

Combustion Synthesis of BN/AlN and BN/B₄C Ceramic Composite Powders

*Hayk H. Khachatryan, and Suren L. Kharatyan
Institute of Chemical Physics, National Academy of Sciences
Yerevan 375044, Republic of Armenia*

*Jan A. Puszynski
South Dakota School of Mines and Technology
Rapid City, SD 57701*

Abstract

This paper presents recent experimental data on combustion synthesis of BN-based composite powders (BN/AlN, BN/TiB₂, and BN/B₄C). Based on thermodynamic analysis of BN-AlN system, composite powders with different AlN content were prepared by one step high pressure combustion synthesis ($P_{N_2} > 2$ MPa) using aluminum diboride (AlB₂) reactant diluted with AlN and/or BN powders. It was demonstrated that synthesis of BN-B₄C composites in self-sustaining process by direct interaction of B-C-N₂ system is not feasible because of stronger thermodynamic favorability of the BN-C formation. A new method of BN-B₄C composite powders synthesis in a combustion regime has been explored. This technique is based on activation of initial mixture by halogen- or nitrogen- containing reactants with teflon, and melamine in order to promote a gas transport of boron and carbon at a particle level. Based on experimental results BN-B₄C composite powders can be obtained with various content of B₄C using this chemically activated combustion synthesis process.

Introduction

There is a continuous need for new materials with improved mechanical, thermal, and corrosion resistance properties. Many nonoxide ceramic materials and ceramic-ceramic composites have exceeding properties of metals, especially in high temperature and corrosive applications. Aluminum nitride has proven to be an excellent material exhibiting high thermal conductivity and resistance to molten aluminum. However, this material does not possess superior thermal shock resistance. An addition of hexagonal boron nitride to aluminum nitride or other non-oxide ceramics significantly improves thermal shock resistance of resulting composites. Wear resistance, corrosion resistance, and machinability of such composites are also improved¹⁻³. Aluminum nitride - boron nitride composites along with their good machinability, are characterized by high thermal conductivity, high electrical resistivity, and good dielectric properties. Similarly, titanium diboride and boron nitride composites have similar machining properties and in addition they are electrically conductive and therefore suitable for evaporation of different metals, including very reactive aluminum.

In this study combustion synthesis technique has been explored for one step formation of BN nitride based composites. The combustion synthesis is very economical method of producing non-oxide ceramics⁴. This technique allows synthesizing nonstoichiometric

composites or solid solutions, which are difficult to obtain by the traditional furnace technology. The principle of this method is to form desired products by igniting strongly exothermic reaction between condensed-phase reactants ($Ti+2B\rightarrow TiB_2$) or solid and gaseous reactants (e.g. $Al+1/2N_2\rightarrow AlN$). These SHS reactions, once ignited, generate high temperatures (typically $>2000^\circ C$) and the combustion front propagates with the velocity in the range of millimeters or centimeters per second. In addition, combustion synthesized powders may exhibit higher homogeneity and better sinterability⁵. The versatility of combustion reaction allows synthesis of different materials with relatively high throughput.

The objective of this study was focused on investigation of the formation of BN-AlN, BN-TiB₂, and BN-B₄C composites by SHS technique.

Experimental

Boron Nitride – Aluminum Nitride Composite Powders

Based on thermodynamic calculations done by using thermodynamic software THERMO from ISMAN Chernogolovka, Russia, it was found that free boron is still present in the product at lower nitrogen pressures and low degree of reactant dilution ($P_{N_2} < 2 \text{ MPa}$)⁶. The results were confirmed by using FACT and HSC thermodynamic software packages⁶. Increased concentration of AlN or BN in the initial mixture leads to the significant reduction of free boron in the final product. Therefore, in order to find compromise between high and low pressures and adequate level of dilution, the nitrogen pressure of 2 MPa was chosen. Thermodynamic analysis of AlB_2 -AlN- N_2 system indicates that the nitridation of AlB_2 occurs in three stages (Figure 1): a) formation of aluminum nitride and aluminum boride, AlB_{12} ; b) further nitridation of AlB_{12} resulting in the formation of AlN and partial nitridation of boron; c) final nitridation of boron.

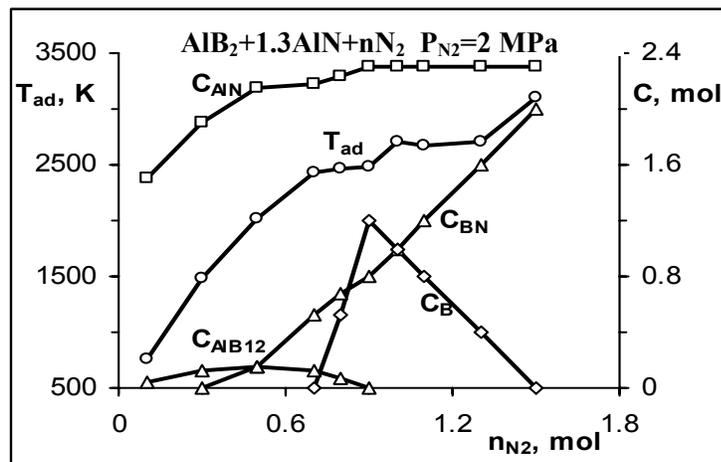


Figure 1. Thermodynamic analysis of AlB_2 - $1.3AlN$ - N_2 system at $P_{N_2} = 2 \text{ MPa}$ ⁶

The conclusions from this thermodynamic analysis are supported by the experimental results presented by Zhang et al⁷. They showed that nitridation of AlB_2 at 1 atm nitrogen pressure follows a consecutive reaction scheme. First AlN and $Al_{1.61}B_{22}$ are formed followed by the formation of AlN-BN composite.

All combustion synthesis experiments were performed in high-pressure reactors. The experimental setup used in this study was described elsewhere⁸.

The following reactant powders were used in the experiments: 1) AlB_2 with $d_{50}=4.5\mu\text{m}$ and $d_{90}=24\mu\text{m}$; 2) BN with different average particle sizes, $10\mu\text{m}$, $25\mu\text{m}$, $50\mu\text{m}$, $65\mu\text{m}$, $70\mu\text{m}$, $80\mu\text{m}$, $125\mu\text{m}$, and $>125\mu\text{m}$, and 3) AlN $d_{50}=4.9\mu\text{m}$, and $d_{90}=29\mu\text{m}$. Nitrogen gas with 99.97% purity was used in all experiments.

The reactant powders were mixed in a ball mill for 8 hrs. After that cylindrical pellets with a diameter of 35mm and height of 40-50mm were pressed. An average bulk density of pressed pellets was between $0.5\text{-}0.6\text{g/cm}^3$. The pressed pellets were placed in the high pressure reactor, which was evacuated, purged, and pressurized with nitrogen prior to the ignition. The ignition was done by a resistively heated tungsten coil at 2 MPa nitrogen pressure. Combustion temperature, T_c , and average combustion front velocities, U_c , were measured by tungsten - rhenium thermocouples with 0.1mm diameter. These thermocouples were placed at different axial positions in the pellet. After combustion process was completed, the product was grinded and milled in the ball or vibratory mill.

Combustion synthesis experiments, conducted under 2 MPa nitrogen pressure, showed that the maximum combustion temperature ($\sim 2200^\circ\text{C}$) is rather not affected by the dilution with boron nitride in a wide range of concentrations (0-65 wt%). Interestingly above the higher level of dilution ($>65\text{ wt}\%$), the nitridation reaction is not self-sustaining. In contrary, the combustion front propagation velocity is significantly affected by the level of BN dilution (see Figure 2). Up to 40 wt% BN this velocity increases with increasing degree of dilution. At low BN concentrations, the aluminum diboride powder decomposes above 2100K and the resulting molten boron and aluminum tend to coalescence prior to the nitridation. Examination of pellet's microstructure has clearly indicated melting of intermediate Al and B products. The increase of the content of BN diluent reduced the effect of intermediate products coalescence and their sintering. In addition, the dilution enhances a nitridation process by providing additional surface area of a refractory materials carrier.

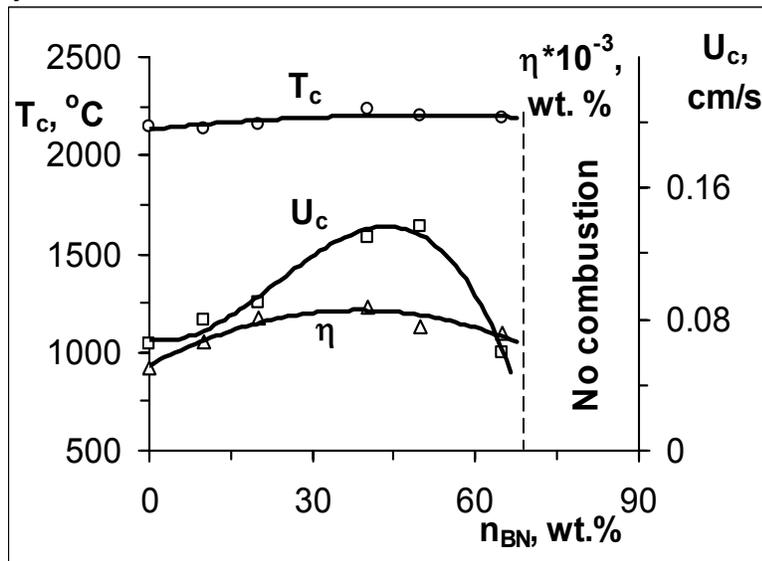


Figure 2. Combustion parameters of $\text{AlB}_2\text{-}n\%\text{BN-N}_2$ system vs. amount of the diluent at $P_{\text{N}_2}=2\text{ MPa}$.

At higher dilution ratios (above 40 wt%) the combustion front propagation velocity decreases with the increasing concentration of the diluent. This decrease might be caused by increased resistance to a nitrogen transport within the pellet. The overall conversion, η , of AlB_2 calculated from the total weight change is always less than 100%. This is caused by incomplete reaction close to the pellet's surface. Significant heat losses from the outer surface of the pellet are responsible for a low level of conversion in that region.

The effect of an average boron nitride particle size on key combustion characteristics was investigated as well. Figure 3 shows the variation of maximum combustion temperature, overall pellet conversion, and combustion front velocity as the function of an average particle size of BN diluent. It can be clearly seen that maximum combustion temperature is not affected by the size of diluent. It is interesting to note that the overall pellet's conversion and the combustion front propagation velocity are increasing with the average particle size of diluent. These results also support the strong effect of nitrogen transport limitation within the pellet.

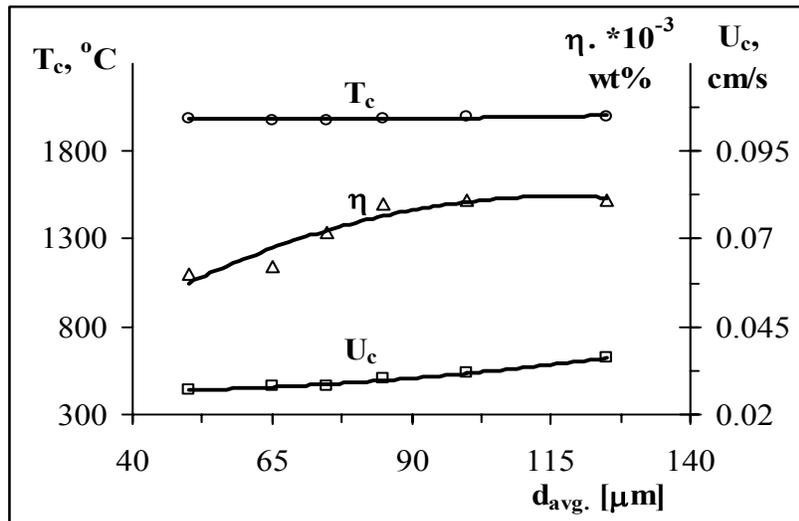


Figure 3. Combustion parameters of AlB_2 -65 wt%BN- N_2 system vs. particle size of the diluent at $P_{\text{N}_2}=2 \text{ MPa}$.

X-ray diffraction pattern of the combustion synthesized AlN -BN composite is shown in Figure 4. Only two, BN and AlN phases were detected. Specific surface area analysis (BET) of ball milled products showed specific surface areas of combustion synthesized powders to be between 8 and 24 m^2/g .

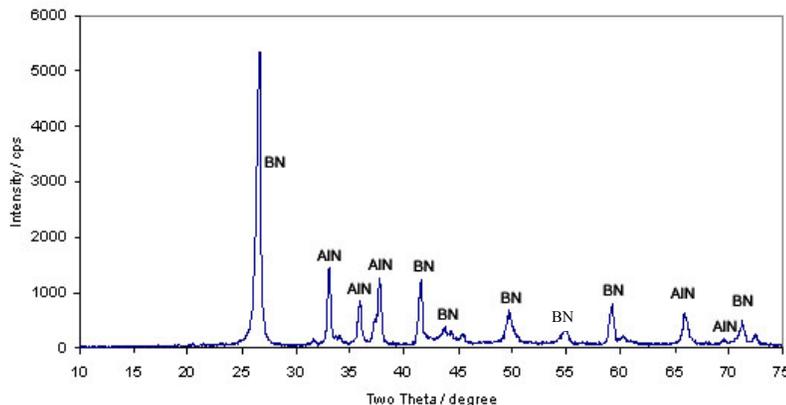


Figure 4. X-ray diffractogram of AlN (25 wt%) and BN (75 wt%) composite.

Boron Nitride – Titanium Diboride Composite Powders

Combustion synthesis of TiB_2 -BN composite powders from amorphous boron and SHS-derived titanium nitride was explored in a similar reactor configuration as that described in the previous section. This particular combustion reaction between boron and titanium nitride represents so-called “gasless” process. In this case, starting reactants and combustion products are in solid state. Thus, during the combustion process nitrogen is primarily exchanged between both solid reactants. Thermodynamic calculations (performed by the “THERMO” software) have shown that combustion in 3B-TiN mixture in argon medium leads to the formation of a product consisting of TiB_2 and BN. During that reaction, the adiabatic combustion temperature may be as high as 1630°C . Unfortunately, experiments have shown that this mixture does not burn both in argon or nitrogen media in the pressure interval 0.1-5 MPa because of insufficient exothermicity of the combustion reaction. In order to increase an overall heat of the reaction: 3B-TiN, a certain amount of titanium was introduced into the initial mixture to satisfy the stoichiometry as follows: $n(\text{Ti}+2\text{B})+(3\text{B}+\text{TiN})$.

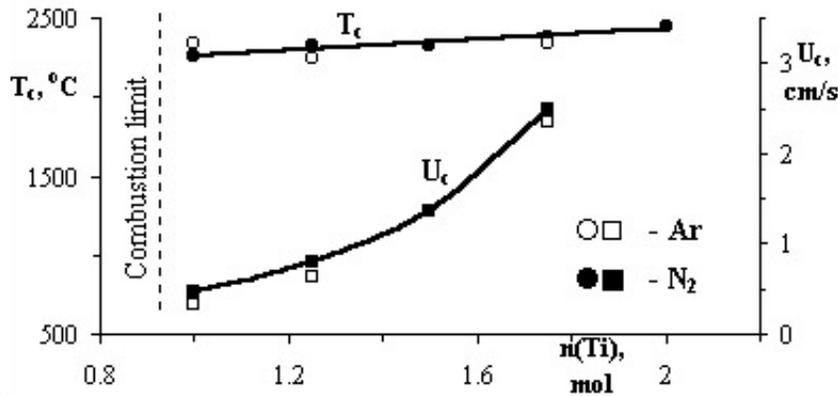


Figure 5. Maximum combustion temperature and combustion front velocity as a function of number of moles of Ti in the reactant mixture: $n(\text{Ti}+2\text{B})+(3\text{B}+\text{TiN})$

Combustion experiments in the $n(\text{Ti}+2\text{B})+(3\text{B}+\text{TiN})$ system were conducted in the nitrogen or argon atmospheres. The obtained results have indicated (see Figure 5) that in both argon and nitrogen atmospheres increasing content of titanium in the initial mixture up to $n=2$ leads to the increase of combustion temperature (approximately 200°C). In both cases, the combustion velocity depends on n value and increases approximately 5 times. The combustion front velocity and combustion temperature increases can be explained by contribution of $\text{Ti}+2\text{B}$ exothermic reaction into the overall combustion process. The lower combustion limit on titanium content has also been established ($n=0.9$).

The combustion products obtained in nitrogen and argon atmospheres were analyzed by XRD and other chemical methods. The results have shown that all products contained three phases, namely, TiB_2 , BN and TiN. It should be noted that at the combustion products formed in argon atmosphere have shown relatively small content of titanium nitride.

Chemical analyses of products obtained in both nitrogen and argon atmospheres have shown that increasing value of n leads to the decrease of the nitrogen content (see Figure 6; curves 1 and 2). Theoretical amounts of nitrogen (without taking into account the contribution of nitrogen from gaseous atmosphere, i.e. the nitridation occurs only at the expense of nitrogen

from TiN) calculated as a function of n are also shown in Figure 6 (curve 3). It can be seen that within the examine range of n values, the nitrogen content in samples reacted in argon atmosphere is significantly lower than those formed in the nitrogen medium.

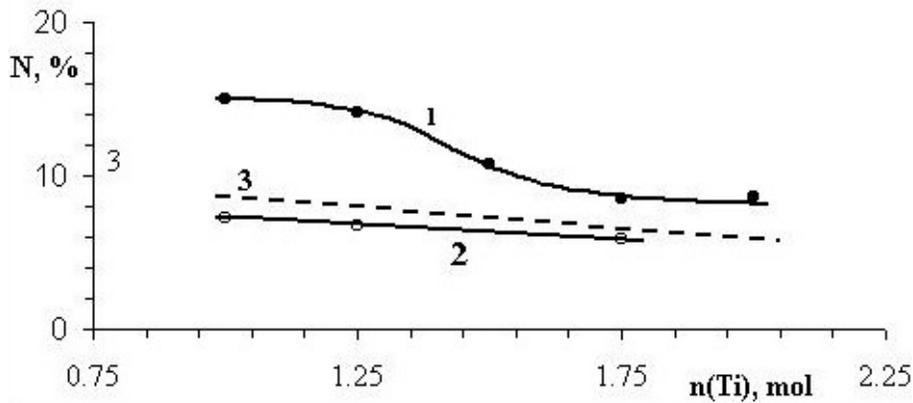


Figure 6. Nitrogen content as the function of n in the $n(\text{Ti}+2\text{B})+(3\text{B}+\text{TiN})$ system with nitrogen (1) and argon (2) atmospheres at $P=3$ MPa. Curve (3) represents theoretical nitrogen content in gasless reaction.

In addition, the effect of initial pellet density on maximum combustion temperature and combustion front velocity in the $1.25\text{Ti}-5.5\text{B}-\text{TiN}$ was determined (see Figure 7). It was shown that the increase of relative density of reactants result in the increase of both combustion parameters.

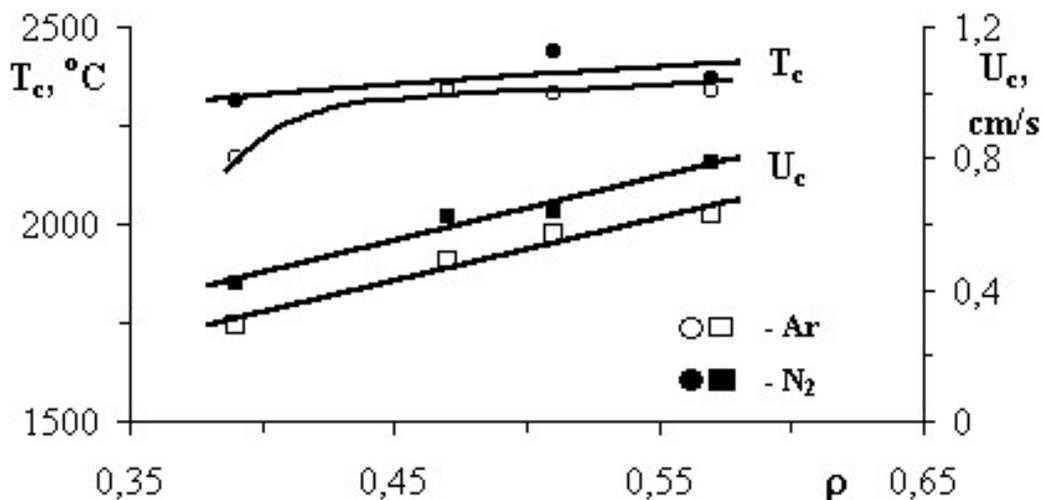


Figure 7. Combustion temperature (T_c) and combustion front velocity (U_c) vs. relative density of reactants' mixture at $P=3$ MPa, argon atmosphere.

The phase content of major phases in combustion products as the function of gas atmosphere and relative density is shown in Table 1.

Table 1. XRD analysis of combustion products generated from 1.25Ti-5.5B-TiN in argon or nitrogen atmospheres

Relative density	Atmosphere	
	Nitrogen	Argon
0.39	TiB ₂ , BN, TiN	TiB ₂ , BN
0.47	TiB ₂ , BN, TiN	TiB ₂ , BN
0.51	TiB ₂ , BN, TiN	TiB ₂ , BN
0.56	TiB ₂ , BN, TiN	TiB ₂ , BN, small amounts of TiN

In the case of argon the combustion product mainly consists of TiB₂ and BN. The results of chemical analyses have shown that nitrogen content in samples burned at 0.39-0.51 relative densities makes about 7.5 wt.% nitrogen (theoretical value is 7.75 wt.%).

It can be concluded that combustion of 1.25Ti-6.5B-TiN mixture (with 0.39-0.51 relative densities) in argon medium leads to formation of double-phase TiB₂-BN composite containing 10 wt.% BN. Currently investigations are in progress aimed at obtaining BN-rich composites.

Boron Nitride – Boron Carbide Composite Powders

Combustion synthesis of boron nitride-boron carbide composite powders was investigated using two different approaches: i) combustion of a B-C mixture in the nitrogen medium and ii) combustion of B-C mixture in the presence of fluorine-containing organic compounds as combustion promoters.

The first approach is based on utilizing the heat released by a strongly exothermic reaction between boron and nitrogen (T_{ad} can be as much as 3000 K) which could generate sufficient conditions for the reaction between boron and carbon.

Based on thermodynamic calculations it has been shown that there is no possibility of forming pure BN and B₄C phases in B-C-N system without proper control of nitrogen intake. In the case of nitrogen excess (normal situation) boron carbide will react with nitrogen and the final product will contain only boron nitride and free carbon (see Figure Fig. 8). These results were confirmed experimentally, showing that the final product contains only boron nitride and carbon at the nitrogen pressures of $P_{N_2}=1-7$ MPa. In addition, boron carbide cannot be obtained within extended ranges of the combustion temperature and velocity. Note, that combustion temperature and velocity were controlled by introducing various amounts of a diluent, changing the nitrogen pressure, sample density, etc.

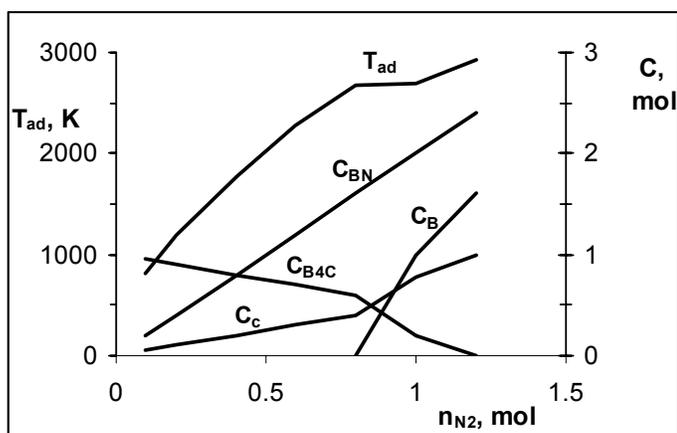


Figure 8. Adiabatic combustion temperature and equilibrium composition of products vs. nitrogen amount in the B_4C+nN_2 system; $P_{N_2}=0.1$ MPa.

The investigation of B-C-N system has led to the conclusion that it is impossible to obtain a boron nitride – boron carbide composite via direct nitridation of the B-C mixture.

Therefore, the second technique involving fluorinated hydrocarbons was explored. Thermodynamic calculations have shown that the interaction of boron and tetrafluoroethylene ($B-(C_2F_4)_n$) system is strongly exothermic. One could assume that it is possible to obtain a BN- B_4C composite using the heat released by the $B+(C_2F_4)_n$ reaction in the presence of a solid source of nitrogen, e.g. $C_xH_yN_z$. Initially, melamine - $C_3H_6N_6$ was chosen as a potential source of nitrogen. As thermodynamic calculations did show, the combustion in $B-(C_2F_4)_n-C_xH_yN_z$ might lead to adiabatic temperatures above 2500 K. Unfortunately, the experiments have shown that this system could not be ignited in the inert (argon) atmosphere at $P < 3$ MPa. In order to increase the exothermicity of the system, boron reactant was replaced with magnesium polyboride. In this case, ignition was accomplished. The product of the reaction was partially reacted (core of the cylindrical sample). The XRD analyses have shown that the reacted part mainly contained the target composition (BN- B_4C), but an amorphous mass was also detected.

Presently, a new technique based on thermal activation by oxygen containing compounds, in the presence of boron and solid sources of carbon and nitrogen has been explored. The results will be presented elsewhere⁹.

Conclusions

The experimental research has demonstrated that boron nitride based composite powders, especially BN-AlN and BN-TiB₂ can be successfully synthesized using combustion technique. It was also demonstrated that the BN- B_4C composite powder is not possible to form by direct nitridation of B-C mixture.

Acknowledgment

The authors would like to acknowledge the financial support from the Civilian Research Development Foundation (Grant № NFSAT CH 123-02/CRDF 12047).

References

1. K.S. Mazdidasni, R. Ruh, E.E. Hermes, "Phase Characterization and Properties of AlN-BN Composites". *J. Am. Ceram. Bull.*, 64 [8] 1149-54 (1985).
2. S. Du, Zh. Liu, L. Gao, F. Li, L. Li, "Dielectric Properties of AlN-BN Composite Ceramics", *J. Am. Ceram. Bull.*, 69-73 (1997).
3. T.D. Xiao, K.E. Gonsalves, P.R. Stritt, "Synthesis of Aluminum Nitride/Boron Nitride Composite Materials", *J. Am. Ceram. Soc.*, 76 [4] 987-92 (1993).
4. A.G. Merzhanov, "Theory and Practice of SHS: Worldwide State of the Art and the Newest Results," *International Journal of Self-Propagating High-Temperature Synthesis*, 2 [2] 113-158 (1993).
5. J. Lis, S. Majorowski, J.A. Puszynski and V. Hlavacek; "Densification of Combustion Synthesized Silicon Nitride", *Ceram. Bull.* 70 [2], 244, (1991).
6. Khachatryan, H.H., Hobosyan, M.A., Kharatyan, S.L., and Puszynski, J.A.; "Combustion Synthesis of BN/AlN Ceramic Composite Powders", accepted for publication in *Ceramic Transactions*, (2004).
7. G.J. Zhang, J.F. Yang, M. Ando, T. Ohji, "Reaction Synthesis of Aluminum Nitride-Boron Nitride Composite Based on the Nitridation of Aluminum Boride", *J. Am. Ceram. Soc.*, 85 [12] 2938-44 (2002).
8. L.S. Abovyan, H.H. Nersisyan, S.L. Kharatyan, R. Saiu, R. Orru, G. Cao and D. Zedda. "Synthesis of Alumina Silicon Carbide Composites by Chemically Activated Self-Propagating Reactions", *Ceramics International*, 27 [2] 163-169 (2001).
9. Khachatryan, H.H., Hobosyan, M.A., Kharatyan, S.L., and Puszynski, J.A.; "Chemically Activated Combustion Synthesis of Boron Nitride-Based Composite Powders", in preparation 2004.