

# LABORATORY PRODUCTION OF $MgB_2$ BY A THERMAL EXPLOSION OF MECHANOACTIVATED Mg-B MIXES

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Abstract. Magnesium diboride  $MgB_2$  is one of the promising compounds to use as a high-energy material in the ramjets and solid rocket motors because it possesses very high mass- and volume-heat of combustion.  $MgB_2$  is usually produced by a long heating of mixes of boron and magnesium at a temperature of 1000°C, or higher. Mostly, the  $MgB_2$  is produced along with small amounts of MgO and impurities. In this research a possibility has been explored of producing the  $MgB_2$  by thermal explosion method when using the components preliminary mechanical activation. Thermal explosion was conducted in the flow through reactor under atmospheric pressure of argon. According to the data of X-ray phase analysis the products of thermal explosion are monophasic  $MgB_2$  with impurity traces in the form of MgO. On the basis of the analysis of thermal explosion thermograms it is stated that an interaction of reagents in mechanically activated mixes starts before the magnesium melting. Results of radiographic and electron microscope studies of the mixes of reagents after mechanical activation and the products of thermal explosion are presented.

## INTRODUCTION

Boron possesses the greatest mass and volume heat of combustion among practically important elements [1]. Thus, it is promising high-energy additive in solid propellants or in the fuel for ramjet propulsion engines. However, formation of a liquid oxide layer on a surface of boron particles during combustion slows down its oxidation and leads to reduction of the heat release rate [2]. In this regard as for high-energy additives, the boron compounds are considered to be more perspective. In particular, it can be  $MgB_2$  -

magnesium diboride. Its theoretical combustion heat is equal to 9.2 kcal/mol and density 2.69 g/cm<sup>3</sup> [3]. Usually, the magnesium diboride is obtained via long heating of mixes of boron with magnesium at a temperature of 1000°C and above [4]. In work [5], monolithic samples of MgB<sub>2</sub> were prepared by the method of hot pressing combined with thermal explosion. The method of the dynamic thermal explosion for synthesis of the MgB<sub>2</sub> powders was used in work [3]. Realization of this mode of synthesis is based on the exothermicity of reaction in the mixes Mg + 2 B. It was established that thermal explosion in the mixes of powders of initial reagents is realized only after magnesium melting. Therefore for magnesium evaporation suppression (T<sub>boil</sub> = 1090°C) the experiments were made in a sealed reactor at elevated pressure of argon. According to the X-ray phase analysis the thermal explosion products consisted of MgB<sub>2</sub> with Mg and MgO [3] impurity.

Mechanical processing is successfully used to treat powders before heat treatment [6], self-propagating high-temperature synthesis [7], or reactive hot pressing [8]. It is commonly believed that mechanical processing enables homogenization and size reduction down to a nanoscale level, promotes the formation of new, oxide free surfaces, reduces the interparticle distance diffusion range, produces structural defects, and activates reactants. Mechanical processing that leads to chemical changes is referred to as mechanochemical.

Preliminary mechanical processing enables successful MgB<sub>2</sub> synthesis at 650°C in 1 h [6, 9]. The processing time influences the temperature of MgB<sub>2</sub> formation, which decreases with increasing milling duration. In particular, magnesium diboride was obtained by heating to 500°C a mixture of Mg and B powders milled for 60 min [6, 9]. The average particle size of MgB<sub>2</sub> was 7 nm [6] to 70–80 nm [7], which is almost three orders of magnitude lower of that value for magnesium diboride prepared from a mixture of fresh (unmilled) powders. A major impurity in magnesium diboride synthesis is magnesium oxide, MgO, which results from the reaction of magnesium with the residual oxygen in the furnace [9].

Magnesium diboride exists in both crystalline and amorphous forms. Grinding of crystalline magnesium diboride in a SPEX 8000 Mixer/Mill vibratory ball mill for 20 h at a maximum ball acceleration of  $100 \text{ m/s}^2$  was reported to lead to the formation of an amorphous phase [10]. On the other hand, amorphous  $\text{MgB}_2$  can be prepared by milling a mixture of pure magnesium and boron powders for 25 h.  $\text{MgB}_2$  crystallization from the amorphous phase thus produced begins at a reduced (compared to reported crystallization temperatures) temperature of  $450^\circ\text{C}$  [11].

In [12], it was studied the phase composition of materials obtained by mechanochemical processing and subsequent heat treatment of mixtures of magnesium and boron powders in the atomic ratio 1 : 2. During annealing of the activated powder mixture, X-ray amorphous magnesium diboride forms at  $340^\circ\text{C}$  and crystallizes at  $480^\circ\text{C}$ . As shown by high-resolution transmission electron microscopy, the unreacted crystalline magnesium is covered with amorphous layer consisting of magnesium diboride and boron. The amorphous material obtained by milling contains nuclei of  $\text{MgB}_2$  crystallites of 3–5 nm in size. During subsequent heating of the activated mixture, magnesium and boron react further to form amorphous magnesium diboride and then amorphous phase crystallizes. Heating of mechanically activated mixtures to just below the crystallization temperature allow  $\text{MgB}_2$  nanoparticles to be produced. The formation of nanocrystalline magnesium diboride nuclei along with the amorphous phase during mechanochemical processing facilitates mechanochemical synthesis as compared to thermal synthesis.

The goal of the reported study was investigation of the effect of mechanical activation (MA) of the mix of magnesium and boron particles on the parameters of thermal explosion (TE) resulting in the synthesis of  $\text{MgB}_2$ .

## TECHNIQUE OF EXPERIMENTS

For preparation of initial reactionary mix of (Mg + 2.1B) there were used the reagents: magnesium (MPF-3) and amorphous boron (black, B-99a). Small excess of the boron content in the mix, as compared with the stoichiometry quantity, was intentionally made

in order to compensate inevitable losses of this component due to sticking to the 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 [13]. Volume of each of two steelpans of a mill is 160 cm<sup>3</sup>. 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 was 400 m/s<sup>2</sup> (40 g). For prevention of oxidation during MA the drums with samples were filled with argon. After MA treatment the samples were unloaded from drums in the box filled with the argon.

Time of activation varied in the range of 1- 5 min with a step in 1 min. At duration of MA exceeding 5 min, the activated samples ignited when unloading in air from the box with inert gas, even in the case of cooling of drums to room temperature. That is, these samples became pyrophoric.

The basic constructional element of experimental installation for carrying out reaction in the mode of dynamic TE is the specialized reactor manufactured on the basis of the induction oven. The scheme of experimental installation is presented in [14]. Synthesis was carried out in argon. Rate of heating and temperature of the heater were controlled with use of the control unit of the oven. To control the temperature and recording thermograms there were used tungsten - rhenium thermocouples (WRe5/WRe20) with a diameter of 100 micron. The signal from the thermocouple was sent on the analog-digital converter LA- 2USB – 14 and further on the computer.

Rate of heating of samples was chosen constant (45 K/min). Reactionary mixes after MA and products of thermal explosion were investigated by means of the X-ray phase analysis (RFA) and the scanning electronic microscopy. Roentgenograms were obtained on the DRON-4.0 S diffractometer with use of Cu Ka radiation. Electronic and microscopic studying was carried out on the scanning TM-1000 and S-3400 N (Hitachi) microscopes.

## RESULTS AND DISCUSSION

It is well known that while treating in planetary mills, the morphology and microstructure of initial reagents [14-20] significantly changes. The data obtained so far testify that as a result of the intensive plastic deformation (IPD) which is realized at MA of reactionary mixes in a planetary spherical mill, the mechanocomposites with considerable dispersing of reagents are formed; the area of their contact increases and high concentration of nonequilibrium defects and internal tension develops. As a result of these processes the part of the mechanical energy brought at MA is accumulated by a sample.

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

The data on the effect of preliminary MA of exothermic systems, which are available so far, testify that all these factors considerably increase reactionary ability of mixed components and reduce temperature of the beginning of chemical interaction of reagents. For some compositions it comprises hundreds of degrees [1, 14, 15, 19 - 21]. It is found that the size of the effect depends on structure of concrete system, the nature of components and the conditions of MA (duration, power intensity and type of the used activator).

As a result of studying the morphology of treated by MA mixes of magnesium with boron, it is established that after 30 sec treatment there is a formation of dense mechanocomposites of a lamellar form with the cross size  $\approx 30 \div 300$  microns and  $2 \div 5$  microns thick. At increase in treatment duration up to 5 min the cross sizes of these lamellar particles increase to 1 – 2 mm. On the roentgenograms of MA treated samples only the broadening of lines of magnesium is observed. Even after 5 min treatment the products of interaction of magnesium with boron are absent. The value of adiabatic

temperature of combustion for stoichiometric mix of initial reagents calculated with use of data [22] equals 1613K.

The typical thermogram of TE of a sample after 30 sec preliminary MA is given in fig. 1. The lack of isothermal site corresponding to magnesium melting is an unusual finding here. The heat release begins at a temperature  $\approx 525^{\circ}\text{C}$ , and at the temperature of  $560^{\circ}\text{C}$  TE is initiated. The maximum temperature of reaction is equal to  $1060^{\circ}\text{C}$ . According to data [6, 3], in the samples of studied composition without preliminary MA or activated in less power intense mills, the isothermal site of melting of magnesium is presented always.

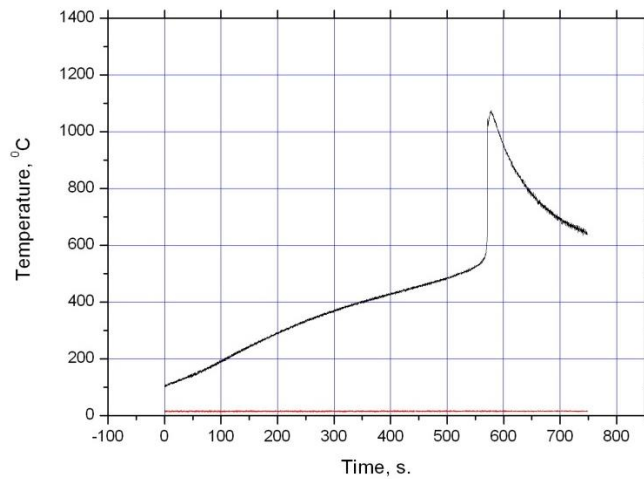


Fig. 1. The temperature record in thermal explosion of Mg + 2.1B composition preliminary treated by MA for 30 s.

The increase in time of MA up to 4 - 5 min leads to decrease in the values of temperature of the TE initiation to  $500 - 480^{\circ}\text{C}$ . The maximum temperature of reaction decreases to  $970 - 860^{\circ}\text{C}$ , respectively.

It has to be noted that decrease in values of TE initiation temperatures and in the maximum temperatures of reaction is observed practically in all exothermic compositions after preliminary MA in the powerful planetary spherical mills. For example, preliminary MA of mix 3Ni + Al in a planetary spherical mill AGO-2 within only 2.5 - 3 min leads to decrease in temperature of TE initiation of from  $660$  to  $180^{\circ}\text{C}$ . The maximum reaction temperature decreases from  $1350$  to  $1050^{\circ}\text{C}$  [19,20].

On the basis of the X-ray phase analysis data it is established that irrespective of duration of preliminary MA of the studied composition, the products of TE consist of  $MgB_2$  with a small  $MgO$  impurity. The typical X-ray phase diagram of TE products is presented in fig. 2.

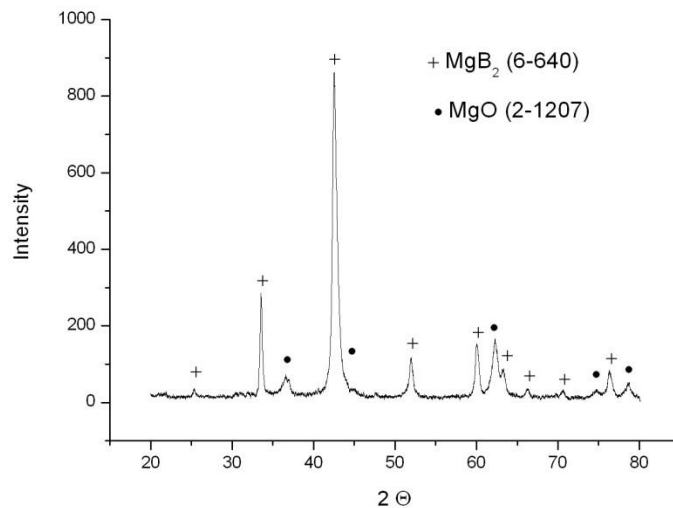


Fig. 2. X-ray phase diagram of the products of thermal explosion.

The electronic and microscopic studies of  $Mg-B$  mix showed that irrespective of duration of preliminary MA, the TE products practically preserve morphology of initial mechanocomposites. As shown in fig. 3, the products of TE consist of the same lamellar particles. Differences are in the presence in TE products of quite large number of fine particles and in changed microstructure of a surface of plates. Based on the data of X-ray phase analysis it is possible to assume that fine particles consist of  $MgO$ . The micro photo of a surface of separate lamellar particle is given in fig. 4. Unlike microstructure of an initial mechanocomposite having almost smooth surface, the surface of TE products consists of grains with the sizes from 0.3 to 1.2 micron.

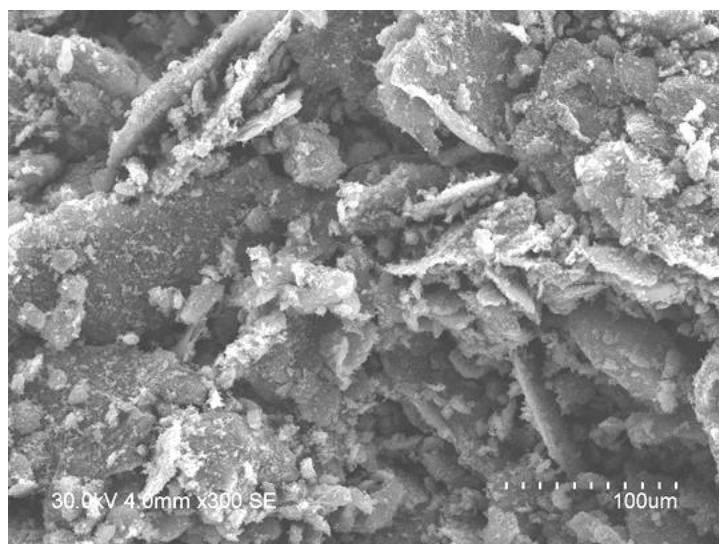


Fig. 3. Microphotography overview of the TE products.

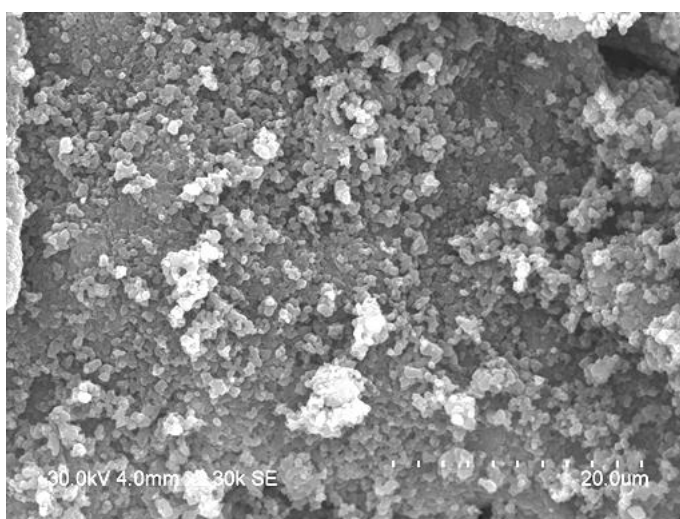


Fig. 4. Enlarged view of the surface of separate lamellar particle of TE products.

## CONCLUSIONS

1. Preliminary MA of powdered mixes of studied composition leads to decrease in the temperature of TE initiation to the values, which are smaller the magnesium melting temperatures. Interaction begins to proceed between solid reagents.
2. Irrespective of duration of preliminary MA, the TE products consist of  $MgB_2$  and small amount of  $MgO$ .



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