ENERGETIC BORIDES: COMBUSTION SYNTHESIS AND PROPERTIES

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Introduction

Borides are advanced materials for use as fuel additives for rocket motors. The potential of use of metal powders (Al, Mg and others) 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.

Vacuum-heat technology is 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 (SHS-process). Large scale furnace equipment is not necessary in this case, and what is the most important the synthesized materials have better performance characteristics.

At the same time there are a lot of systems including boride ones which do not have enough heat liberation for SHS-processes [1]. In such cases there are two possible variants of organization of SHS-process: energy 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. This method is widely used in aluminothermy in the process of production of complex ferroalloys.

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.

Table 1. Heat of combustion of energetic borides

Borides	Heat of combustion, cal/g
AlB_2	9.430
AlB_{12}	12.160
MgB_2	9.050
TiB_2	5.700
$Mg_{0,5}Al_{0,5}B_2$	9.240
ZrB_2	4.230

A.G. Merzhanov pointed out five most typical situations in the process of classification of chemical routes of SHS-reactions [2]. 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. 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.

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.

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:

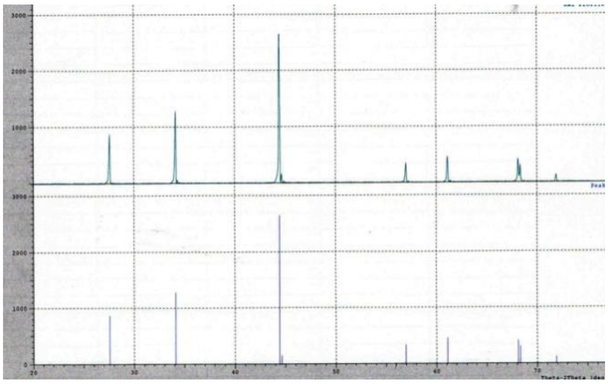
$$Ti + 2B \rightarrow TiB_2$$

$$Al + 2B \rightarrow AlB_2$$

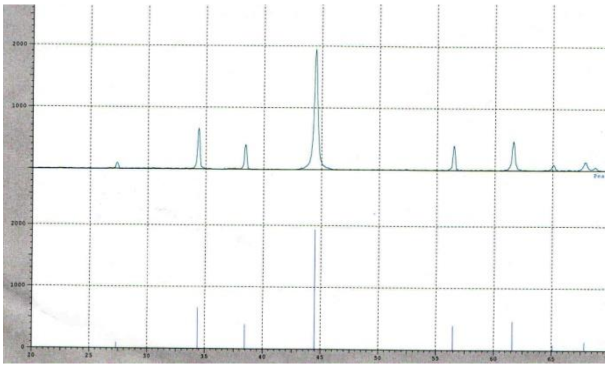
$$Zr + 2B \rightarrow ZrB_2.$$

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 $\delta_{50} \approx 10\mu m$. The results of X-ray phase analysis of some synthesized borides are shown in Figure 1 as an example. Particle size distribution (Figure 2(a)) as well as DTA (Figure 2(b)) data for AlB_2 were obtained.

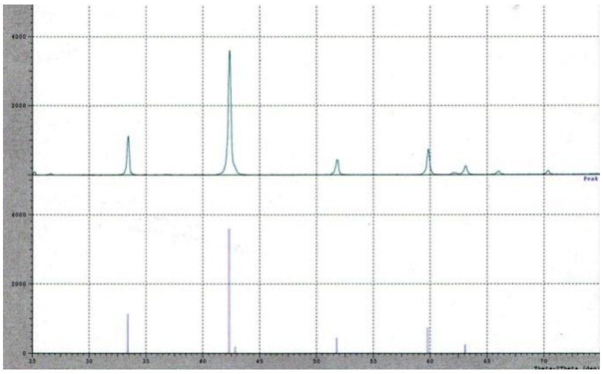
According to X-ray phase analysis data the content of target phases in the powders studied comprised: 88,04% for $Al_{0,5}Mg_{0,5}B_2$ phase, 93,18% for AlB_2 and 98,43% for TiB_2. The average CSR size for target phases did not exceed 30-40 nm.



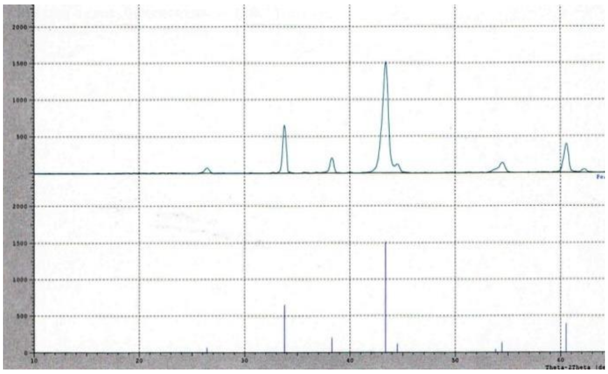
TiB_2



AlB_2



MgB_2



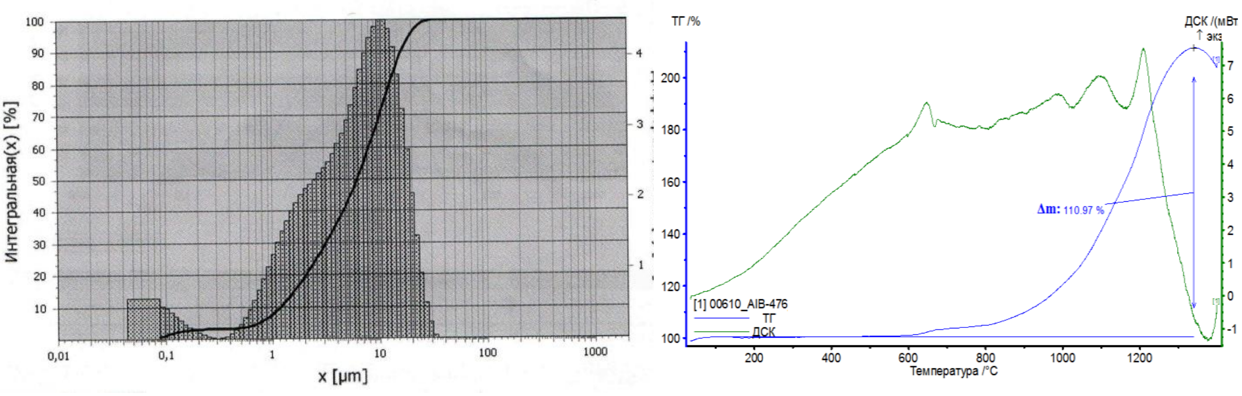
$Al_{0,5}Mg_{0,5}B_2$

Figure 1. Typical X-ray images of SHS of energetic borides

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} – 24,9μm. According to DTA data sample mass increased ~2,17 times. Estimated increase of mass for reaction:

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

comprises ~2,26. 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 SH synthesis

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%.

Acknowledgments

This study (research grant No 8.2.28.2015) was supported by The Tomsk State University Academic D.I. Mendeleev Fund Program in 2015, was financially supported from the Ministry of Education and Science of the Russian Federation within the framework of the Federal Target Program Agreement No. № 14.578.21.0034 (RFMEFI57814X0034) and financial support by Grant President RF MK - 5883.2014.8.

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