Mechanochemical Method of Increasing of Reaction Ability of Mixtures of Aluminum and Magnesium with Oxidizers

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1 Introduction

Now in the world the significant attention is given for development of ways of producing of new energetic materials on the basis of nanotechnology. One of the effective method to obtain nano-sized energetic composites is mechanical activation of metal-oxidizer mixtures in ball mills. Previously, it was shown that preliminary mechanical treatment allows obtaining mechanoactivated energetic composites (MAEC) with high burning rate. This paper analyses the rules of formation under mechanical treatment, the structure and reactivity of nano-sized MAEC based on aluminum and magnesium with solid oxidizers (MoO_3 and Teflon).

2 Experimental

The mixtures of Me/Ox (Me = Al, Mg Ox = MoO_3, Teflon) powders were mechanically activated by vibration mill. For preparing mixtures different types of metal and oxidizer powders were used as initial components. The Al powder of ASD-6 mark has a spherical shape with the mean particle size of 3.6 μm, whereas the particles of the remaining Al powders are flat with different mean size and thickness (flake particles: PP-2 – 70*1 μm, PAP-2 – 30*1 μm, Al No4 – 21*0.5 μm). The initial Mg powder of MPF-3 brand looks like curved particles with maximal size of 150–200*5-10 μm and equivalent diameter of 35 μm. Three types of MoO_3 powders have mean particles size 30 μm, 3-8 μm, and 30-50 nm (preliminary activated MoO_3). Initial Teflon powder F4-PN have particle size of 10–300 μm.

The conditions of mechanoactivation were chosen so that the maximum homogenization of the mixture was ensured in the absence of the reaction between components in the course of treatment. Some details of specimen preparation procedure are described in [1, 2]. Mixtures were treated in the vibrating mill designed by Aronov [3]. The mechanical treatment of energetic systems Me/Ox is affected by a danger of explosion directly during ball milling. That is why ball milling was performed in the presence of the hexane, which was subsequently removed by drying the mixture. To prevent overheating of the mixture and initiation of the reaction in the activator, the treatment was carried out in 30 - 45-s cycles. The ratio of components and the dose of activation were varied. The total activation dose was changed in the range from 1.6 to 11 kJ/g (time of activation - from 6 to 40 min).

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The structure of mechanoactivated specimens was investigated with examined by X-ray diffraction X-ray diffraction (XRD) and microscopy (optical, scanning and transmitting electron (SEM, TEM) and atom-force (AFM)), differential scanning calorimetry (DSC), as well as the value of the BET specific surface.

The measurements of burning rate were carried out to analyze influence of mechanoactivation on reactivity of Me/Ox mixtures in burning regime. The powders of mixtures were charged in portions into the casing (plastic or metal tube of internal diameter of 8-12 mm) and slightly compressed. Ignition was effected by electric heating of Ni-Cr wire. Burning rate was measured by registration of burning product radiation. Optical light fibers made of quartz-polymer with the core of 0.5 mm were mounted into holes along the tube 2-3 mm deep inside the mixture. The charge length from the ignition point to the first optical fiber was 20-200 mm. Radiation of burning products was transmitted to the photodiodes through optic fibers, and analogue-digital converter recorded it.

Optical pyrometry was used to obtain information on temperature of burning products. Loose packed samples of Me/Ox in duralumin tube were ignited by Ni-Cr wire, heated by electric current. PMMA plates, about 5 mm of thick, were used as window material. Radiation emitted from the sample-window interface was converted by dual-channel optical pyrometer with effective wavelengths 420 and 627 nm into electric signals, which were recorded by analogue-digital converters. Electric signals were recalculated to brightness temperatures with using of usual pyrometric procedure.

The research of an opportunity of detonation-like propagation of chemical reaction has been executed for mixtures with the greatest speeds of burning. The experiments were carried out in metal tubes (10-30 mm in diameter with a height of 150-300 mm). The mixture was charged in portions into the tube and slightly compressed. The mixture of ammonium perchlorate (AP) and acrylic plastic (PMMA) (95/5) with a mass of 5 - 10 g and a density of 0.55 g/cc was used as the initiator. The AP/PMMA mixture was detonated by the ED-8 electric detonator. The velocity was measured by electric contact gauges and quartz optical fibers inserted into the mixture to half the diameter.

3 Results

The structure of obtained mixtures depends on the type of initial powder particles and dose of activation.

Maximum homogenization of the mixtures was obtained for Me+Teflon systems (see Fig. 1a and 1b). In this case we obtain mechanoactivated energetic composites (MAEC), consisting of oxidizer and metal fragments of the submicron- and nano-size in a Teflon matrix. The particles of composite have the shape of flakes. The linear size of the main fraction of particles ranges from 5 to 50 μm, while their thickness varies from fractions of a micrometer to 1 μm. X-ray diffraction analysis of the MAEC shows that mechanical activation is followed by the broadening of x-ray lines for the components. This effect may be due both to a decrease in the size of crystallites (coherent scattering regions) and to the accumulation of dislocations. In particular, the analysis indicates that the broadening of the X-ray lines of Al and Mg is caused by the formation of dislocations. The formation of dislocations is apparently associated with the intense plastic deformation of metals under mechanical actions. Deformation is accompanied by change in the shape (flattening) of the initially spherical Al particles.

The results for Me+MoO_3 demonstrate strong dependence on the type of initial powder particles. More rigid in comparison with Teflon MoO_3 interferes with crushing of particles of metal. The most homogeneous composite can be received at use of the finest initial components. For this purpose initial MoO_3 was exposed to preliminary machining with crushing up to nano dimensional sizes of 50-60 nanometers. For composites with spherical Al particles (ASD-6) the micronsized Al particles are preserved and they are covered by MoO_3 particles. In the case of “flat” Al the “inverse” structure is observed: particles of micron-sized MoO_3 are covered with a layer of Al. For MAEC with “flat” Al of PAP-2 mark and nanosized activated MoO_3 the micronsized fragments of flake Al are covered by nanoparticles of MoO_3 (see Fig. 1c). From the viewpoint of maximal homogenizing of mixture, the use of flake-like metal powder with minimal particle dimensions and preliminary activated nanosized

MoO_3 is the most promising way. In this case it is possible to prepare MAEC, in which the components are mixed at the nano-level (tens nm).

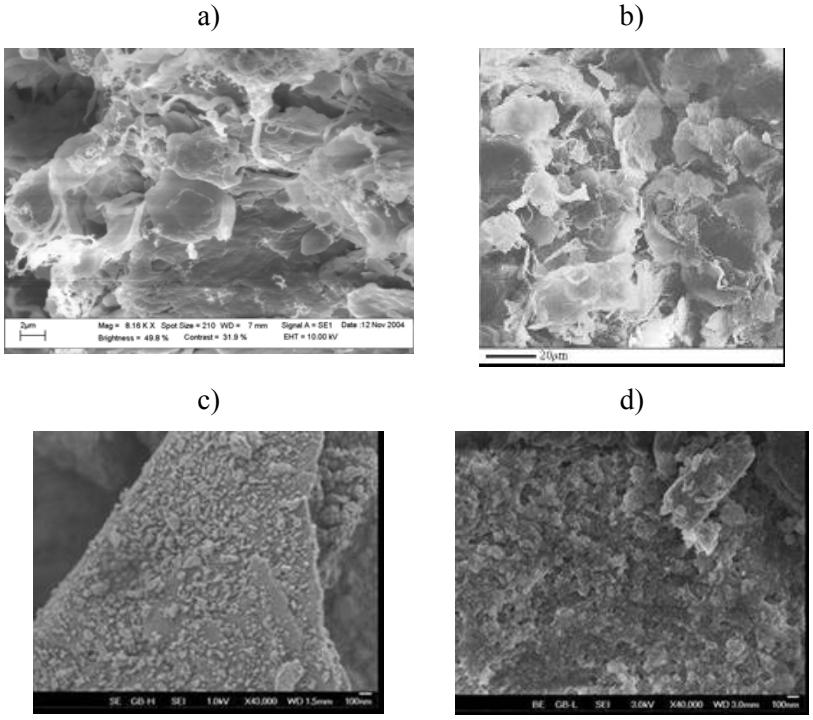

Figure 1. SEM images of activated composites:

a) Al (ASD-6) + Teflon;

b) Mg (MPF-3) + Teflon;

c) Al (PAP-2)+ nano MoO_3;

d) Mg (MPF-3)+ nano MoO_3.

The mechanical activation provides an opportunity of the fullest use of the energy reserved in metal-oxidizer mixtures at initiation of processes of burning and a detonation.

The burning rate of MAEC changes from several meters to several hundred meters depending on activation dose, type of metal and density. The highest velocities were obtained for MAEC Al/MoO_3, based on flake Al and preliminary activated MoO_3. The burning rate grows as the dose of activation increases up to 7 kJ/g, and the density of sample decreases. In the case of loose-packed MAEC Al/MoO_3 at the relative density of 0.3 TMD the process of burning proceeds in explosive regime with high velocities (up to 400 m/s). For pressed samples with the density of 0.7-0.8 TMD the burning rate is varied through the range: 1.5 - 20 cm/s.

The measured brightness temperature lies in the range between 2200 and 4100 K in dependence on type of initial particles, activation dose and component ratio. Maximum temperature is registered for MAEC based on the Mg and nanosized preliminary activated MoO_3

Magnesium has shown high activity during mechanical treatment. Reaction begins already during treatment at excess of some doze of activation. For MAEC Mg/MoO_3 the maximum reactivity and the highest parameters of burning were obtained for the dose of activation 2.7-3 kJ/g (see Figures 2 and 3). For loose-packed MAEC Mg/MoO_3 at the relative density of 0.3 TMD the process of burning proceeds in explosive regime with velocities at the level 280 m/s with maximum brightness temperatures of about 4000 K. The further increase of activation dose (more 3 kJ/g) results in partial reaction of components during ball milling as well as in essential decrease of parameters of burning. The optimum doze of activation for Mg + Teflon is equal 7-8 kJ/g.

The results of investigations have demonstrated the possibility of initiation of steady-state detonation-like process in Teflon based MAEC. Velocity of self-sustaining detonation-like process depends, first of all, on a degree of homogeneity of mixtures (or an effective surface of contact of reagents). The maximum of detonation velocity are achieved at a weight ratio of components close to stoichiometric ratio (see Fig. 4). The optimum doze of activation for Mg/Teflon for maximum velocity is equal 7-8 kJ/g (see Fig. 5).

Thus, metal-oxidizer nanocomposites prepared by the mechanochemical method have increased reactivity of their components in various processes. This may be used for the development of various energetic materials, materials for hydrogen power systems, cermets, etc. Formation of nanocomposites is the intermediate stage of the mechanochemical synthesis, and, depending on the formulated problem, one can prepare the specimens with different properties

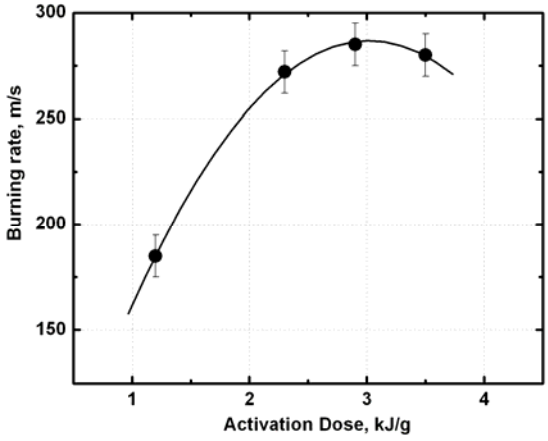

Figure 2. Burning rate in loose-packed samples Mg/MoO_3 34/66 vs. dose of activation

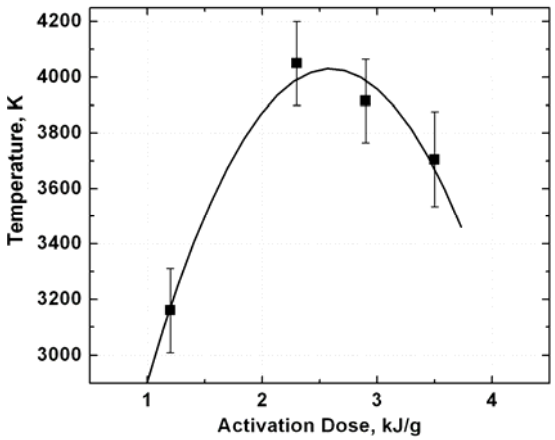

Figure 3. Brightness temperature in loose-packed samples Mg/MoO_3 34/66 vs. dose of activation

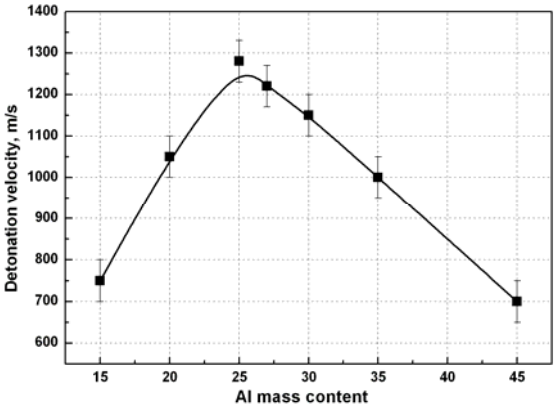

Figure 4. Detonation velocity vs. Al mass content for MAEC Al/Teflon

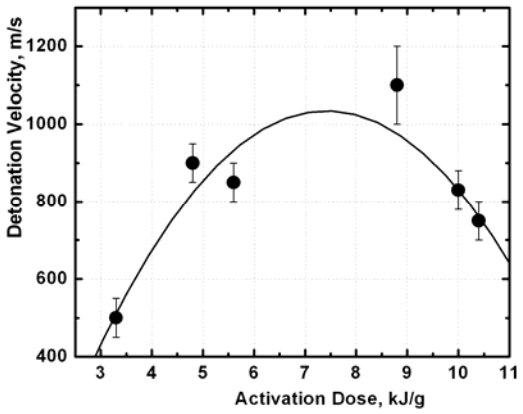

Figure 5. Detonation velocity vs. dose of activation for MAEC Mg/ Teflon 35/65.

Acknowledgements

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