Effect of mechanical activation duration on combustion parameters of Al-Mg-based high-energy systems

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Abstract. The paper studies dispersion, oxidation degree, burning rate and combustion heat in high-energy mixtures obtained from of Al-Mg powder materials depending on the duration of mechanical activation in a planetary mill. According to dispersion analysis by laser diffraction method, 3 h mechanical activation gives Al-Mg particles with average particle size of 30 μm compared to 180 μm particles obtained after 2 h activation. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were used to record TG/DSC curves and measure burning rate and combustion heat for synthesized powders in comparison with engineered Al-Mg powder PAM-4 (Novosverdlovsk Metallurgical Company, Yekaterinburg, Russia). It has been found that the injection of 6 h mechanically activated Al-Mg powder into high-energy compositions leads to 24 and 45% increase of burning rate and combustion heat compared to the compositions without additive.

1 Introduction

Modern high-energy materials (HEMs) consist of 3 main components: perchlorate and ammonium nitrate used as an oxidizer, polymer rubber as a fuel binder, and metal powders (aluminum, magnesium, beryllium, zirconium, boron, etc.) or their alloys as metal fuel. Fine-dispersed powders of metals mainly used as components for adjusting the burning rate and combustion heat of HEMs, which depend on the dispersion of introduced powders. In works [1-4], the effect of additives dispersion on the burning rate of HEMs compositions was described. Meanwhile, there are research showing that metal powder mechanical activation may improve thermophysical properties HEMs [5–10].

There are basic parameters used for powder selection in combustion study as scarcity, cost, combustion heat, burning rate, density and environmental friendliness of combustion products. The optimal components of high-energy systems providing basic complex of parameters are aluminum and magnesium. Aluminum powder is the most available and effective additive (10…20%) providing a high temperature of combustion [11-13], while magnesium provides easy ignition and high burning rate of HEMs compositions [13]. The alloys of the Al-Mg system ignite with lower ignition delays, lower temperatures and higher burning rates as compared to pure powders. At present, obtaining aluminum-magnesium powder (PAM) according to GOST 5593-78 from an alloy of aluminum and magnesium by spraying it into a sealed chamber is known. The fusion of technically pure aluminum and magnesium with further milling and mechanical activation in planetary mills can serve as an alternative. Mechanically activated particles have an increased reactivity, much easily enter into chemical reactions than powder mixtures obtained by other methods [14].

Despite the considerable interest in studying the effect of mechanical activation of eutectic alloys on the combustion parameters of high-energy systems, quantitative information about their burning rate, combustion heat, oxidation degree and other important parameters remains limited. In particular, there are practically no studies on integrated effect of duration and mode of mechanical activation on the combustion parameters of Al–Mg system in the content of high-energy additives.

The purpose of this work is an experimental study of the properties such as dispersion, oxidation degree, burning rate and combustion heat in the composition of high-energy compositions obtained from of Al-Mg powder materials depending on the duration of mechanical activation in a planetary mill.

2 Materials and methods

In our experiments we prepared five HEMs compositions as shown in the table 1. Ingots of technically pure aluminum A0 (99.0 wt.% of Al, Rusal, Moscow, Russia) and technically pure magnesium Mg-95 (99.95 wt. % Mg, Ruskhim, Moscow, Russia) in the mass ratio of 1:1 were used to obtain Al-
Mg alloy additives which added after to traditionally used HEMs. Powders mixture in the weight ratio of 1:1 [8, 9] was mechanically activated in a chamotte-graphite crucible of a planetary mill (AktivNano, Saint Petersburg, Russia). Mechanical activation is fully described in [14]. Balls from steel 40XC having a diameter of 9.5 mm were used as milling bodies. The mass ratio of the milling bodies to the powder mixture was 3:1. Mechanical activation of the material was carried out in argon medium with a preliminary evacuation. The treatment time of the powder mixture was 9 h with sampling in an hour.

Obtained additives after 2 and 7 h treatment were added to HEMs consisted of ammonium perchlorate powder (PHA) with a diameter of 160...315 µm; divinyl rubber based on butadiene rubber and plasticized with transformer oil (SKDM–80); of black amorphous boron powder (B-99) with diameter of 13 µm (Polena, Russia), Industrially produced Al-Mg powder PAM-4 with diameter 65 µm (Novosverdlovsk Metallurgical Company, Yekaterinburg, Russia) was selected as a control for determining burning rate and combustion heat. Also we added the mixture of industrial powders (Al-Mg powder mixture) consisting of 50 wt.% of Al powder ASD-0 with diameter of 50 µm (Rusal, Moskow, Russia) and 50 wt.% of Mg powder MPF-4 (Ruskhim, Moskow, Russia) with size of 45 µm.

Calorimetric studies of HEMs compositions were carried out using a thermal analyzer of Mettler Toledo (module TGA / SDTA 851) in the temperature range 25...1200 °C at a heating rate of 50 °C/min in air medium using an aluminum oxide crucible.

Disparsity material study for each hour of mechanical activation was carried out with the help of an Analysette 22 MicroTec Plus instrument (Fritsch company) using laser diffraction method in the range of 0.08...2000 µm. The dispersing was performed in ethanol medium (concentration of particles was 10 vol. %). The theory of Fraunhofer was used for calculating.

X-ray fluorescence analysis (XRF) was performed using a Shimadzu XRD 6000 X-ray diffractometer with filtered CuKα radiation from 20 to 80 angular degrees with a step of 0.2 degrees. Qualitative phase analysis was made using the PDF 4+ database, as well as the full profile analysis program POWDER CELL 2.4.

Samples of a cylindrical shape having a diameter of 10 mm and a height of 30 mm were produced by pressing the powder mixture in fluoroplastic assemblies. The determination and calculation of burning rate and combustion heat was performed according to the methods presented in [15, 16]. The burning rate of compositions was determined using high-speed digital video camera Citius Centurio C100 (Citius Imaging Ltd, Finland). Obtained in the combustion process of samples of the video files were processed using a software video processing “TimeLapse (Al Devs, Russia). For each composition we conducted at least three duplicate experiments.

Measurement of combustion heat was carried out using a calorimetric installation. A basic element of calorimetric installation was the calorimetric bomb of constant pressure. Samples was weighed and placed in a calorimeter bomb. In a vessel of a calorimeter installation poured distilled water, lowered a bomb and took water temperature the metastatic Beckmann thermometer allowing to receive a high precision of measurements. After the executed measurements ignition and step-by-step measurement of water temperature in a calorimeter was carried out and then the calculation of combustion heat.

| Component | Composition of prepared HEMs. |
|-----------|------------------------------|
| SKDM-80   | 10.5 10.5 10.5 10.5 11       |
| PHA       | 70.5 70.5 70.5 70.5 74       |
| B-99      | 14.3 14.3 14.3 14.3 15       |
| PAM-4     | 4.7 4.7 4.7 4.7             |
| Al-Mg powder mixture | 4.7 4.7 4.7 4.7                   |
| Al-Mg alloy (after 2 h treatment) | 4.7 4.7 4.7 4.7                     |
| Al-Mg alloy (after 7 h treatment) | 4.7 4.7 4.7 4.7                         |

3 Research results

Obtained Al-Mg alloy additives (after 6 h activation) were compared with industrial powder PAM-4 via dispersion analysis. It has been demonstrated that particle size distribution (PSD) for the samples is 3...127 and 6...127 µm and an average size is 37.8 µm and 65 µm for Al-Mg alloy and PAM-4, respectively (Fig.1).

According to laser diffraction method, PSD character strongly depends on the duration of the mechanical treatment: we see that the main peak on PSD curve moves to the left – to the side of smaller particles. For instance, the mode diameter is 551 µm (5.8 %), 80 µm (3.4 %) and 50 (3.2 %), respectively, after treatment duration during 2, 4, and 7 h (Fig.2). Further it has been calculated that longer mechanical activation causes particles dispersing: the average particle size is 180 and 30 µm, respectively for 2 and 7 h activation (Fig.3). The data show that after 2 h of mechanical activation, the average particle size of powder mixture decreases sharply from 180 µm (2 h) to 50 µm (3 h).

The analysis of thermogravimetric data shows that exothermic peak of HEMs shifts to a zone of lower temperatures with an increase of mechanical activation duration. The PAM-4 oxidation degree was 77.65 % at an exothermic peak of 550 °C; the degree of powder oxidation after 2 h activation was 70.65 % at an exothermic peak of 600 °C; after 4 h mechanical activation was 77.31 % at an exothermic peak of 520 °C; after 7 h activation was 74.74 % at an exothermic peak of 520 °C (Fig. 4).
Fig. 1. Particle size distributions of PAM-4 compared to Al–Mg alloy obtained by 6 h activation.

Fig. 2. Particle size distribution of Al-Mg alloy additives obtained by mechanical activation.

Fig. 3. Influence of mechanical activation duration (t) on the average particle size (d).

The DCS analysis (Fig.4) has shown that the addition of Al-Mg alloy additives to composition #5 (SCDM-80 + ammonium perchlorate + amorphous boron) after 7 h activation leads to the growth of burning rate by 45% compared to the composition without the additive (Table 2).

Table 2. Burning rates and combustion heat of HEMs compositions.

| HEMs composition | Density, $\rho$ (g/cm$^3$) | Burning rate, $u$ (mm/s$^2$) | Combustion heat, $Q$ (kal/g$^3$) |
|------------------|-----------------------------|-------------------------------|-------------------------------|
| 1                | 1.44                        | 2.28±0.2                     | 1710±17.1                     |
| 2                | 1.47                        | 2.06±0.2                     | 1762±18                       |
| 3                | 1.47                        | 2.17±0.2                     | 1745±22                       |
| 4                | 1.47                        | 2.47±0.2                     | 1765±13                       |
| 5                | 1.47                        | 1.71±0.2                     | 1432±12                       |

The addition of mechanically activated Al-Mg alloy powder obtained during 7 h mechanical activation, to the HEMs increased the combustion heat by 24% compared to the composition #5 - without a mechanically activated Al-Mg powder. It has been established that the injection of a mechanically activated Al-Mg powder into the composition #5 (SKDM-80 + ammonium perchlorate + amorphous boron), regardless of the mechanical treatment duration and dispersity does not affect the combustion heat.

4 Conclusion

We have shown the influence of mechanical activation duration on Al-Mg alloy particles dispersion, and oxidation degree, burning rate and combustion heat in high-energy mixtures obtained with the addition of Al-Mg powder materials of different origin as engineered Al-Mg powders and mechanically activated Al-Mg alloy powders. It was established a significant reduction in particle sizes of Al-Mg alloy powder, particularly, from 180 to 30 μm occurred, respectively after a 2 h and 3 h mechanical activation. The thermogravimetric analysis showed that the exothermic peak shifted to a zone of lower temperatures with an increase of mechanical
activation duration and mechanical treatment for more than 4 h does not significantly affect the characteristics of the material.

It has been also stated that the injection of mechanically activated Al-Mg powder into the composition containing SKDM-80, ammonium perchlorate, amorphous boron causes 1.4-fold growth of it’s burning rate in air and 1.2- times increase of heat release of boron-containing high-energy compositions from 1432 $\pm$ 1 % kal•g$^{-1}$ to 1765 $\pm$ 1 % kal•g$^{-1}$. At the same time, the dispersity of the injected Al-Mg powder does not have a significant effect on the heat release indices.

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