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Semenov Institute of Chemical Physics
Russian Academy of Sciences, Moscow*



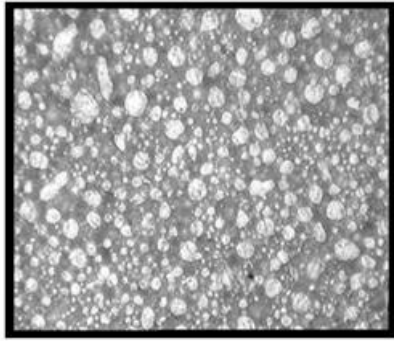
MECHANOACTIVATION AND DETONATION OF AMMONIUM PERCHLORATE – NANOALUMINUM MIXTURE

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M. A. Brazhnikov**

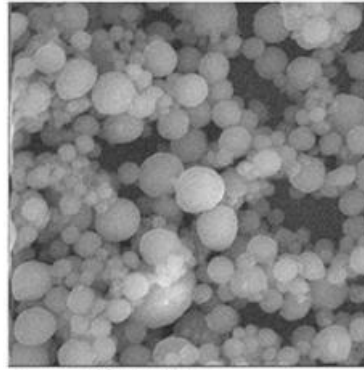
SHOCK INDUCED CHEMICAL REACTIONS IN OXIDIZER-FUEL MIXTURES

Composition (wt.)	ρ_{\max} g/cc	Reaction	Q, kcal/kg	$Q \cdot \rho \cdot 10^{-3}$, kcal/m ³
Al/S, 36/64	2.26	$2\text{Al} + 3\text{S} = \text{Al}_2\text{S}_3$	1150	2600
Al/MoO₃, 27/73	3.91	$2\text{Al} + \text{MoO}_3 = \text{Al}_2\text{O}_3 + \text{Mo}$	1120	4380
Al/Fe ₂ O ₃ , 25.5/74.5	4.23	$2\text{Al} + \text{Fe}_2\text{O}_3 = \text{Al}_2\text{O}_3 + 2\text{Fe}$	950	4020
Al/WO ₃ , 19/81	5.45	$2\text{Al} + \text{WO}_3 = \text{Al}_2\text{O}_3 + \text{W}$	710	3870
Al/CuO, 18.5/81.5	5.13	$2\text{Al} + 3\text{CuO} = \text{Al}_2\text{O}_3 + 3\text{Cu}$	970	4980
Al/BaO ₂ , 17.5/82.5	4.32	$4\text{Al} + 3\text{BaO}_2 = 2\text{Al}_2\text{O}_3 + 3\text{Ba}$	560	2420
Al/CrO ₃ , 35/65	2.76	$2\text{Al} + \text{CrO}_3 = \text{Al}_2\text{O}_3 + \text{Cr}$	1680	4640
Al/(-C₂F₄-), 26.5/73.5	2.31	$4\text{Al} + 3(-\text{C}_2\text{F}_4-) = 4\text{AlF}_3 + 6\text{C}$	2070	4780
Zr/(-C ₂ F ₄ -), 47.5/52.5	3.20	$\text{Zr} + (-\text{C}_2\text{F}_4-) = \text{ZrF}_4 + 2\text{C}$	1380	4420
Zr/MoO ₃ , 48.5/51.5	5.41	$3\text{Zr} + 2\text{MoO}_3 = 3\text{ZrO}_2 + 2\text{Mo}$	770	4170
Ti/(-C ₂ F ₄ -), 32.5/67.5	2.63	$\text{Ti} + (-\text{C}_2\text{F}_4-) = \text{TiF}_4 + 2\text{C}$	1350	3550
Ti/MoO ₃ , 33.5/66.5	4.63	$3\text{Ti} + 2\text{MoO}_3 = 3\text{TiO}_2 + 2\text{Mo}$	740	3430
Mg/(-C₂F₄-), 32.5/67.5	2.02	$2\text{Mg} + (-\text{C}_2\text{F}_4-) = 2\text{MgF}_2 + 2\text{C}$	2280	4610
Mg/Fe ₂ O ₃ , 31.5/68.5	3.21	$3\text{Mg} + \text{Fe}_2\text{O}_3 = 3\text{MgO} + 2\text{Fe}$	1010	3240
Mg/MoO₃, 33.5/66.5	2.99	$3\text{Mg} + \text{MoO}_3 = 3\text{MgO} + \text{Mo}$	1170	3500
Mg/TiO ₂ , 38/62	2.74	$2\text{Mg} + \text{TiO}_2 = 2\text{MgO} + \text{Ti}$	490	1340
Mg/SiO ₂ , 44.5/55.5	2.15	$2\text{Mg} + \text{SiO}_2 = 2\text{MgO} + \text{Si}$	670	1440

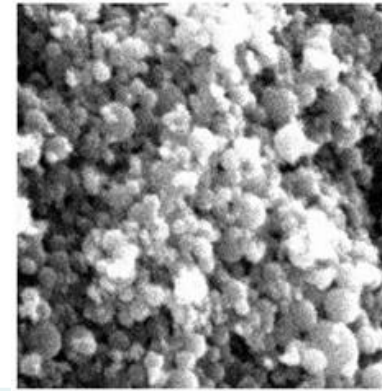
Auminium



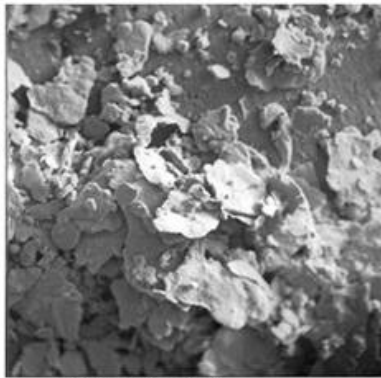
ASD-4 ($\langle d \rangle \sim 7 \mu\text{m}$)



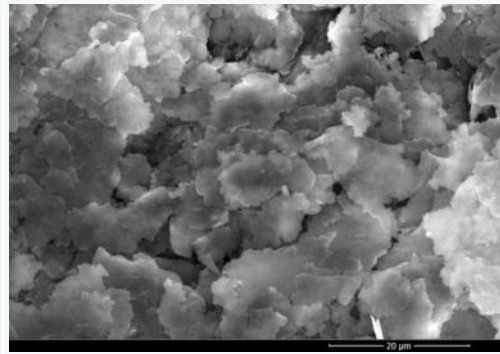
ASD-6 $\langle d \rangle \sim 3,6 \mu\text{m}$



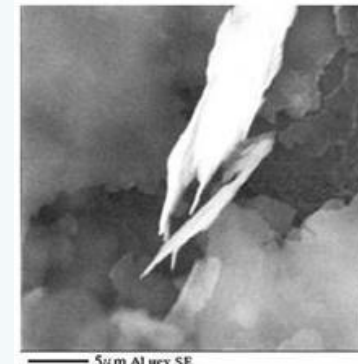
nAl $\langle d \rangle \sim 100 \text{ nm}$



PP-2
 $\langle L \rangle \sim 70 * 1 \mu\text{m}$

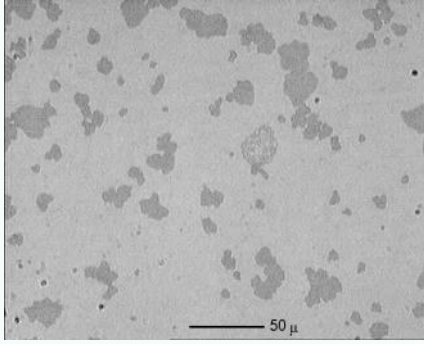
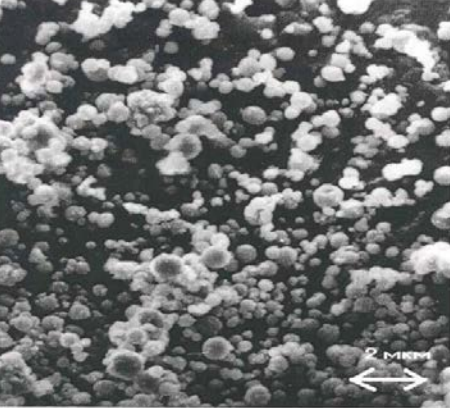
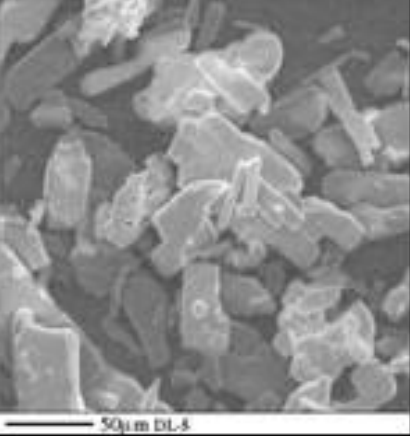
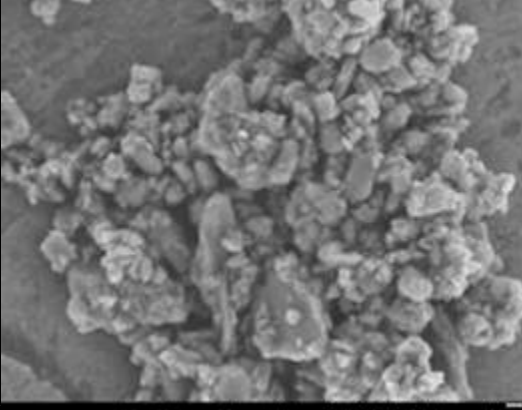


Al - PAP-2
 $\langle L \rangle \sim 30 * 1 \mu\text{m}$



Al(N4), ($S=2.7 \text{ m}^2/\text{g}$)
 $\langle L \rangle \sim 0.5 * 21,3 \mu\text{m}$

Initial Powders (oxidizers)

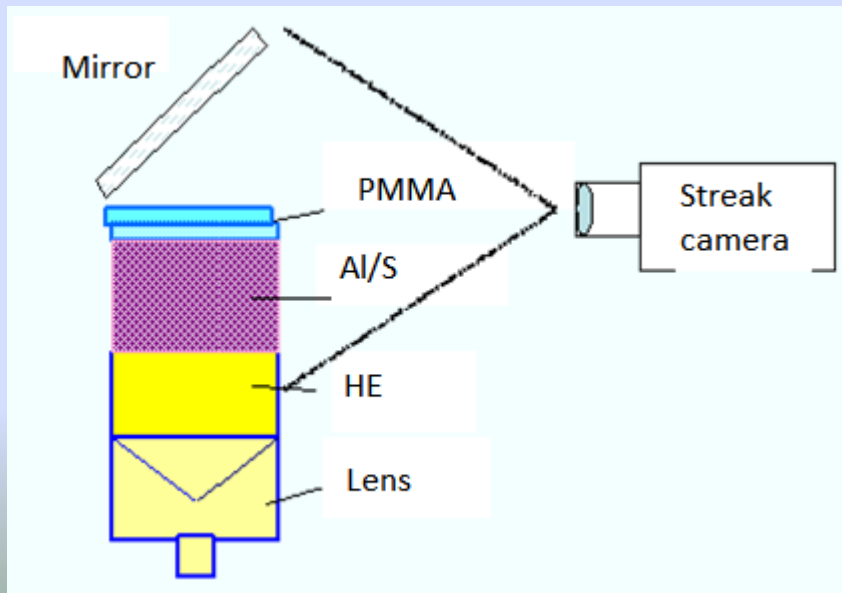
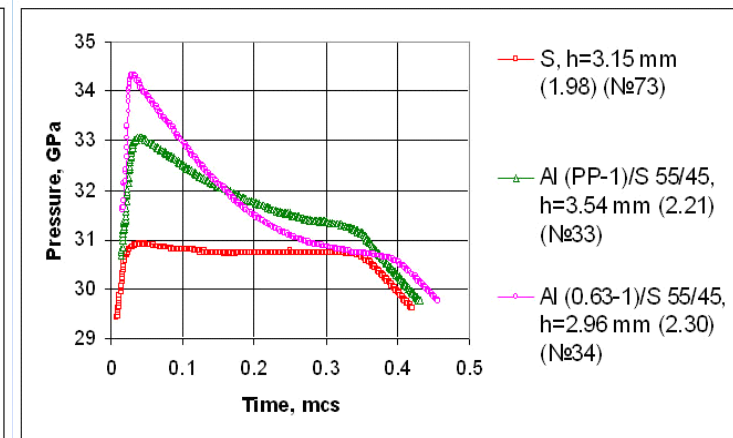
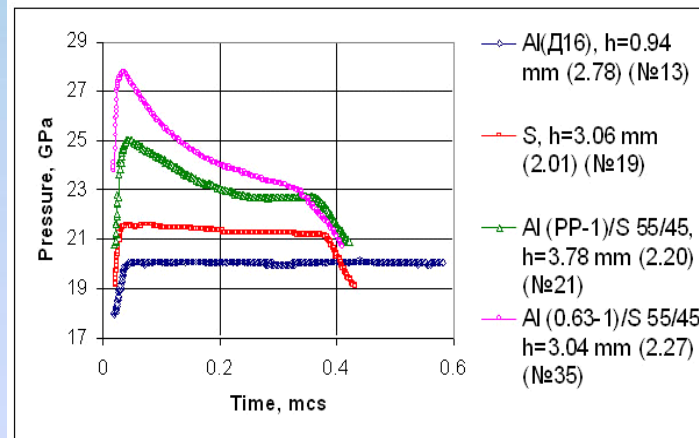
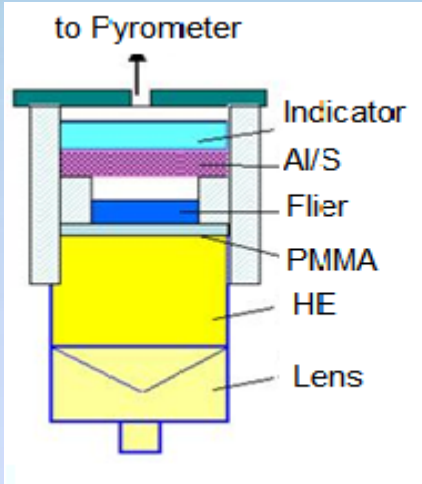
Teflon (F4-PN)	Teflon (FORUM)	MoO ₃	Nano-MoO ₃
			
<p>$\langle d_1 \rangle \sim 10 - 300 \mu\text{m}$ (Most of particles)</p> <p>$\langle d_2 \rangle \sim 1.5 - 2.5 \mu\text{m}$</p>	<p>$\langle d \rangle \sim 0.6 \mu\text{m}$</p>	<p>$\langle d \rangle \sim 30 \mu\text{m}$</p>	<p>Preliminary activation - $\langle d \rangle \sim 60 \text{ nm}$</p>

- Tested charges were prepared from the initial components by mixing in vibromill with consequent pressurizing.
- Mechanochemical activation was also used for mixture manufacturing

Shock induced reaction in Al/S

$W = 3.61 \text{ km/s} - \text{CCl}_4$

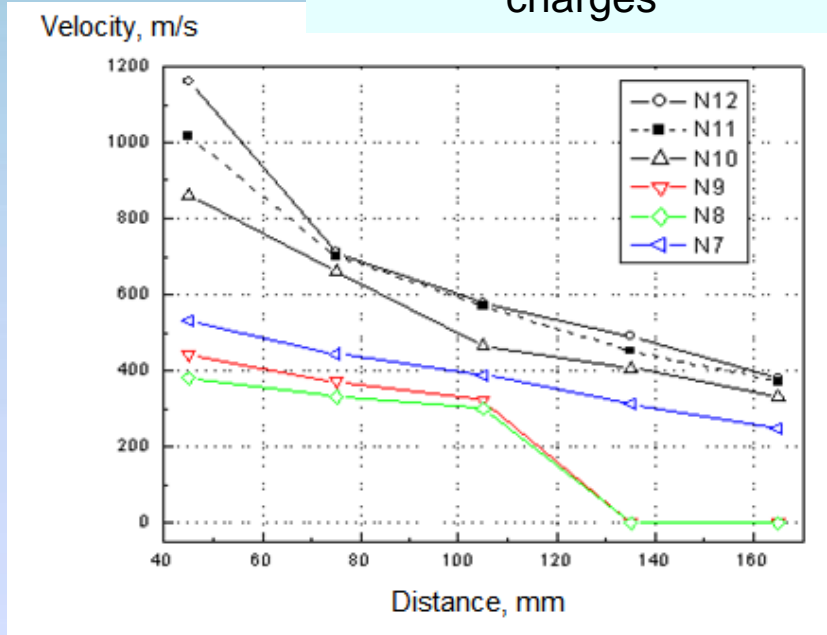
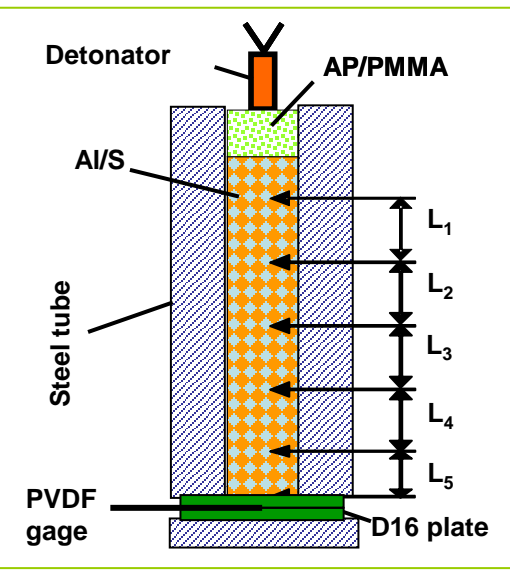
$W = 3.61 \text{ km/s} - \text{CHBr}_3$



The reaction quickly decays in dense samples under powerful initiating

Detonation-like process in Al/S mixture

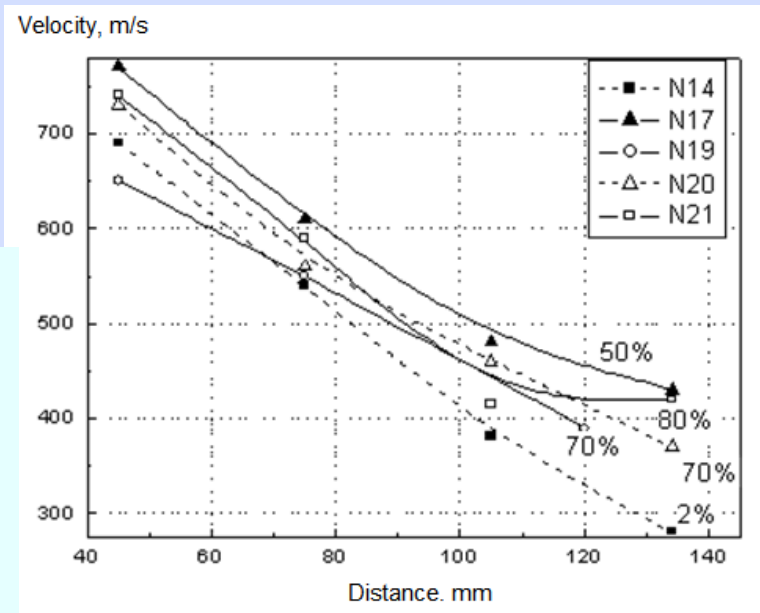
Fading mode in low dense charges



Fast reaction propagation due to formation of hot spots and jets of reaction products

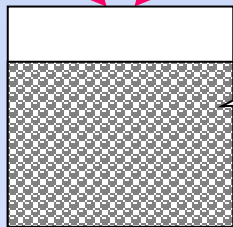


To accelerate the solid state reactions necessary to increase the effective surface area of contact of the reactants. Mechanochemical activation is one of the ways to increase the reactivity of the oxidizer fuel mixture



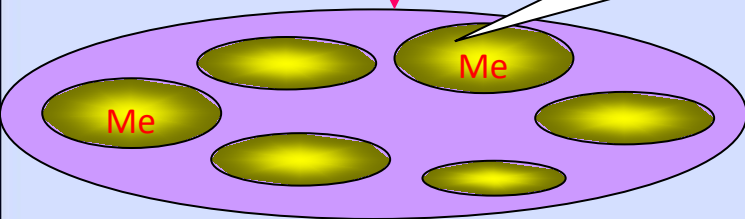
Mechanoactivated Energetic Composites (MAEC)

Initial Particles of micron size

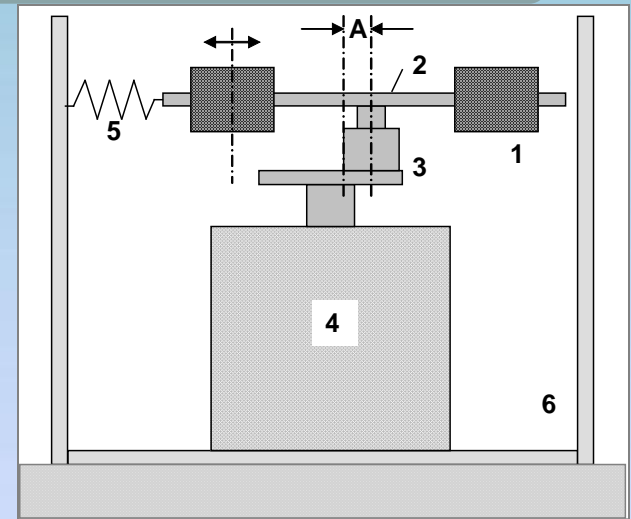


Activation
in ball mill

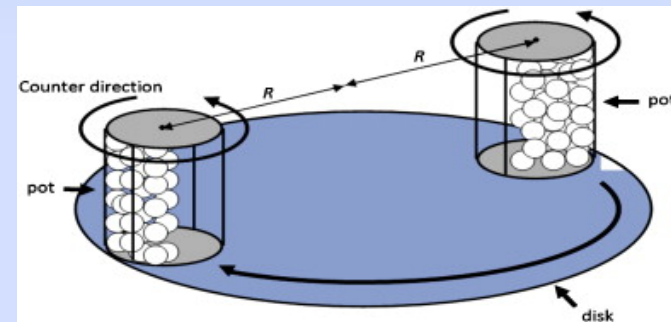
Nanocomposite
Fuel – oxidizer



"Aronov" type
Vibration mill

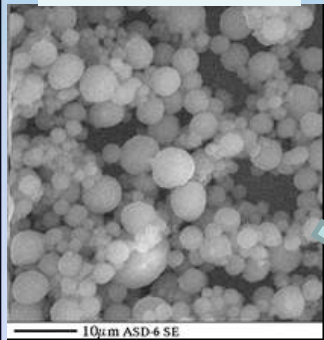


planetary ball mill "Activator – 2SL"

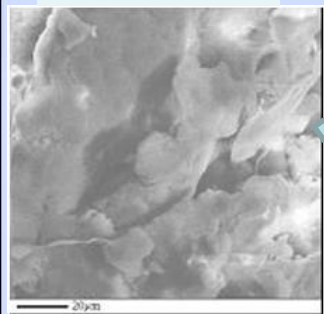


Formation of Mechanoactivated Energetic Composites Me/Teflon

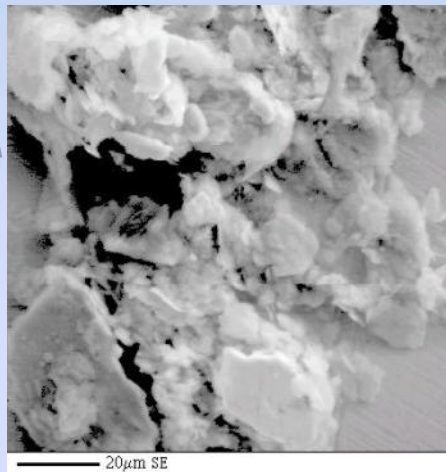
Al-ASD-6



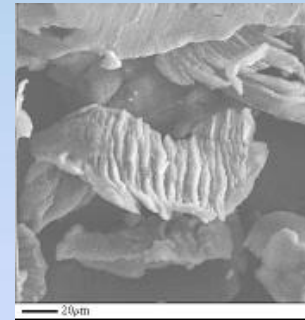
Teflon F4



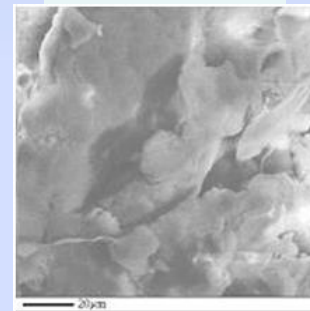
MAEC Al/Teflon



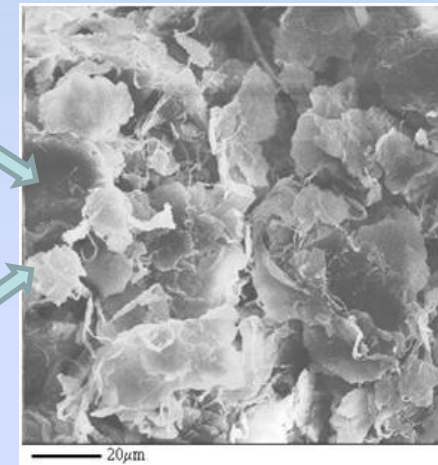
Mg-MPF-4



Teflon F4



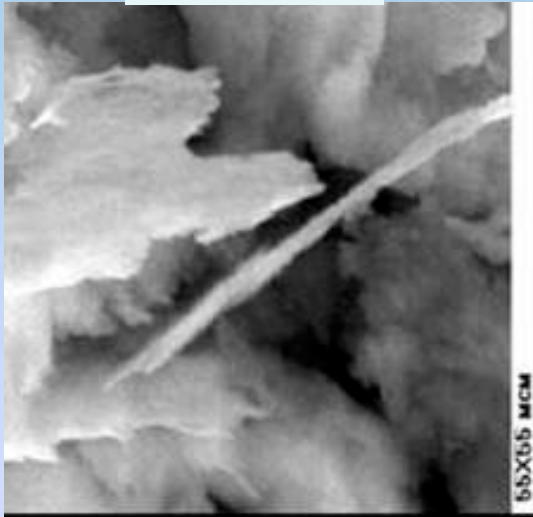
MAEC Mg/Teflon



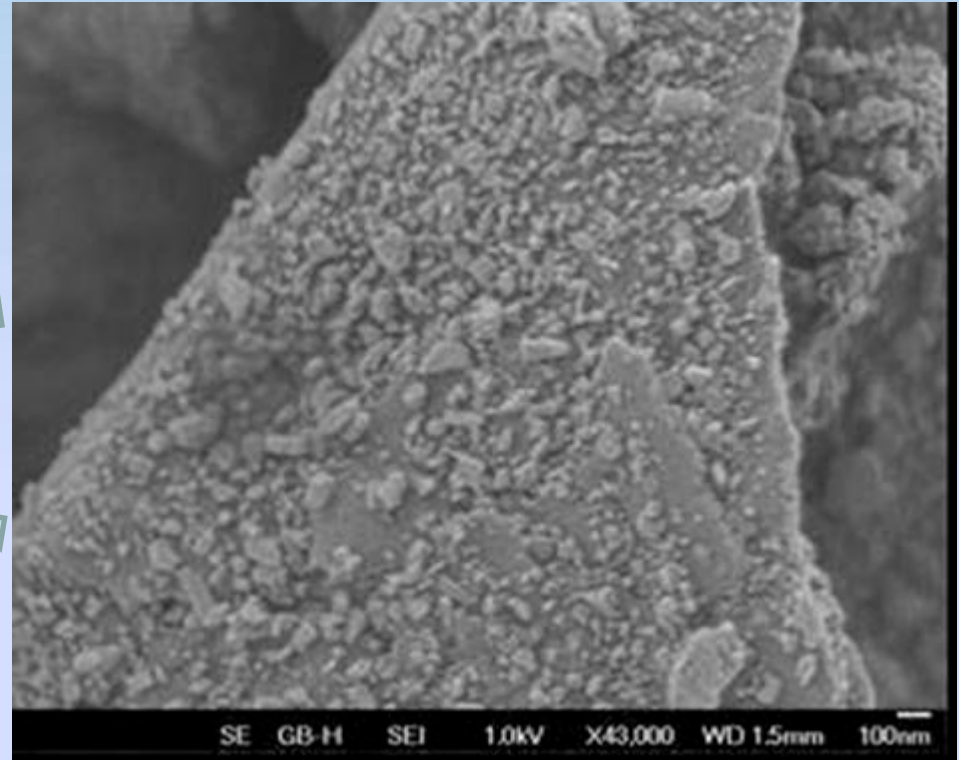
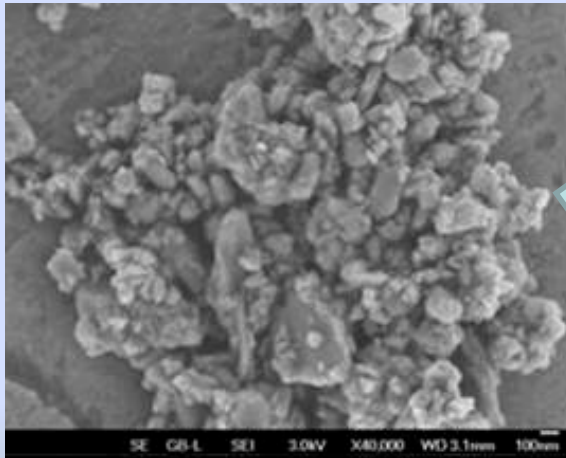
Obtained composites consists of flake particles of Teflon matrix with Metal inclusions

MAEC Al/MoO₃

Al-PAP-2

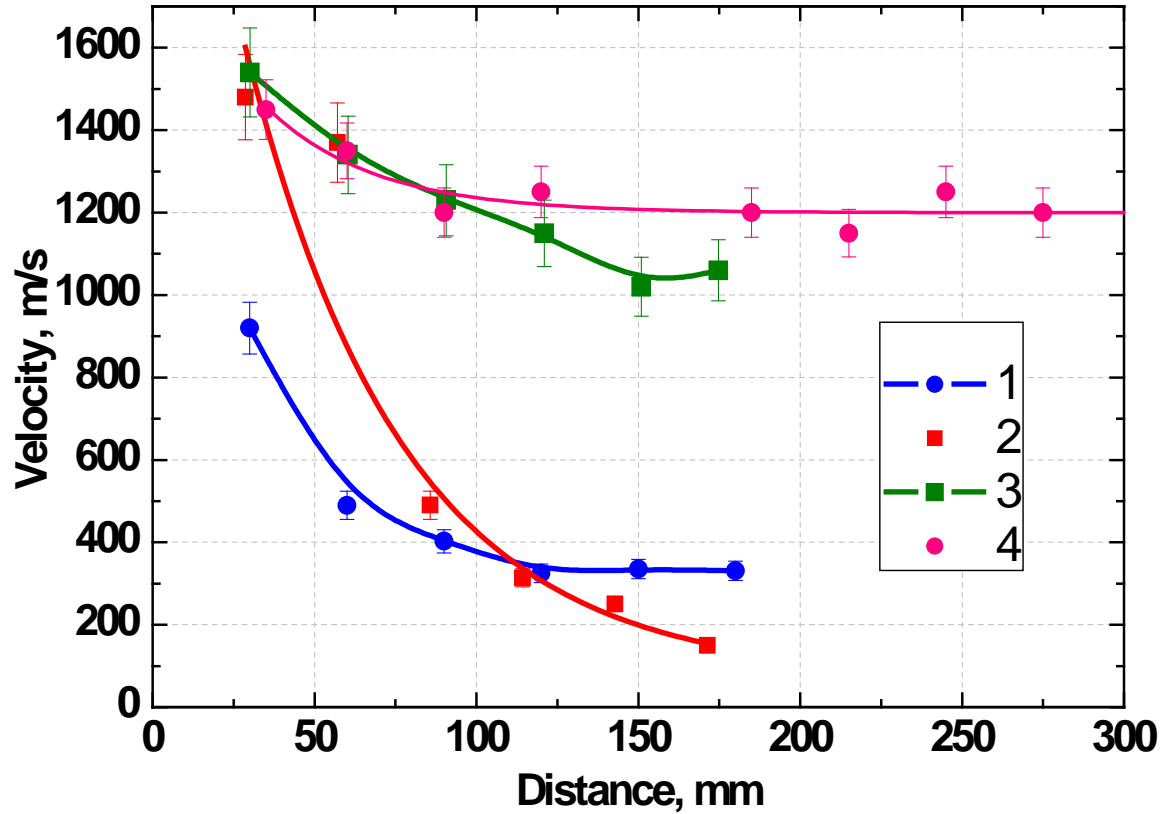


Nano MoO₃



Self-accelerating combustion regime with transition to explosion obtained for low-dense mixtures Al/MoO₃
For usual mixtures burning rate $u < 1 \text{ m/s}$
Mechanoactivated mixtures $u > 400 \text{ m/s}$

Detonation-like processes in MAECs Al, Mg + Teflon, MoO₃



Velocity of propagation of shock induced reaction in different MAECs:

- 1 – Mg/MoO₃ 34/66 ($\rho_0=1.13$ g/cc, $\epsilon=62\%$);
- 2 – Al/MoO₃ 32/68 ($\rho_0=1.43$ g/cc, $\epsilon=62\%$);
- 3 – Mg/Teflon 35/65 ($\rho_0=0.49$ g/cc, $\epsilon=75\%$);
- 4 – Al/Teflon 27/73 ($\rho_0=0.59$ g/cc, $\epsilon=74\%$)



Detonation - supersonic process
with constant velocity
(sound speed $C < 100$ m/s,
 $D = 800-1300$ m/s)

Materials Tested

Thermal effect of reactions Si, Al + PP, AP

Composition, Stoichiometric ratio	ρ_{\max} , g/cc	Reaction	Q, kcal/kg	$Q \cdot \rho \cdot 10^{-3}$, kcal/m ³
Si/KClO ₄ 28.8/71.2	2.46	$2\text{Si} + \text{KClO}_4 = 2\text{SiO}_2 + \text{KCl}$	2240	5515
Si/NH ₄ ClO ₄ 35/65	2.07	$9\text{Si} + 4 \text{NH}_4\text{ClO}_4 = \text{SiCl}_4(\text{g}) + 8\text{SiO}_2(\text{s}) + 2\text{N}_2 + 8\text{H}_2$	2230	4612
Al/KClO ₄ 34.2/65.8	2.58	$8\text{Al} + 3\text{KClO}_4 = 4\text{Al}_2\text{O}_3 + 3\text{KCl}(\text{s})$	2544	6560
Al/NH ₄ ClO ₄ 27.7/72.3	2.11	$10\text{Al} + 6\text{NH}_4\text{ClO}_4 = 5\text{Al}_2\text{O}_3 + 6\text{HCl} + 9\text{H}_2\text{O} + 3\text{N}_2$	2385	5032

Deflagration to Detonation transition MAEC Si + NH₄ClO₄ (30 min)

DDT in stainless steel tube (10 mm dia) L = 2 cm stady-state regime D = 1900 m/s
nano-Si/NH₄ClO₄ (<d> = 60 - 100 nm) 29/71 density = 0.48 g/cc (24% TMD)



Ni-Cr wire initiation

D = 1900 m/s

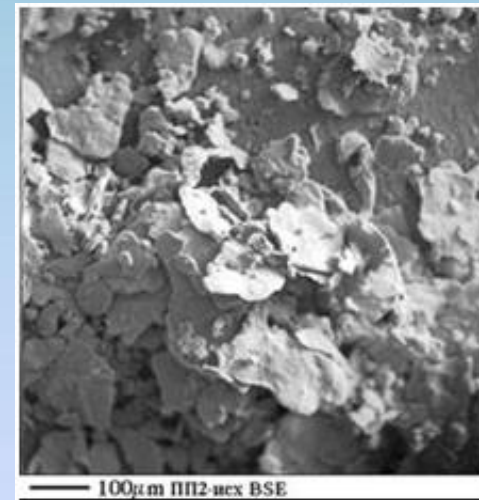
Materials Tested



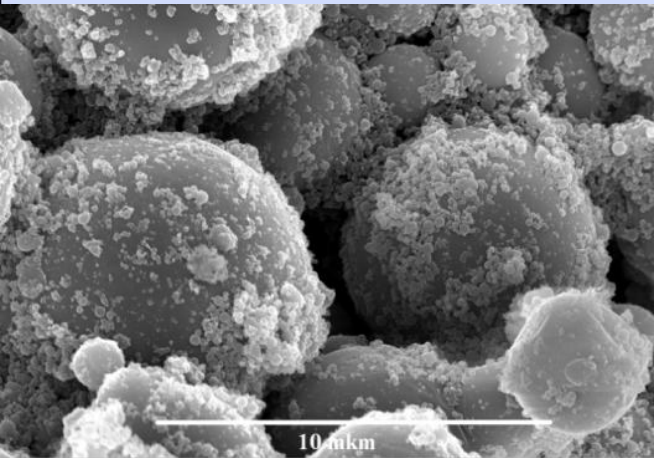
NH_4ClO_4
PA1. $\langle d \rangle \sim 200 \mu\text{m}$



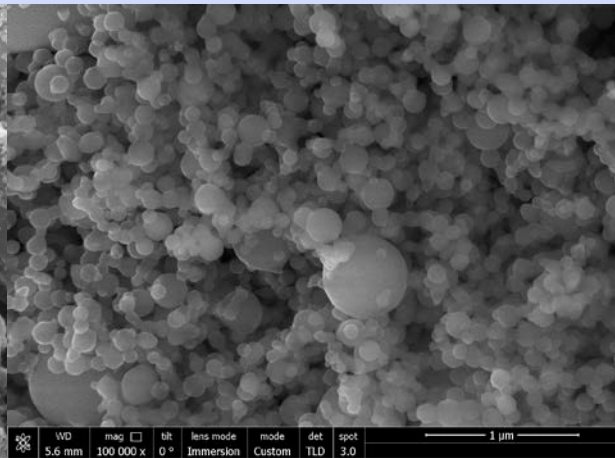
NH_4ClO_4
PA2. $\langle d \rangle \sim 20 \mu\text{m}$



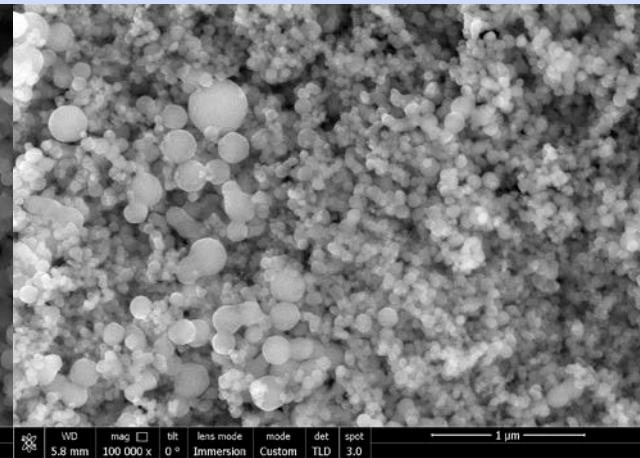
Al – PP-2
 $\langle L \rangle 70 * 1-5 \mu\text{m}$



Al ($8 \text{ m}^2/\text{g}$) (*GNIICHTEOS*)
 $\langle d \rangle \sim 260 \text{ nm}$ two fraction
3-5 μm and 100-300 nm

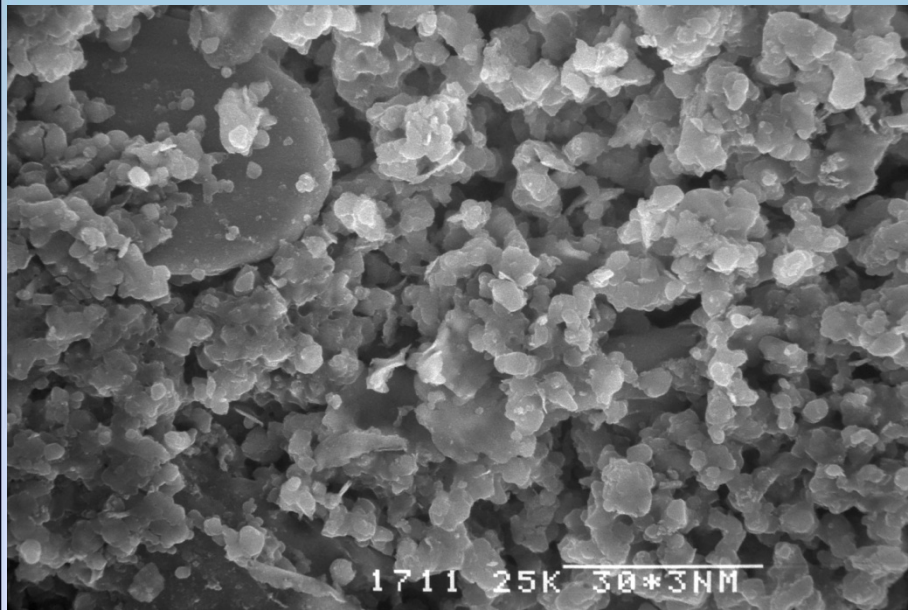


Alex (*Tomsk*)
 $\langle d \rangle \sim 100-200 \text{ nm}$

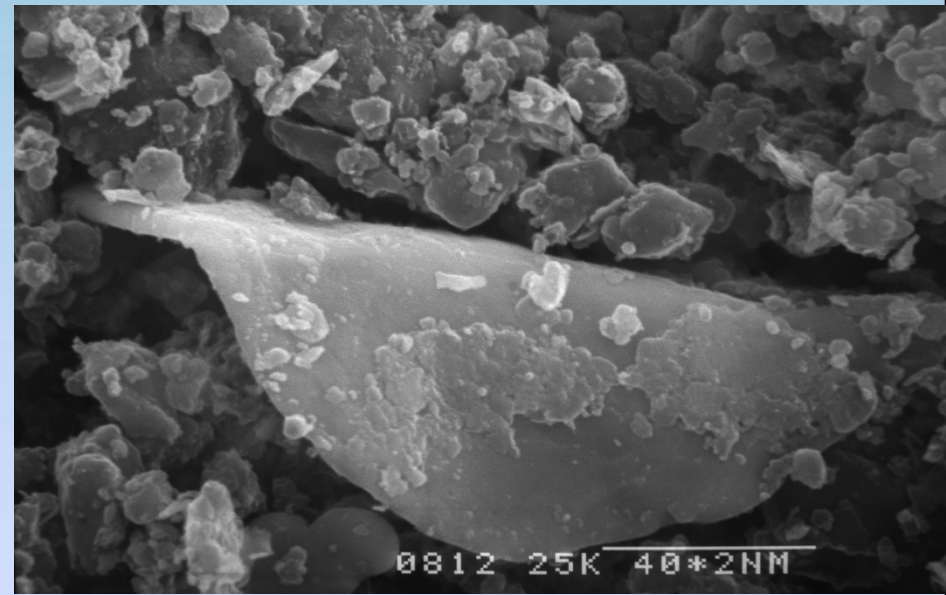


nAl (*INEP*)
 $\langle d \rangle \sim 100 \text{ nm}$

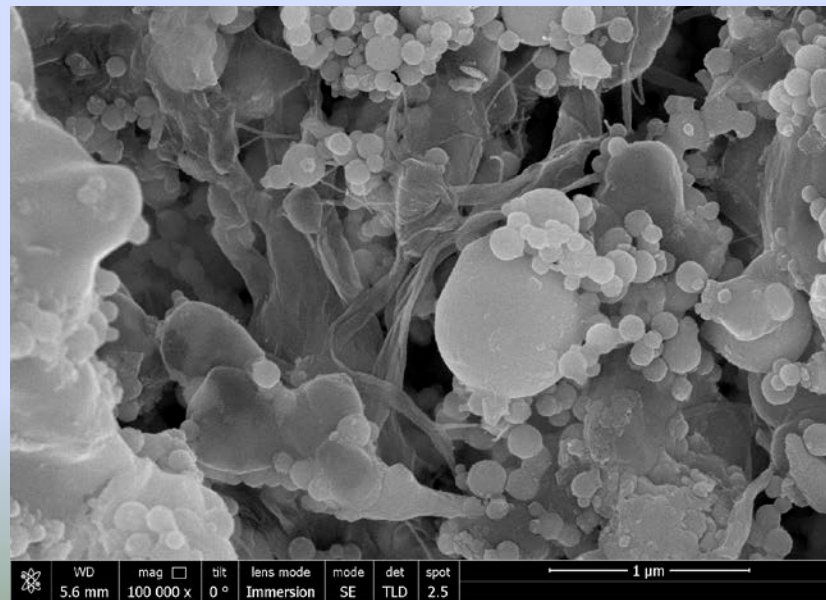
MAEC Al+AP



Al(PP-2)+AP

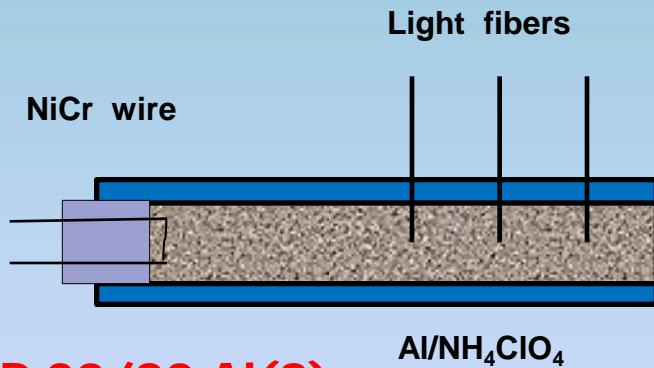


Al(8)+AP



Alex+AP+3%Fluoroplast-42

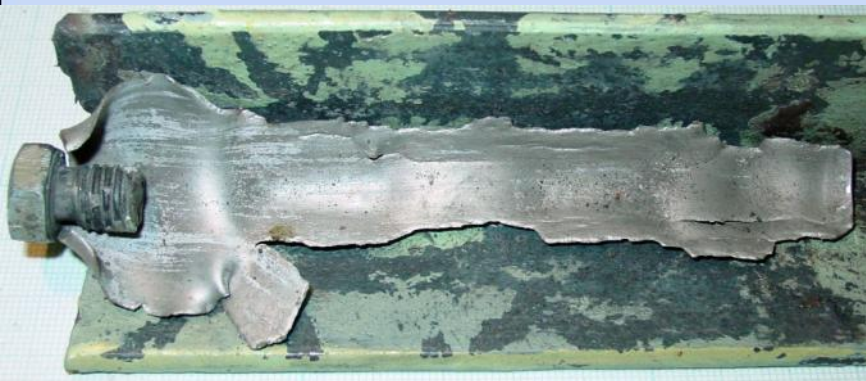
Deflagration to Detonation Transition DDT



metal tube \varnothing 10 mm length 120 mm
charge with electric gauges or light fibers
porosity of charges – $\varepsilon = 80-82\%$



Al/AP 20/80 Al(8)



$t_a = 35$ min, $D = 2380$ m/s
steel tube



$t_a = 20$ min, $D = 2310$ m/s
duralumin tube

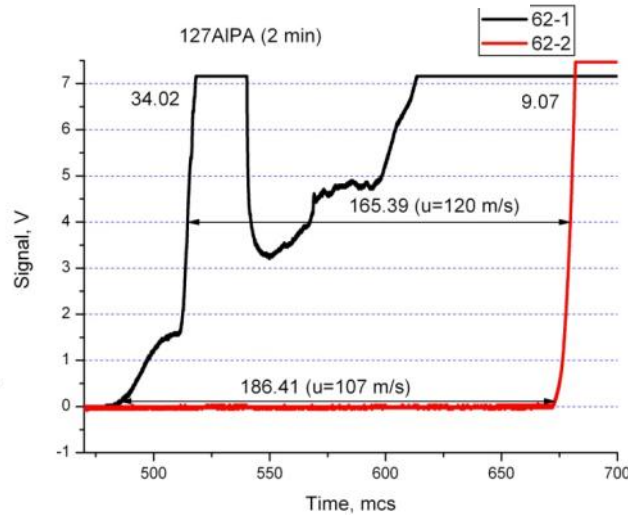


$t_a = 40$ min, $D = 2300$ m/s
duralumin tube

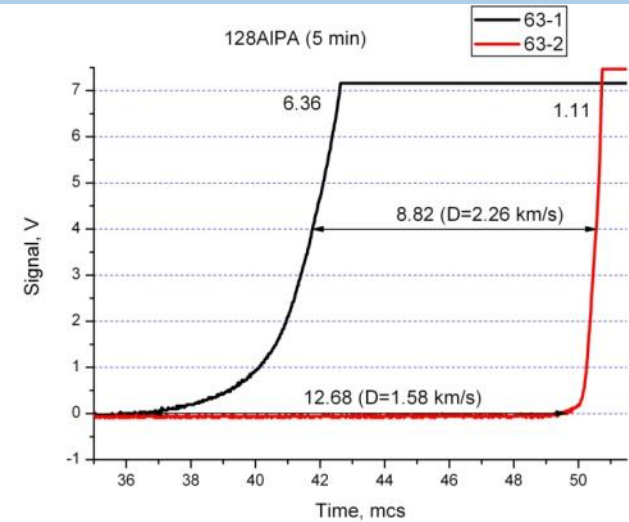
DDT Al/AP 20/80 Al(8) $\epsilon = 80-82\%$

Al/NH₄ClO₄
Al(8)
Signals

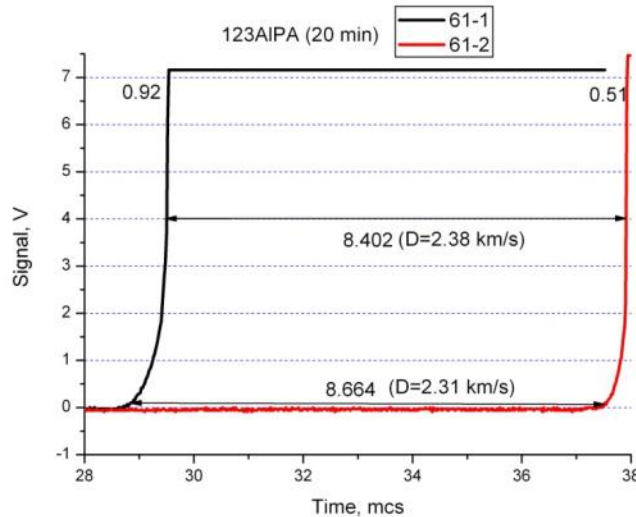
$t_{act} = 2 \text{ min}$ $u=110 \text{ m/s}$



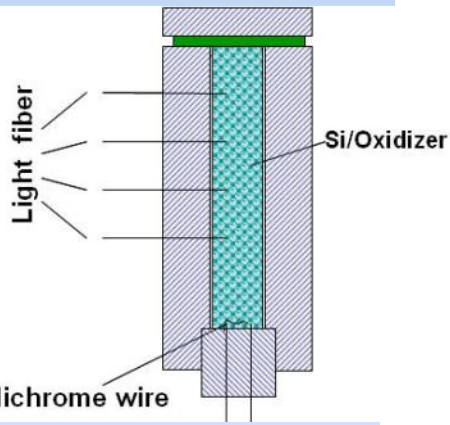
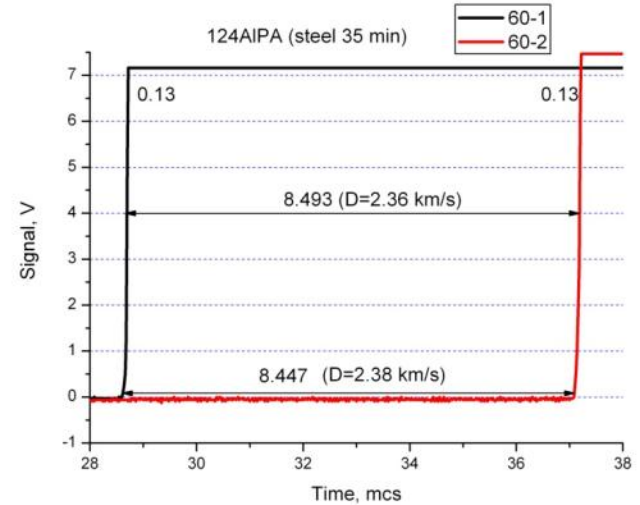
$t_{act} = 5 \text{ min}$ $D=1600 \text{ m/s}$



$t_{act} = 20 \text{ min}$ $D=2310 \text{ m/s}$

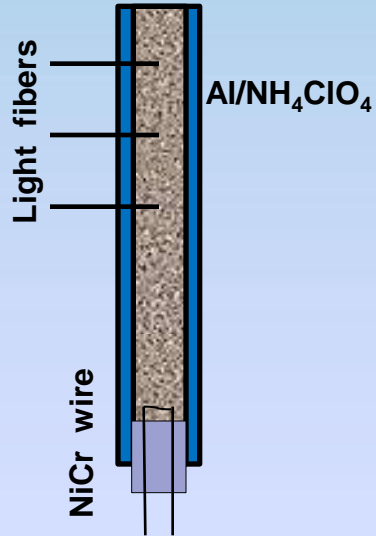


$t_{act} = 35 \text{ min}$ $D=2380 \text{ m/s}$

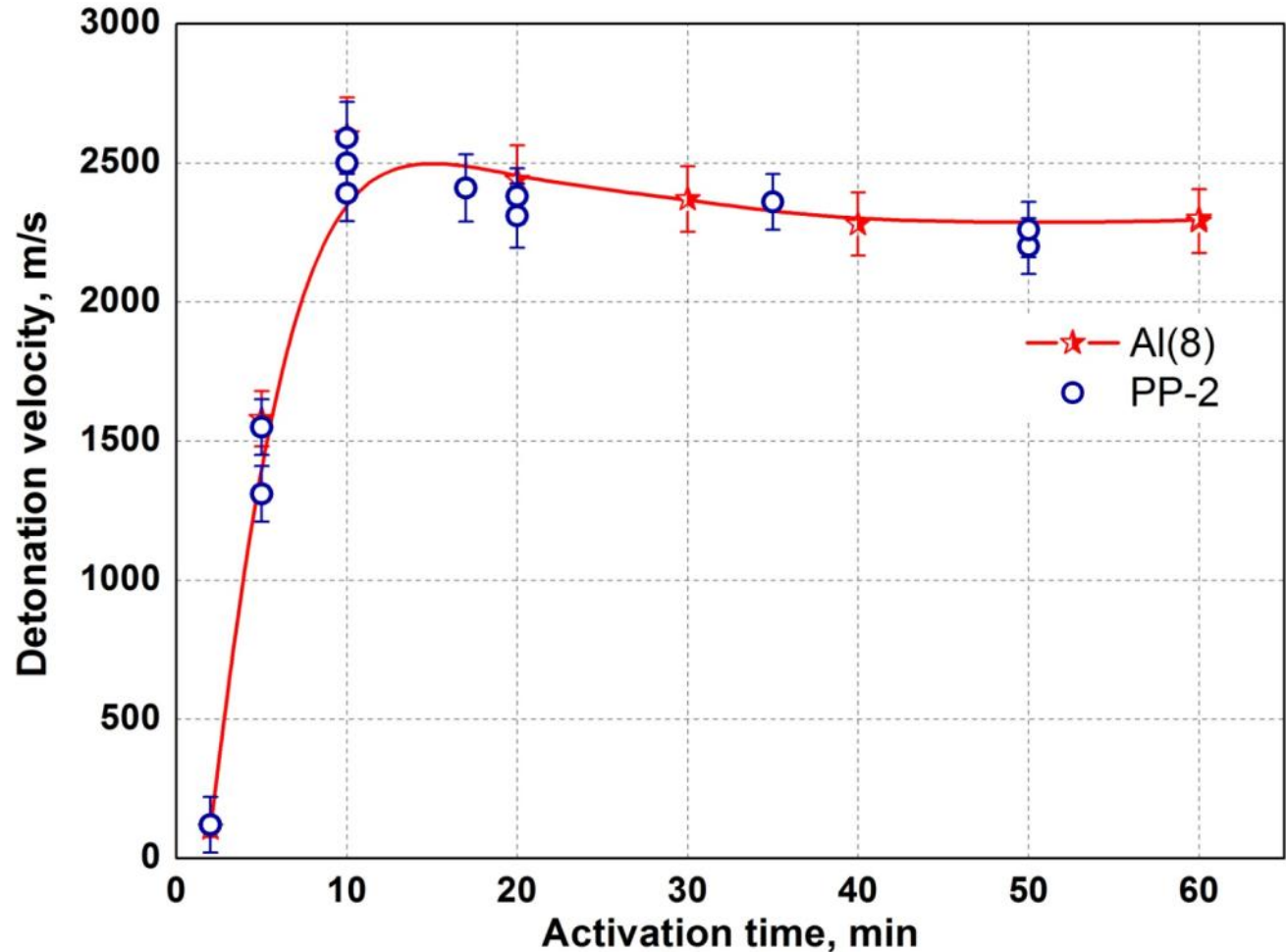


metal tube
 $\varnothing 10 \text{ mm}$
length 120 mm

DDT Al/AP 20/80 $\epsilon = 80-82\%$



aluminum
tube
Ø 10 mm
length 120 mm
 $\epsilon = 80-82\%$



Det. Vel. vs Time of activation

Mechanical sensitivity

P_{cr} activated Al/AP
in comparison with HE

BB	$P_{кр}, \Gamma Pa$
Lead aside	$0,38 \pm 0,03$
BTNEN	$0,79 \pm 0,02$
HMX	$0,99 \pm 0,03$
Al/AP (20/80)	$0,61 \pm 0,02$

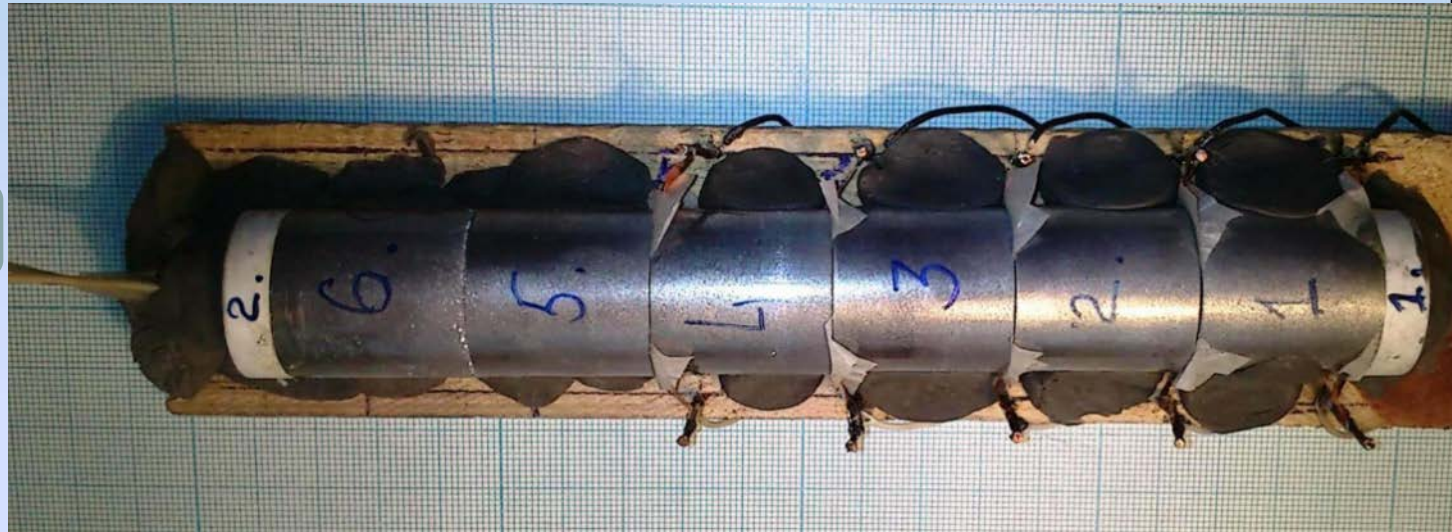
P_{cr} - critical pressure corresponding to the transition from mechanical destruction of charges in the shell of PMMA without an explosion to destruction with explosion

(method of the collapsing shell)
[Schetinin V.G. // *Physics of combustion and explosion*, 1999, V. 35]

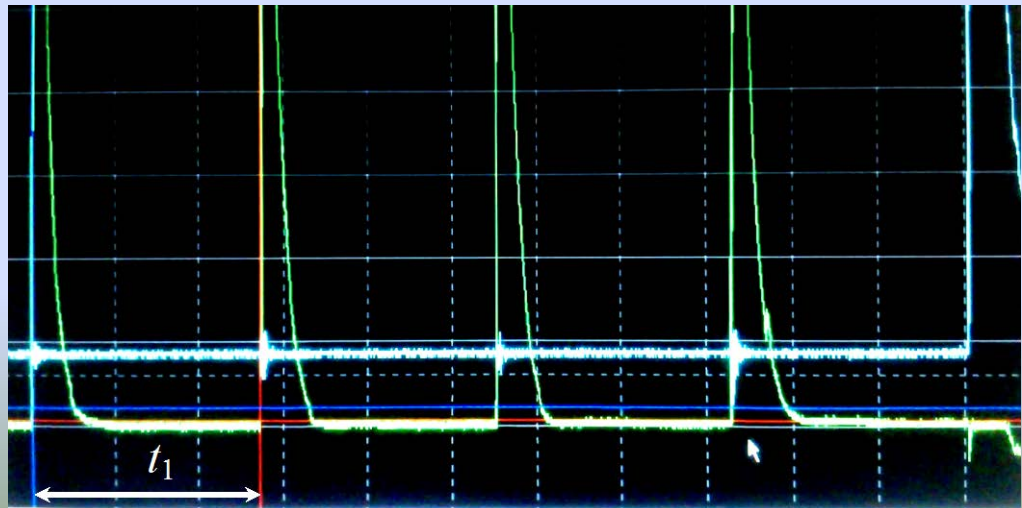
Detonation in pressed charges

Al/AP different densities and diameters

Experimental set up

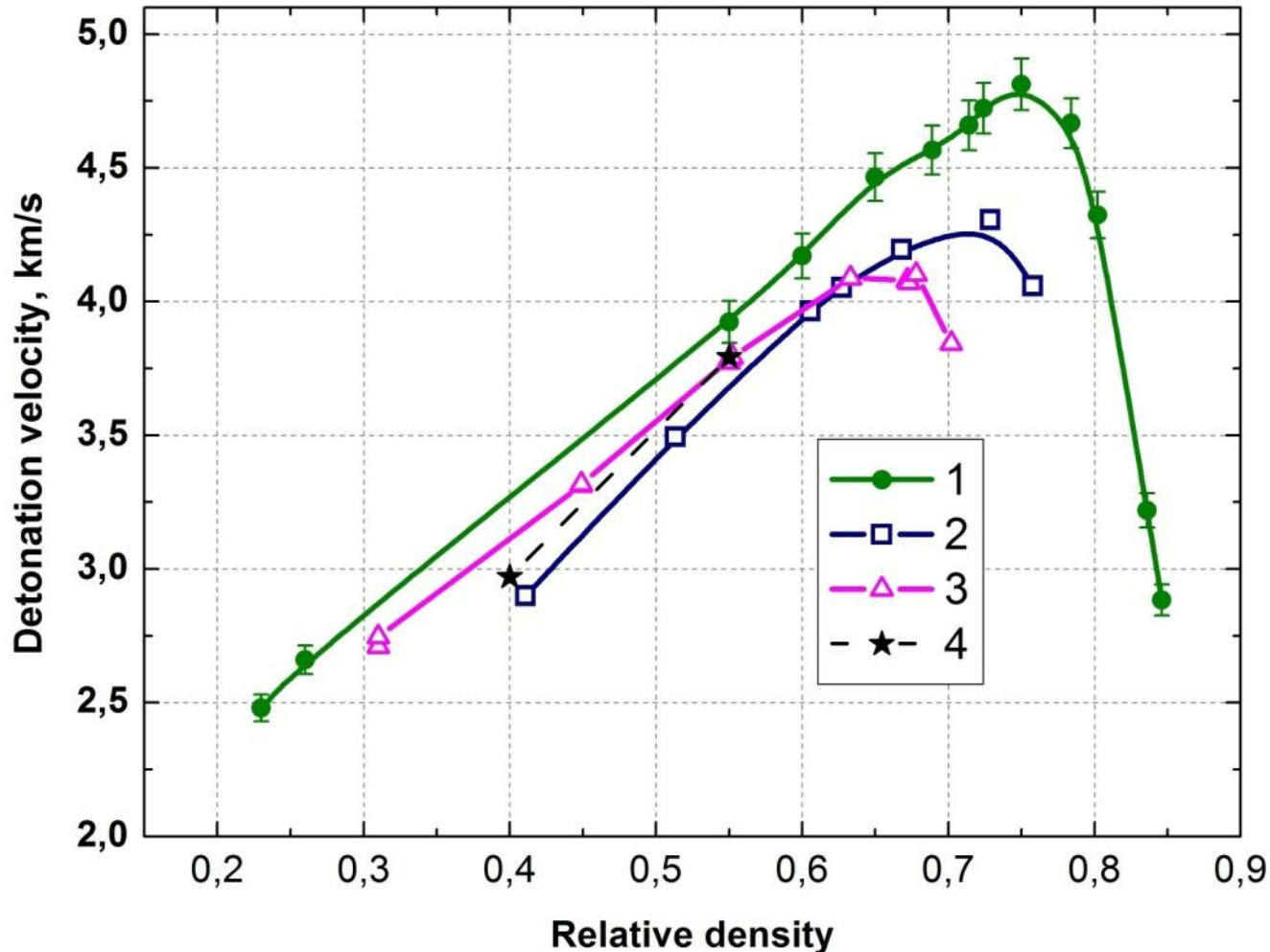


Signals



Detonation velocity vs relative charge density

Al (PP-2)/AP 20/80 (charge diameter $d = 25$ mm)



1 - Al/AP 20/80
 $t_{act} = 10$ min
Al - PP-2

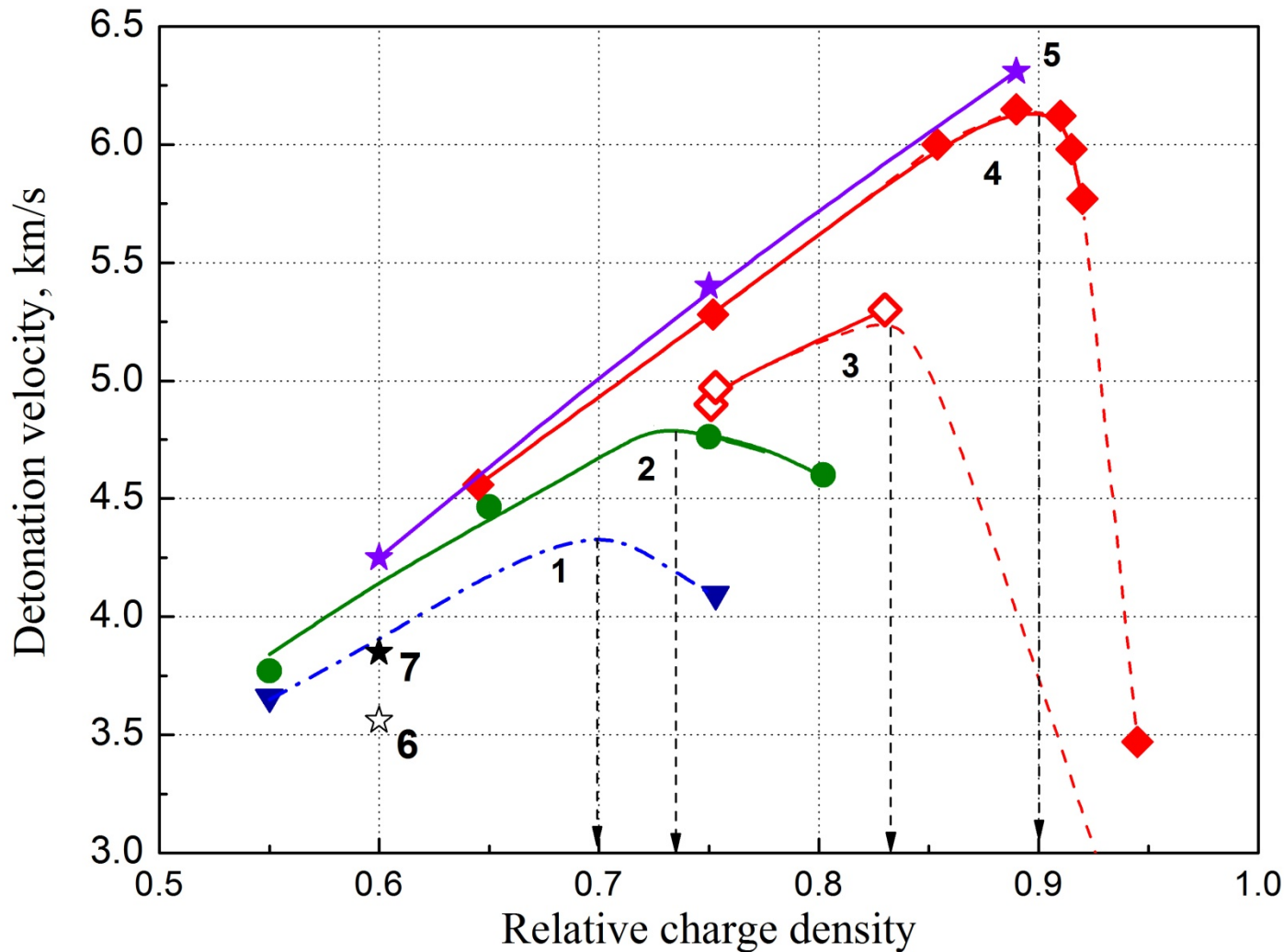
Donna Price data

2 - AP,
3 - Al/AP 10/90,
4 - Al/AP 20/80

[Donna Price,
A.R. Clairmont,
J.O. Erkman. *Explosive
Behavior of Aluminized
Ammonium Perchlorate*
Naval Ordnance
Laboratory Report
NOLTR 72-15, White
Oak, MD, USA, 1972].

Detonation velocity vs relative charge density

Al(PP-2), Alex/AP and nAl/AP 20/80 d = 25 mm



1 - nonactivated

2 - Al - PP-2
 $t_{act} = 10$ min

3 - Al - Alex
 $t_{act} = 1$

4 - Al - Alex
 $t_{act} = 10$

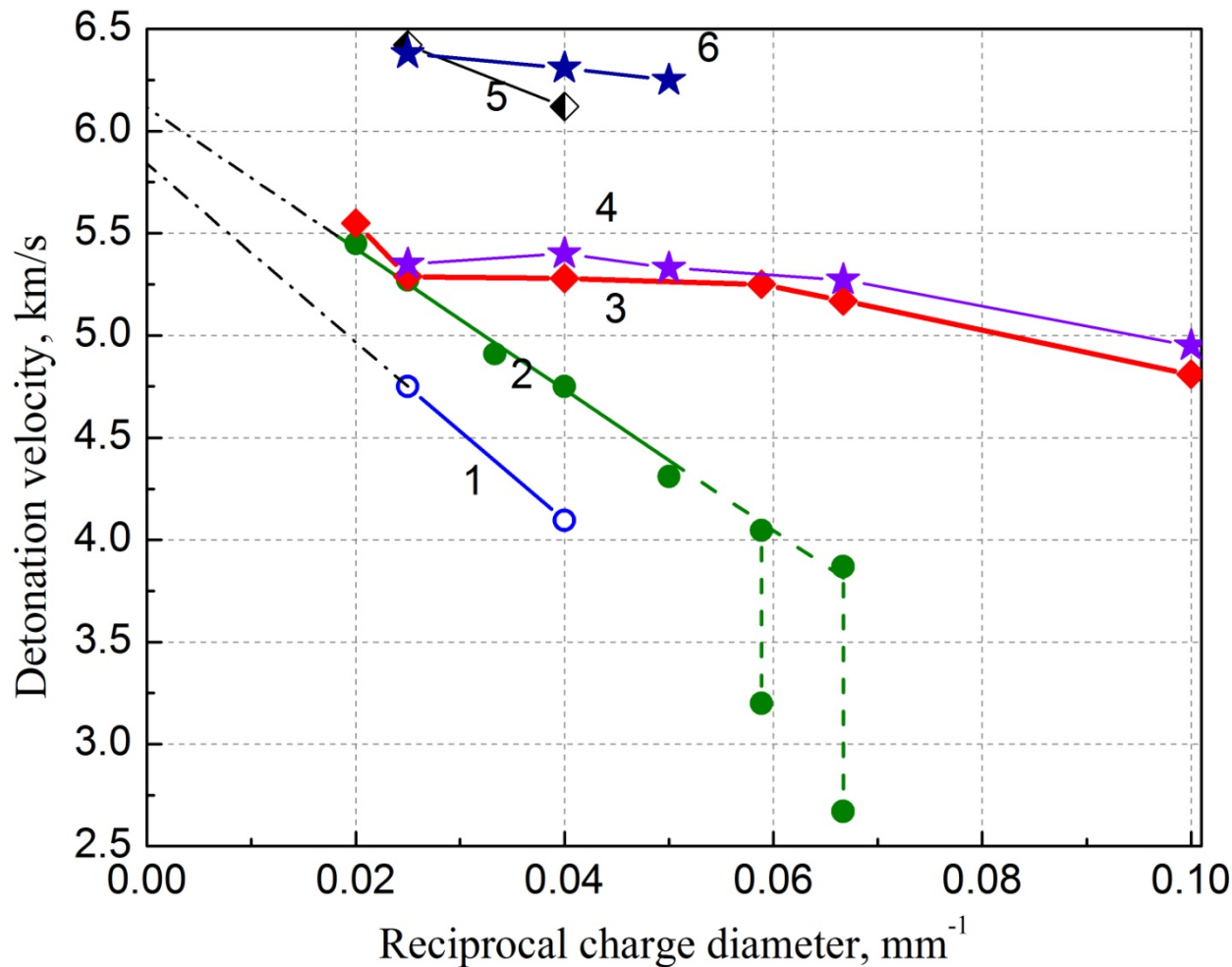
5 - Al - nAl
 $t_{act} = 10$

6 - AP(non-act)

7 - AP($t_{act} = 10$)

Detonation velocity vs reciprocal charge diameter (1/d)

Al/AP 20/80 (charge density 0.75 and 0.9 TMD)



0.75 TMD (1-4)

1 – non-activated

$t_{\text{act}} = 10$ min (2-6)

2 - Al - PP-2

3 - Al - Alex

4 - Al - nAl

0.9 TMD (5-6)

5 - Al - Alex

6 - Al - nAl

Conclusion

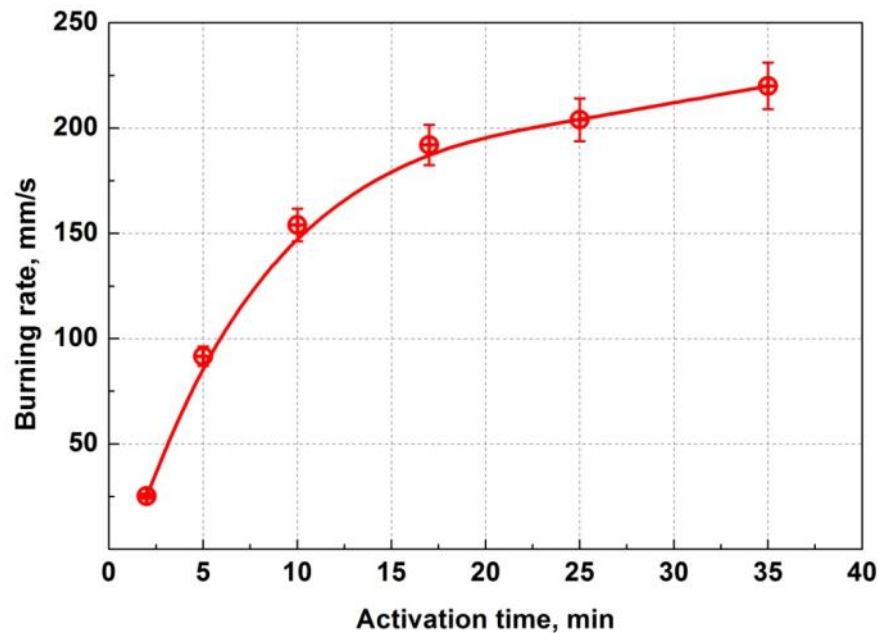
- **The results of work allow to consider a method of mechanoactivation as a way to control detonation velocity of explosive compositions on the base of oxidizer-fuel mixtures**
- **Sharing nano-scale components and mechanical activation can significantly improve the detonation ability of oxidizer - fuel mixtures**
- **Mechanoactivated energetic composites on the basis of aluminum and perchlorates can be of interest as perspective energetic materials for new initiating and incendiary devices with increased requirements on rate of energy realize**

Burning velocity of Al/KClO₄ (30/70) composite

Pressed charges, $\varnothing = 12$ mm, porosity = 10-15%

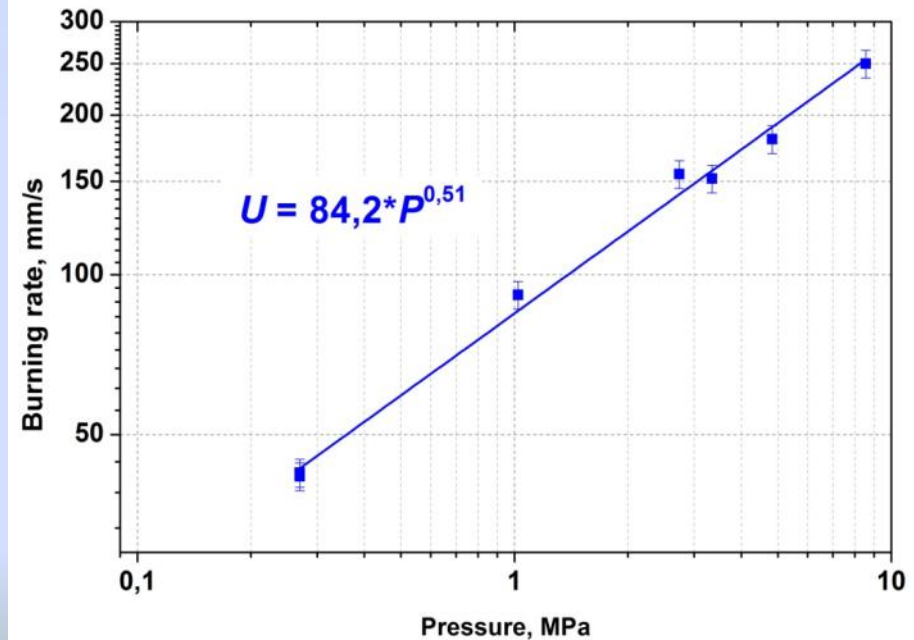
Burning velocity vs activation time

$P_0 = 2$ MPa

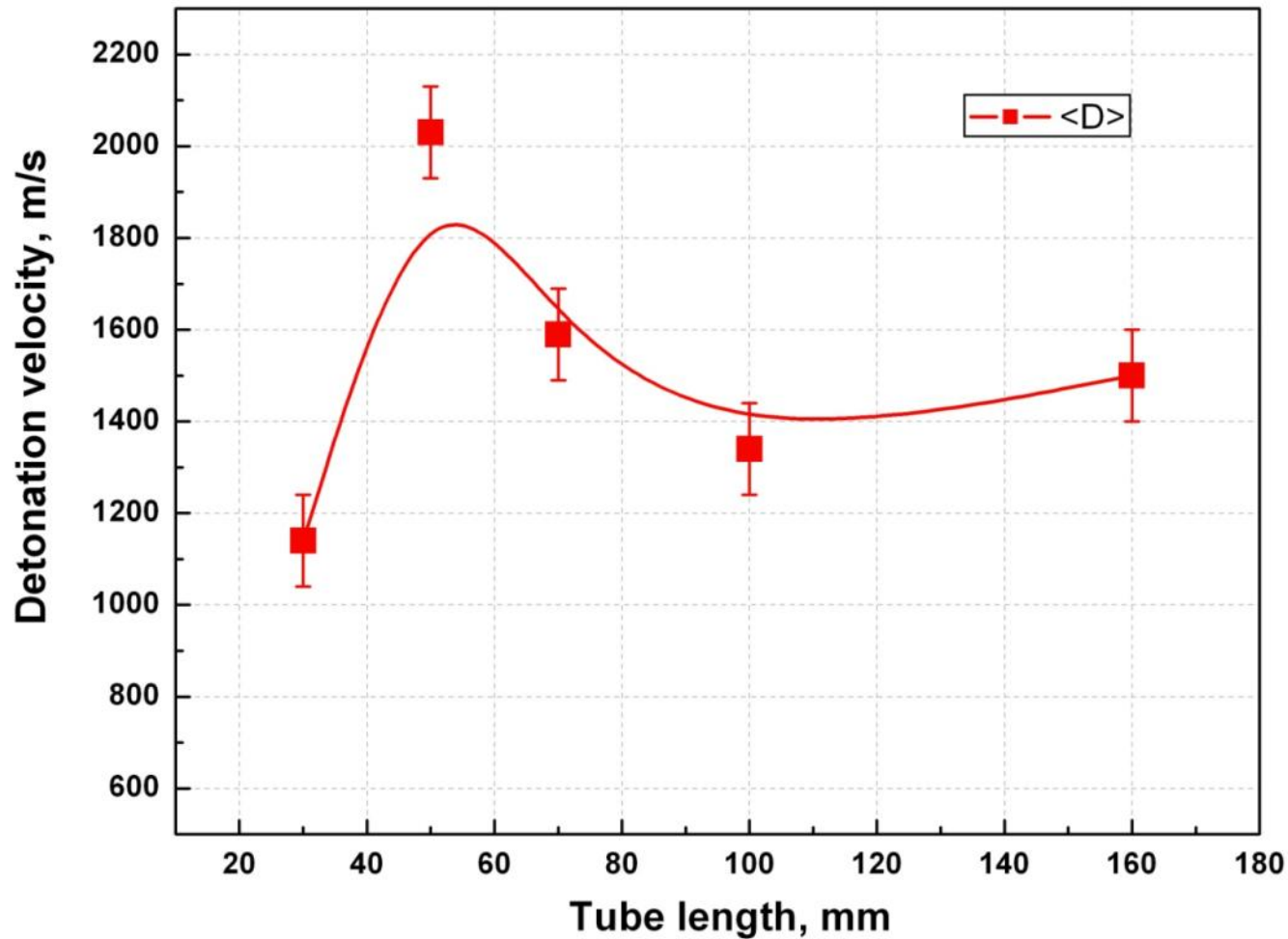
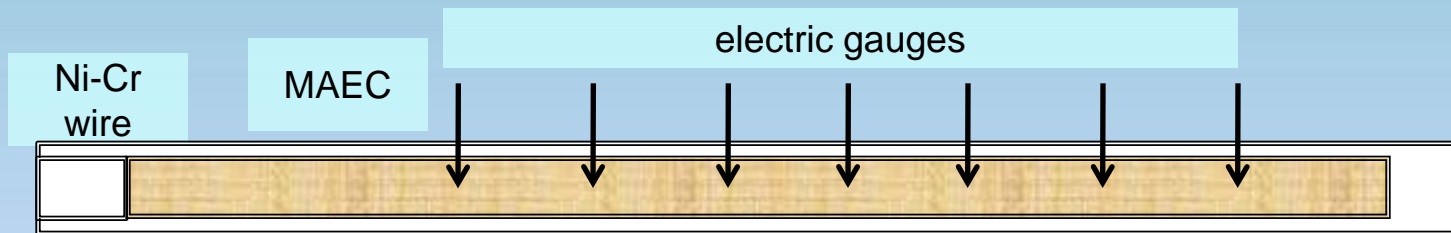


Burning velocity vs pressure (nitrogen)

$t_{act} = 10$ min



Detonation velocity Al/KClO₄ vs charge length



$\varnothing = 18 \text{ mm}$
charge length
= 180 mm
porosity
= 82-84%