates, so the product was sifted

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through the sieve with the mesh size of 0.4 mm. Initial components and the produced MAECs were analyzed using X-ray diffraction technique and scanning electron microscopy (SEM).
X-ray diffraction analysis showed no chemical reaction between components, which were activated up to t_{act}= 30 min. Only the lines of two phases of AP and Al are seen in the X-ray diffraction diagrams, and slight Fe traces (about tenth of percent) can be detected. Fe impurity in the MAECs is produced as the result of grinding of steel drums and balls.

3 Experimental Results

Mechanical sensitivity of the MAECs was investigated by the disintegrating-shell method [4]. The sensitivity was characterized by critical pressure P_{cr} (the pressure corresponding to the transition from mechanical destruction of charges in the shell of PMMA without an explosion to destruction with explosion). Sensitivity of activated Al/AP (P_{cr} = 0.61 ± 0.02 GPa) occupies an intermediate position between such sensitive explosives as lead azide (0.38 GPa) and bis(trinitroethyl)nitramine (0.79 GPa).
The results of research of explosive properties (deflagration to detonation transition in loose-packed charges, dependence of detonation velocity on density and diameter of the pressed charges) have been received also.
For loose-packed MAECs (18-20% of TMD - percentage of theoretical maximum density), both burning and detonation velocities were measured in stainless steel tubes 10 mm in diameter and 120 mm of length. The tubes were charged in portions with consequent mixture hand-pressing to a given density. The tested mixtures were ignited by heated Nichrom wire, which was located nearby the closed end of the tube. The rate of the burning process along the tube was measured using optical fibers inserted into the tube on a half of its diameter in order to prevent possible influence of flame passage along the tube wall. The fibers transmitted the light emitted by burning products in the reaction zone to photodiodes. The electrical signals were recorded by digital oscilloscopes.

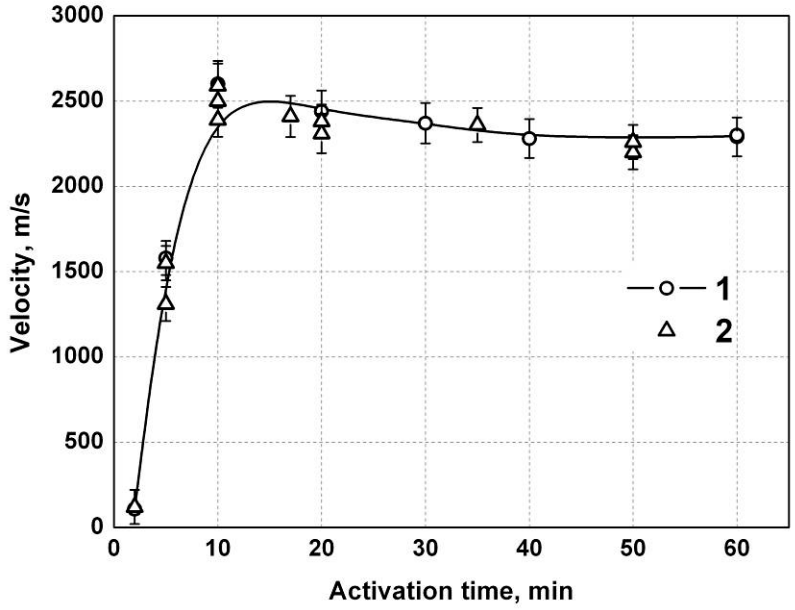


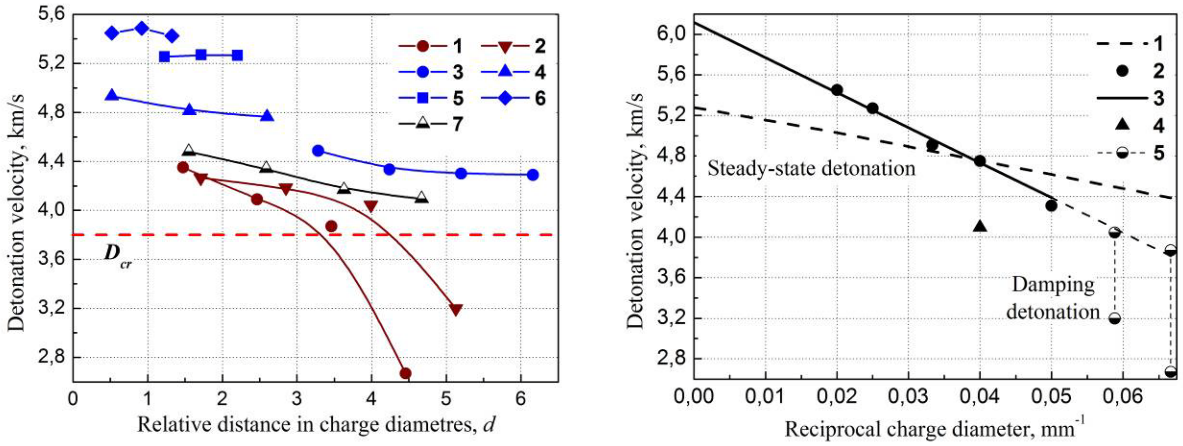
Figure 1. The velocity of burning and detonation processes in loose-packed charges of Al/AP (20/80) (20% of TMD) versus activation time (1 – PP-2, 2 – Al(8)).

In general, it was found that lengths of deflagration-to-detonation transition (DDT) and detonation velocity (*D)* depend on activation time and components mass ratio as well. For example, for loose-packed Al/AP (20/80) (t_{act} = 10 min) the DDT length ranges from 65 to 75 mm and *D* ranges from 2.0 to 2.5 km/s. The experimental data on *D* for Al/AP (20/80) composition with different t_{act} are shown in

Fig. 1 (*D* was measured at 20-mm base situated in 70 mm from the ignition wire). So, the velocity of the reaction propagation increases from 120 m/s (t_{act} = 2 min) – convective burning to 2500 m/s (t_{act} = 10 min) – detonation. While longer activation (up to t_{act} = 60 min) slightly decreases the velocity (*D* = 2350÷2400 m/s). It is also seen from the Fig. 1 that the type of Al (PP-2 or Al(8)) doesn't affect the measured velocity.

The dependence of detonation velocity on density was investigated in pressed charges of Al/AP with addition of 3% fluoroplast F-42.

Al/AP MAECs (20/80+3% F-42 with t_{act} = 10 min) pressed up to 85% of TMD were studied in the charges which diameters (*d*) varied from 15 to 50 mm. The charges were initiated by detonator through RDX thin pellets and booster charge of the same density as the charges tested; for 40-mm and 50-mm charges in diameter plane-wave generator made from RDX with wax was used. The time of detonation wave travelling along the base was measured with assistance of contact foil gages, in so doing there were measured detonation velocity, *D*, averaged over the base equal approximately to the charge diameter. The *D*-values ascribed to the middles of the measuring bases versus the distance from the end of the booster charge are given in Fig. 2a and 2b.



a) b)

Figure 2. *D* vs relative distance from the booster charge in charge diameters (a) and *D* vs reciprocal charge diameter (b) in Al/AP (20/80) (2a - charge diameters *d*: 1 – 15 mm; 2 – 17; 3 – 20; 4 – 25; 5 – 40; 6 – 50; 7 – 25 (non-activated); 2b - 1 – linear approximation of the D. Price data [5]; 2 – *D*-values for steady-state detonation in activated mixtures; 3 – linear approximation of the *D*-values; 4 – experimental point for non-activated mixture; 5 – *D*-values for damping detonation in activated mixtures

According to the experimental results obtained for activated Al/AP composites 75% of TMD, it was found steady-state detonation in the charges of $d \geq 20$ mm. While the steady-state mode for different charge diameters does occur at different lengths from the booster charge, the lesser is the diameter than the longer is the relative distance of the transition, see Fig. 2a. We assume that critical diameter of the MAEC tested lies in the range of 17÷20 mm. For the charge diameters of 15 mm and 17 mm, the detonation is observed to be of slow-damping character with charge length until the velocity decreases below D_{cr} ≈3800 m/s. Further distance growth results in sharp detonation failure. All experimental data in the field of steady-state detonation can be approximated by linear dependence: $D = 6.12 - 34.5/d$, where [*D*] = km/s [*d*] = mm (line 3 in Fig. 2b).

For the charges 17- and 15-mm in diameter one can see the detonation process has damped, so it would not be correct to use the *D*(*d*) relation given above. Nevertheless, the detonation velocities measured at the distance of 3-4 diameters from the booster charge belong to the constructed linear dependence (see the points on the dash line in Fig. 2b). *D* measured at the last bases are also given in the figure in order to show the detonation sharp decrease in the velocity along the measuring base, so the damping detonation in 17- and 15-mm charges is illustrated by two points for each charge diameter

in Fig. 2b. The constructed approximation $D(d)$ (line 3 in Fig. 2b.) is able to predict detonation velocity for quasi-steady-state regime in wide range of charge diameters.

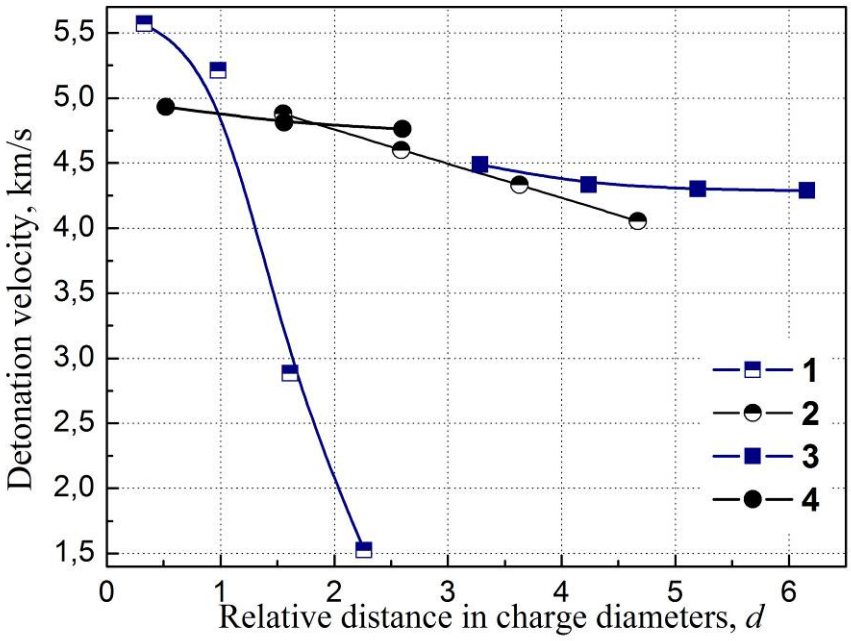


Figure 3. D vs relative distance from the booster charge in Al/AP (20/80) (t_{act} = 10 min): 1, 3 – d =20 mm, 85% and 75% of TMD; 2, 4 – d =25 mm, 80% and 75% of TMD.

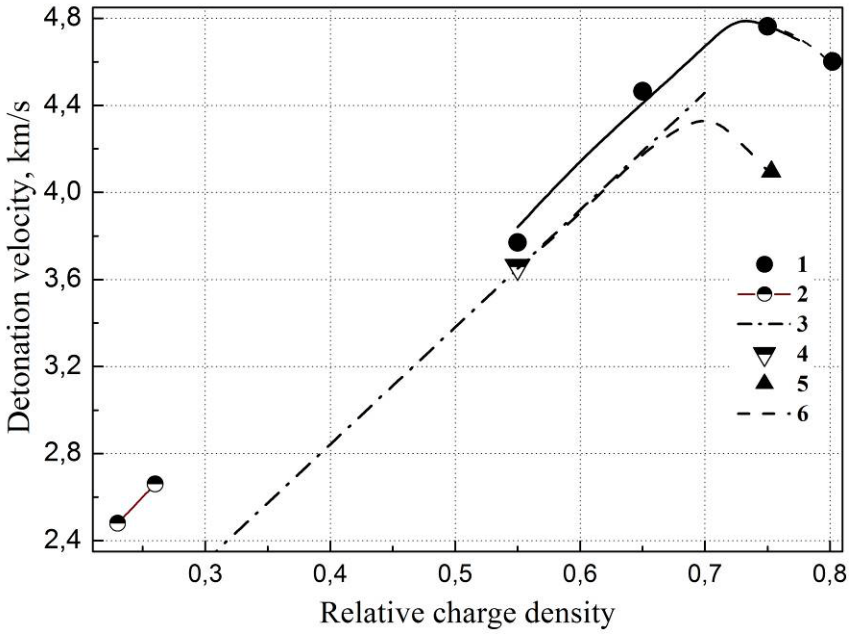


Figure 4. Detonation velocity versus relative charge density for Al/AP (80/20).
d =25 mm: 1 – D-values and their approximation (t_{act}=10 min); 4, 3 – D-value and linear approximation for non-activated mixture [5]; 5 – D-value (t_{act}=0.5 min); 6 – possible D for non-activated mixture
d=10 mm: 2 – D-values for the loose-packed mixture in steel tube (t_{act}=10 min), present data.

Studied MAECs demonstrate higher detonation velocities than one could expect basing on Donna Price data obtained for non-activated mixtures [5]. This issue correlates with the data obtained for

activated and non-activated compositions, for which *D* was measured in the charges of 25-mm diameter. For non-activated mixture (t_{act} = 0.5 min), we can observe larger distance of the detonation transition to steady-state regime and less final detonation velocity. Possible decrease of critical diameter resulted from mechanoactivation of the mixture is one of the reason for such effects, which demands for further investigation.

Perchchlorate-based compositions are the explosives of Group II according to Donna Price classification [6], i.e. *D*-values dependence on charge density demonstrates maximum with further attenuation. So, increase of charge density from 75% of TMD results in velocity decrease and detonation failure, see Fig. 3, 4. For 20-mm charge diameter detonation failure at 85% of TMD is obvious, while for the charge of 80% TMD and 25-mm diameter one can see detonation slow-damping with length.

Detonation velocity versus charge density varied from 55% to 84% of TMD was measured for charges 25 mm in diameter, see Fig.4. For charge density 80% of TMD detonation velocity slow decreases with charge length *L* from *D* = 4.88 km/s (slightly overpressed detonation) at *L* = 1.55*d* to *D* = 4.054 km/s at *L* = 4.67*d*, while for the charges 83.5% of TMD, D = 3.22 km/s at *L* = 2.26*d*. So, we believe that D_{max} corresponds to the charge ≈75% of TMD. *D*-velocities of steady state detonation measured in the Al/AP (20/80) charges of different diameters at 75% of TMD are given in Table 1. The *D*-values calculated by D. Price dependence obtained for non-activated Al/AP mixtures are given in the Table 1 for comparison.

We assume, taking into account our data for *d*=25 mm, that charges of non-activated mixture with diameter less than 25 mm would demonstrate detonation failure. One can deduce analyzing the data presented in the Table 1 that the velocities for the charges with *d* < 25 mm would be overestimated by D. Price approximation, while the charges with d > 25 mm exhibit higher velocities.

The *D*-values for activated (t_{act} = 10 min) and non-activated mixtures (t_{act} = 0.5 min) as well as D. Price data are presented in Table 2.

Table 1: Detonation velocity in mechanoactivated Al/AP (20/80)

d, mm		20	25	40	50
D_{max}, km/s	experiment	4.29	4.77	5.27	5.43
	calculated [5]	4.59	4.73	4.93	5.00

Table 2: Detonation velocity for activated and non-activated Al/AP with different Al content (d = 25 mm)

Al/AP	mixture	TMD,%	D, km/s
10/90	non-activated [5]	63	4.09
		67	4.08
	activated	65	4.68
20/80		66	4.46
		75	4.75
	non-activated		4.10
	non-activated [5]	55	3.66
	activated		3.77

Comparing the data one can see that activation would result in the increase of *D*-value in the charges of *d* = 25 mm at the same relative density. Moreover, we assume that mechanoactivation of Al/AP mixtures could shift the maximum *D*-value to the higher relative densities, this assumption is

illustrated by the curve 6, see Fig. 4, constructed for the charges of d = 25 mm. Of course, the assumption should be verified experimentally for the charges made of the same components and prepared identically.

For Al/AP mixtures, component mass ratio 80/20 was found optimum for detonation in loose-packed charges. While for high-dense charges (75% of TMD) growth of Al content from 10% to 20% results in detonation velocity decrease, this effect is less prominent if one compare the results for the charges of 55% TMD, which were obtained in this work and by D. Price, see Table 2.

Conclusion

Reactivity of mixtures of solid oxidizers and fuels depends largely on the specific surface area of contact of the reagents. Preliminary mechanical activation is one of the most promising ways to improve the reactivity of such mixtures. Under intensive treatment of powders in the ball mill, their grinding and mixing with the consequent increase of the contact surface of the particles takes place, as well as deformation of the particles and generation of different crystal defects. In general, mechanical activation can significantly improve the speed of combustion and detonation. In this paper we found a noticeable increase in detonation ability of explosive mixtures based on powders of micron-sized particles of aluminum and ammonium perchlorate. Comparison of the data obtained for the activated compositions and mechanical mixtures ones shows that mechanochemical activation can result in significant increase in detonation velocity at the same charge density, moreover the shift in the maximum of detonation velocity for Al/AP to higher charge densities at given diameter was observed. Preliminary experiments have also shown that using initial aluminum particles with a size of about 100 nm instead of micron particles can result in both further increase of detonation velocity and the density (to maximum 0,9 TMD) at which steady-state detonation occurs at charges in diameter of 25-40 mm. In the future, we plan to continue this research.

Acknowledgements

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