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Synthesis of Nanocrystalline Magnesium and Aluminum Diborides

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Abstract

For obtaining MgB_2 and AlB_2 with nanometer size of coherent scattering area the technique based on the preliminary mechanical activation (MA) of initial reagents powder mixes and the subsequent reaction in the mode of the thermal explosion (TE) was used. The mentioned diborides are the promising compounds to use as a high-energy material in the ramjets and solid rocket motors because they possess very high mass- and volume-heat of combustion. Mostly, the diborides are produced under conditions of high temperatures and pressures. In this research a possibility has been explored of their producing by thermal explosion method when using preliminary mechanically activated components. The peculiarities of the technique to produce diborides are examined. Results of radiographic and electron microscope studies of the mixes of reagents after mechanical activation and of thermal explosion products are presented.

1. Introduction

Boron (B) has the greatest mass and volume heat of combustion among known important elements [1]. Therefore, it is of great interest as high-energy additive in solid fuels for ramjet propulsion engines. However formation of oxide layer on a surface of B particles during burning slows down its oxidation and leads to reduction in the heat release rate [2]. In this regard the diborides of magnesium and aluminum (MgB_2 and AlB_2) are considered most perspective as high-energy additives. They possess the greatest mass and volume heat of combustion among available condensed compounds. MgB_2 and AlB_2 are usually obtained by long heating of mixes of initial reagents at a temperature of 1000 °C, or above. In work [3] by the method of the thermal explosion (TE) of stoichiometric mixes of an amorphous B with magnesium it was obtained MgB_2 with small MgO and Mg impurities. It was established that TE in mixes of powders of initial reagents is implemented only after magnesium melting. Therefore for preventing evaporation the MgB_2 synthesis was carried out in the closed reactor at elevated pressure of argon. But it wasn't succeeded to obtain AlB_2 with use of this technique. In work [4] monolithic samples of MgB_2 are obtained by TE method combined with hot pressing. However it is obvious that for implying diborides as additives to solid fuels the most perspective would be use of these compounds with the submicron crystalline and nanometer size of grain. In the case of MgB_2 it is possible to obtain such samples sometime with use of the preliminary mechanical activation (MA) of initial mixes of magnesium and B powders in planetary spherical mills with subsequent annealing of the activated samples of mixes [5]. However, there are no data on a possibility of obtaining AlB_2 with the nanometer size of grain.

The goal of this work is development of a technique for obtaining aluminum and magnesium diborides with nanometer size of grain.

2. Experimental

Based on the literature data and results of own experiments [6, 7], for the solution of the problem

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*Corresponding author. E-mail: korchag@solid.nsc.ru it was decided to use the technique implying preliminary MA of powder mixes of initial reagents and subsequent self-propagating reaction in the regime of dynamic thermal explosion.

For preparation of initial reactionary mixes Al + 2.1B and Mg + 2.1B it was used aluminum (PA-4 brand, 98% of Al), magnesium (MPF-3 brand, 99% of Mg) and amorphous boron (brand B 99A, 99.3). Small excess of B in the mixes, in comparison with stoichiometric quantity, is intentionally applied to compensate inevitable losses of this component due to sticking to walls of drums and spheres of a mill during MA.

Mechanical activation of initial reactionary mixes was carried out in a planetary spherical mill AGO–2 with water cooling [8]. The volume of each steel mill drum is equal to 160 cm^3. Diameter of spheres is 8 mm, the mass of spheres in each drum is 200 g, the mass of a sample is 10 g. Centrifugal acceleration of spheres is 400 m s^{-2} (40 g). For prevention of oxidation during MA the drums with samples were filled with argon. After MA samples were unloaded from drums in boxing with argon.

Time of activation changed with a step of 1 min. For mixes with magnesium when duration of MA exceeded 12 min, the activated samples ignited during unloading from boxing on air, even in case of cooling down the mill drums to room temperature. That is, these samples became pyrophoric. For mixes with aluminum the maximum MA time comprised 12 min.

The basic constructional element of experimental installation for carrying out reaction in the mode of dynamic TE is the specialized reactor designed on the basis of the induction furnace. The scheme of experimental installation is provided in [9]. Synthesis was carried out in argon. Speed of heating and temperature of the furnace were controlled with use of the control unit of the furnace. To control the temperature and record the thermograms of TE there were used tungsten – rhenium thermocouples (WRe 5/WRe 20) with a diameter of 100 micron. The signal from the thermocouple arrived on the analog-digital converter LA–2USB – 14 and further on the computer.

Reactionary mixes after MA and products of thermal explosion were investigated by means of the X-ray phase analysis (XPA) and scanning electronic microscopy. Roentgenograms were taken on the DRON-4.0 diffractometer with use of Cu K_α radiation. Electronic and microscopic studying was carried out on the scanning microscopes of TM-1000 and S-3400 N (Hitachi).

3. Results and discussion

It is well known that when machining in planetary mills the morphology and a microstructure of initial reagents significantly change [7, 9, 10]. The data obtained so far demonstrate that as a result of the intensive plastic deformation (IPD) which is implemented at MA of reactionary mixes in a planetary spherical mill the mechanocomposites are formed in which there is a considerable fragmentation of reagents, and the area of their contact increases and high concentration of nonequilibrium defects and internal tension is formed. As a result of these processes a sample accumulates a part of the mechanical energy brought at MA.

Besides, it is obvious that at the earliest stages of activation there is a destruction of the oxide layers and the adsorbed films on particles of initial powders which serve a serious diffusive barrier to start interaction. Especially it is essential for the mixes containing aluminum or magnesium.

The data on the effect of preliminary MA of exothermic systems which are available so far demonstrate that all these factors considerably increase reactionary ability of components of mixes and, in particular, reduce temperature of the beginning of reagents chemical interaction (in some compositions by hundreds of degrees [7, 9, 10]). It is established that the value of this effect depends on the formulation of concrete system, the nature of components and conditions of MA (duration, power tension and type of the used activator).

Via examining the changes in morphology of the activated examples of both mixes it is established that at 1 MA min duration the crushing of particles is observed, both aluminum, and magnesium, and formation of low density agglomerates of these metals with B begins. Further the number of such agglomerates increases; their density is increased. The sizes of the main fraction of these agglomerates increase to 50 ÷ 100 micron. However even after 10–12 min of MA about a half of volume of a sample consists of separate, smaller particles (Fig. 1).

On roentgenograms of activated samples the only widened lines of a metal component are observed. Even after 12 min of MA the products of interaction of aluminum with B, or magnesium with B are not detected.

In Fig. 2 the plot of dependency of the size of coherent scattering area (CSA) of aluminum versus MA time is presented for samples of studied mix. It is seen that the greatest decrease in the values of CSA is observed already at the earliest stages of

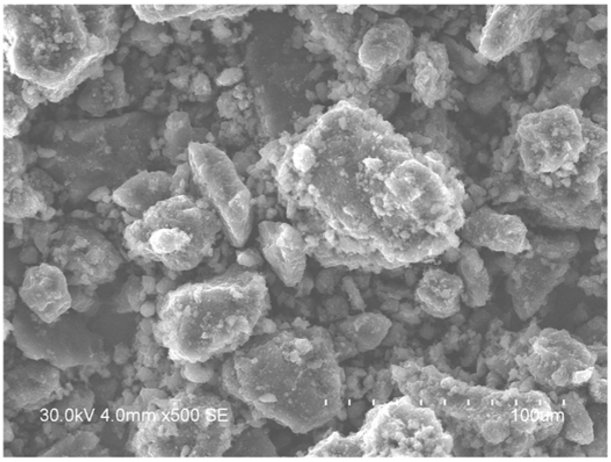

Fig. 1. The microphoto of the Al + 2.1B sample after 10 min of MA.

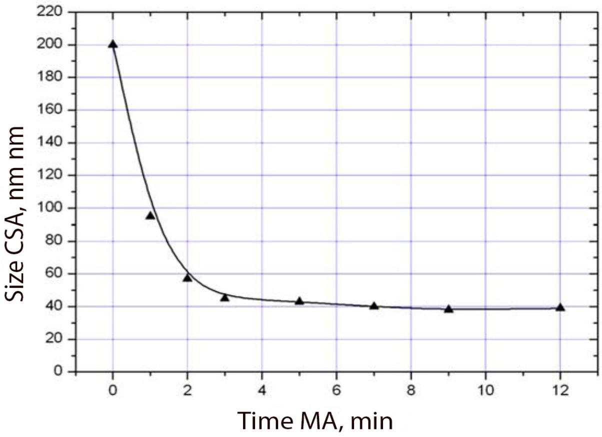

Fig. 2. Dependency of the size of coherent scattering area of aluminum on time of MA of the mixture Al + 2.1B.

activation (at 1–2 min of MA). At increase in time of activation the sizes of aluminum grain change not so considerably, but at these stages there is an increase in a portion of the energy of MA [7] accumulated by a sample.

Similar dependencies for the CSA size were obtained for activated Mg + 2.1B mixture. The minimum value of CSA for magnesium (20 nm) is obtained as a result of MA of initial mixture for 10 min.

On the thermogram of heating the initial mix Al + 2.1B (without MA) at the temperature range of 640–660 °C the extended isothermal segment corresponding to aluminum melting is recorded. The exothermic reaction of aluminum with B leading to TE is observed only after full Al melting. According to X-ray phase diagram the TE products in this case consist generally of AlB_2 with small impurities of Al_2O_3 and unreacted aluminum. Similar thermograms are obtained also when heating the initial, not activated mix of Mg + 2.1B [6].

In Fig. 3 the typical thermogram of TE is presented for Al + 2.1B sample after preliminary MA within 2 min.

The absent of the isothermal segment corresponding to aluminum melting is unusual here. The TE is observed at once at reaching this temperature. Further increase in time of preliminary MA leads to decrease in temperature of initiation of TE to the values below the Al melting temperature. Also the maximum temperature of reaction decreases. Dependencies of the TE parameters on time of MA for Al + 2.1B sample are given in Fig. 4.

Similar changes of character of thermograms and T_{ign} and T_{max} values upon increase in time of preliminary MA are established also in the experiments with Mg + 2.1B samples [6].

As a result of carrying out X-ray phase analysis it is established that at times of MA exceeding 2 min the products of TE are AlB_2 and MgB_2 with the impurity traces of Al_2O_3 and MgO, respectively.

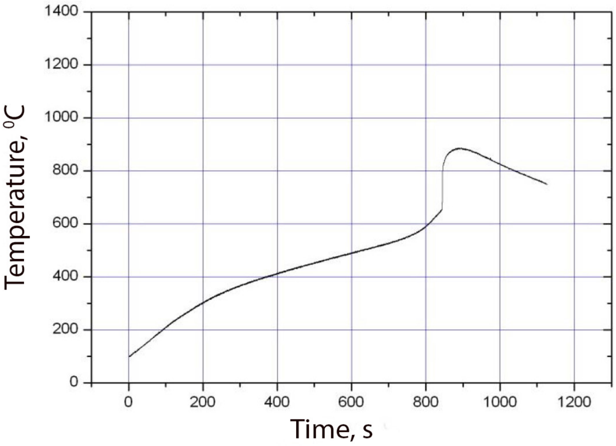

Fig. 3. The thermogram of TE of Al + 2.1B mix after preliminary MA within 2 min.

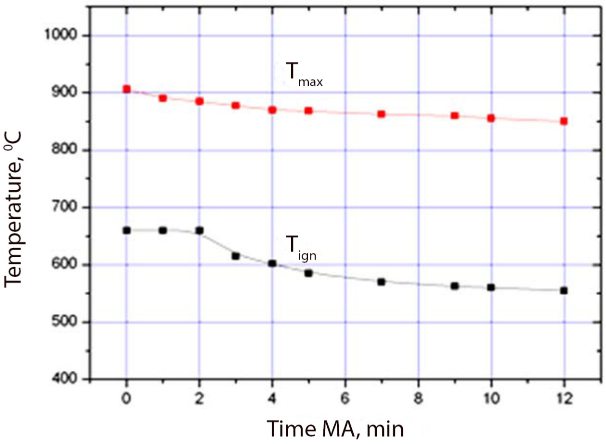

Fig. 4. Dependencies of temperature of initiation of TE (T_{ign}) and the maximum temperature of reaction (T_{max}) for Al + 2.1B sample on time of preliminary MA.

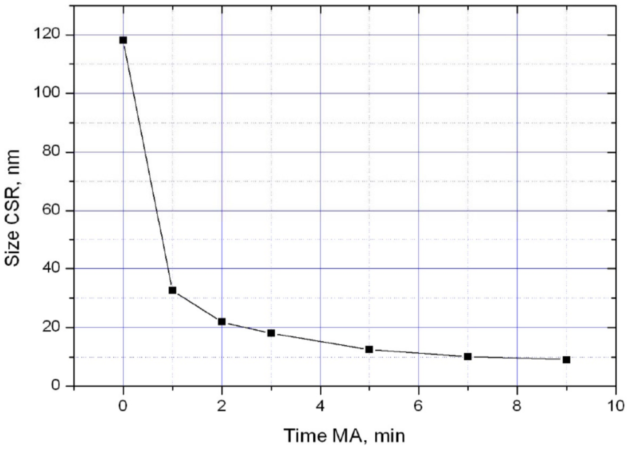

Fig. 5. Dependency of the of AlB_2 CSA sizes on additional MA processing time.

It is known that nanosized powders are of the greatest interest to increase the burning rate of high-energy materials. Therefore experiments on additional MA of the obtained aluminum diboride for the purpose of increasing in its dispersion extent were made. For these experiments some amount of AlB_2 compound has been prepared by the method of vacuum annealing of the examples activated within 5 min. Cylindrical samples with a diameter of 12 mm and 30–35 mm long pressed to relative density 0.55–0.6 were prepared from MA mix. The obtained samples were loaded into the vacuum furnace (for vacuum) and heated up to the temperatures of 750–800 °C. It is found that in this case the mono-phase AlB_2 with small impurity of aluminum oxide is formed.

The effects of additional MA duration on the CSA sizes, parameters of a lattice and morphology of AlB_2 have been investigated. It is established that the CSA values of initial AlB_2 depend on the indexes of diffraction reflection. It demonstrates the difference in the sizes of crystallites in various crystallographic directions. Machining of AlB_2 within 1–2 min leads to formation of equiaxed crystals. The data on dependency of the diboride of aluminum CSA sizes on MA processing time calculated on basis of the line (010) are presented in Fig. 5. According to these data, the values of CSA of aluminum diboride processed during 1 min MA decrease from 118 ± 3.4 nm to 33 ± 0.8 nm. Increase in time of processing up to 9 min leads to decrease in values of CSA up to 9 ± 0.2 nm.

As a result of electronic and microscopic researches it is established that additional MA of a diboride of aluminum leads to essential change of his microstructure. After 1 min of MA the dense particles of initial AlB_2 are practically absent. Essential dispersion of these particles is observed. At further increase in time of MA the formation of friable agglomerates composed of small particles of submicron sizes begins. Increase in time of MA doesn't lead to essential change of a microstructure, but according to the data given above, the size of CSA of these MA of samples decreases to 9 ± 0.2 nm.

4. Conclusions

1. Preliminary MA of the powder mixes Al + 2.1B and Mg + 2.1B leads to decrease in temperature of initiation of TE to the values lower the melting the aluminum and magnesium temperatures, respectively.
2. The MA modes allowing to obtain diborides of aluminum and magnesium as a result of TE are found.
3. Additional machining of AlB_2 in a planetary spherical mill leads to reduction of the sizes of areas of coherent dispersion to nanometer values.

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