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Self-Propagating High-Temperature Synthesis of Energetic Borides

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Abstract. A promising way to synthesize new energy materials based on refactory inorganic compounds is self-propagating high-temperature synthesis of compositions based on boron compounds. This paper describes a laboratory technology of production of aluminum borides. The experimental results of thermogravimetric analysis and particle size analysis obtained for synthesized powders are given. According to thermogravimetric analysis data the degree of oxidation of obtained powders exceeds 95 %. The experimental data have shown that the development of new compositions of high-energy fuel cells using borides can yield high-quality results in the sphere of solid hypersonic engines.

INTRODUCTION

Boron is one of the most favorable elements used as a high-energy source for ramjet engines, in particular, solid fuel ramjet engines due to its greater volumetric and mass heat of combustion [1]. However, practical implementation of the propellant budget of boron poses a challenge because an oxide layer forms on the surface of a particle, which slows down its oxidation and often leads to low combustion efficiency [2]. Including boron into certain energy compositions may intensify its combustion [3-5]. The potential of metal powders (Al, Mg and others) application is almost exhausted today. New additives with higher energy characteristics are required. Boron is the best alternative so far. Heat of combustion for boron is almost two times higher than for aluminum. Production technologies for boron and its compounds are well-known and tested. Moreover, boron is non-toxic, occurs in nature in large quantities and produced on an industrial scale. However, efficiency of its use is decreased due to specific properties of boron oxide (B_2O_3) – low melting point (450°C) and high evaporation temperature (2250 °C). The use of borides can change this situation. The most natural candidates for this role are borides of metals having maximum calorific values: Al, Mg, Zr, Ti and some others. One of such important compositions is magnesium diboride (MgB_2) with a theoretical heat of combustion equal to 9.2 kcal/g and density of 2.69 g/cm^3 vs. 5.9 kcal/g and 1.74 g/cm^3 for magnesium (Mg) [6]. Another compound is aluminum diboride (AlB_2). The theoretical heat of its combustion is 9.1 kcal/g vs. 7.4 kcal/g for aluminum [7,8].

Vacuum-heat technology is commonly used for boride synthesis. At the same time formation of borides is associated with significant heat liberation. This energy is often enough for the process in combustion mode at a self-propagating high-temperature synthesis (SHS). Large scale furnace equipment is not necessary in this case, and what is the most important the synthesized materials have better performance characteristics [9-11].

At the same time there are a lot of systems including boride ones which do not have enough heat liberation for SHS-processes [12]. In such cases there are two possible variants of organization of SHS-process: energy

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pumping from external sources or energy recovery. External energy can be introduced in the form of physical or chemical heat. In case of physical heating initial SHS-mix is placed into electric furnace heated up to required temperature and then an SHS-reaction is initiated. In this case both layer-by-layer and overall combustion modes can be provided. Other possible option of improvement of exothermicity of the mix consists in introduction of additional chemical heat into it [13]. This method is widely used in aluminothermy in the process of production of complex ferroalloys.

Thus, the aim of this work is to synthesize and study the oxidation degree of aluminum (AlB_2) and titanium borides (TiB_2). Preliminary findings were presented at the conference in the American Institute of Chemical Engineers [14]. This article presents a continuation of the theme research.

EXPERIMENTAL PART

In this work, we used powders of amorphous boron with a boron content of 99.5% (average particle size 650 nm) as well as aluminum powders (particle size D=2÷6 μm). For titanium borides we used PTOM-1 titanium powders (particle size D=0÷40 μm). Powders of titanium/aluminum and boron were mixed in a stoichiometric ratio.

Combustion synthesis started with setting up a reaction crucible with dry exothermic mix in the reactor chamber. Ignition electrodes are placed into contact with the surface of the exothermic mix. After that, the reactor chamber was sealed, the air was evacuated, and the chamber was filled with working gas. For gasless synthesis, argon was normally used as a working gas (argon under pressure of 2 MPa). Then a short-term electric pulse was fed to the electrodes. As a result of combustion, the temperature reached 1300-2200ºC [15]. After that, the material synthesized by laminated burning was kept in the reactor chamber for the period sufficient for most of the mix to transform into the target product in the mode of overall combustion. After overall combustion, the product was cooled in the same atmosphere down to the temperature eliminating a powder atmospheric oxidation.

The end-product processing stage started with unsealing the SHS reactor. Before this operation, the pressure in the reactor chamber is set equal to the atmospheric pressure. Then the reaction crucibles are removed from the reactor. The crucibles with end-products are weighed. Then the sintered material retrieved from the crucibles is transferred for crushing. For the synthesis were used of the materials and equipments Russian production.

The structure of powders was examined using a Philips SEM 515 scanning electron microscope. The average size of powder particles was measured with Mastersizer laser diffraction particle size analyzer. The study of the phase composition and structural parameters of powders was performed using an X-ray diffractometer with CuKα radiation. Phases were identified by comparing peaks of X-ray spectra with ASTM (American Society for Testing and Materials) card file.

RESULTS AND DISCUSSION

The use of potentially high boron exothermicity becomes possible if it is used in the form of metal borides which also have high values of the heat of combustion. It was found that borides of Al and Mg as well as Ti and Zr are the most promising ones (Table 1). Values of heat of combustion for such borides are given below. Heat of combustion of borides is significantly higher than the values for corresponding metals. Complex oxides are formed in the process of combustion of borides; these oxides are easier to remove form the particle surface which improves degree of oxidation.

A.G. Merzhanov pointed out five most typical situations in the process of classification of chemical routes of SHS-reactions [16]. One of these types of routes was called "chemically independent routes in thermally coupled systems ("chemical furnace")". In these cases chemical reactions proceed independently, however the heat from the more exothermic reaction provides energy for the less exothermic one.

From the very beginning of the research in the field of combustion synthesis a lot of promising systems from the practical point of view were determined, however, a self-sustaining process was not possible due to their insufficient exothermicity [15]. The first approach was pumping of additional heat by means of pre-heating of initial mix in a resistance furnace. It was the production of intermetallides when the operation of increasing of initial temperature of reaction mix was used for the first time for SHS reactions. The increase of initial temperature of the mix up to 50-500°C made it possible to synthesize aluminides of Ni, Co, Ti, Cr, Mo and other metals in combustion mode. When such furnace SHS technology is used in practice its characteristic advantages such as zero energy consumption, simplicity of equipment and low time consumption are reduced to zero.

TABLE 1. Heat of combustion of energetic borides [15]

Borides	Heat of combustion, cal/g
AlB_2	9 430
AlB_{12}	12 160
MgB_2	9 050
TiB_2	5 700
ZrB_2	4 230

The next step which extended the potential of SH synthesis for low-exothermicity systems was the invention of a so-called "chemical furnace". This term was coined by V.M. Maslov for the process of synthesis of intermetallides in Nb-Al and Nb-Ge systems. Equiatomic mixture of Ni and Al powders with combustion temperature of 1640°C was used as a material of "chemical furnace".

It was offered to use the principle of "chemical furnace" for the synthesis of such compounds as WC, NbC, SiC, B_4C, Al_4C_3, VC, Mo_2C, WB, WB_2 and others which do not have enough heat liberation for a general SHS process. In this case mixtures with higher burning temperatures such as mixtures of Ti or Zr powders with C or B (Table 2) are recommended to be used as materials for a "chemical furnace".

TABLE 2. Heat of formation of energetic borides [15]

Borides	Heat of formation, J/mol / J/mol
TiB_2	70 / 1006.6
ZrB_2	76.5 / 778.3
TiB_{12}	-
ZrB_{12}	120 / 542.8
AlB_2	-
AlB_{12}	-
MgB_2	13.3 / 289.4
MgB_{12}	34.4 / 223.1

In case of insufficient heat liberation combustion synthesis can be combined with elements of furnace synthesis where required energy is pre-pumped into the system providing further combined SHS-process. Initial mix of metal and boron is used for implementation of boride combustion synthesis:

$$Ti + 2B \rightarrow TiB_2$$
$$Al + 2B \rightarrow AlB_2$$
$$Zr + 2B \rightarrow ZrB_2$$

A laboratory-scale production technology for borides of Al, Ti, Mg and other metals including double and mixed compounds is tested and currently available. Particle size for synthesized powders comprised $\delta_{50} \approx 10$ μm. The structure of some powders (AlB_2) is shown in Figure 1. Particle size distribution (Fig. 2(a)) as well as DTA (Fig. 2(b)) data for AlB_2 were obtained.

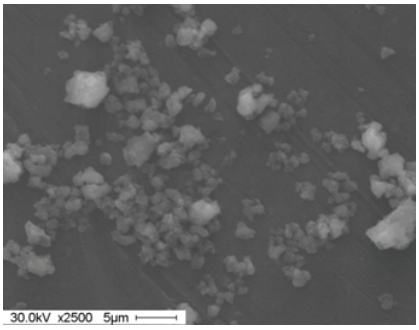


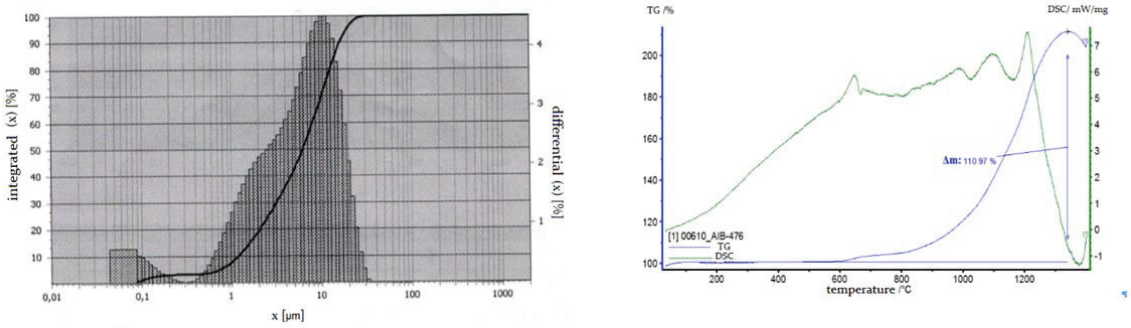
FIGURE 1. Typical structure of energetic borides (AlB_2).

According to X-ray phase analysis data the content of target phases in the powders studied comprised: 88.1 % for $Al_{0,5}Mg_{0,5}B_2$ phase, 93.2 % for AlB_2 and 98,4 % for TiB_2. The average CSR size for target phases did not exceed 30-40 nm.

The analysis of particle size distribution in AlB_2 powders have indicated that average particle size comprises 6.2 μm. The maximum size of the fraction comprised δ_{99} – 24.9 μm. According to DTA data sample mass increased ~2.17 times. Estimated increase of mass comprises ~2.26 for reaction:

$$2AlB_2 + 3O_2 = Al_2O_3 + B_2O_3$$

Oxidation degree comprised 96%.



(a) (b)

FIGURE 2. Particle size distribution (a) and DTA analysis data (b) for AlB_2 powder produced by means of SHS.

CONCLUSION

Synthesis of Al borides is one of the most promising areas in the field of development of new energy materials. Self-propagating high-temperature synthesis is the most suitable method for these purposes which makes it possible to produce ultrapure product with target chemical and phase composition by means of adjustment of synthesis parameters. Preliminary studies have indicated that it is possible to produce borides with high content of target phase. According to DTA data the degree of oxidation of obtained powders exceeds 95%.

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