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Initiation and Combustion of Mechanoactivated Mixtures of Aluminum and Copper Oxide

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Abstract

The optimization of parameters of mechanoactivation of powder mixture of Al + CuO for the purpose of realization of the most powerful energy release at chemical interaction of components was performed. Vibration and planetary type of the ball mills were used. The results of mechanoactivation on burning rate were controlled by means of high-speed photography of burning process of samples. Initiation of burning was carried out in the electro spark way with control of the current impulse. The non-stationary mode of propagation of chemical interaction of mixture components was recorded under low level spark. The influence of parameters of mixture porosity and current amplitude of a spark for induction period and the speed of distribution of the reaction front of was defined. The results of the research indicate the prevalence of filtration nature of distribution of chemical interaction.

Keywords

Thermite mixtures; mechanoactivation; burning rate.

Introduction

Thermite mixtures based on metals and solid oxidants allow obtaining a significant exothermic effect during combustion. Al + CuO mixture allows receiving one of the highest exothermic effects per unit of volume (more than 20 kJ/cm^3). However, the burning rate of initial mixtures of micron powders usually does not exceed several tens of mm/s, which limits the field of their application. This is because that development of chemical reactions in solid mixtures takes place on the contact surface of reactants, which in the case of large particles is rather small. To increase this surface, various methods, such as ultrasonic mixing of nanosized powders, electrochemical deposition of submicron metal-oxidizer layers, etc. are used. [1]. One of the relatively new methods for obtaining thermite composition is the preliminary mechanochemical activation of mixtures of micron-sized particles in high-energy intensity ball mills. Initial components in this process are shredded, mixed and acquire new defects of crystal structure, which leads to an increase in the surface area of contact of the reagents at the submicron and nanoscale levels and to the formation of additional reaction spots. Thus, by means of mechanoactivation of oxidizer-metal mixtures it is possible to regulate the rate of energy release for different of specific application. In Russia, the method of preliminary mechanoactivation of solid oxidant-metal fuel mixtures has been actively used since the beginning of the 2000s [2–5], and the resulting materials are called Mechanically Activated Energetic Composites (**MAEC**).

The practical use of exothermic energy release is associated with the implementation of different parameters: the rate or power of heat release, the quality and intensity of light radiation, etc. However, in all cases, the completeness, or the effectiveness of the chemical interaction, is an important factor. This indicator largely depends on the conditions of application: the physical parameters of the components, the initial parameters of the mixture, the energy and power of initiation, as well as other physical and geometric factors.

In this work, tendencies of manifestations of chemical interaction of MAEC Al/CuO are investigated under different conditions of its realization. An ultimate goal of a research is optimization of mechanoactivation parameters of this mixture for effective application in different conditions.

Before experiments the mixture of Al + CuO powders were subjected to mechanoactivation. Then the mixture was compacted in experimental samples with controlled porosity. The samples were mounted in experimental assemblies and initiation of chemical interaction was made. The characteristics of manifestations of combustion process of samples were an object of research in which mechanoactivation time, the samples porosity, the initiation parameters and the experiment scheme were parameters. High-speed camera, four-channel pyrometer, photoelectronic and electrocontact sensors were used as tools. The characteristics of a luminescence area were speeds of borders and brightness.

Prior to the experiments, a mixture of Al and CuO powders was subject to mechanoactivation under various conditions. The mixture was then compacted into experimental samples with controlled porosity. The samples were mounted in experimental assemblies and produced an electro-spark initiation. The characteristics of the combustion process were the subject of the study, in which the mechanoactivation time, the porosity of the samples, and the energy of the spark initiation were the initial parameters. The speed of the boundaries of the luminous cloud of products and their brightness were measured. High-speed camera, pyrometer, photoelectronic and electro-contact sensors were used as a tool.

Materials and mechanoactivation parameters

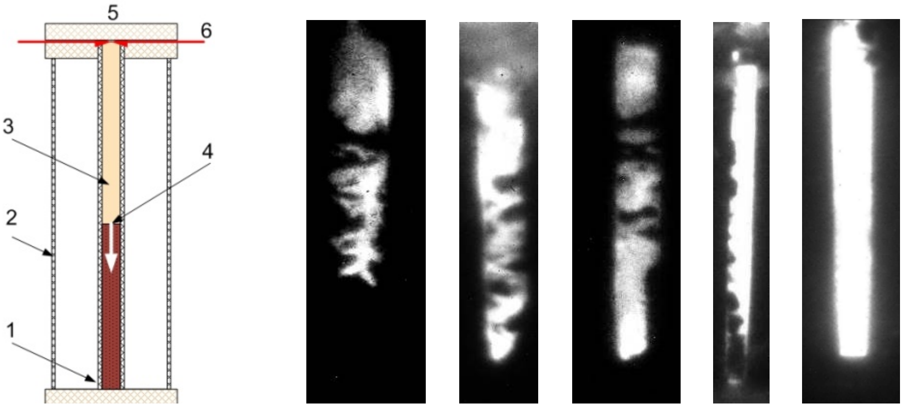
As the initial components, micron and nanosized powders were used. Al weight content was from 18 to 25 %. Mixing and activation was carried out in the vibration mill of the Aronov design or in the planetary mill "Activator-2sl" with steel drums and balls. Estimate of the energy intensity of the two types of mills based on the growth of the specific surface area of the test material (MoO_3) is for "Ativator-2sl" at a total power J = 9.7 W/g, and for the Aronov mill J = 3.7 W/g. Weight load of powders was 10–25 g, the mass of balls was 200–300 g. Hexane was added to reduce frictional heating. The starting powders and MAEC were analyzed by X-ray diffraction, electron microscopy and thermo-gravimetric analysis. It is established that the activation of the obtained material resulted in a polydisperse mixture of fairly large conglomerates of flat fragments of Al particles (~ 1–10 μm) with submicron CuO particles. Owing to different strength characteristics of material, dispersion in sizes and a form of particles, conglomerates represented the disordered structures with numerous, but divided, points of contact of components. These points of contact of components, presumably, can serve as primary centers of chemical interaction.

Experiments

Primary analysis of mechanoactivation influence was carried out by means of determination of dependence between ignition delay time and mixture temperature. As a rule, the ignition delay increases with reduction of temperature. It was defined that temperature of ignition of the mixture, activated in different conditions, lies in range from 200 to 350 ºC.

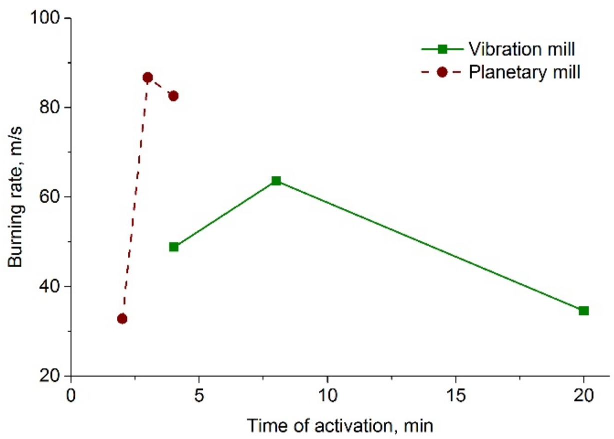
At electro spark initiation of a bulk sample on the horizontal plane (mass from 0.03 g and above) the area of a luminescence is formed. On a set of experimental data, this area should be characterized as the extending stream of the reacting clusters of mixture components in a cloud of the radiating plasma of burning products with a specific resistance of 10^7 Om·mm^2/m. By pyrometric measurements, the brightness temperature of a luminescence area changes from 2400 to 3700 K depending on mixture activation time. Characteristic scattering rate of burning products of local samples and also the burning rate of linear samples (with a linear density from 0.2 g/cm and above) are tens of meters per second. The existence of small air intervals between separated samples does not interfere with distribution of burning and does not influence the burning rate. An increase in the mass of separated samples leads to the growth of the expansion speed of the chemical reaction.

The burning initiation of the compacted mixture sample (porosity of 50–70 %) was carried out in the electrospark way in a glass tube with a diameter of 5.5 mm (Fig. 1). The tube end face on the initiation side, as a rule, was closed. The spark gap between wire electrodes with a diameter of 0.1–0.5 mm was 0.1–1.0 mm. The current through a spark interval was changed in the range of 40–350A. The current impulse duration of a spark was ~ 1 μs on the basis. The moment of sparking was used for synchronization of the high-speed photo recorder Cordin 222-4G. The photo recorder took 16 photos of process in beforehand determined time points.

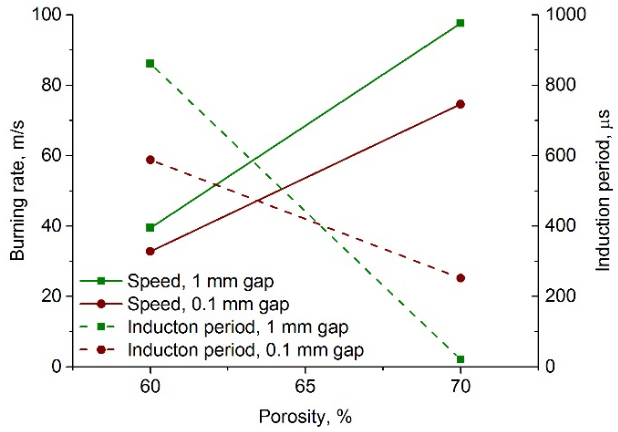


a) *b*)

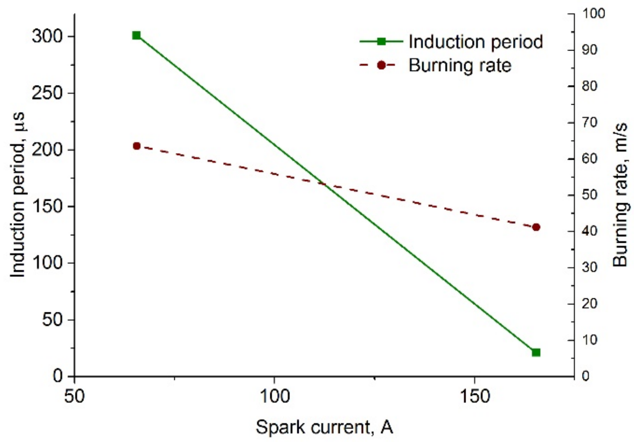
Fig. 1. Initiation with the maximum current through a spark interval:
a – experimental scheme: *1* – dark part of glass tube (no combustion); *2* – glass vessel with water; *3* – light part of tube (combustion); *4* – a boundary between dark and light parts of tube; *5* – spark gap; *6* – electrodes;
b – photos of luminescence inhomogeneity at various spark currents



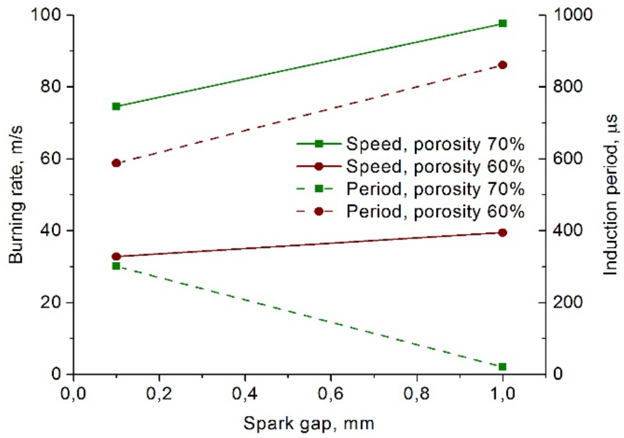
Influence of mechanoactivation time: achievement of the maximum burning rate



Influence of a sample porosity (planetary mill): considerable reduction of induction period and increase in burning rate



Influence of spark current (vibration mill): considerable reduction of the induction period at insignificant reduction of burning rate (insufficient warming up of cold mix)



Influence of length of a spark interval (planetary mill): minor changes in the induction period and increase in burning rate (increase in volume of an electrospark energy contribution)

Fig. 2. Set of experimental data

In the photos, a border between dark and light parts of a tube was fixed (Fig. 1). This border was identified with some stage of chemical interaction characterized by a certain temperature. In case of the disordered structure of our mixture, it may concern thermal explosion in the neighborhood of contact points of components. At small currents through an electric spark (< 150 A) the area of burning has pronounced non-uniform character. Zones of a bright luminescence of hot products alternate with dark zones at photos. With increase in spark current, the uniformity of a luminescence increases.

The long luminescence abroad of the section of zones in process of its movement is caused by hashing and interaction of initially not contacting parts of components. Time interval between the moment of initiation and formation of border is usually called the induction period. Movement of this border in time was taken for the speed of burning of mixture in a tube.

Results

By set of experimental data is determined the tendency of change of characteristics of burning depending on parameters of mechanoactivation, compaction and initiation (see Fig. 2). Each tendency is created according to two experiments with identical other conditions.

Analysis of dependences of Fig. 2 reveals the strongest influence of mechanoactivation time, mixture porosity and a spark current amplitude for induction time and the rate of chemical interaction. It assumes the leading role of the filtration mechanism in energy transfer for initiation of chemical interaction in cold sites of mixture.

Conclusions

In general, the results of the work have shown the promise of preliminary mechanochemical activation for the production of fast-burning thermite compositions. For each type of mills, there are optimum conditions of activation at which the greatest reactionary ability, rate and temperature of burning are reached. At excess of this value, there is a partial interaction of components in the activation process and decrease in burning characteristics.

References

1. Energetic Nanomaterials: Synthesis, Characterization, and Application / Ed. by V.E. Zarko and A. Gromov. 2016. Elsevier Inc.

2. Dolgoborodov A.Yu., Gogulya M.F., Makhov M.N., et al. Detonation-like phenomena in Al/S mixture”, *Proc. Twenty-Ninth Intern. Pyrotechnics Seminar*, 2002, pp. 557-563.

3. Dolgoborodov A.Yu., Makhov M.N., Kolbanev I.V., Streletskii A.N. Mechanically activated pyrotechnic composition, *RF Patent No. 2235085*, 2004.

4. Dolgoborodov A.Yu. Mechanically activated oxidizer-fuel energetic composites. *Combustion, Explosion, and Shock Waves*. 2015, vol. 51 issue 1, pp. 86-99.

5. Streletskii A.N., Sivak M.V., Dolgoborodov A.Yu. Nature of high reactivity of metal/solid oxidizer nanocomposites prepared by mechanoactivation: a review. *J. Mater. Sci.* 2017, vol. 52, issue 20, pp. 11810-11825.