Structural Modification of La$_2$O$_3$-TiO$_2$-B Mixture After Mechanical Activation

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Abstract. Accelerators require development of new and more powerful installations, generating the streams of the charged particles, affecting the development of machine building industry, energy power industry and other fields of science and technology. Great attention is paid not only to the modernization of the installations, in whole, but also to their individual elements. Cathode is the most important element of the installations, generating the stream of charged particles.

Using lanthanum hexaboride as a cathode material allows getting maximum efficiency of cathode assembly due to the thermodynamic and emission properties of lanthanum hexaboride. This paper studies the properties changes of lanthanum oxide mixture, titanium and boron oxides under the influence of mechanical activation to obtain the final product, based on lanthanum hexaboride and titanium diboride, corresponding to the high performance properties of the emitter. The study resulted in determination of time and frequency of mechanical activation to obtain the particles with the smallest average size of 6.3 microns for the mixture of lanthanum oxide, titanium and boron oxides powders.

1. Introduction

Nowadays, the world faces with an acute problem of creating electron flows generating devices used in charged-particle accelerators, electron tubes, microscopes and other devices with operating principle based on the physical phenomenon – the electron emission.

Operating consistency of the emission cathode depends on the material from which it is made. The use of rare earth metals hexaborides as cathode materials ensures the greatest efficiency of the cathode assembly. Among the compounds of the borides with the rare earth metals lanthanum hexaboride stands out, because of the possibility to obtain a number of the advantages over traditional materials used in cathode technology: minimal work function of the electrons (~ 2.7 eV); high melting point (2800 K); ability to retain the emission properties at low vacuum and under intense ion bombardment; high density of obtained emission current ($\approx 2 \cdot 10^3$ A/cm^2, at a temperature of 2000 K); no poisoning in the air; high performance [1, 2].

Powder metallurgy methods, which are currently used to obtain the lanthanum hexaboride compound, have a number of drawbacks: poisoning of the final product as a result of the synthesis process; technologically sophisticated equipment; large energy losses due to prolonged annealing and synthesis of the products. One of the latest technologies for the production of lanthanum hexaboride is a self-propagating high-temperature synthesis (SHS), which allows obtaining materials with desired properties. SHS method is based on local initiation of the reaction, resulting in moving of the chemical

transformations along the mixture in the combustion wave mode (self-propagation) to form solid products.

SHS is possible to control during three stages of implementation: preparation of the batch components, conducting self-propagating synthesis and cooling of the final products. Preparation stage is considered to be more sophisticated, since changing the parameters of the batch, it is possible to control the final properties of synthesized materials, for example, the use of mechanical activation of the initial components of the mixture [3]. The solid body adopts the energy, acquired during the activation, in the form of point and line defects, and the accumulated excess energy is released during the synthesis process [4, 5].

2. Experiment
During the research the experiment was carried out to study the influence of mechanical activation on the morphological properties of the mixture of chemically pure (99.9 wt. %) powders of lanthanum oxide, titanium oxide and boron mixed at the stoichiometric coefficients for the following reaction:

$$La_2O_3 + 3TiO_2 + 24B \rightarrow 2LaB_6 + 3TiB_2 + 3B_2O_3 \qquad (1)$$
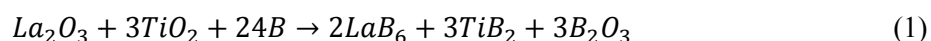
Titanium dioxide was added to obtain titanium diboride, which provides structural properties improvement and reduces the work function of the final product.

Starting reagents were thoroughly mixed in KB-15S pin type cubic mixer using ERWEKA AR 403S universal drive for 30 minutes. The powder mixture was pre-dried in a muffle furnace at 100 $^{\circ}$C for 5 hours at atmospheric pressure. Mechanical activation was carried out in a planetary ball mill of AGO-2C type; grinding was carried out using metal balls with a diameter of 4 mm; the ratio of the balls mass to the mass of the processed mixture was 10/1.

In the first part of the experiment, the dependence of the average particle size of the mixture from the rotational rate of activating mill was studied. Rotational rate varied in the range of 10 to 40 Hz at a pitch of 10 Hz at a constant rotation time of the activating mill of 10 minutes.

3. Results and discussion
The pictures of the powders before mechanical activation, made by a scanning electron microscope Philips SEM 515, clearly show large particles (Figure 1, a). After mechanical activation (Figure 1, b) the size of the particles decreases significantly as a result of the shock-abrasive interaction of the grinding balls with the particles in a planetary mill.
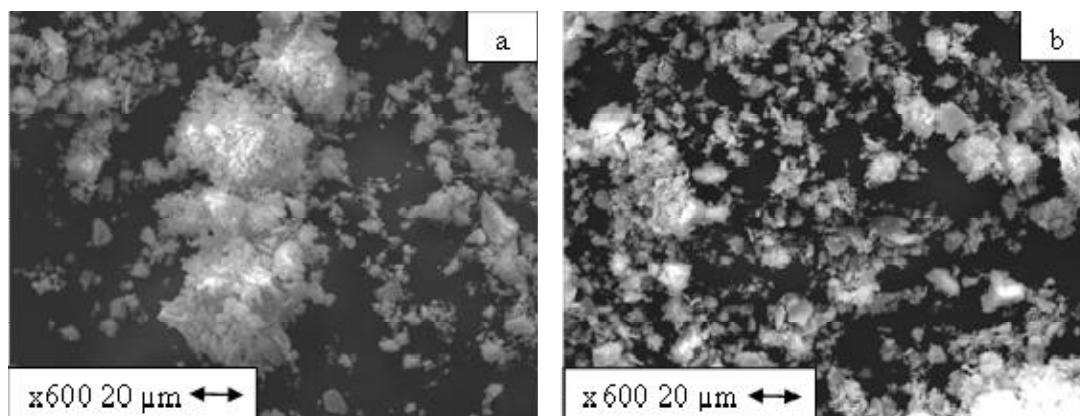
Figure 1. Pictures of the powders mixtures ($La_2O_3 + TiO_2 + B$):
a – before mechanical activation; b – after mechanical activation

To measure the surface area of the mixture components, the initial samples were BET-analyzed using surface area analyzer META SORBI-M. The results are shown in Table 1.

Table 1. Measurement of the surface area of the mixture components ($La_2O_3 + TiO_2 + B$) (activation time is 10 minutes).

Mill rotation rate (Hz)	Centripetal acceleration, made by the balls (m/s^2)	Measured Value A$_{sp.}$ (m^2/g)
Without mechanical activation		1.19±0.02
10	27.03	2.00±0.01
20	54.05	3.16±0.04
30	81.08	5.14±0.05
40	108.11	5.03±0.05

It may be noted that the largest surface area for the mixture ($La_2O_3 + TiO_2 + B$) is observed at a frequency of 30 Hz. This is the threshold value and increase of the rotational rate leads to decrease of the specific surface area.

In order to determine the particle size distribution, the components of the initial batch were subjected to the grain-size analysis using a laser particle size analyzer SALD-7101.
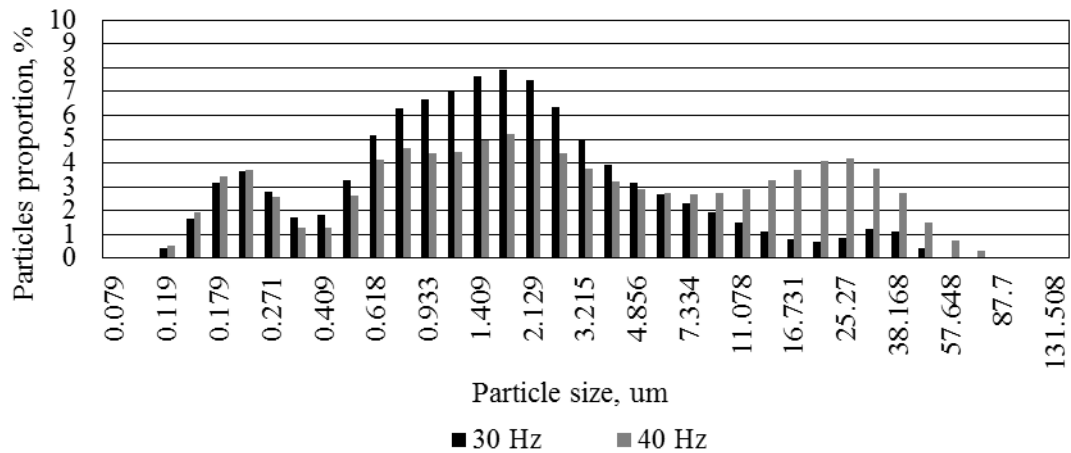
Figure 2 shows the particle size distribution before and after mechanical activation at a frequency of 10 Hz.
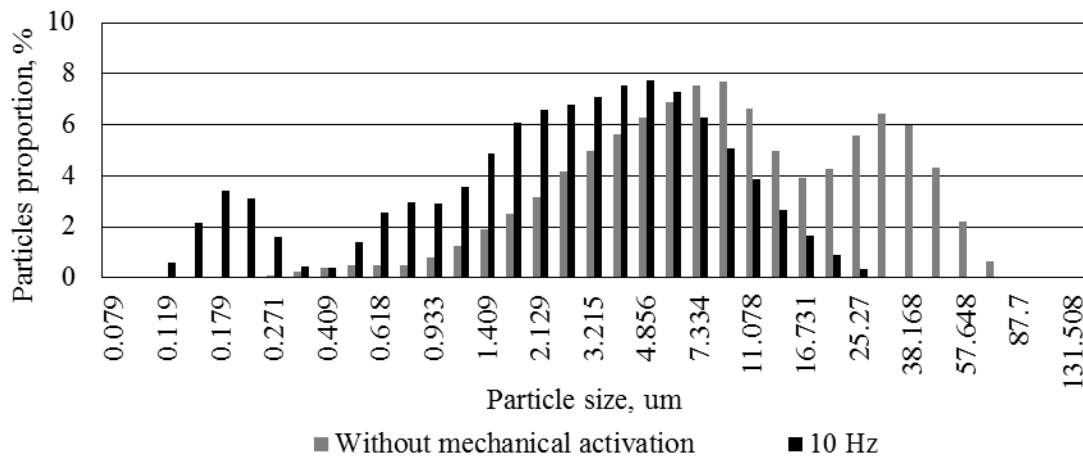
Figure 2. Grain-size composition of the batch before and after mechanical activation with a frequency of 10 Hz

Comparison of the size distributions shows that the particle size of the mixture after mechanical activation significantly reduces due to the distribution displacement to smaller sizes area.

At increasing the activation frequency up to 20 Hz and 30, the distribution displacement to smaller sizes area continues. However, at increasing the frequency up to 40 Hz, the proportion of the particles with a large size significantly increases. Figure 3 shows the particle size distribution after mechanical activation with frequency of 30 and 40 Hz.

Figure 3. Grain-size composition of the batch after mechanical activation with frequency of 30 and 40 Hz.

Comparing the distribution of particle size after mechanical activation with frequency of 30 and 40 Hz, it can be seen that with an increase of the activation frequency, the maximum particle size increases, the proportion of the particles with a large size also significantly increases. Such negative effect of mechanical activation at increasing the rotational rate is due to the fact that the particles under the action of the shock-abrasive forces reach their minimum size, begin to "glued" to one another under the action of mechanical forces, arising in mechanical activation mill, and form agglomerates.

For complete analysis it is necessary to compare the average size of the mixture particles before and after mechanical activation. The average particles size is a universal characteristic of all mechanical activation modes of the batch components, so, the obtained results could be used in all installations, where mechanical activation is able to be implemented. Calculation of average particle size of the mixture is made as using grain-size analysis. The obtained values are presented in Table 2.

Table 2. Measurement of average particle size

Mill rotation rate (Hz)	Centripetal acceleration, made by the balls (m/s^2)	Average particle size of the mixture, um
Without mechanical activation		15.05
10	27.03	9.51
20	54.05	7.31
30	81.08	3.67
40	108.11	8.49

The data presented in Table 2 and in Figures 2 and 3 show the reduction in particle size, indicating an increase of the surface contact area. According to [6, 7], the higher the surface contact area, the lower the temperature gradient, which high values negatively influence on obtaining the final product. However, comparing the particles size, obtained at rotation rate of 30 Hz and the rotation rate of 40 Hz (see Figure 3), it can be seen that the maximum particle size increases, the proportion of the particles with a large size significantly increases.

In the second part of the experiment the effect of activation time on average particle size in the mixture was studied. The activation time was varied in the range from 5 to 30 minutes at a pitch of

5 minutes and at a frequency of 30 Hz, provided the smallest size and the greatest average specific surface area of the particles.

As a result of the surface area analysis, the following experimental data were obtained and presented in Table 3. The highest specific surface area of the particles is observed for 25 minutes of activation time.

Table 3. Measurement of the surface area of the mixture components ($La_2O_3 + TiO_2 + B$).

Activation time, minutes	Measured value A_{sp}, m²/g
5	13.650±0.053
10	9.938±0.052
15	9.942±0.079
20	9.4765±0.057
25	36.840±0.313
30	4.063±0.036

Conducting grain-size analysis of the batch composition shows that at short-time activation (5 minutes) and at rotation frequency of 30 Hz of activation mill, there is a significant decrease of the average particle size of the mixture in comparison with the initial value of 15.05 um (Figure 4).
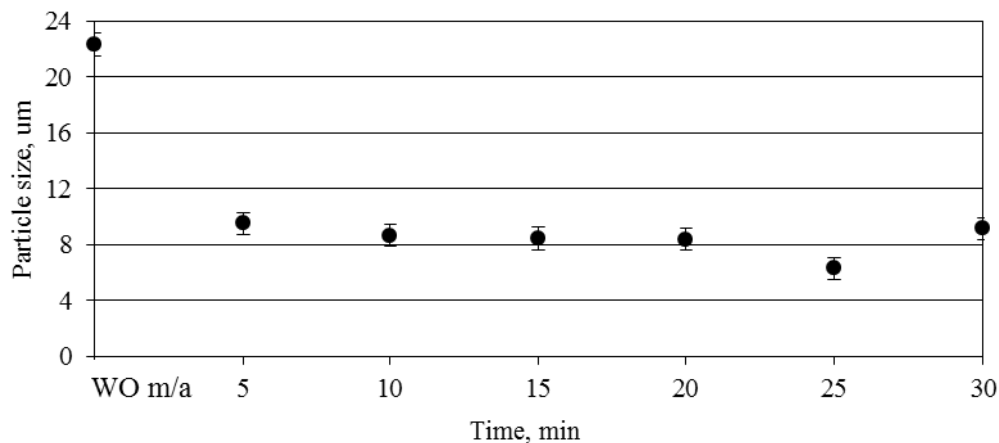
Figure 4. Dynamics of the changes of average mixture particle size ($La_2O_3 + TiO_2 + B$) depending on the activation time in a planetary ball mill.

Also, it should be noticed that the average particle size at mechanical activation ranging from 5 to 20 minutes slightly decreases, but at 25-minute activation a strong decrease of the average size is observed and, then, the average size increases in the case of 30-minute activation. Activation time of 25 minutes is a threshold, at increasing time there is an agglomeration of the particles, because of riveting one particle on the other to form agglomerates.

4. Conclusion
The study revealed that because of conducting reagents mechanical activation, there is a decrease of average particle size, leading to an increase of the contact area of the particles. In turn, this increases the reaction rate and improves the uniformity of the combustion wave flow, providing obtaining homogeneous and high-quality samples.

For the system ($La_2O_3 + TiO_2 + B$) the dependence of the average particle size on the activation frequency and time in a planetary mill is experimentally proved; the values of the rotation frequency

and time of the activating mill are determined, at which particles with the smallest dimension of 6.3 mm – 30 Hz and 25 minutes, respectively, are formed. Further uncontrolled increase of the activation frequency or time could lead to the "saturation".

Thus, starting with certain values, mechanical activation will have a negative impact on obtaining the desired product due to reducing the particles contact area, which leads to a decrease of the reaction energy yield and the nonuniformity of SH-synthesis flow. Therefore, for each reagent structure the values of frequency and time of mechanical activation must be individualized, because they have a strong influence on obtaining of the final product.

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