# Regulation of the burning parameters for energetic materials based on ammonium nitrate and metal nanopowders and nonmetals

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**Abstract**. The results of study for the influence of metallic and nonmetallic nanopowders on the combustion parameters of mixed energetic materials based on ammonium nitrate are presented and compared with materials, containing micropowders of metals. The catalytic activity rank of the powders is plotted showing their effect on the combustion characteristics of mixed energetic materials.

## 1. Introduction

The use of metallic and nonmetallic nanopowders (NPs) as a fuel in mixtures of energetic materials (EMs) with various compositions has a long history [1–3]. Rather extensive material has been collected to date on the thermal–kinetic parameters of NP oxidation and the NP impact on ignition and combustion parameters and the thermal decomposition and combustion of EMs based on ammonium perchlorate (AP), inert hydrocarbonaceous and active combustible binders (CBs), containing primarily nitroesters and energetic supplements, predominantly nitramines [4, 5]. It should be noted that a significant part of compositions used in the studies underlying the EMs does not meet the requirements of processibility and component compatibility of compositions obtained on the basis of metallic and nonmetallic NPs or other solid components of EMs, including oxidizers and energy supplements. The chemical compatibility requirement practically eliminates the possibility of using most components of EMs with NPs of aluminum, as well as transition metal oxides, which are of high interest for the combustion catalysis of EMs. Technological problems associated with the use of NPs are related with the substantial reduction of the critical filling characteristics (filling limit, the degree of filling corresponding to the percolation transition), leading to an increase in the viscosity of EMs of 10 and 100 times more than with EM-based microdispersed powder fillers. In addition to the abovementioned arrangements of the EMs based on AP (relating to rapidly burning materials), the necessary increase in their combustion rate and the reduction of aluminum agglomeration during combustion and of the level of other energy losses is implemented more effectively by methods, which do not require the use of NPs, primarily aluminum, containing usually no more than 90 wt % of the base material. As applied to fast burning EMs based on active combustible binders and nitramines, including ballistic gunpowder, the use of aluminum instead of microfine NP leads to insignificant effects when increasing the combustion rate or even the inhibition of burning. Therefore, it is

advisable to focus on the use of metal and nonmetal NP as a primary fuel or additives to EM compositions for fundamental solutions to existing problems of their combustion, including metallized mixtures.

The use of NP in slow burning EMs is of great interest. The high efficiency of using NP in such EMs may be due to the increase in the reaction time of EMs components and products of their thermal decomposition (pyrolysis) with NP, as well as the features of the physicochemical interaction associated with the high catalytic activity and high content of oxide layers on a nanoparticle surface. For example, an oxide layer of aluminum NP predominantly contains a catalytically active γ-modification and an amorphous modification of $Al_2O_3$ in an amount of 10–20 wt %. Industrial brands of microfine granular aluminum powder (ASD-1, ASD-4, ASD-6, ASD-8) used in EMs contain up to 0.5 wt % of catalytically inert α-$Al_2O_3$ particles on their surface.

One of the promising applications of NP objects are EMs based on ammonium nitrate (AN), which is widely studied and used in compositions for various purposes, being an ecologically clean and safe chlorine_free oxidizer. The ammonium nitrate, AN-based EMs, and various CBs have low burning rate and temperature values, high values of the lower ignition limit and burning by pressure (2 – 10 MPa), and inad_missibly great losses in energy and mass due to incomplete combustion, as well as an anomalously high agglomeration of metallic fuel and slagging during the combustion of metallized nitrates in EMs. The combustion efficiency of nitrate EMs (diminishing the losses on agglomeration and slagging and increasing the rate of burning) can be increased using nanodispersed powders of metals and nonmetals.

In this work we continue earlier investigations presenting the experimental results on the influence of the type of metallic and nonmetallic powders and their microdisperse equivalents on the burning rate of nitrate energetic materials (EMs).

## 2. Objects and methods

We investigated regularities of the influence of metallic (Al, Cu, Fe, Ni, Zn, B) and nonmetallic (B, C), aluminum oxide $Al_2O_3$, and aluminum-magnesium alloy powders with different dispersivities on the combustion rate of nitrate EMs. To obtain a comparative base, we used certified micropowders with a size from units to hundreds of micrometers: aluminum (spherical) ASD-1, ASD-4, ASD-6, and ASD-8; titanium PTEM; tungsten PV-1; iron PZhV-1; copper PMS-1; and nickel PNE-1. These materials were prepared by the electrodeposition of zinc, aluminum-magnesium alloy (PAM) with a weight ratio Al:Mg = 1:1, and aluminum oxide micropowders in α and γ forms. As the nanopowders we used certified metallic powders of aluminum, nickel, and zinc obtained under the electroexplosion of wires and nonmetallic powders of C and B. The choice of α and γ-$Al_2O_3$ micropowders (MP) for studying the combustion catalysis and thermal decomposition of EMs is motivated by the fact that an oxide film on the MP of Al represents a catalitically "inert" α-$Al_2O_3$, whereas the oxide film on the NP of Al contains γ-$Al_2O_3$ used as the catalyst in various chemical processes [2]. In addition, the NPs of Al are used predominantly in most metallized EMs.

The base EMs included SKDM-80 combustible binders (divinyl rubber SKD plasticized by transformer oil), which is very compatible with nearly all metallic and nonmetallic powders [2] in an amount of 12.3 wt %, MP ASD-6 15 wt %, ammonium nitrate and the rest of the substance is a two-component NP mixture with a ratio of coarse to small fraction of 1/1. The effect of the metal fuel type was analyzed upon the full replacement of aluminum powder on the metal powder. The B and C powders were introduced into EMs with the partial replacement of aluminum for connecting the mixtures thereof. In studying the burning processes of the base EMs, the powders were introduced with a concentration of 2 wt % from the mass of the mixture (100%). Experimental data on the burning rate ($u$) were approximated by the powerlike function of pressure of the form $u(p) = b \cdot p^v$.

## 3. Experimental results and discussion

Figure 1 shows the determined burning rates of EMs with different microdispersed metallic fuels depending on pressure (experimental data in the figure are approximated by curves). All EMs are

incapable of sustained combustion at pressures below 1-2 MPa (as well as at normal conditions in atmosphere of air). All MPs except for Ti increase the burning rate of the base EMs (at low pressures up to ~5 MPa). For MP of Ti, W, and Cu, parameter b is diminished, whereas zinc and PAM increase the value of b. The exponent $v$ of the power law increases when replacing aluminum (ASD-6) by metallic powders used in this series of experiments. A MP of Ni is similar to a MP of W in regards to its catalytic activity. The PZhV-1 iron powder causes a decrease in the burning rate of the mixture when compared to the base EM and considerable growth in the lower threshold (up to 6-8 MPa) of the pressure of stable ignition and burning the mixture. For the considered EM composition, one can plot the following relation of metallic (alloy) activity corresponding to the increasing burning rate: Fe < ASD-6 ≈ Ti < Ni ≈ W < Cu < Zn < PAM.

Figure 2 samples the data on the impact of metallic MPs and aluminum oxide additives on the burning rate of the base EM. The series of additive activity is fully consistent with the series obtained upon complete replacement of aluminum powder by the metals considered: the most active MP is Zn; the next are the MPs of W and Ti (there is almost no impact of the latter on the rate of base EM burning).
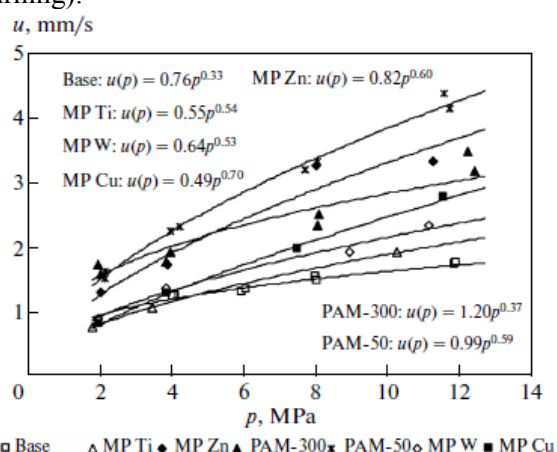


**Figure 1.** Impact of fine-dispersed metallic fuel on the burning rate of the base EM
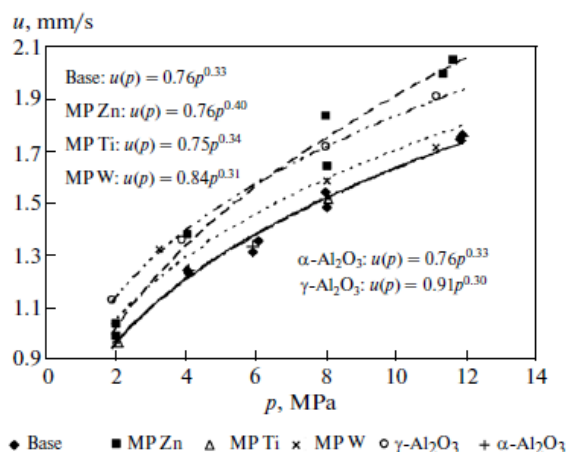


**Figure 2.** Impact of metallic MP additives (2 wt % above 100 wt % of mixture) and aluminum oxide on the burning rate of the base EM

All other MPs of metals also have an insignificant impact on the rate of base EM burning. This figure also shows the data of EM catalysis by oxides with different crystalline modifications. Additives of W and $\gamma$-Al$_2$O$_3$ cause the growth of parameter b; other additives of MPs do not affect the value of this parameter, while the values of parameter $v$ are nearly constant. This allows one to make a qualitative conclusion on the effects of W and $\gamma$-Al$_2$O$_3$ on the processes in condensed phase. The activity of tungsten in the condensed phase (c-phase) is likely caused by its solubility in the melt of AN. A significant influence of $\gamma$-Al$_2$O$_3$ on the combustion characteristics of nitrate based EMs is qualitatively similar to that observed upon the burning of EMs based on the ammonium perchlorate (AP) as an oxidizer [2].

Figure 3 samples the data showing the impact of metallic and nonmetallic NPs on the burning rate of EMs upon the full or partial replacement of aluminum ASD-6 (EMs with NPs of B and C). As a rule, the intercalation of NP into EMs results in a considerable decrease in the lower pressure of stable ignition and burning up to 0.2-0.5 MPa. However, at a pressure close to atmospheric pressure, only Al and C NPs can maintain the stable combustion of EMs that do not contain other effective combustion catalysts like o-carborane or fast-burning additives. Nanodispersed Cu powder slightly increases the rate of EM burning when compared to a copper micropowder. This is likely caused by the interaction of copper with the melt of ammonium nitrate accompanied by the formation of solutions of basic materials and reaction products (metal, oxide, nitrate, and ammoniates), which is characteristic for the

powders of Ni and Zn. The partial replacement of ASD-6 by NP of C (4 wt %) and NP of B (8 wt %) leads to a significant growth in the burning rate of the base EM. Replacing the ASD-6 powder of Al by NP of Al, B, and C increases the burning rate of EMs from three to five times. Additives of Cu nanoparticles result in a decrease in parameter b and a significant increase in parameter ν (by more than two times). Additives of Al NP in EM and the partial replacement of Al MP in the base EM by B and C nanoparticles result in an increase in parameter b by three and more times. Moreover, the NP additives of Al and B lead to an increasing value of ν, while the additive of C practically does not alter this parameter. In addition, the rate of burning of nitrate EMs in the studied interval of pressures corresponds to the AP-based compositions. In general, in the case of nanodispersed powders, the impact of energy efficiency of metals and nonmetals when used as a primary fuel is crucial. One should also take into account strong catalysis of the AN decomposition when using NP of C and $\gamma$-$Al_2O_3$, as well as the solubility of metals and their oxides in the melt of AN. Figure 4 shows data on the impact of metallic NP on the burning of the base EM. The results allow one to plot the following row of metallic NP activity in increasing order of the combustion rate of base EM: NP Ni < (NP Fe $\approx$ NP B) < (NP Cu $\approx$ NP Al) < NP C.
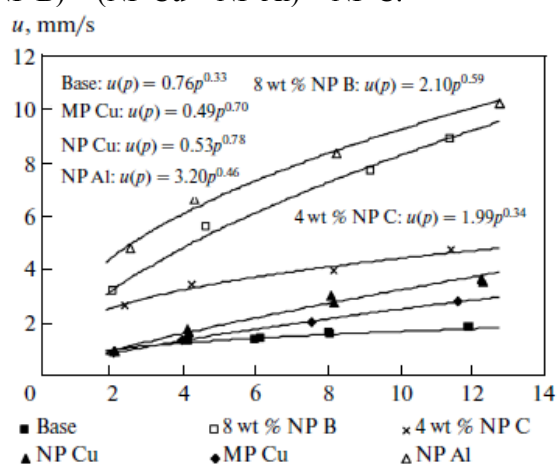


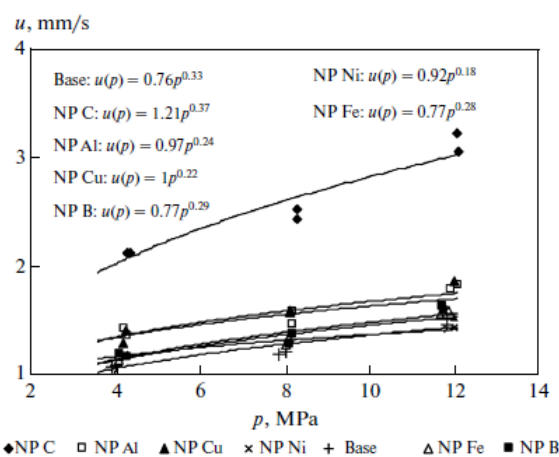**Figure 3.** Impact of nanodispersed metallic fuel on the burning rate of the base EM



**Figure 4.** Impact of NP additives (2 wt %) on the burning rate of the base EM

## 4. Conclusion

The resulting activity row of metallic and nonmetallic NP does not match the series of energetic and catalytic activity upon the combustion and thermal decomposition of EM [6]. With allowance for the area of possible reactions (c-phase and gaseous phase), one can plot the partial activity rows compatible with the rows of catalytic and energetic activity upon thermal decomposition in the mixtures with AN. The aluminum NP additive (2 wt %) has the maximum activity among the metals, increasing the burning rate of EM, but its activity nearly equals the activity of copper NP. Except for the carbon NP, all NP additives diminish the value of parameter ν. Parameter *b* is not altered when using EM with additives of boron and iron NPs; the other NP additives cause an increase in this parameter, indicating the presence of catalysis for reactions in c-phase.

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