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The Effect of Preliminary Mechanical Processing of Mg and B mixture on the Parameters of Its Thermal Explosion and Reaction Products Characteristics

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Investigation of the effect of preliminary mechanical processing the mixes of magnesium with amorphous boron (Mg + 2.1B) on major parameters of the thermal explosion and phase structure of the formed reaction products has been conducted. The mechanical processing parameters providing realization of the condensed phase thermal explosion regime are defined. Results of X-ray phase analysis and electron microscopic studying the mechanically treated mixture components and reaction products of thermal explosion are presented.

I. Introduction

Due to its efficient energetic properties (greatest mass and volume heat of combustion) the boron can be used as a high-energy additive in solid propellants or in the fuel for ramjet propulsion engines [1]. Unfortunately, there are some drawbacks in practical use of boron because the formation of a liquid oxide layer on the boron particles surface during combustion slows down its oxidation and leads to reduction of heat release rate [2]. Therefore, the boron compounds, in particular, MgB_2 - magnesium diboride, can be also considered as perspective ones for combustion applications. The MgB_2 theoretical combustion heat is equal to 9.2 kcal/mol and its density 2.69 g/cm^3 [3].

Usually, the magnesium diboride is obtained via long heating of mixes of boron with magnesium at a temperature of 1000^0C and above [4]. In [5], monolithic samples of MgB_2 were prepared by the method of hot pressing combined with thermal explosion. The method of the thermal explosion for synthesis of the MgB_2 powders was used in [3]. It was established that the thermal explosion in the powders mixes of initial reagents is realized only after magnesium melting. Therefore for magnesium evaporation suppression (T_{boil} = 1363K) the experiments [3] were conducted in a sealed reactor at elevated pressure of argon. According to the X-ray phase analysis data the thermal explosion products consisted of MgB_2 with Mg and MgO impurity. Realization of this mode of synthesis is based on the exothermicity of reaction in the mixes Mg + 2 B. The magnitude of adiabatic combustion temperature for stoichiometric Mg-B mixture equals 1615K [6].

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Mechanical processing has been successfully used to prepare raw powders before heat treatment [7], self-propagating high-temperature synthesis [8], or reactive hot pressing [9]. 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_2 synthesis at 650°C in 1 h [7, 10]. The processing time influences the temperature of MgB_2 synthesis, which decreases with increasing the milling duration. In particular, magnesium diboride was obtained by heating to 500°C a mixture of Mg and B powders milled preliminary for 60 min [7, 10]. The average particle size of MgB_2 was 7 nm [7] or 70–80 nm [8], which value is almost three orders of magnitude less than that for magnesium diboride particles prepared from a mixture of non-processed powders. A major impurity in magnesium diboride synthesis is magnesium oxide, MgO, which results from the reaction of magnesium with residual oxygen in the furnace [10].

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 m/s^2 was reported to lead to the formation of an amorphous phase [11]. On the other hand, amorphous MgB_2 can be prepared by milling a mixture of pure magnesium and boron powders for 25 h. MgB_2 crystallization from the amorphous phase thus produced begins at a reduced (compared to reported crystallization temperatures) temperature of 450°C [12].

In the [13], it was performed study of the phase composition of materials obtained by mechanochemical processing and subsequent thermal 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°C and crystallizes at 480°C. As shown by high-resolution transmission electron microscopy, the unreacted crystalline magnesium is covered with an amorphous layer consisting of magnesium diboride and boron. The amorphous material obtained by milling contains nuclei of 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 the amorphous phase crystallizes. Heating of mechanically activated mixtures to just below the crystallization temperature allows MgB_2 nanoparticles to be produced. The formation of nanocrystalline magnesium diboride nuclei along with the amorphous phase during mechanical processing facilitates mechanochemical synthesis as compared to thermal synthesis.

The effects of the reaction mixture preparation on the Mg + 2 B system and the heating rate on the magnesium diboride formation mechanism were investigated by using time-resolved X-ray diffraction in [6]. There were investigated the dynamics of phase formation during the thermal explosion and the effects of preliminary mechanical activation. As described, the MgB_2 phase emerged with no formation of intermediate compounds. A further increase in the mechanical processing time to 60 min has no effect on T_{ign}. For the purpose of mechanical activation, the reactants were mixed in Activator-2 S high-speed ball planetary mill. The ratio between the ball weight and the raw mixture was 35:1. The components were mixed in Ar at 1 atm. No mechanochemical synthesis occurred while mechanically processing the mixture in the range from 15 to 60 min. The self-ignition temperature (T_{ign}) of the non-activated mixture is ~ 656°C, which corresponds to the melting point of magnesium. The self-ignition temperature decreases by 500°C after 15 min of mechanical activation. A further increase in the mechanical processing time to 60 min has no effect on T_{ign}.

The aim of the present study was the detailed investigation of the effect of the raw materials preliminary mechanical processing via use of high energy planetary ball mill AGO-

2 on dynamics of heat release and phase composition of the products of Mg-B mixture reaction.

II. Experimental Technique

For preparation of initial reactionary mix of (Mg + 2.1B) there were used the reagents: magnesium (MPF-3, 99 % Mg) and amorphous boron (black, B-99a, 99,3 % B). 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 mechanical processing.

Mechanical processing the initial reactionary mixes was carried out in a planetary spherical mill AGO – 2 with water cooling [14]. Volume of each of two steel pans of a mill is 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 was 400 m/s^2 (40 g). For prevention of oxidation during mechanical processing the drums with samples were filled with argon. After mechanical processing treatment the samples were unloaded from drums in the box filled with argon too.

Time of activation varied in the range of 0.5-12 min. At duration of mechanical processing exceeding 12 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 thermal explosion is the specialized reactor manufactured on the basis of the induction oven. The scheme of experimental installation is presented in [15]. 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 microns. 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 mechanical processing and the 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.

III. Experimental Results and Discussion

It is well known that while treating in planetary mills, the morphology and microstructure of initial reagents [16-22] significantly changes. The data obtained so far testify that as a result of the intensive plastic deformation which is realized at mechanical processing of reactionary mixes in a planetary ball mill, the mechanocomposites with considerably dispersing reagents are formed; the area of the components contact increases and high concentration of nonequilibrium defects and internal tension is developed. As a result of these processes, the part of the mechanical energy brought at mechanical processing is accumulated by a sample.

Besides, it is obvious that at the earliest stages of activation there is destruction of oxide layer as well as of the adsorbed films on initial particles which serve a serious diffusive barrier to start chemical interaction. The data on the effect of preliminary mechanical processing 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 the reagents chemical interaction. For some compositions it comprises hundreds of degrees [16 - 22]. It is found that the size of the effect depends on structure of concrete system, the nature of components and the conditions of mechanical processing (duration, power intensity and type of the used activator).

As a result of studying the morphology of treated by mechanical processing mixes of magnesium with boron, it has been established that after first 30 sec treatment there is a formation of dense mechanocomposites of a lamellar form with the cross size ≈ 30 ÷ 300 microns and 2 ÷ 5 micron thick (Fig.1). The lamellar Mg particles are evenly covered with small B particles. At increase in treatment duration up to 5 min the lamellar particles decrease in size. In Fig. 2, the overview of aggregates formed is presented. Even after 12 min treatment approximately half of the volume of the sample consists of relatively small particles of 1-5 micron size. In the roentgenograms of mechanically treated samples only the broadening of Mg lines is observed. After 12 min treatment the products of chemical interaction of magnesium with boron are absent.

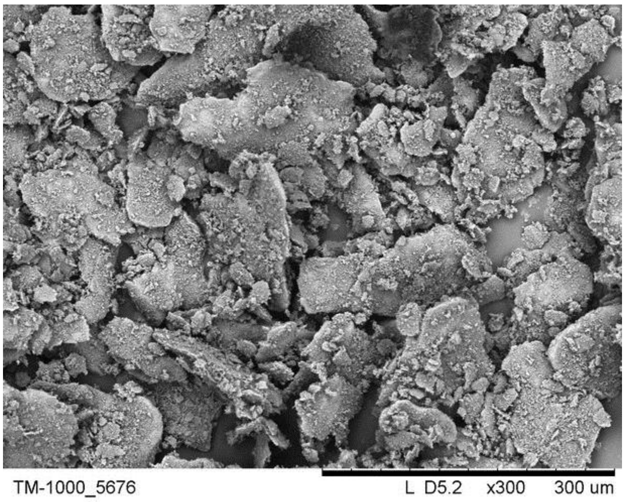

Figure 1.Microphotography of Mg+2.1B mixture after 30 s mechanical processing.

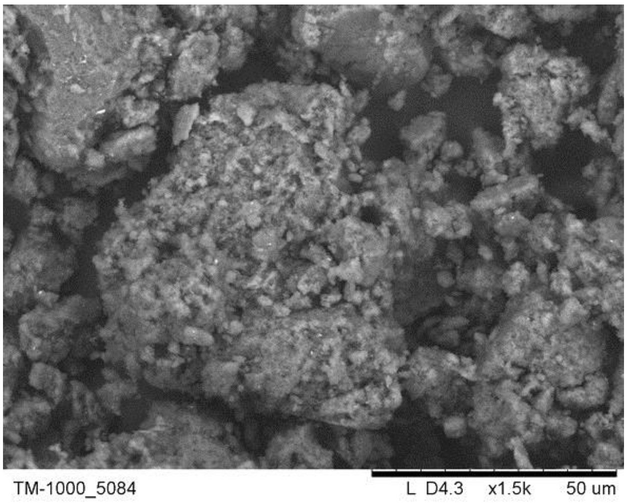

Figure 2. Microphotography of Mg+2.1B mixture after 5 min mechanical processing.

The typical thermogram of thermal explosion of a sample after 30 sec preliminary mechanical processing is presented in Fig. 3. The heat release begins at a temperature ≈

500°C followed by almost horizontal curve fragment corresponding to Mg melting. After total Mg melting the slow exothermic reaction continues resulting in increase in temperature up to 800°C.

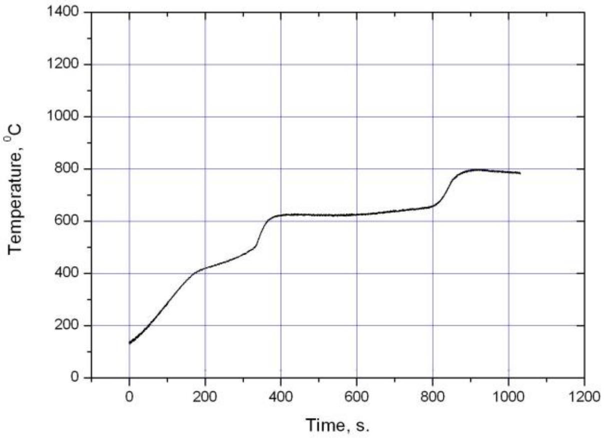

Figure 3.A typical thermogram of thermal explosion of Mg+2.1B mixture (30 sec preliminary mechanical processing).

As shown in Fig. 4, the reaction products consist of MgB_2, MgO и Mg. Besides, the elongated Mg melting stage leads to partial evaporation and deposition of Mg on the walls of crucible.

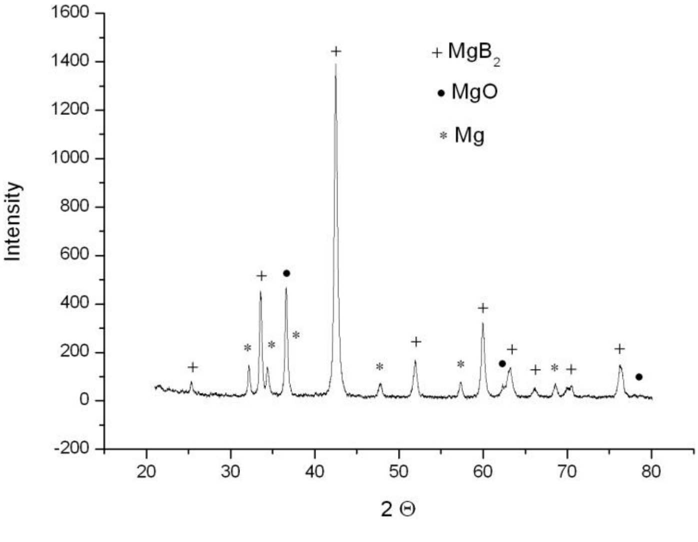

Figure 4. X-ray phase diagram of the Mg+2.1B mixture thermal explosion (30 sec preliminary mechanical processing).

The increase in time of mechanical processing leads to gradual diminishing the time period corresponding to Mg melting in thermal explosion. As it is seen in Fig. 5, the heat release in the case of the raw mixture 2 min mechanical processing starts at the temperature ≈ 500°C. Then during relatively short period the Mg melting is observed followed by sharp increase in the temperature up to 940°C. The reaction products roentgenogram demonstrates essentially decreased peaks of unreacted Mg.

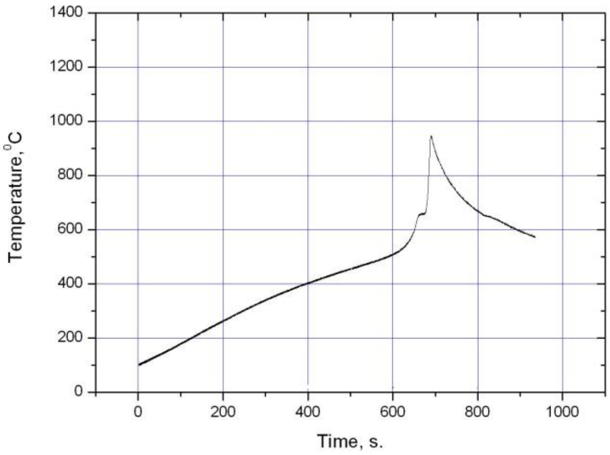

Figure 5. A thermogram of thermal explosion of Mg+2.1B mixture exposed to 2 min preliminary mechanical processing.

At further increase in the mechanical processing treatment up to 5-6 min the melting temperature fragment on thermal explosion record disappears. It is seen in Fig. 6 that thermal heat release starts at the temperature ≈ 460°C and then the fast thermal explosion develops. Maximal reaction temperature increases up to 1000°C. Thus, the reaction initiation temperature for such samples becomes noticeably lower than the melting temperature of Mg.

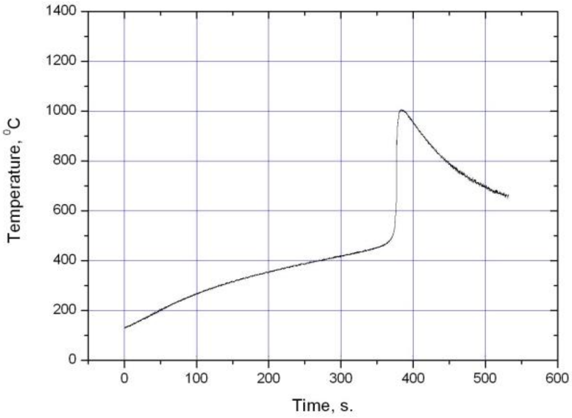

Figure 6. Thermogram of thermal explosion of Mg+2.1B mixture exposed to 5 min preliminary mechanical processing.

The X-ray phase diagram of thermal explosion products in this case demonstrates only MgB_2 peaks and small intensity MgO peaks (Fig.7). The electron microscopic study revealed no melted mixture components that is illustrated by the photography of the reaction products of the mixture exposed to 6 min preliminary mechanical processing (Fig. 8). The absence of the melting curve piece on thermocouple records and microstructure of the reaction products serve as an evidence of condensed phase reaction mechanism of thermal explosion for long preliminary mechanically treated Mg-B mixture.

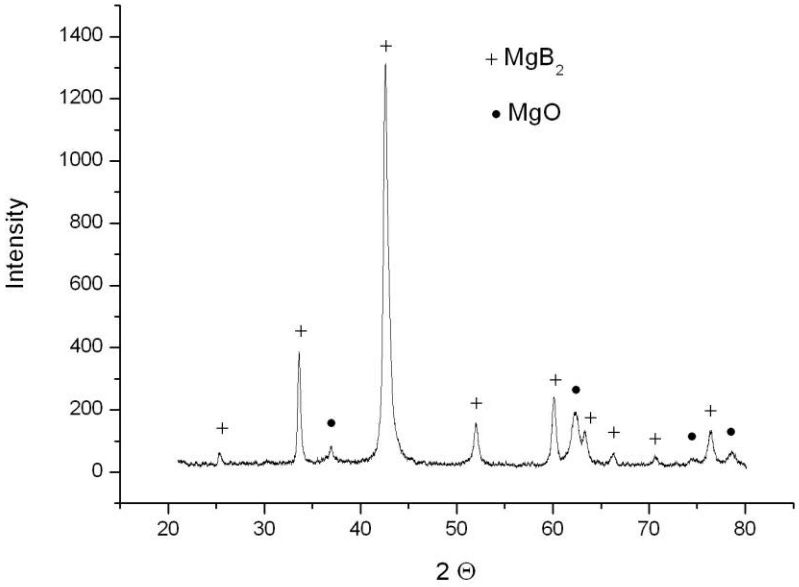

Figure 7. X-ray phase diagram of the Mg+2.1B mixture thermal explosion (6 min preliminary mechanical processing).

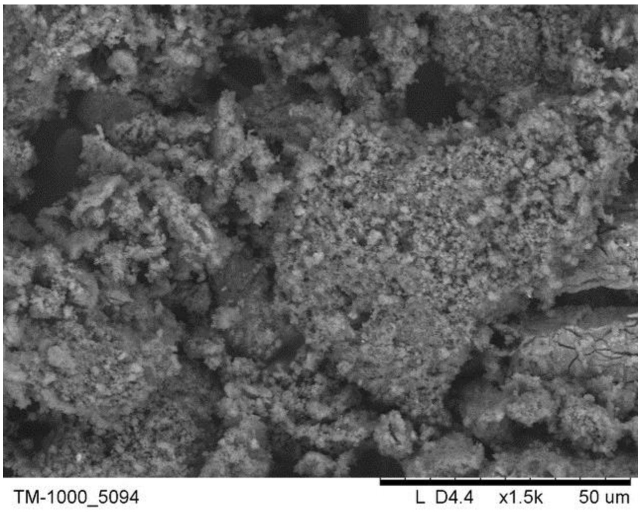

Figure 8. Microphotography of Mg+2.1B mixture thermal explosion products (6 min preliminary mechanical processing).

Increase in duration of preliminary mechanical processing of the mixture up to 12 min does not lead to changing the thermogram shape, phase diagram and microstructure of the reaction products. The magnitude of thermal explosion initiation temperature remains at the level of 5000°C and the maximal reaction temperature only slightly increases (up to 1050 ± 200°C).

Thus, it is revealed in this study that elongation over 6 min of preliminary mechanical processing the Mg+2B mixture leads to disappearing of Mg melting stage upon mixture thermal explosion and to proceeding the condensed phase reactions with formation of MgB_2 and small impurities of MgO. The temperature of exothermic reactions beginning comprises approximately 500°C and maximal reaction temperature can reach 1050°C.

The compound obtained can be used as a component of gas generating mixtures that provides the needed level of temperature of the combustion products.

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