

# Formation of Ceramic Nanopowders and Composites in a Self-sustaining Reaction Regime

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## ABSTRACT

Synthesis and densification of nanosize powders in a combustion regime have been demonstrated. Several reacting systems were examined and SiC, AlN-BN, BN-B<sub>4</sub>C, and Si<sub>3</sub>N<sub>4</sub>-MoSi<sub>2</sub> nanopowders as well as TiAl<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> dense nanostructures were synthesized. Both, chemically-assisted combustion synthesis of nonoxide ceramic nanopowders and in-situ densification of combustion synthesized intermetallic-ceramic composites from nano-reactants in a uniaxial press were conducted. All synthesized powders and dense structures were characterized using X-ray, EDX, BET, and scanning electron microscopy.

**Keywords:** *Combustion synthesis, nonoxide ceramics, nanopowders*

## 1. INTRODUCTION

A combustion synthesis, also called self-propagating high-temperature synthesis, has been found to be an effective and economical production method of advanced ceramic and intermetallic compounds [1-4]. This method is very suitable for the formation of nonstoichiometric compounds, solid solutions, and refractory composites. Many reacting systems, especially those involving elemental reactants, may generate a sufficient amount of energy to be self-sustaining. In such cases, a reacting system, once initiated by a local energy source, generates a high temperature combustion wave, which propagates throughout the reactants forming more thermodynamically stable

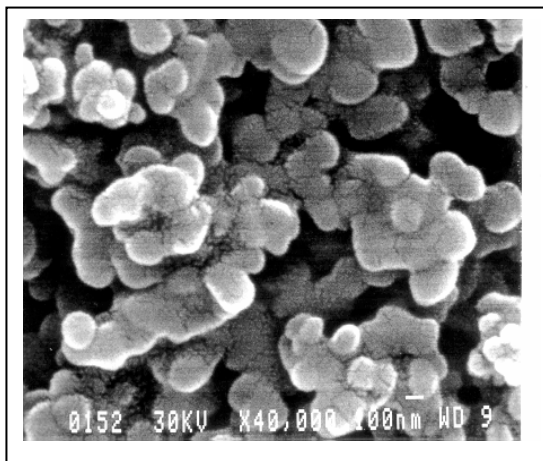
products. Combustion temperatures are typically in the range of 2000-3800K. The velocity of a propagating front combustion front may vary from millimeters per second to several hundreds of meters per second depending on the initial size of reactants [1,5]. However, when the energy release is too fast, the reacting system might be suitable for energy generation rather than synthesis of advanced materials. For these fast reacting systems, the rate of energy release, and the maximum combustion temperature can be controlled by diluting the initial reactant mixture with the final product. In recent years, it has been also demonstrated that this method can be applied to less energetic systems, which are not self-sustaining under ambient conditions. Addition of certain reactive additives and chemical promoters may result in the significant alteration of the reaction mechanism and increase in the overall exothermicity of the reaction and the formation of compounds with different phase structures. Due to a gas transport of key reactant(s) on a particle-to-particle level, products with average particle sizes at nanoscale level can be obtained by using this high temperature technique. For example, the nitridation of silicon-silicon nitride mixture at elevated nitrogen pressures (15-40 atm) resulted primarily in the formation of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase via solid/liquid. However, when the same mixture was nitrided with the addition of ammonium halide,  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> was formed instead [6]. In this case, silicon was transferred from the solid to a gas phase in a form of Si<sub>x</sub>F<sub>y</sub> volatile compounds, which subsequently reacted with nitrogen nucleating desired  $\alpha$ -phase. Many other

nonoxide ceramics can be synthesized using that approach. This paper summarizes experimental results of synthesizing pure SiC, Al-BN, BN-B<sub>4</sub>C, and MoSi<sub>2</sub>-Si<sub>3</sub>N<sub>4</sub> composite nanopowders using chemically activated self-propagating high temperature synthesis. In addition, results of in-situ densification of TiAl<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> nanocomposite formed from Al and TiO<sub>2</sub> nanoreactant powders are presented as well.

## 2. RESULTS AND DISCUSSION

### 2.1 Combustion Synthesis of Silicon Carbide

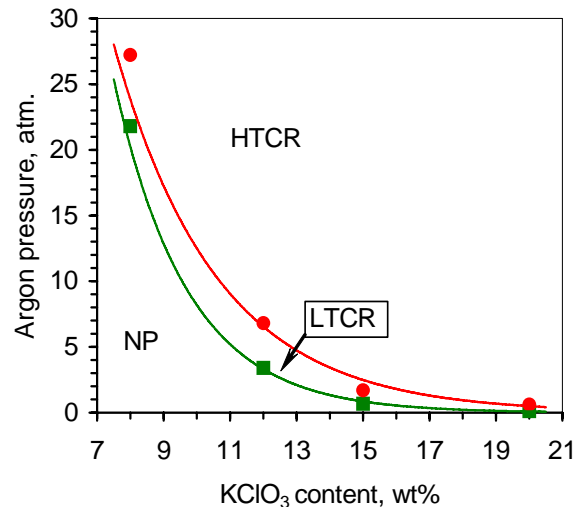
Direct reaction between silicon and carbon powders is not self-sustaining without very significant preheating of reactants. Typically, preheating temperature in excess of 1100°C are needed and the reaction takes place in so called volume combustion regime, which is characterized by sudden ignition of the entire reactant mixture. In order to make this reaction self-sustaining in a room temperature teflon and KClO<sub>3</sub> additives were considered [7,8]. Nanosize SiC powders with an average particle size between 60 and 200 nm was successfully synthesized using that approach (see Figure 1).



**Figure 1.** SEM image of SiC powder combustion synthesized from elemental powders in the presence of KClO<sub>3</sub>.

The effect of KClO<sub>3</sub> or teflon reactive additives on maximum combustion temperature, reaction heating rate, and the combustion front

velocity have been studied in detail. With increasing concentrations of KClO<sub>3</sub> (5-20 wt%) and teflon (8-20 wt%), the maximum combustion temperature increases from 1400 °C to approximately 2000°C.



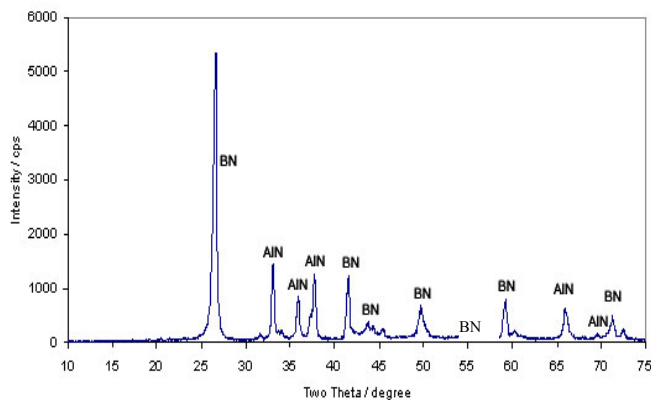
**Figure 2.** Combustion propagation diagram in Si-C-KClO<sub>3</sub> reacting system; NP-no propagation; LTCR-low temperature regime; HTCR-high temperature regime [7].

However, the combustion front velocity in the case of KClO<sub>3</sub> varies from 0.5 cm/sec to 2 cm/sec and it was ten times faster than in the case when teflon was used as the additive. It was found that the gas pressure has a very significant effect on the combustion characteristics. When the concentration of additives is greater than the minimum concentration, three different combustion regimes might exist (see Figure 2) [7]. If the gas pressure is lower than minimum pressure, no propagation can be achieved. However, when the gas pressure is higher, low-temperature or high-temperature combustion waves might be generated, depending on the absolute value of that pressure.

### 2.2 Combustion Synthesis of AlN-BN Nano-Composite Powders

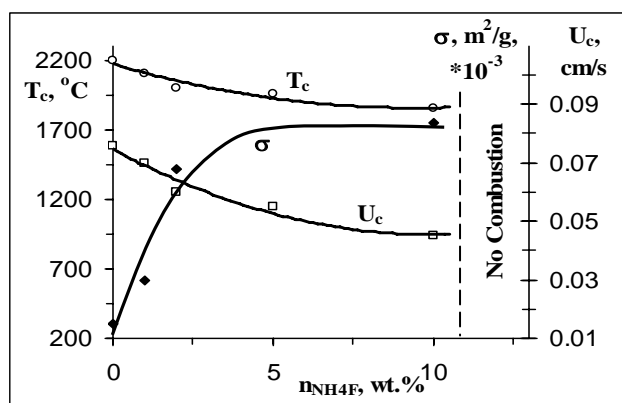
Based on thermodynamic calculations AlN-BN composites may be obtained by several ways using aluminum and boron powders or

aluminum diboride as initial reactants [9]. It should be noted that these compounds react readily with nitrogen releasing significant amount of energy. Due to generated high combustion temperatures boron nitride and aluminum nitride products may partially dissociate at these conditions. In order to prevent such dissociation dilution of the initial reactant mixture with the product is necessary. It was also determined that the use of aluminum diboride ( $AlB_2$ ) instead of aluminum and boron powders led to the formation of composites with a better homogeneity. X-ray diffraction pattern of the combustion synthesized AlN-BN composite nanopowders is shown in Figure 3.



**Figure 3.** X-ray diffractogram of AlN (25 wt%) and BN (75 wt%) composite.

Only two BN and AlN phases were detected in the combustion synthesized product. The specific surface area of the composite synthesized by direct nitridation of aluminum diboride was  $24 \text{ m}^2/\text{g}$ . In order to increase the specific surface area even further gasifying compounds (e.g., ammonium fluoride or chloride) were introduced into the initial powder mixture. Experiments did show that the addition of such compounds have a profound impact on combustion parameters, especially on combustion temperature and combustion front velocity (see Figure 4). BET analyses have shown that the specific surface has increased two- to four-fold for the most of the examined conditions. The maximum specific surface area ( $\sim 86 \text{ m}^2/\text{g}$ ) was observed for the 80%BN + 20%AlN composite.

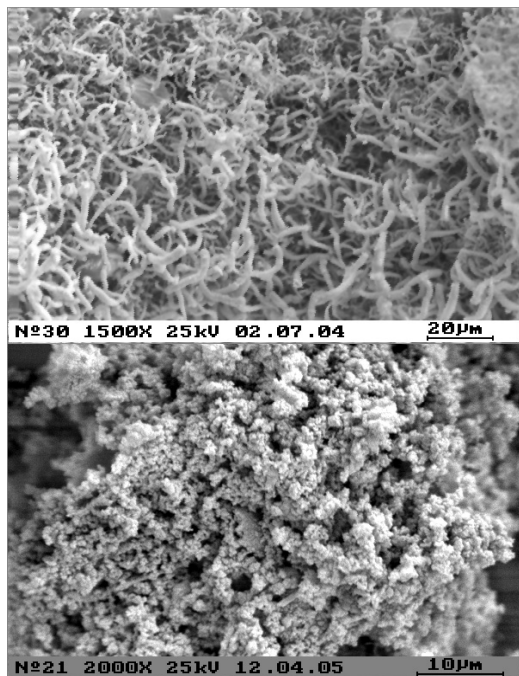


**Figure 4.** Combustion parameters and specific surface area ( $\sigma$ ) of products for the  $AlB_2$ -BN- $nNH_4F$ - $N_2$  system vs. the amount of ammonium fluoride at  $P_{N_2}=2.5 \text{ MPa}$  [9].

### 2.3 Combustion Synthesis of BN- $B_4C$ Nano-Composite Powders

The previous research studies indicated that the presence of oxygen in the initial  $B/B_2O_3/C$  system favors the formation of boron carbide at elevated temperatures [10]. The presence of oxygen not only affects the rate of carbide formation but also affects the mechanism of solid phase growth via solid-gas or gas-phase mechanism, which may result in the growth of nanowhiskers.

In order to obtain nanosize BN- $B_4C$  nanocomposite powders chemically-activated combustion synthesis was explored. In this case, a magnesium polyboride ( $MgB_{12}$ ) powder and a combination of oxygen-containing inorganic oxidizer (e.g., nitrates) and organic fuel (in particular, melamine, urotropine, urea, etc.) were used in an argon atmosphere. Several key parameters, including reactants' composition, pressure and gas atmosphere, type and quantity of additives, and pellet density were investigated to find optimum synthesis conditions leading to the product with desired morphology and composition. It was determined that a stable combustion and complete conversion are possible for the gas pressure not less than 2.5-3 MPa.



**Figure 5.** Microstructure of the boron nitride-boron carbide composite.

At lower pressures, generated gases from the decomposition of organic and inorganic solids ( $N_2$ ,  $NH_3$ ,  $CO$ , and others) are expelled easily from the porous sample and the partial pressure of nitrogen-containing gaseous compounds was insufficient to complete nitridation process. It was also found that the quantity and ratio of oxygen-containing components in the initial mixture are greatly affecting the composition and specific surface area of synthesized composite powders (see Figure 5). The experimental results also revealed that the initial density of burned sample also has a significant effect on the product properties. It was determined that with increasing density of the pellet the conversion and product homogeneity were not as good as for higher pellet porosities. Pellets with relative density  $\Delta=0.25$  were found to be the most optimal. Under these conditions, composite nanopowders with the specific surface area in the range of  $36-40 \text{ m}^2/\text{g}$  were obtained. X-ray analysis revealed that the final product after leaching contained only boron nitride and boron carbide crystalline phases.

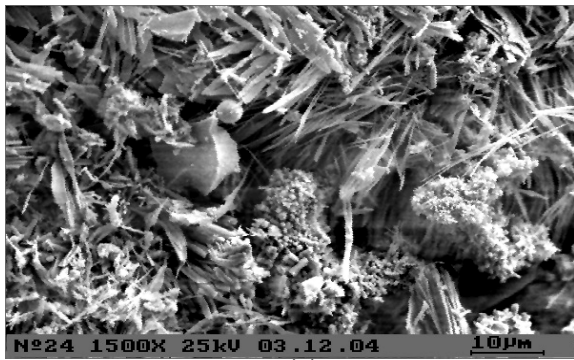
## 2.4 Combustion Synthesis of $MoSi_2-Si_3N_4$ Nanocomposite Powders

Composite powders consisting of  $Si_3N_4-MoSi_2$  were synthesized in combustion regime from elemental silicon and molybdenum in nitrogen atmosphere. The experiments were conducted without and with the presence of additives. In this case, sodium or potassium chloride salts were used as additives. In the case, when only pure elemental powders were used, the measured combustion temperature was approximately  $2100^\circ\text{C}$ . Under these conditions, multiphase products containing  $MoSi_2$ ,  $Si_3N_4$ ,  $Mo_5Si_3$  and non-reacted silicon were obtained. Besides that, the product powder exhibited rather large average particle sizes ( $5-15 \mu\text{m}$ ). By addition of inorganic salts, an additional diffusion barrier for nitrogen transport was created preventing excessive nitridation of  $MoSi_2$  formed in the initial stage of the process. It should be noticed that these salts do not react with any component in the mixture and are considered as inert diluents affecting combustion temperature

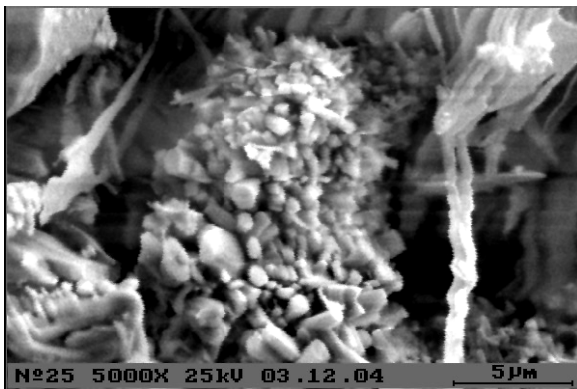
It is well known that at the initial stages of the combustion process, the size of product's nuclei is in submicron- or nano-size range. However, during the post-combustion stage a significant growth and agglomeration of particles takes place and product's grains become significantly larger.

The experiments showed that the growth of such grains can be prevented by the presence of inert molten salts in the hot zone. It was found that the average particle size obtained under these conditions was in a submicron range. Also, the experiments revealed that there is the limit for the amount of added salts, beyond which the self-sustaining character of the reaction process cannot be accomplished. However, there is a possibility of extending the concentration range by the addition of other additives, such as  $KClO_3$ ,  $NH_4NO_3$ , or Teflon. The preliminary results, did show that small addition of Teflon (1.5 wt%) extended the

propagation limit and led to the formation of whisker-like materials (see Figure 6).



(a)

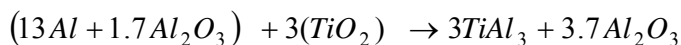


(b)

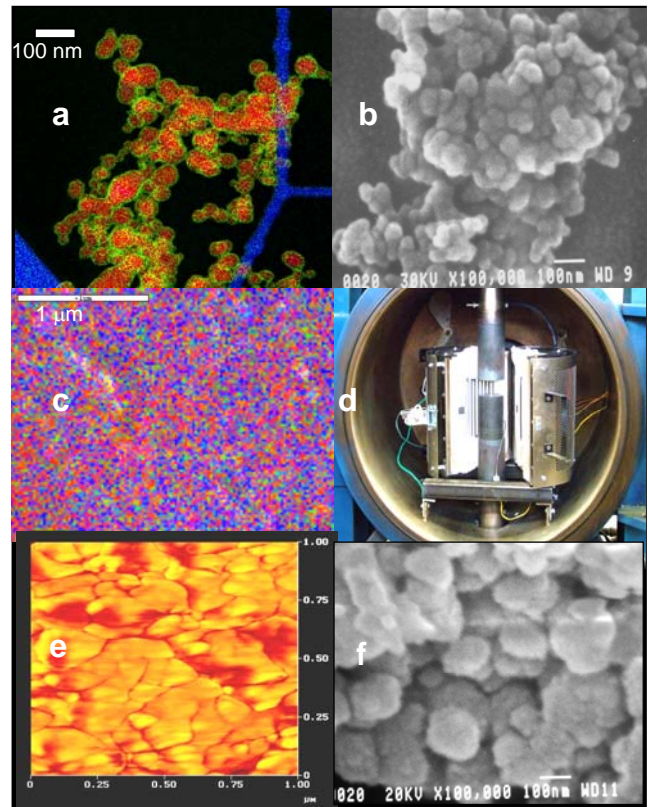
**Figure 6.** Micrographs of combustion synthesized  $\text{Si}_3\text{N}_4\text{-MoSi}_2$  composites: (a) whiskers-like and (b) particulate structures.

### 2.5 In-Situ Densification of Combustion Synthesized Nanocomposites

Nanoreactant energetic system,  $\text{TiO}_2\text{-Al}$ , was selected for simultaneous combustion synthesis and densification experiments [11]. The TEM and SEM images of Al and  $\text{TiO}_2$  nanoreactants are shown in Figures 7a and 7b. The EDS image of the reactant mixture prepared by a wet mixing technique is shown in Figure 7c. The red and blue dots represent Al and Ti dominant aggregates, respectively. Gasless reaction between aluminum/ alumina and titanium dioxide nanopowders was followed by the uniaxial densification:



In-situ densification of combustion synthesized titanium aluminides-alumina composites was conducted in the uniaxial press shown in Figure 7d. The system has preheating capability up to 1500K in vacuum or inert gas atmosphere and densification pressures up to 200 MPa. It was demonstrated that the densified composite material retained submicron grain structure after completion of the simultaneous synthesis and densification processes without a significant grain growth. AFM and SEM images of titanium aluminide-alumina composites prepared by this technique are shown in Figures 7e and 7f. The best samples of densified composites had a residual porosity less than 3%.



**Figure 7.** Combustion synthesis of  $\text{TiAl}_3\text{-Al}_2\text{O}_3$  nanocomposite structures: a) and b) aluminum and anoreactants, respectively; c) EDS of reactant mixture; d) experimental set-up; e) and f) AFM and SEM image of the product, respectively.

### 3. CONCLUSIONS

- It was found that the addition of ammonium fluoride as a gasifying agent during nitridation of  $AlB_2$  powder in a combustion regime resulted in the formation of AlN-BN composite powders with specific surface up to  $85 \text{ m}^2/\text{g}$ .
- Silicon carbide with average particle size in a nanometer range can be synthesized from micron-size silicon and nanosize carbon elemental powders with the addition of  $KClO_3$  or Teflon as gasifying agents.
- BN- $B_4C$  composites can be synthesized in the combustion regime using nitrogen-containing organic compounds (e.g. melamine) as a source of nitrogen and carbon, combined with an oxidizer (ammonium nitrate).
- $TiAl_3$ - $Al_2O_3$  composites with the density of 96-98% of the theoretical one with average grain sizes between 100-200 nm were in-situ densified during the combustion synthesis from nanosized Al and  $TiO_2$  reactants.
- It was demonstrated that silicon nitride-molybdenum disilicide submicron composite powders can be synthesized from micron size elemental powders in the presence of sodium or potassium chloride salts, which inhibit a grain growth and reduce the rate of molybdenum disilicide nitridation. The addition of gas-transport promoting additives has led to the further particle size reduction and the formation of whiskers.

### ACKNOWLEDGMENT

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### REFERENCES

1. A.G. Merzhanov; *International Journal of Self-Propagating High-Temperature Synthesis*, vol. 2, no. 2, pp. 113-158, 1993.
2. Z.A. Munir and U. Anselmi-Tamburini, *Mater. Sci. Rep.*, vol. 3, pp. 277-365, 1989.
3. A.G. Merzhanov, "Condensed-Phase Combustion," Russian Academy of Science, 2000.
4. A. Varma, A.S. Rogachev, A.S. Mukasyan, and S. Hwang; *Adv. in Chem. Eng.*, vol. 24, pp. 79-225, 1998.
5. S. Valliappan, J.J. Swiatkiewicz, and J.A. Puszynski; *Journal of Powder Technology*, Vol 156 (2-3), 164-169, 2005.
6. B. Liebig and J.A. Puszynski; *Int. J. of Self-Propagating High-Temperature Synthesis*, 7(1), 75-85, (1998).
7. J.A. Puszynski and S. Miao; *Int. J. of Self-Propagating High-Temperature Synthesis*, 8(3), 265-275, (1999).
8. S.L. Kharatyan and H.H. Nersisyan; First Sino-Russian Workshop on SHS, Progress of SHS Facing a New Millennium, Beijing, China, 2000, pp.96-104.
9. H.L. Khachatryan, M.A. Hobosyan, S.L. Kharatyan, and J.A. Puszynski; *Ceramic Transactions "Innovative Processing and Synthesis of Ceramics, Glasses, and Composites"*. Vol 166, 3-10, 2004.
10. R. Ma, Y. Bando, "High purity single crystalline boron carbide nanowires". *Chemical Physics Letters*, 2002, 364, pp.314-317.
11. S. Dargar, L. Groven; J. Swiatkiewicz, and J.A. Puszynski; *Mat. Res. Soc. Symp. Proc.* Vol. 848, FF1.7, 1-6, 2005