Mechanical activation influence on the morphological properties of La_2O_3-TiO_2-B

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Abstract. The influence of mechanical activation of the powder mixture used to obtain the high-perfomance cathode for accelerating engineering with the SHS-method has been explored. The mechanically processed mixtures have been morphologically analyzed. The optimal modes of mechanical activation have been determined for the mixture.

1. Introduction

Accelerating engineering requires creation of new and more powerful plants, which generate flows of charged particles. This fact has a significant influence on the industrial, machine-building, energetic development and other fields of science and engineering. A great attention is paid not only to a plant modernization as a whole, but to its individual parts. The most important element of the devices generating flows of charged particles is a cathode. The use of hexaborides of rare earth metals as a cathode secures the maximal effectiveness of the cathode assembly by some parameters. The main advantages of the cathode made of lanthanum hexaboride are: the minimal work function (~2.7 eV); the high density of obtained emission current ($\approx 2\cdot 10^3$ A/cm^2, at T=2000 K); the high melting point (2800 K); the ability to retain emission properties in the conditions of low vacuum and intensive ion bombardment; the absence of air pollution; high exploitation characteristics [1].

The methods of powder metallurgy used for obtaining lanthanum hexaboride have some disadvantages: poisoning of the finished product as a result of a fusion process; technically complicated equipment; great energy expenditures for a long-lasting synthesis and annealing of products. One of the alternative methods is a self-propagating high-temperature synthesis permitting to obtain materials with specified properties [1].

A self-propagating high-temperature synthesis (SHS) is an exothermic reaction initiated locally as a result of specific chemical transformations, which occur in the mixture in the mode of a combustion wave (self-propagation) with the formation of solid products.

SHS has a controllable character and is realized in three stages: preparation of burden components, realization of SHS and cooling of finished products. A preparation stage is regarded as the most technological one, at which burden parameters can be changed. So, the possibility to control terminal properties of synthesized materials has appeared. One of such parameters is a mechanical activation [2].

The mechanical activation is a formation of a substance with a higher chemical activity owing to preliminary mechanical processing. The energy acquired during the activation time is assimilated by solid in the form of point and line defects. The accumulated dump energy is released during the synthesis. In addition, during mechanical activation a particle size is decreased, what increases the contact area. The process of mechanical activation can be observed in devices capable of grinding in impact, impact-rubbing or rubbing modes (the VSI, planetary and jet mills and other apparatus, where high values of frequency and force of mechanical impact are combined). Compared with other apparatus planetary mills have a higher efficiency. As a result of its use the maximum accumulation of structure defects is observed, the curvature value of surface is increased [3].

As a result of mechanical activation of reagents the decrease of the initial particle size and the increase of reactivity of solid reagents are observed; the temperature of reaction initiation is reduced; the structure becomes more uniform; the mechanical properties of materials are improved (the porosity is reduced, the strength is risen, the plastic properties are improved) [4-6].

This article represents a study of property changing of the mixture (La_2O_3+TiO_2+B) under the action of mechanical activation with the purpose of obtaining of finished product based on lanthanum hexaboride and titanium diboride and meeting the properties of a high-performance emitter.

2. Experiment

During the experiment burden parameters were studied according to the rotational frequency of the mill activating. In order to study the influence of mechanical activation parameters a special mixture was used: a mixture of chemically pure (99.9 mass %) fine-dispersed powders of lanthanum oxide, titanium oxide and boron (La_2O_3+TiO_2+B) mixed in a stoichiometric proportion for reaction propagation:

$$La_2O_3+3TiO_2+24B \rightarrow 2LaB_6+3TiB_2+3B_2O_3. \quad (1)$$

The initial reagents were being thoroughly intermingled in a pin cubical mixer with the help of the universal drive ERWEKA AR 403S during 30 minutes. The powder mixture had been dried before being placed in a muffle furnace during 5 hours at 100 °C and at atmospheric pressure. The mechanical activation was carried out in the planetary ball mill AGO-2S. The rotational frequency was varied within the limits of 10 to 40 Hz while the mechanical activation time was from 5 to 60 min. The grinding objects were metal balls with a diameter of 4 mm. The ratio of the ball mass to the mass of the processing substance was 10/1.

3. Results and discussion

The analysis of initial reagents was carried out on the BET-analyzer of specific surface META SORBI-M. Table 1 presents the results of the BET-analysis.

Table 1. The measurement of the specific particles surface area of the mixture (La_2O_3+TiO_2+B) (the activation time – 10 min).

Rotational frequency of mill (Hz)	Measured value of A_{sp} (m^2/g)
0	1.19 ± 0.02
10	2.00 ± 0.01
20	3.16 ± 0.04
30	5.14 ± 0.05
40	5.03 ± 0.05

In the pictures of powders before mechanical activation, taken by means of the raster electronic microscope Philips SEM 515, the large-sized particles are distinctly observed (Figure 1).

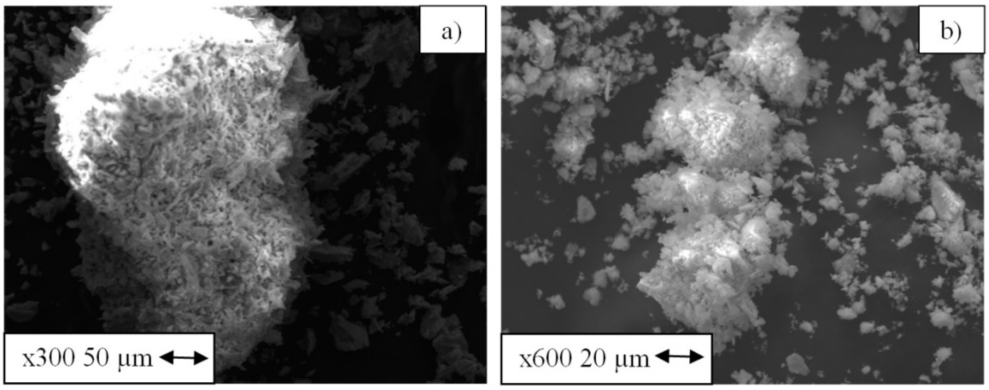

Figure 1. Photographs of the powder mixture ($La_2O_3 + TiO_2 + B$) before mechanical activation at magnification a) of 300 times; b) of 600 times.

After mechanical activation (Figure 2) the particle size has noticeably diminished as a result of particle rubbing and collision in the planetary mill.

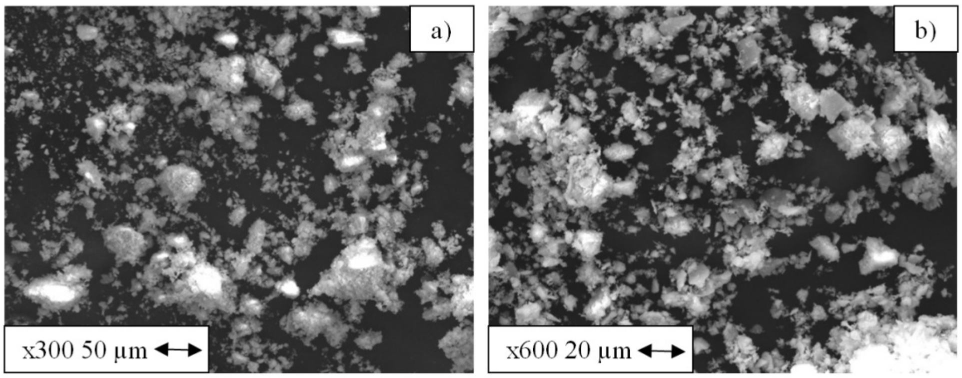

Figure 2. Photographs of the powder mixture (La_2O_3+TiO_2+B) after mechanical activation at magnification a) of 300 times; b) of 600 times.

In order to estimate the derived information it is necessary to plot the dependence of the specific surface area of processing burden on the rotational frequency of the activating mill. The graph is presented in Figure 3.

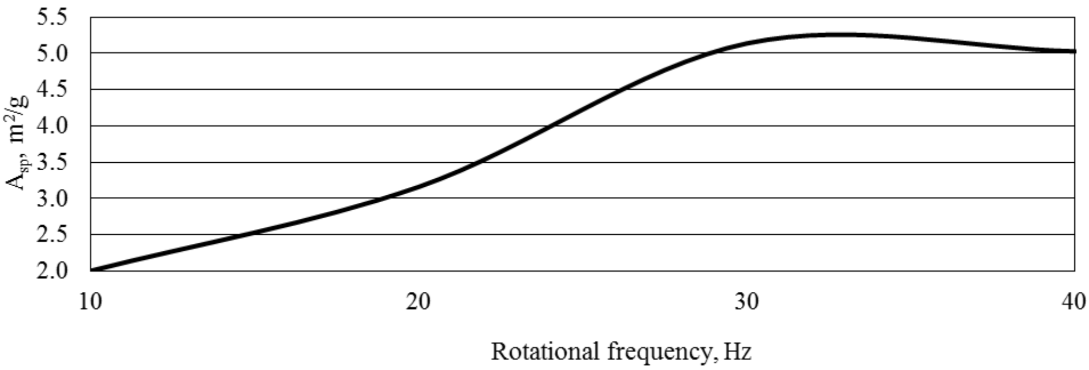

Figure 3. Dependence of the specific surface area of processing burden on the rotational frequency of the activating mill.

It can be seen from the plot that for the mixture (La_2O_3+TiO_2+B) the maximum value of the specific surface area is observed at the frequency of 30 Hz. This value decreases if the rotational frequency increases. In order to understand this process it was necessary to carry out the granulometric analysis of burden composition with the use of the laser analyzer of a particle size SALD-7101.

Figure 4 presents the particle size before grinding in the planetary ball mill.

Figure 5 presents the particle distribution according to sizes after mechanical activation with the frequency of 30 Hz during 10 min.

Figure 6 presents the particle distribution according to sizes after mechanical activation with the frequency of 40 Hz during 10 min.

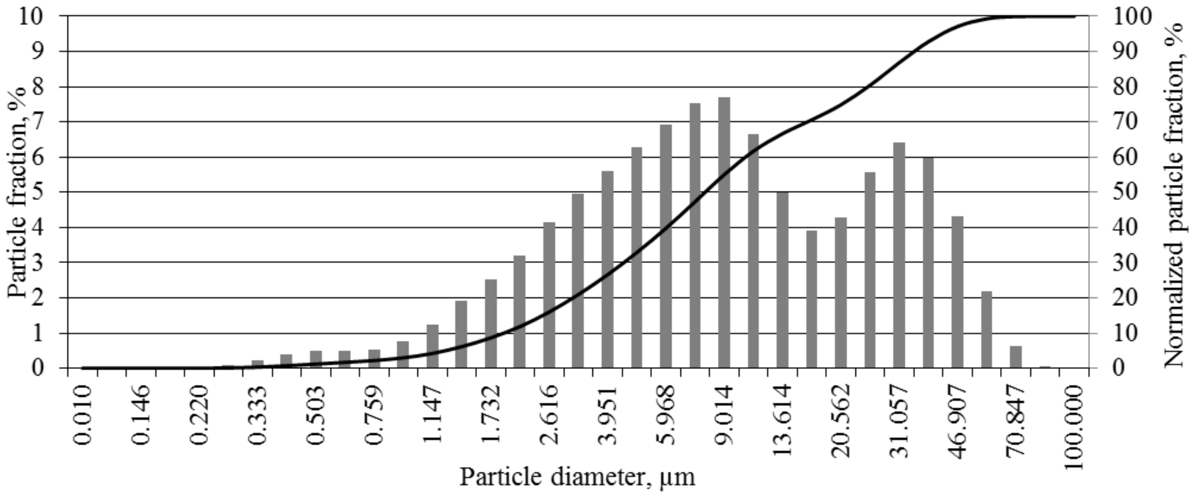

Figure 4. Granulometric composition of burden without mechanical activation.

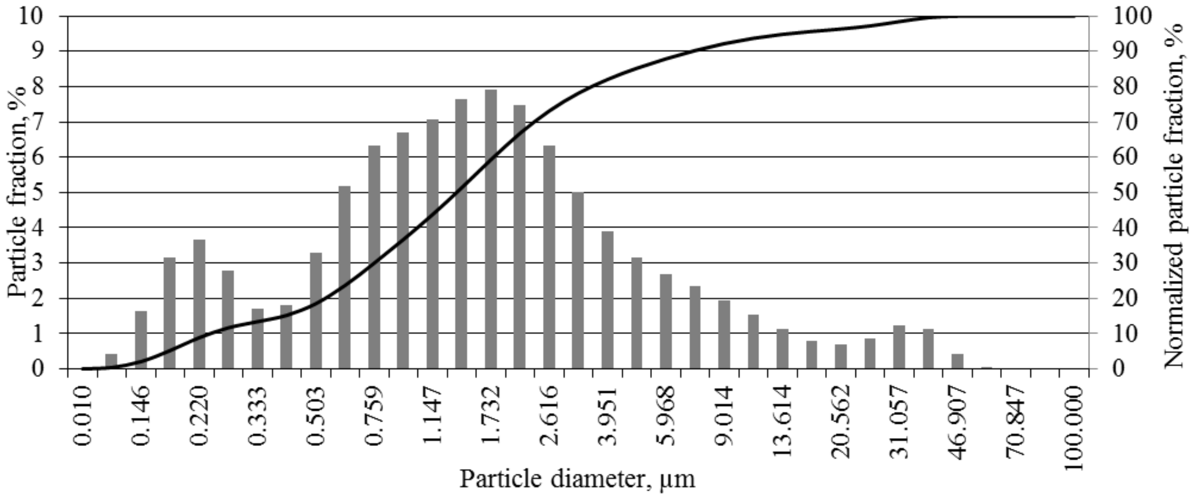

Figure 5. Granulometric composition of burden after mechanical activation with the frequency of 30 Hz during 10 min.

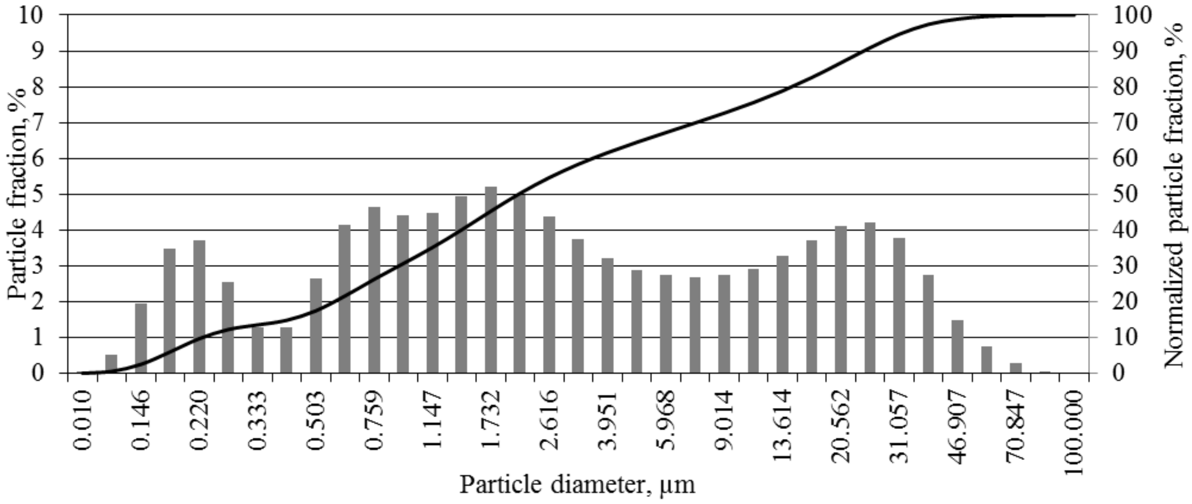

Figure 6. Granulometric composition of burden after mechanical activation with the frequency of 40 Hz during 10 min.

The comparison of Figure 4 and Figures 5, 6 clearly demonstrates the decrease of a particle size as a result of mechanical activation. It can be seen that the maximum value of the particle fraction is displaced to the less side. The decrease of the particle size increases the surface contact area reducing a temperature gradient, which has a negative influence on obtaining of finished products. However, when comparing the particle sizes obtained at the rotational frequency of 30 Hz (Figure 5) and the rotational frequency of 40 Hz (Figure 6) one can notice that the maximum particle size is increased, so the particle fraction with a larger size is raised. This process is also observed in Figure 3 in the frequency interval from 30 to 40 Hz. A similar negative influence of mechanical activation during the increase of rotational frequency is explained in the following way: the particle size stops diminishing under the action of impact-rubbing forces; particles start to collide with each other forming agglomerates (the particles of a larger size).

The integral curve in Figures 4–6 allows defining the particle fraction among all mixture compositions by a specified maximum size. In addition, it is possible to define the average particle size of the mixture, which serves as a more descriptive parameter. An average particle size is a universal characteristic for all modes of mechanical activation what allows using derived results in all devices, where mechanical activation is possible to realize.

4. Conclusions

During the research it has been discovered that as a result of mechanical activation of reagents the average particle size is decreased. The small particle size increases the surface contact area of particles thereby increases a reaction rate and improves the uniformity of combustion wave passing, thus promoting the obtainment of uniform and high-quality samples.

As a result of the research the dependence of the average particle size on the rotational frequency of the planetary mill has been found experimentally. The optimal value of rotational frequency of activating mill equaling to 30 Hz has been derived for the system (La_2O_3+TiO_2+B). It has been ascertained that the unregulated increase of rotational frequency may lead to the so-called «saturation threshold». In other words a mechanical activation will have a negative influence on SHS starting from certain values.

Mechanical activation allows controlling SHS what gives the opportunity to obtain material with specified properties: hardness, strength, porosity, density. In order to obtain a high-quality product with the help of mechanical activation it is necessary to calculate a frequency value individually for every reagent composition.

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