

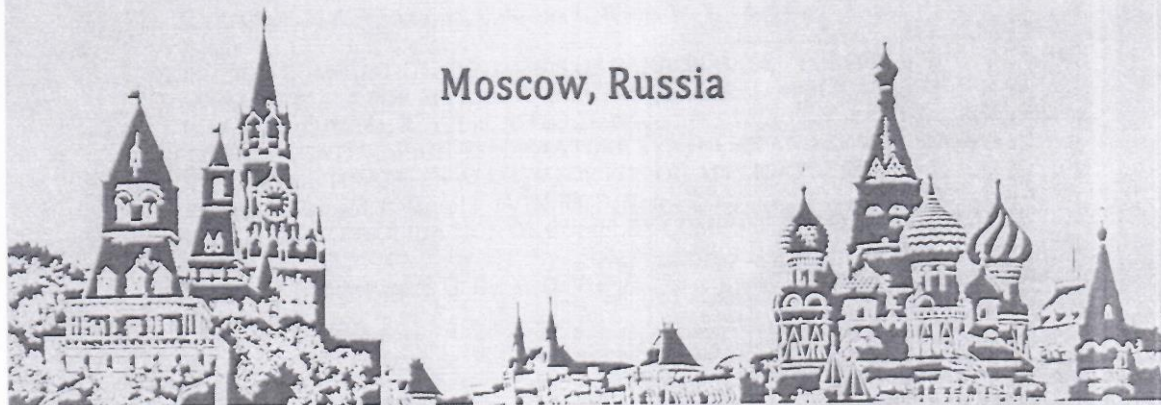


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ENERGY INTENSITY OF SOLID FUEL SYSTEMS WITH MECHANICALLY ACTIVATED ALUMINUM

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Aluminum is widely used in energy-intensive systems for various purposes, both in hydrogen energy and in technological combustion processes in the synthesis of various composite materials [1]. In the rocket-engine area, aluminum is used mainly to improve the gravimetric and volumetric specific impulse of solid-fuel rocket motors or to increase the regression rate of hybrid fuels [2]. In both cases, the reactivity of the aluminum powder plays a key role, which is related with the processes occurring in the combustion chamber. Micrometric aluminum is the most commonly used in space power plants with a high metal content (for example, 97.7% by weight of aluminum of grade PA4, dispersion of 50 μm) and low toxicity. However, its low reactivity is due to the presence of an oxide film on the surface of the particles, which reduces the specific impulse and burning rate in solid-fuel motors [3]. To increase the activity, different methods are used: chemical activation, mechanical and mechanochemical treatment (MCT) [4]. It is known that addition of metal powders to solid rocket fuel leads to an increase in system performance due to high energy per unit mass.

Studies on the MCT of aluminum were carried out on the powder grade PA4. Figure 1 presents the electron microscopic image, the energy dispersion spectrum, and the mass fraction of the elements of the original aluminum powder. From the presented picture it follows that the particles of Al have a spherical shape. According to the particle size analysis, the average particle size is about 50 μm .

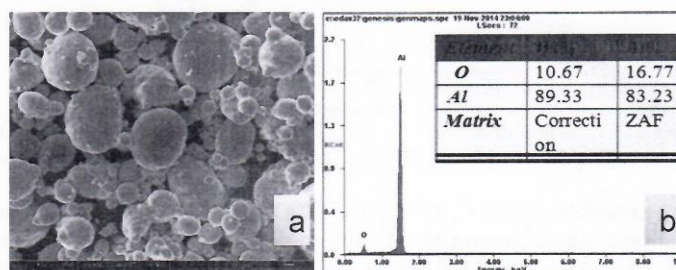


Fig. 1. Characteristics of the original aluminum powder of grade PA4: (a) electron microscopic image; (b) energy dispersive spectrum and mass fraction of elements.

From the results of energy dispersive analysis of the initial powder, it follows that the amount of aluminum metal is 89.33 wt %, and that of oxygen is 10.67 wt %. The presence of oxygen atoms indicates the presence of a sufficiently dense layer of oxide film on the surface of particles. Powder particles are gray in color with metallic luster and do not contain foreign inclusions.

Mechanochemical treatment of aluminum was carried out with graphite (C), stearic acid ($C_{17}H_{35}COOH$), and polyvinyl alcohol ($(C_2H_5OH)_n$) with different amounts of the modifying additive (from 3 to 20%). The processing time was 20 minutes. The choice of the optimal time of MCT was determined by the results of previous studies [5]. In order to prevent aluminum particles from oxidizing with oxygen of the air after MCT and to estimate the changes actually associated with the mechanical action, the samples of the dispersed mixture were passivated with hexane (C_6H_{14}).

Studies have been conducted on the effect of mechanochemical treatment (MCT) of aluminum powder on the mechanism of combustion of solid fuels and the structure of combustion. Measurements were made of the burning rate and the visualization of the burning process using a high-speed video camera. To study the effect of MCT on the ballistic properties, we used the standard formulation: AP/Al/HTPB: 68%/18%/14%. The fuels were distinguished by organic additives during the mechanochemical synthesis of aluminum powders. The MCT of metal aluminum was carried out for 20 min with the ratio of powder to grinding balls 1/4 Mp/Mb. Graphite, stearic acid and polyvinyl alcohol were used as modifiers. During processing, the amount of modifying additives varied from 3 to 20%, as well as the presence of silicon oxide (SiO_2) in an amount of from 5 to 20%.

The measurement of the steady-state burning rate was performed using samples of $4 \times 4 \times 30$ mm. They were burned in a nitrogen atmosphere in a bomb with windows. As can be seen from in Fig. 2, the base fuel containing aluminum in the initial state with a particle size of $50 \mu m$ has a low burning rate and a high pressure exponent ($n = 0.5572$). When replaced with aluminum treated with 3% graphite, an increase in the burning rate by 22% and a decrease in the pressure exponent ($n = 0.456$) are observed. The obtained data indicate the fact of the combustion process stabilization.

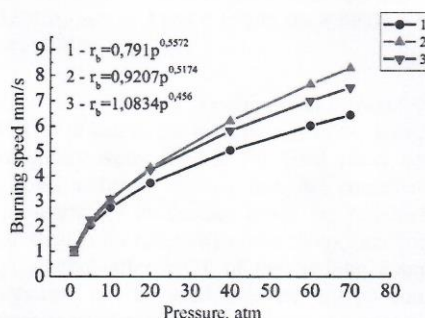


Fig. 2. Change of the burning rate of AP/HTPB/ Al_x fuels with non-activated aluminum and after MCT of composites: 1 Al initial; 2 [Al + 3% C]_{MCT}; 3 [Al + 20% C]_{MCT}.

Compositions based on PA/HTPB/(Al + $C_{17}H_{35}COOH$ + SiO_2) demonstrated the best result in burning rate and exponential pressure (Fig. 3). At present, stearic acid is used for the passivation of aluminum powders on an industrial scale [6]. Firstly, stearic acid is hydrophobic, secondly, with MCT, it fills cracks in the oxide film on the surface of aluminum particles and, thirdly, increases the chemical resistance of aluminum in relation to other fuel components, thereby increasing the shelf life of solid fuel. Aluminum particles in solid rocket fuels are initially localized between large oxidizer particles. When the melting point reaches $660^\circ C$, the aluminum particles become liquid, but they are still in the bulk of the oxide film, i.e. in an isolated state. The melting point of aluminum oxide is three times higher than the melting point of aluminum. In our case, as in the opinion of Price [7], liquid aluminum can leak due to cracks in the oxide shell formed during the MCT and filled with stearic acid, which can facilitate the

ignition of particles. Perhaps the subsequent agglomeration of particles may occur in the heating zone adjacent to the burning surface layer.

After introduction of the mechanically activated composite ($\text{Al} + 3\% \text{C}_{17}\text{H}_{35}\text{COOH} + 5\% \text{SiO}_2$) into solid fuel, there is a good increase in the burning rate by 13.5% at 5 atm and by 15.9% at 40 atm. The use of powder ($\text{Al} + 3\% \text{C}_{17}\text{H}_{35}\text{COOH} + 20\% \text{SiO}_2$) caused only minor changes in the burning rate as compared to ($\text{Al} + 3\% \text{C}_{17}\text{H}_{35}\text{COOH} + 5\% \text{SiO}_2$) within $\Delta r_b = 17.6\%$ in the considered pressure range. The content of active aluminum, which was determined by the volumetric method, was no more than $\sim 85.1\%$ in the system. A possible factor of this result is that the active combustible system is fully composite $[\text{Al} + 3\% \text{C}_{17}\text{H}_{35}\text{COOH} + 20\% \text{SiO}_2]$.

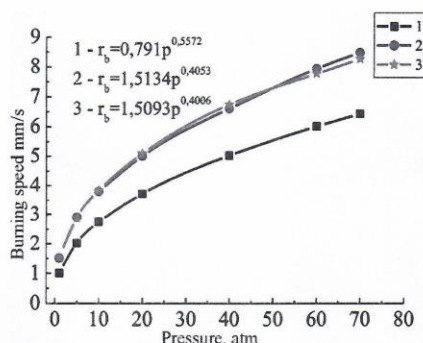


Fig. 3. Change of burning rate of fuels PA/HTPB/ Al_x with non-activated aluminum and after MCT of composites: 1 Al initial; 2 $[\text{Al} + 3\% \text{C}_{17}\text{H}_{35}\text{COOH} + 5\% \text{SiO}_2]_{\text{MCT}}$; 3 $[\text{Al} + 3\% \text{C}_{17}\text{H}_{35}\text{COOH} + 10\% \text{SiO}_2]_{\text{MCT}}$.

Mechanically activated aluminum-based powders with a modifier were prepared using a centrifugal mill. After MCT of powders, the morphology of the particles, the metal content in the composite, and its reactivity were studied. The final effect depends on the activation modifier and promoter. Solid additives (silicon dioxide) contributed to finer grinding of aluminum powder and loosening of its surface oxide layer, which led to more effective activation, as well as an increase in the reactivity of the composite. Formulations of powders of aluminum with polyvinyl alcohol after MCT of the burning composition occurs with an explosive effect. Such systems can be used in other energy compositions such as: gas generators, explosives, thermite compositions to obtain porous ceramics.

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