Central European Journal of Energetic Materials, **2009**, *6*(3-4), 277-289
ISSN 1733-7178

Mechanical Activation of Al/MoO_3 Thermite as a Component of Energetic Condensed Systems to Increase Its Efficiency

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Abstract: In the present work a stoichiometric energetic compositions Al+MoO_3 prepared by dry mixing and by reactive milling of micro-scale particles were investigated. Morphology, particle size and surface structure of produced powders were examined using scanning electron microscopy, atomic-force microscopy, laser diffractometry and BET analysis. DSC/TG data were processed to obtain kinetic mechanism of the reaction between Al and MoO_3. The combustion rate of Al+MoO_3 thermite mixture increases with pressure, reaching a maximum at ~10 atm, and then decreases with further pressure increase. The rise of combustion rate at the low range of pressure is associated with the rise in the extent of the vapour phase penetrating the pores of the pressed sample as the ambient pressure increases. However, at a higher pressure the gas formation is suppressed, and the melt formed in the combustion process can selectively wet the pores resulting in inhibition of reaction. Burning rates of mechanical activated system Al+MoO_3 are two times higher then not-activated system at ambient pressure ~10 atm and 8 times higher at ~40 atm. In additional experiments, nano-scale MoO_3 powder was prepared by evaporation with a subsequent condensation onto cooled plate in an inert-gas flow. Scanning electron microscopy showed that nano-MoO_3 particles are absolutely spherical with mean diameter ~100 nm, and atomic-force microscopy

reveals smaller particles with mean diameter ~5-30 nm. DSC/TG data showed that the nano-MoO_3 starts to sublime earlier than micro MoO_3. The use of nano-sized components could considerably increase the burning rates of energetic condensed systems, because of its large specific surface, lower temperature of sublimation, and high reaction ability.

Keywords: thermites, burning rates, nano-MoO_3

Introduction

The decrease in the size of energetic materials particles, e.g., metal fuels and oxidizers, leads to an increase of the reaction surface area, which considerably enhances the combustion rate of propellant compositions. The crystal grid defects considerably accelerate the process of the thermal decomposition of energetic materials [1]. One of the most important types of defects – dislocations – in a great extent defines the mechanical and physical properties of crystalline materials. The chemical reactions on dislocations proceed much faster than on an ideal crystal. Mechanical-activated and nano-materials are known of having a high defect concentration, which is along with the large surface area the reason to expect the higher chemical activity of such materials in comparison to the conventional compounds. To show the influence of particle size distribution and mechanical-activated mixtures on combustion parameters, we have selected two compositions: stoichiometric thermite $2Al+MoO_3$ (two mole of aluminium and one mole of molybdenum trioxide) and multi-component mixture used in pyrotechnic torches [2], based on as-received powders and prepared by arrested reactive milling (ARM) $27\%Al/51\%MoO_3/19\%KClO_4/3\%(C_2F_4)_n$.

Experimental

To reduce the particle size of as-received MoO_3 and to prepare mechanical-activated mixture ($Al+MoO_3$) the arrested reactive milling (ARM) [3, 4] was used. The specific material for this study was prepared by milling of the component powders in 100-ml steel vials using a shaker mill (ICP RAS). Starting blends were prepared in stoichiometric proportions from powders of elemental aluminium (75% pure, flakes aluminium powder) and molybdenum trioxide MoO_3 (99% pure). Steel balls of 5 mm and 8 mm diameter were used as a milling media, the balls mass were 15 times higher than mixture mass. Milling for 60 min was carried out in ambient atmosphere.

To synthesize the nano-sized MoO_3 we have created the lab-device presented in Figure 1. It works on the principle of evaporation with a subsequent condensation onto cooled plate in an inert-gas flow. The micro-sized prouder 7 evaporates with hitting element 4 and transits with inert gas flow onto plate cooled with liquid nitrogen 8. The temperature of evaporation is 900 °C. The velocity of the inert (N_2) gas flow is 10 litres per hour.

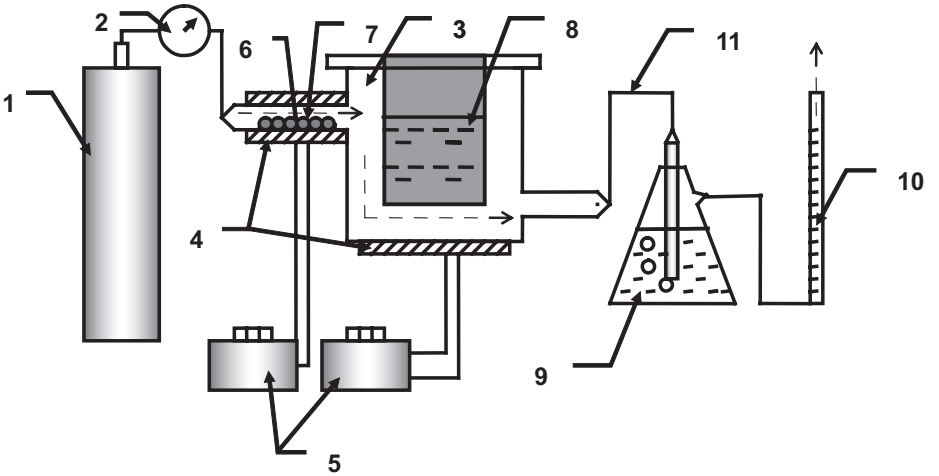


Figure 1. Scheme of experimental set-up to synthesize nanopowders (1- inert gas container, 2- reducer, 3- device reactor, 4-heaters, 5-heating controller, 6- thermostable holder, 7- precursor powder, 8- liquid nitrogen, 9-water filter, 10- gas flow-meter, 11- gas trace).

Materials

In the present study, as-received molybdenum trioxide and aluminium powder of different grades, alone with the stoichiometric thermite mixture 27%Al+73%MoO_3 were studied. Different fabrication techniques to obtain smaller particles were applied*, i.e.,* dry mixing, arrested reactive milling (ARM) of as-received powder, and evaporation with a subsequent condensation technique of as-received MoO_3 as a precursor. Table 1 shows the investigated powders and compositions along with the fabrication technique. In addition, the multi-component pyrotechnic compositions Al/MoO_3/$KClO_4$/$(C_2F_4)_n$, which is of use for pyrotechnic torches were investigated. These samples (#8-#10 in Table 1) were fabricated by adding three different variations of treated Al/MoO_3 stoichiometric compositions into $KClO_4$/$(C_2F_4)_n$ mixture.

Table 1. List of investigated powders and fabrication techniques

Sample	Composition	Fabrication technique
1	MoO_3	As-received
2	MoO_3	Arrested reactive milling (ARM)
3	MoO_3	Evaporated and subsequently condensated
4	Al	As-received flaky powder
5	Al+MoO_3	Mixing of as-received powders
6	Al+MoO_3	Mixing of Al(as-received) and MoO_3(produced by ARM)
7	Al+MoO_3	ARM of sample 5
8	Al/MoO_3/$KClO_4$/$(C_2F_4)_n$	Mixing of sample 5 with $KClO_4$/$(C_2F_4)_n$
9	Al/MoO_3/$KClO_4$/$(C_2F_4)_n$	Mixing of sample 6 with $KClO_4$/$(C_2F_4)_n$
10	Al/MoO_3/$KClO_4$/$(C_2F_4)_n$	Mixing of sample 7 with $KClO_4$/$(C_2F_4)_n$

Equipment

To investigate materials morphology scanning electron microscope (SEM) Phenom (FEI, Netherlands) was used.

Atomic force microscopy (AFM) images were recorded with NTEGRA Prima (NT-MDT, Russia) operated in a tapping mode at ambient conditions. Cantilevers with curvature radius less than 10 nm were used.

The BET surface area was determined with FlowSorb III 2305 (Micromeritics, USA) by measuring adsorption of gas mixture (30%N_2/70%He) on powder surface.

To determine the particle size distribution of the investigated powders laser diffractometer "Laska-1" (Lumex, Russia) was used.

Investigation of thermal behaviour was carried out using the DSC/TG simultaneous thermal analyzer NETZSCH STA 409PC (Germany). The samples were loaded into alumina crucibles and a dry argon purge flow of 35 ml/min. Calibrations of TG mass, DSC baseline, and temperature were conducted before the experiments.

A theoretical evaluation of the adiabatic temperatures for studied ECS was conducted using the TERMPS computer code.

The experimental investigations of burning rate were performed using a constant pressure bomb in nitrogen atmosphere. The calculated average accuracy of the burning rate measurements is ±3%. The sample pellets were cylindrical (8 mm in diameter) for burning rate experiments. Due to the quartz windows, the combustion process was recorded for the subsequent digitizing.

Results and Discussion

Components

Aluminium. SEM analysis reveals as-received particles of aluminium flaky powder have a lamellar shape with an average particle thickness 0.2-0.5 μm and effective size of 20-30 μm (Figure 2). Effective diameter of 7.6 μm was measured by laser diffractometry, and BET surface area of Al was found to be of 7.2 m^2/g. Active aluminium content was obtained by comparative DSC-analysis: the calculated integral melting effect of investigated powder was compared to that of the reference powder with the standard activity. The powder activity thus obtained was found to be about 75%.

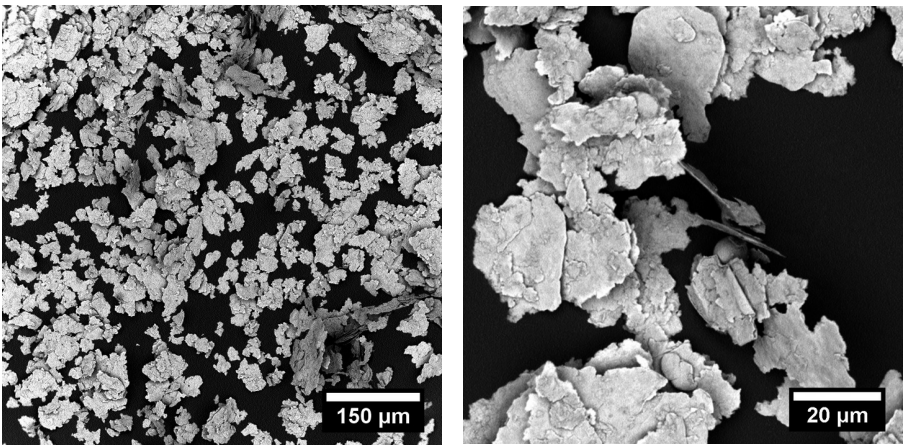
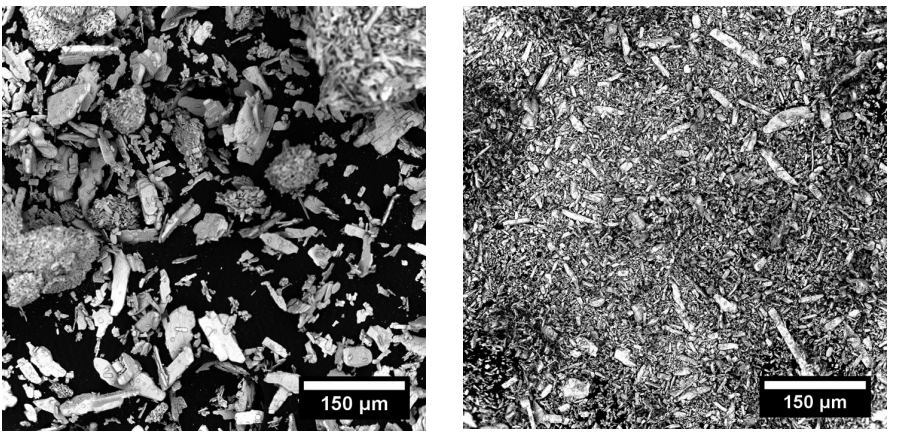


Figure 2. SEM images of aluminium as-received flaky powder.

Molybdenum trioxide − as-received powder (sample 1, Table 1). SEM image of conventional MoO_3 powder is shown in Figure 3a. Micro-sized molybdenum trioxide powder consists of large crystals of irregular shape with the size about 10-50 μm. The effective diameter of as-received powder d_{eff}=16.5 μm was obtained with laser diffractometry measurements (Figure 4).



a) *b)*

Figure 3. SEM images of MoO_3 powder: a) as-received; b) produced by ARM

Molybdenum trioxide − fabricated by arrested reactive milling (sample 2). The structure of as-received powder after arrested reactive milling (milled MoO_3 powder) is represented by small crystals with the particle size less than 10 µm (Figure 3b). The effective diameter value of milled MoO_3 powder (d_{eff} =1.5 µm) was obtained by laser diffractometry method (Figure 4). Effective size derived from BET surface area measurements is 1.26 m^2/g.

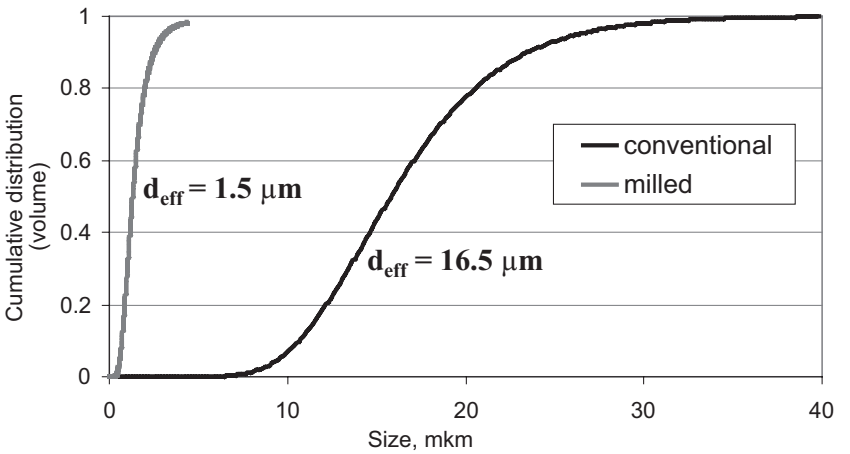
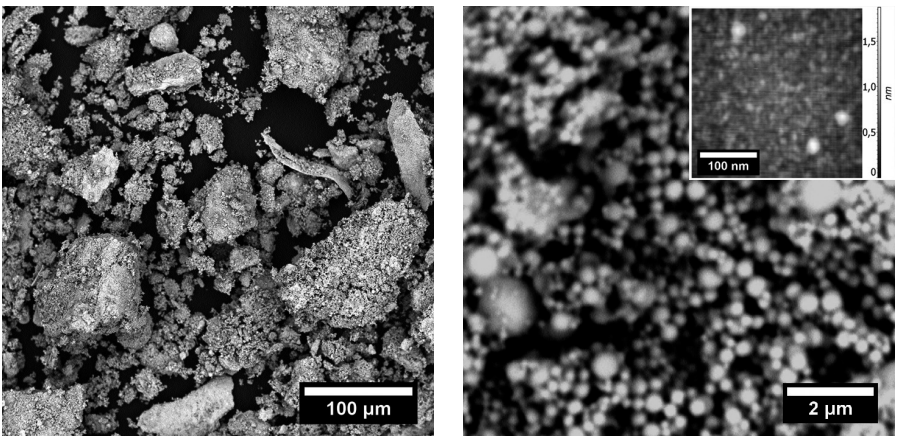


Figure 4. Particle size distribution of MoO_3 powders made by laser diffractometry, sample 1 (as-received MoO_3 black curve) and sample 2 (milled MoO_3, grey curve).

Molybdenum trioxide − nano-sized powder (sample 3). Nano-sized MoO_3 powder has a complex structure with at least three levels, as indicated in Figure 5: conglomerates of nano-particles with the average particle size of 10-100 μm (Figure 5a), which in turn consist of ideally spherical particles with several hundred nanometres in diameter (Figure 5b). Atomic-force microscopy allows detecting smaller particles fraction with diameter 5-30 nm (insertion in Figure 5b).



a) *b)*

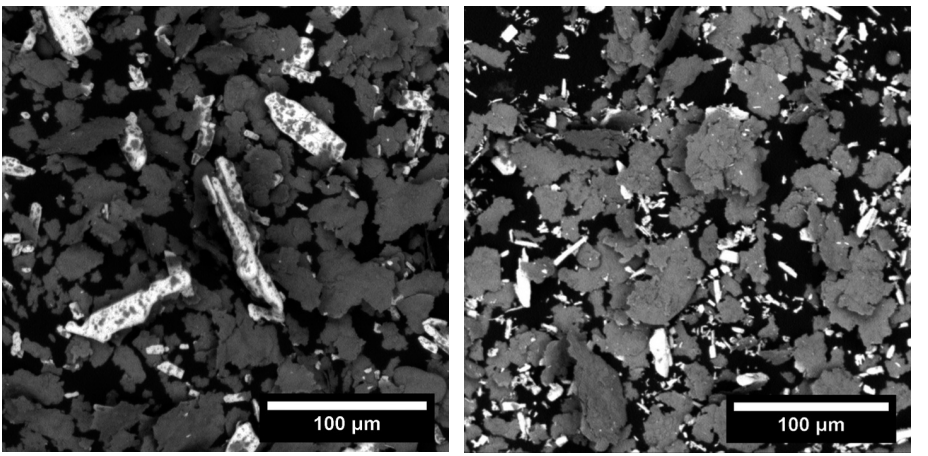
Figure 5. SEM and AFM images of MoO_3 nano-sized powder: a) conglomerates; b) nano-sized particles.

Binary compositions (thermites)

Al(as-received)/MoO_3(as-received). Figure 6a represents SEM images of aluminium/ molybdenum trioxide thermite (sample 5, Table 1). The lightest component is molybdenum trioxide. Large MoO_3 crystals are partially covered with aluminium flakes.

Al(as-received)+MoO_3(produced by ARM). SEM images of mixture with ARM-produced MoO_3 (sample 6) are similar to composition with as-received components, but molybdenum trioxide particles are much smaller (Figure 6b).

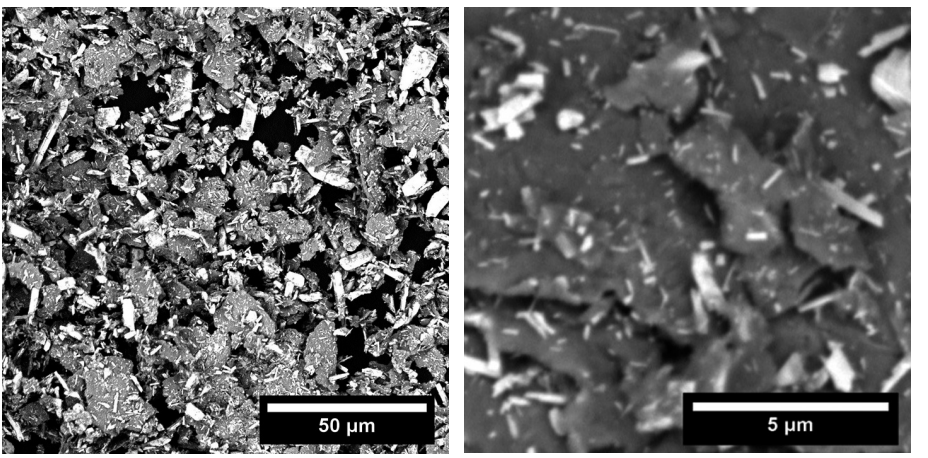
Initial components were mixed by conventional "dry" process (mixer "Turbula" type, time of process –1 hour, mass of load – to 5 g). However, the resulting microstructure uniformity is quite far from the ideal mixing. To improve the mixture uniformity, the mechanical activation process was elaborated and applied (so called ARM). It is known, that ARM technique allows not only grinding particles of the components, but also enhancing homogeneity of composition.



a) *b)*

Figure 6. SEM images of Al/MoO_3 powder: a) Al(as-received)+MoO_3(as-received); b) Al(as-received)+MoO_3(produced by ARM).

Sample 7 (Table 1) was produced by ARM of as-received mixture of Al and MoO_3. Figure 7 shows that mechanically-activated mixture is much more homogenous then compositions prepared by conventional "dry" process. Aluminium flakes entirely covered with small particles of MoO_3 having an average size even less then 200 nm.



a) *b)*

Figure 7. SEM images of (Al+MoO_3) activated by ARM.

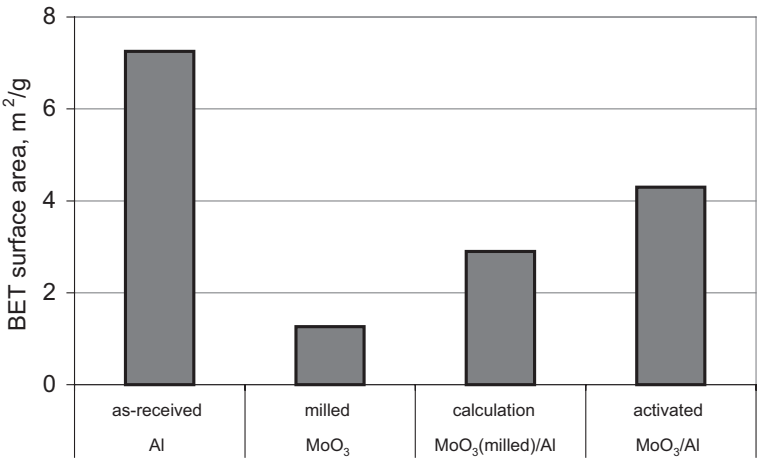


Figure 8. BET surface area for initial powders and final mixtures.

Figure 8 shows the BET-surface area values of the initial components and final mixture of activated components (sample 7) in comparison to the calculated as additive function surface area. Surface area of thermite mixture prepared by ARM is about 1.5 times higher, than calculated surface area of as-received Al and milled MoO_3.

Thermal analysis

Molybdenum trioxide. In Figure 9 the DSC and TG curves of as-received MoO_3 and of the milled powder are presented. The endothermic peak at 800 °C has been assigned to melting point of as-received MoO_3, whereas for milled powder it occurs at lower temperature (790 °C). The evaporation temperature of powders is close to 800 °C, but for milled powder the evaporation proceeds more intensively. The nature of the large exotherm on the DSC curve of milled MoO_3 needs further investigation.

Thermites Al/MoO_3 with as-received components milled MoO_3 and mechanically activated mixture. There is no strongly marked exothermic peak of reaction for the every composition, important that MoO_3 melting peak disappeared. Content of unreacted aluminium in mechanically activated mixture at 660 °C (sample 7), which was evaluated by the endothermic aluminium melting peak, is six times less than that one for composition with as-received components (sample 5). The reaction is represented by complex combination of exothermic and endothermic processes: diffusion of oxygen through an Al_2O_3 product layer and a multi-staged MoO_3 decomposition [5].

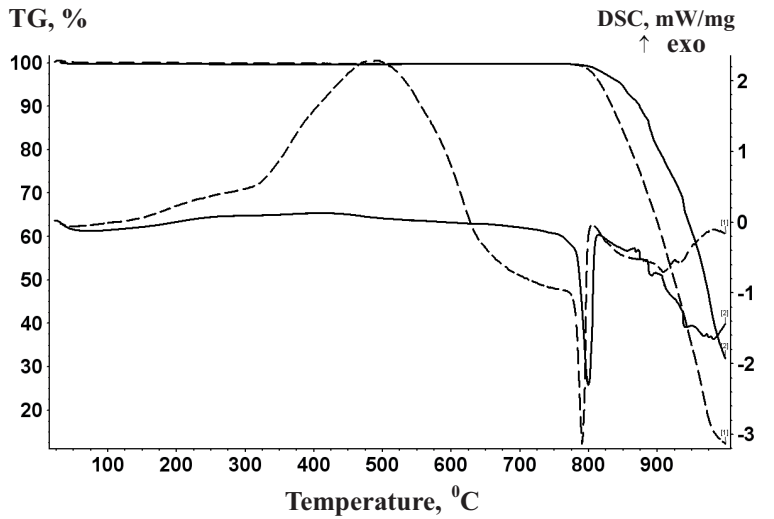


Figure 9. DSC/TG curves for sample 1 (as-received MoO_3 solid curves) and for sample 2 (milled MoO_3, dash curves).

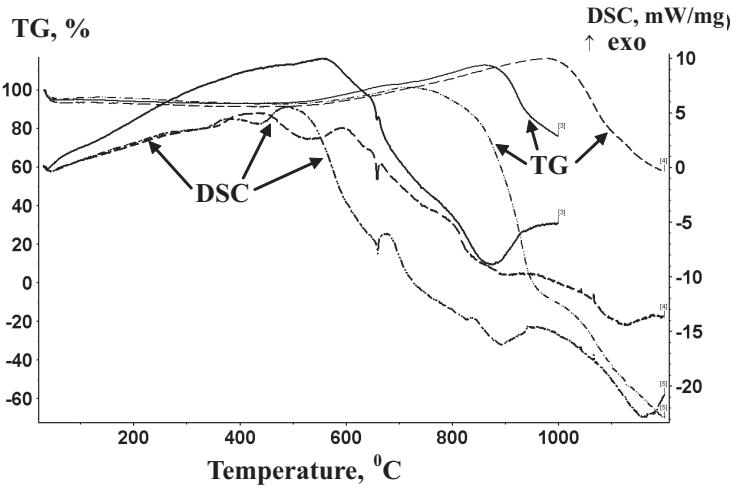


Figure 10. DSC/TG curves for activated mixture (sample 7, solid curves), mixture with milled MoO_3 (sample 6, dashed curves) and with as-received components (sample 5, dash-doted curves).

Combustion parameters

Burning rate of Al/MoO_3 thermites with activated and as-received components. Burning rates of two mixtures (samples 7 and 5) was measured under nitrogen in the pressure range 1-40 atm, and presented in Figure 11. The combustion rate of Al+MoO_3 thermite mixture increases with pressure, reaching a maximum at ~10 atm, and then decreases with further pressure increase. The rise of combustion rate at the low range of pressure is associated with the rise in the extent of the vapour phase penetrating the pores of the pressed sample as the ambient pressure increases. However, at higher pressure the gas formation is suppressed, and the melt formed in the combustion process can selectively wet the pores resulting in inhibition of reaction. Burning rates of mechanically activated system Al+MoO_3 (sample 7) is two times higher than that of the not-activated system (sample 5) under pressure ~10 atm and about 8 times higher under pressure 40 atm. In contrast to activated thermite, mixtures with as-received components do not burn at one atmosphere. The samples porosity of mixtures (sample 5 and 7) are about the same and indicated in Table 2.

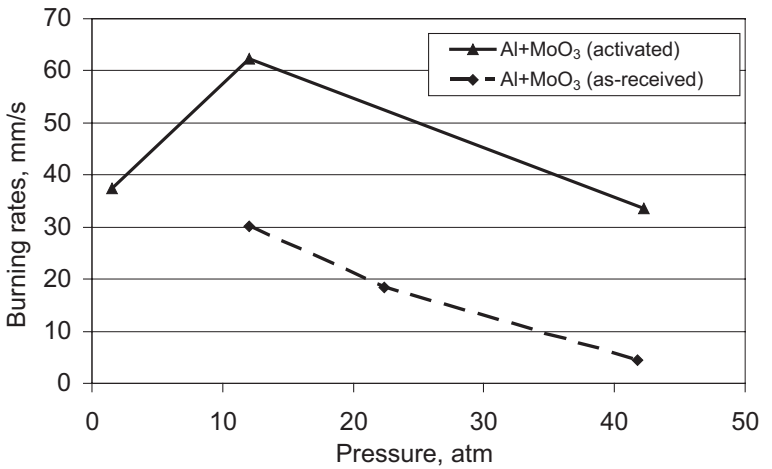


Figure 11. Thermite burning rates with as-received (sample 5) and activated components (sample 7).

Table 2. Burning parameters of thermite mixtures with as-received and activated components

27%Al+73%MoO_3	Porosity, %	U, mm/s		
		1 atm	10 atm	40 atm
sample 5 (as-received)	28	no burning	30	4.5
sample 7 (activated)	28	37	64	34

Multi-component pyrotechnic mixture 27%Al/51%MoO_3/19%$KClO_4$/3%$(C_2F_4)_n$ based on as-received and activated thermite components (Al/MoO_3). Preliminary thermodynamic calculations reveal that this composition (sample 9, Table 1) has a high adiabatic reaction temperature T > 4000 °C, the large volume of gas products Vg = 170 l/kg. Condensed phase of the reaction products consists mostly of Al_2O_3-40% and Mo-20%. To increase the efficiency of these pyrotechnic compositions we have treated the "thermite" part Al/MoO_3 (samples 9, 10) and add it to $KClO_4$/3%$(C_2F_4)_n$.

Burning rates of composition with activated components (sample 10) is two times greater then that of the composition with as-received powders (sample 8), as shown in Figure 12. Under pressure above 10 atm the pressure exponent of the burning rate law ν for the composition with activated thermite decreases from 0.9 to 0.17, which is favourable for the use in pyrotechnic torches at high pressures.

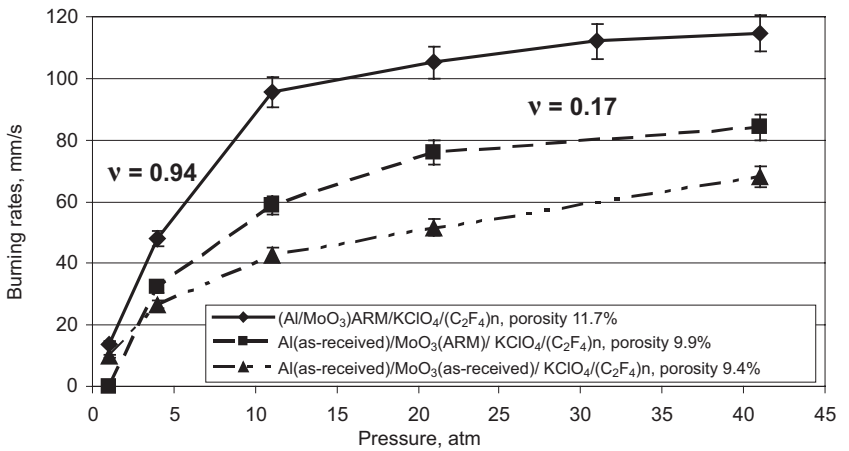


Figure 12. Burning rates for multi-component mixtures based on as-received and activated thermites.

Conclusion

Microstructure and combustion parameters of compositions based on aluminium and MoO_3 were studied with the particle size and the mixing technique variation.

Morphology, dispersity and thermal behaviour for as-received, milled and activated powders were investigated. Obtained, the average size of as-received flakes aluminium is 10-50 μm and chemical activity 75%. Micro-sized MoO_3 consists of crystals of about 50 μm, for nano-sized MoO_3 the structure is spherical and generally formed by particles about 100 nm.

For milled MoO_3 the temperature of the melting peak is shifted to lower temperatures.

Arrested reactive milling of stoichiometric thermite mixture Al/MoO_3 considerably increases the burning rate. The same effect was experimentally observed for pyrotechnic compositions Al/MoO_3/$KClO_4$/$(C_2F_4)_n$ where two components Al/MoO_3 were pre-treated by ARM before adding to final composition. The use of ARM does not reflect on the pressure exponent in the burning rate law.

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