

## SHS OF NANO-POWDERS

A.G. MERZHANOV, I.P. BOROVINSKAYA, A.E. SYTSHEV  
Institute of Structural Macrokinetics and Materials Science, Russian  
Academy of Sciences, Chernogolovka, Moscow, 142432, Russia

*Production of nano-sized powders is a new line of SHS research (hereinafter termed nano-SHS), despite the fact that synthesis of materials with a fine structure has been known for a long time. Meanwhile, the SHS method was considered to be inappropriate for manufacturing fine products because of the presence of high temperatures leading to crystallization of combustion products, which restricted further advance in the field. It was only recently that SHS had been found to be promising for fabrication of nanophased materials. In this paper, we will analyze some primary results obtained in the field.*

### 1. BASIC IDEAS ABOUT NANO-SHS PROCESSES

In this Section, we will consider the modern notions about the mechanism of SHS, appropriate means of control, and methods for SHS-production of nano-powders <sup>1</sup>. Some concrete examples of the processes will be given in Section 2.

#### 1.1. Structure of combustion wave in SHS processes

Fig. 1 presents the still frames of SHS process<sup>1, 2</sup>. Here, one can distinguish between the stages of initiation (ignition), formation and propagation of the combustion wave, and cooling the product-typical stages of any SHS process.

The combustion front separating the reagents from the combustion products is clearly seen in the photo. It is necessary to emphasize that the starting reagents do not instantly transform into the combustion products in the combustion front, but this process occurs within some extended zone (combustion zone). The combustion front represents only the frontal part of the combustion wave.

The structure of the combustion wave plays a very important role in SHS, specifically in nano-SHS processes. The structure of the combustion wave

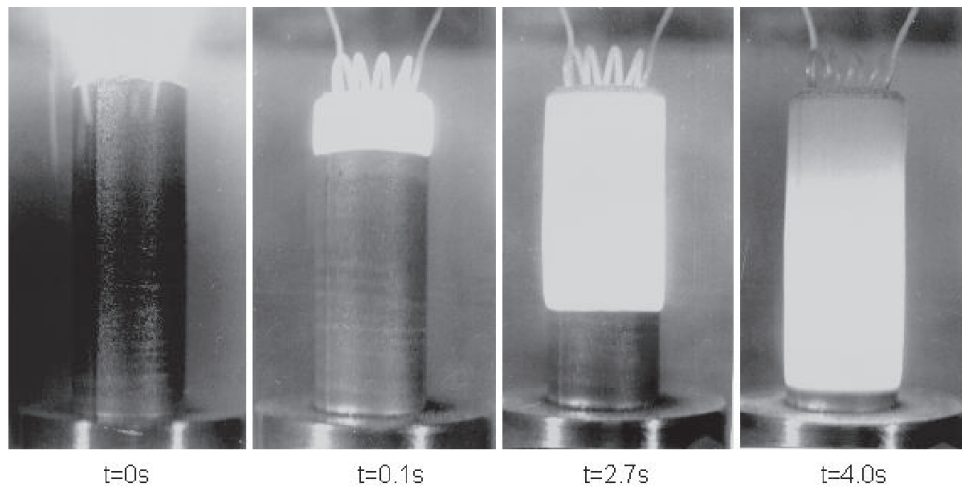


FIGURE 1 - Still frames of SHS.

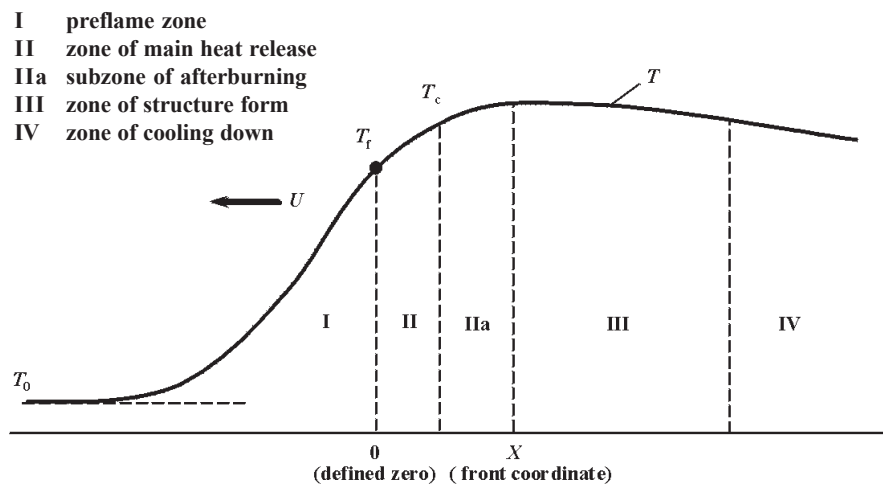


FIGURE 2 - Typical temperature profile.

is normally represented in the form of the temperature profile (Fig. 2) exhibiting a multi-zone structure (Fig. 2).

In zone **I**, the charge warms up to high temperatures due to heat transfer from the zones with higher temperatures. In this zone characterized by intense heat transfer, phase transformations can occur but chemical reactions still do not take place. This is the so-called “preflame zone”.

In zone **II**, the main exothermic chemical reactions occur. Here the charge is warmed up to the combustion temperature. The heat generated in this zone is transferred into zone **I**. The processes taking place in zone **II** promote propagation of the combustion front located on the border between the zones and define its rate.

Sometimes the chemical reactions are not completed in zone II; in this case, they continue to react (afterburn) in sub-zone **IIa** which does not affect the rate of wave propagation.

Extended zone **III** is characterized by the absence of chemical reactions. In this zone, structure formation (phase and structure transformations) in final products takes place. These processes (not typical of combustion of propellants) are very important for SHS because they determine the structure and properties of final products.

In zone **IV**, combustion products undergo cooling down. In case of rapid cooling, zones **III** and **IV**, so that the processes in zone **III** are quenched to form a non-equilibrium product.

In order to affect the burning velocity and combustion temperature, one has to influence the processes taking place in zone **II**. In order to affect the product structure, the processes occurring in zones **III** and **IV** should be influenced.

## **1.2. Mechanisms of transformation of reagents into final nano-products**

In order to control a multiparameter SHS process yielding nano-products, one has to have detailed information about all its stages.

According to Ref. 3, the formation of nano-product is closely associated with the pattern of combustion in the system. To date, the following basic classes of SHS have been investigated: (i) solid-flame combustion in the solid-solid systems (including combustion with intermediate melted layer); (ii) gas-phase SHS (including cool flames and combustion of condensed systems with an intermediate gas-phase zone); (iii) combustion in the solid-gas systems (infiltration combustion, combustion in gas suspensions).

As is known<sup>3</sup>, an ideal solid-flame SHS combustion occurs in the mode of reactive diffusion whose rate is determined by the diffusion of a reagent through the product layer formed on the particle surface. The size of product grain does not differ significantly from that of starting one. The contacts between the particles are highly resistant to diffusion, so that the recrystallization is almost absent. This implies that, in an ideal solid-flame process, nanosized products can only be obtained from nanoscale particles of starting reagents.

For the systems with an intermediate melted layer, formation of nanocrystals is defined by crystallization and recrystallization processes, combustion temperature and product cooling conditions after the reaction is complete.

Gas-phase synthesis (combustion of gases followed by condensation of solid product) is especially promising for producing nano-materials. Agglomeration of product particles condensed from the gas phase leads to formation of the nuclei on whose surface the reaction continues. The size of product particles grows until the reagents are completely consumed. At rapid expansion of the reaction mixture, the process is terminated, i.e., the reaction is quenched. This method can be used to stop the particle growth. In case of gas-phase combustion, the product particle size can be easily controlled by performing continuous combustion with continuous quenching of the system at some certain degree of conversion.

Nano-powders manufactured by condensation from gas phase can be used for various applications. Of especial interest is flame cladding of powders with metal. Ni-Mo-cladded nano-powders of TiC could be used a wonderful raw material for manufacturing hard alloys.

Cool flames - also a kind of gas-phase SHS<sup>4</sup> - can be used to prepare nano-sized oxides<sup>5,6</sup>. It is worth mentioning that, upon introducing solid bodies into a cool flame, heterogeneous condensation can be performed.

Of significant interest is almost unexplored chemical-condensation combustion of condensed mixtures. In such processes, the reagents undergo transition into the gas phase (evaporation, sublimation, dissociation). The reaction occurs in the gas phase with condensation of the product that can form a solid sheet of crystals. If the reaction yields completely or mostly condensed products, the gas-phase stage can be unnoticed during the experiment. In gas-phase SHS (more precisely, in SHS processes with gas-phase reaction) formation of nanoscale products mostly depends on chemical condensation that can be readily controlled.

SHS in the solid-gas systems yielding nano-materials can exhibit very interesting mechanisms, such as infiltration-assisted combustion of porous bodies (powdered and pelleted samples) and gas suspensions.

According to Ref. 3, various physicochemical transformations<sup>3/4</sup>chemical reactions, reactive diffusion, melting, dissolution, crystallization, recrystallization, evaporation, sublimation, dissociation, chemical condensation, etc. can affect the crystallization of products. For formation of nano-structures, of special importance are the processes of nucleation and grain growth (crystallization and recrystallization).

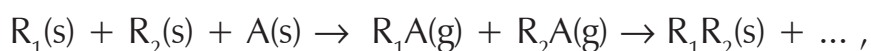
### **1.3. Regulative additives and external influence**

Regulative additives and external influence play an important role in nano-SHS. The action of additives can be different. The most primitive one is the absorption of heat and reduction of combustion temperature. In such

cases, inert additives with submicron or micron particles are introduced into the system. The final products that do not change the composition of the combustion products are the best controlling additives of this kind. A number of successful results were obtained due to implementation of the above approach. For example, dilution of the  $\text{Fe}_2\text{O}_3 + 2\text{Al}$  thermite mixture with one of the final products ( $\text{Al}_2\text{O}_3$ ) allowed us to suggest the first model of the gasless combustion<sup>7</sup>. Dilution of a metal with its nitride ensures high degree of metal nitration upon its combustion in nitrogen<sup>8</sup>. This approach may be applied to provide favorable conditions for formation of nano-crystallites.

Another approach to the use of regulative additives is associated with their melting. Reaction of the reagents dissolved in a low-melting additive occurs in the liquid phase and is followed by crystallization of final product from the solution. This method was found to be efficient for fabricating nano-crystallites.

In a more complicated situation, additives react with reagents to yield gas-phase intermediates leading to nanoscale crystallites. Such a process can be schematically presented as follows:



where  $\text{R}_1$  and  $\text{R}_2$  are the reagents, A is the regulative additive, while “s” and “g” stand for solid and gas, respectively. Generally, the action of additives can proceed also through a more sophisticated mechanism.

Another efficient tool for controlling SHS is the action of external influences. This action can be achieved in the following ways: (a) influence on the charge (pretreatment of reagents), (b) influence on the process (during SHS) and (c) influence on combustion (processing aiming at manufacturing target products). External influences can be classified according to their nature: electric, magnetic, electromagnetic, mechanical, and physicochemical. For nano-SHS, of especial importance are mechanical influences.

Mechanical influence on green mixture (in various mixing facilities, such as planetary stirrers, ball mills, etc.) results in either its mechanoactivation (MA) or mechanochemical synthesis (MS).

Being a very important stage of SHS, the MA of reagents increases the reactivity of particles. The effect is maximal in case of “ideal” solid-flame SHS [9]. If the activated particles undergo melting and reaction in the liquid phase, the effect is either pronounced only slightly or absent altogether. The MA can affect the reagents in two ways: (1) macrokinetically (influenced are the rate and conditions of front propagation) and (2) structurally (influenced are the size and shape of crystallites and the process of pore formation).



TABLE 1 - Combustion modes at various depth of MA.

Depth of MA	Combustion mode
Low	Heat release during mechanical treatment is low. The process is isothermal. MA takes place upon prolonged treatment. MS is absent.
Moderate	Heat release is noticeable. The process is slightly exothermic. Hot spots releasing heat into the bulk can form. MA takes place at initial stages of treatment while MS, upon prolonged treatment.
High	SHS process is initiated in the hot spots formed during mechanical treatment of charge. The reaction mostly occurs in the SHS mode and partly (in the hot spots), in the MS mode.

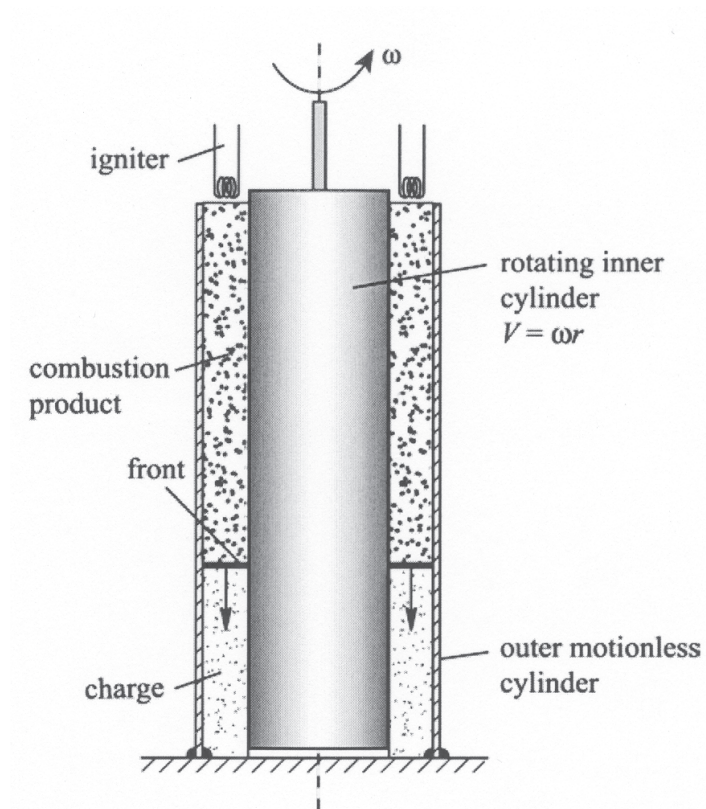


FIGURE 3 - Schematic diagram of SHS rotational viscous meter.

Combination of MS with SHS can lead to very interesting results. Some feasible modes of the process combining MS and SHS in the simplest way - intense MA of charge - are presented in Table 1. At intense effect, the energy dissipation results in appearing hot spots in the charge where SHS is initiated.

In this case, MS almost does not take place, since the reaction occurs in SHS mode.

However, modeling of the MS + SHS processes faces a number of difficulties associated with uncertainty of the conditions for the particle motion in real apparatuses, which does not allow correct describing a source of heat release during mechanical action. This problem can be resolved<sup>10</sup> by simulating the MS + SHS process in terms of the rotational viscous meter model that is convenient for both theoretical and experimental studies (Fig. 3). The charge is placed into a gap between two cylinders, one of which (inner or outer) is rotating. SHS is initiated at steady rotation.

Mechanical treatment of SHS product is of significant interest as well. The simplest method is grinding combustion product to nanoscale powders that facilitates further consolidation of the particles.

Such a primitive method for fabricating nano-powders is very attractive since the vast variety of the process issues is reduced to the only main task, that is, the development of efficient disintegration techniques. In some cases, the production procedure is simple from the technical point of view. If an intermediate melt is formed during combustion, the combustion product can be obtained in the form of nano-structured foam with thin walls (in the presence of a blowing agent) which can be then easily disintegrated.

#### **1.4. Additional comments**

Summing up the above material, it should be stressed that nano-SHS is characterized by two principal stages (Fig. 4):

- synthesis of polycrystalline intermediate products (cakes or ingots) with nanosized crystallites,
- isolation of the crystallites from the intermediate products and fabrication of nano-powders.

These result in appearing two issues:

- how to control (decrease) the crystallite size in the intermediate product,
- how to isolate crystallites from the intermediate product in a most efficient way and obtain a nano-powder.

As was mentioned above, crystallites form upon crystallization or condensation in the combustion wave. The crystallite size can be decreased upon an increase in the number of nucleation (crystallization or condensation) sites by performing quenching at different stages of the process.

Production of nano-powder from an intermediate product is also an important task that can be accomplished by using disintegration procedures and thermochemical treatment.

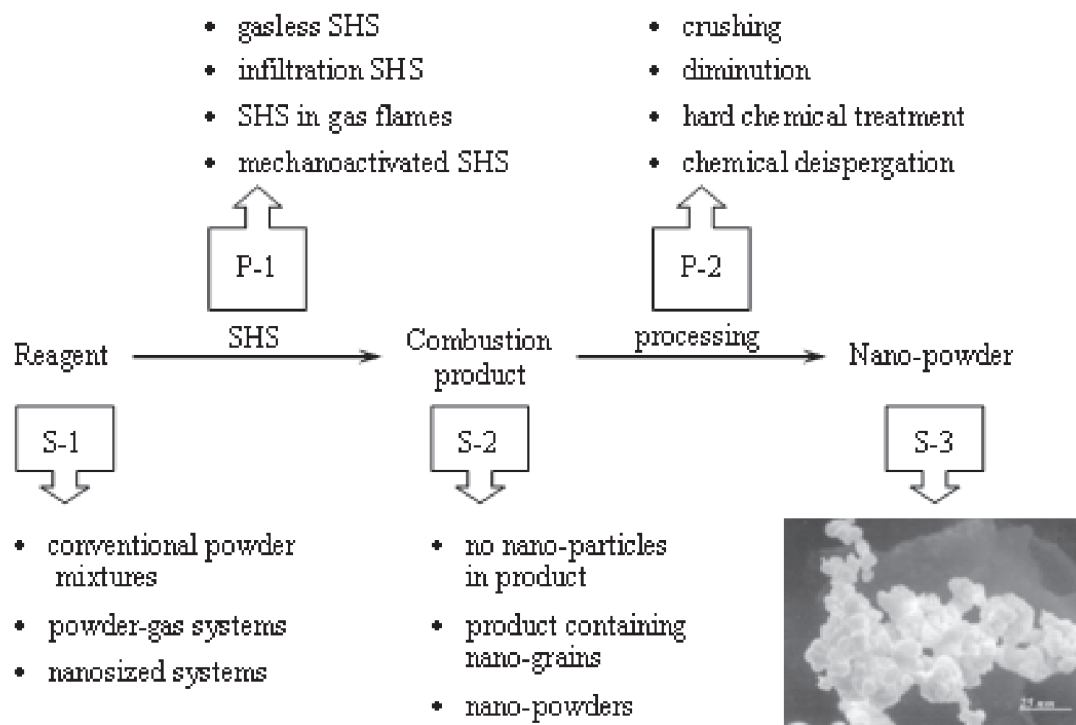


FIGURE 4 - Two stages of nano-SHS.

Disintegration aims at:

- preparation of the combustion product to thermochemical treatment for separation of the crystallites,
- destruction of the crystallites to obtain nanoscale debris (nano-powders).

Obviously, the latter approach is more universal and represents force solution of the task. The efficiency of this method depends upon characteristics of the milling facilities. Separation of the crystallites from intermediate product requires a very accurate approach. Here two methods are usually applied: severe thermochemical treatment of the intermediate product in acids or bases and mild thermochemical one in acids, bases or salt melts (solutions).

Harsh thermochemical treatment is applied to eliminate by-products (for example, MgO in magnesiothermal synthesis) while the mild one, to disintegrate of polycrystalline cakes or ingots. Chemical dispersion<sup>11</sup> is an original method of mild treatment allowing to dissolve the boundary layers of the crystallites without any impact on the bulk.

Let us consider still another aspect of nano-SHS. As a rule, SHS systems are heterogeneous (powder mixtures, powder-gas and powder-liquid systems). In most cases, homogenization of the media, i.e. formation of melt-solution or gas mixture takes place before formation of an intermediate product in the form of heterogeneous nano-structure and final nano-product.



What if one performs SHS in homogeneous systems, solutions or gas mixtures? No doubt, this promising approach would give new interesting results.

Nowadays, SHS in gas systems is under active development. Gas-phase SHS is very attractive due to simplicity of direct manufacturing of nano-particles, absence of an intermediate product, feasibility and expediency of development of continuous process. The next task is performing SHS in solutions.

The most interesting examples for fabrication of nano-powders by SHS are given in Section 2.

## 2. SOME EXAMPLES

Three lines of SHS research can be distinguished as most advanced: traditional, mechanochemical, and gas-phase SHS.

### 2.1. Traditional SHS

As was mentioned above, key points here are controlling the size of crystallites in combustion products and methods for their separation.

For the first time, SHS of aluminum nitride was carried out through combustion of Al in  $N_2$  in the presence of regulating additives<sup>12, 13</sup>. The resultant cake was found to exhibit porous a polycrystalline structure with a particle size of about 100 nm. To transform the cake into powder, the method of chemical dispersion was applied<sup>14</sup>. The photo of the cake (formed by hollow polycrystalline particles) and boron nitride nano-powder is presented in Fig. 5.

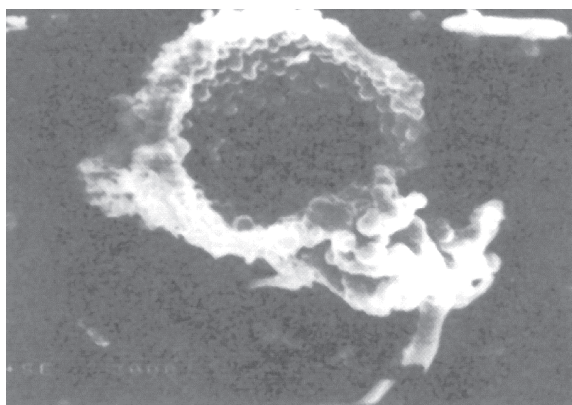


FIGURE 5a - Hollow agglomerate particles (partial diminution)<sup>14</sup>.

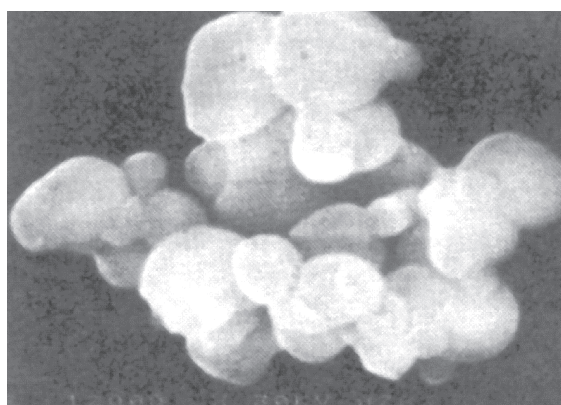


FIGURE 5b - Crystalline grain (0.1  $\mu m$ ) (complete diminution)<sup>14</sup>.

The mechanism of nano-crystallite formation is of significant interest. The authors suppose that the additives transferring a part of the reagents into a gas phase play the main role in formation of the nano-crystallites. The gas-phase reaction yields AlN nucleus that undergoes condensation growth. A set of grown particles forms crystallites. Their size is determined by the time of crystal growth that and can be readily controlled.

SHS was carried out in nitrogen gas in the presence of  $\text{NH}_4\text{F}$  as a regulating additive. The formation of the intermediate gaseous product  $\text{AlF}_3$  is followed by its reaction with nitrogen to yield the final product AlN in the form of nano-crystallites. The crystallite size can be controlled by varying concentration of the additive in the reaction mixture.

The task objective in Ref. 14 was manufacturing the boron nitride powder with a high specific surface according to the scheme:



Reaction (3) was found to be most suitable for practical implementation. The target product BN can be separated from the BN + MgO mixture by treatment with MgO to dissolve acids or bases. The time of the product milling is an important factor determining the specific surface of BN. The specific surface of intermediate and final products as a function of milling time is presented in Fig. 6. A very high specific surface (about  $60 \text{ m}^2/\text{g}$ ) was attained in Ref. 14.

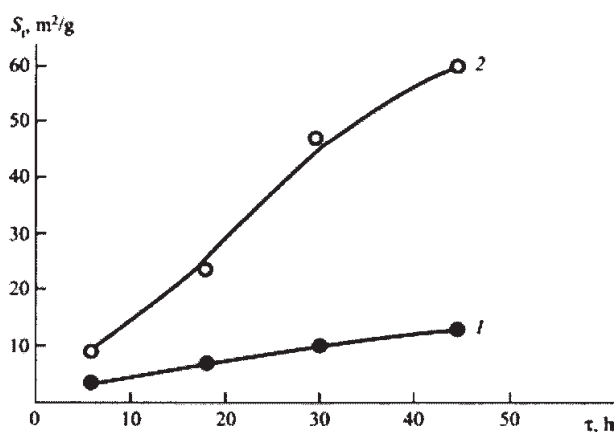


FIGURE 6 - Specific surface as a function of milling time<sup>14</sup>.

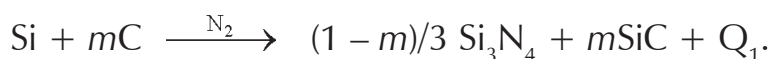
TABLE 2 - Physicochemical characteristics of the WC-Co and WC alloys manufactured by SHS and WC alloy manufactured by furnace synthesis.

Characteristic	SHS-produced WC alloy	VK6-OM alloy (reference)
Density, g/cm <sup>3</sup>	14.9	14.7
Hardness, HRA	91	90.5
Coercive force	270	280
Stability coefficient	1.4	1.0
Porosity, %	0.04	0.2
Grain size up to 1 mm	75 %	60 %

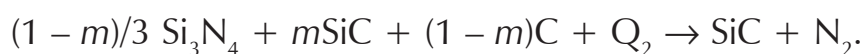
The methodology developed in Ref. 11 and Ref. 14 was applied to fabricate the fine powder of WC, TiB<sub>2</sub>, and SiAlON. The WC powder is taken as an example of the high efficiency of the manufactured powders for production of hard alloys (Table 2).

A number of projects is devoted to synthesis of  $\beta$ -SiC nano-powders, a popular ceramic product. Being slightly exothermic, the synthesis of SiC from the elements requires a charge to be warmed-up. This is performed by using gas burners moving along a charge with a velocity identical to that of front propagation<sup>15</sup>. The SiC grain size ( $\sim 200$  nm) was found to slightly depend on the particle size of starting silicon. The mechanism of the final product formation has not been discussed in Ref. 15.

A very interesting experiment was described by Pampuch *et al*<sup>16</sup>. The method for two-stage synthesis of silicon carbide nano-powders is schematically presented in Fig. 7. During the first stage, the mixture of Si and C powders burns in nitrogen gas:



Then the mixture of Si<sub>3</sub>N<sub>4</sub> and SiC is annealed in a furnace in the presence of carbon:



The only product of this two-stage process is nano-grained SiC. It is interesting that direct reaction of Si and N in the SHS mode results in formation of bigger carbide particles.

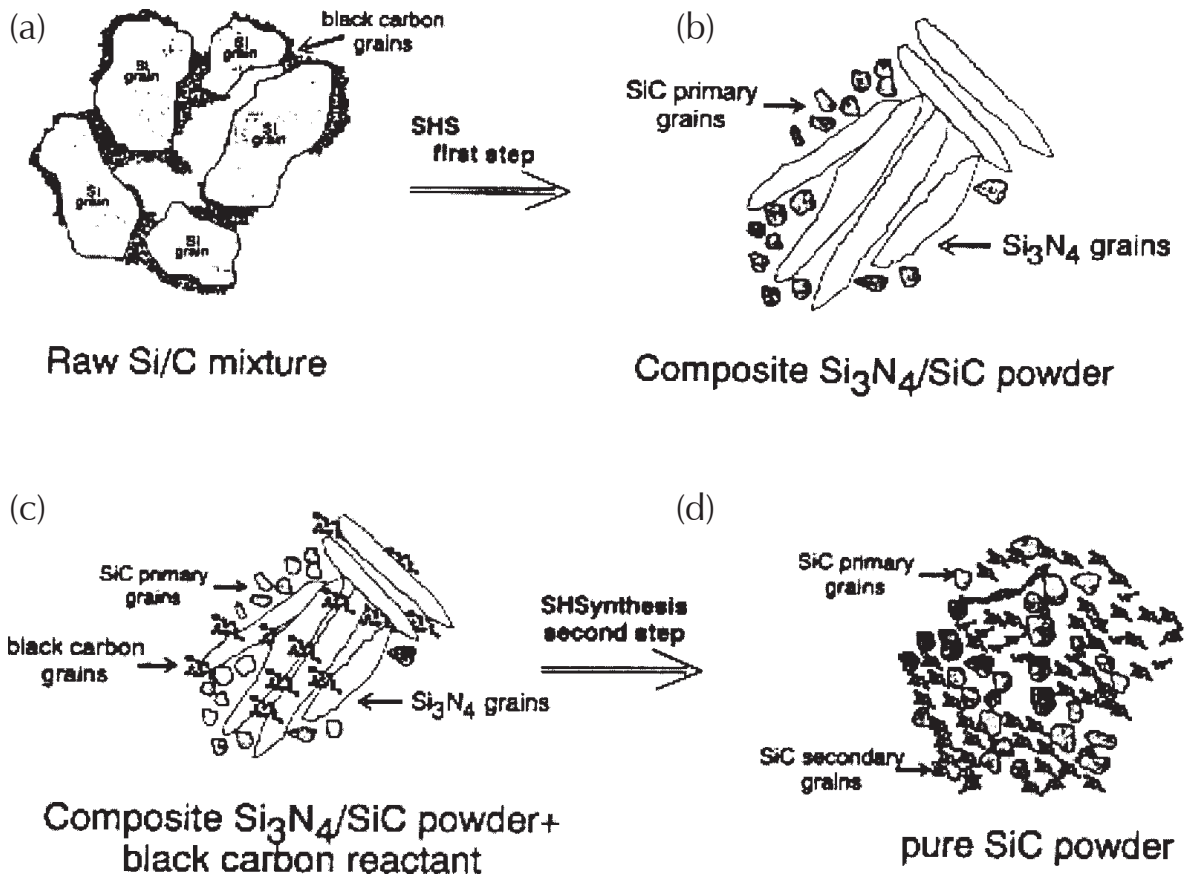
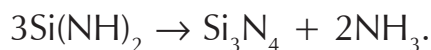


FIGURE 7 - Changes in the morphology of the Si-C-N system containing coarse particles of Si and fine particles of C (primary stage) during SHS: (a) starting mixture; (b) combustion product; (c) intermediate morphology of the  $\text{Si}_3\text{N}_4$  + primary SiC + C composite; (d) resultant morphology of primary and secondary particles of SiC<sup>16</sup>.

A number of research projects is devoted to development of methods for fabricating prolonged nano-particles (fibers, whiskers, etc.). In this context, the synthesis of  $\text{Si}_3\text{N}_4$  was studied in details<sup>17, 18</sup>. In this case, the most efficient regulative additive is  $\text{NH}_4\text{F}$  just as in the synthesis of  $\text{AlN}$ <sup>12, 13</sup>. The main intermediate product is supposed<sup>19</sup> to be silicon imide  $\text{Si}(\text{NH})_2$  that yields the target product upon thermal decomposition:



The fibrous product  $\text{Si}_3\text{N}_4$  was also fabricated in Ref. 20 and 21. In Ref. 20, the reaction was carried out in the SHS mode in the presence of sodium azide  $\text{NaN}_3$  as a nitriding agent:



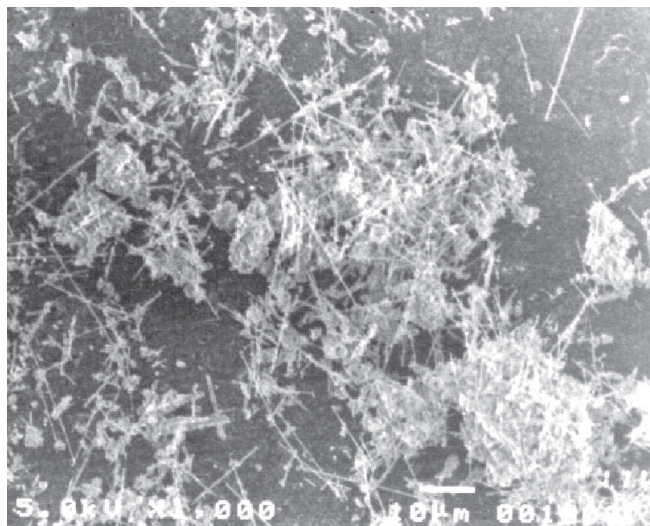
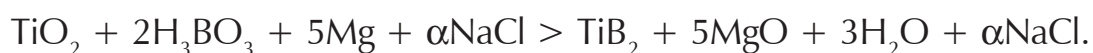


FIGURE 8 - Morphology of the silicon nitride microstructure<sup>21</sup>.

The combustion product is obtained as a mixture of powders and fibers (Fig. 8<sup>21</sup>), which implies non-uniqueness of the  $\text{Si}_3\text{N}_4$  formation route.

For SHS production of  $\text{SiC}$  and  $\text{TiB}_2$  nanoscale crystallites, regulative additives of polytetrafluoroethylene  $(\text{C}_2\text{F}_4)_n$ <sup>22</sup> and  $\text{NaCl}$ <sup>23</sup> were used respectively.

Methods for manufacturing nano-powders of reduced metals (Ti, Ta, Nb, W, Mo) have been discussed in Ref. 22. Fabrication of  $\text{TiB}_2$  crystallites based on the reaction presented below is described in Ref. 23:



The size of  $\text{TiB}_2$  crystallites was found to depend on the amount of additive in the charge (Fig. 9).

The mechanism for action of additive (not discussed in the paper) seems to be associated with formation of the  $\text{NaCl}$  melt in which the reagents dissolve, react in the liquid phase, and crystallize. The plateau on the curve reflects the situation when all the reagents have been transferred to the liquid phase and formation of the final product occurs according to the only route. In this case, the reaction rate becomes independent of combustion temperature (plateau in the curve).

The range of the nano-powders fabricated by SHS is constantly widening due to the use of various reagents, combustion conditions, and regulative additives.

A number of important works on synthesis of nanoscale powders for

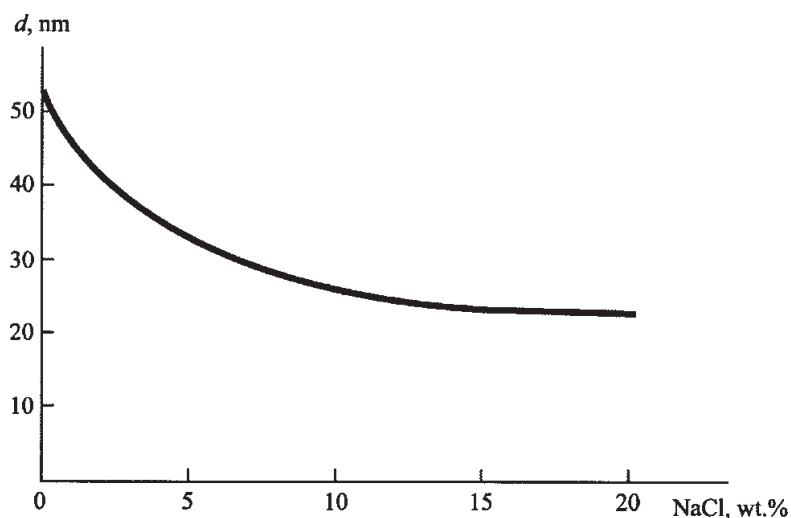


FIGURE 9 - The size of  $TiB_2$  crystallites as a function of additive concentration<sup>23</sup>.

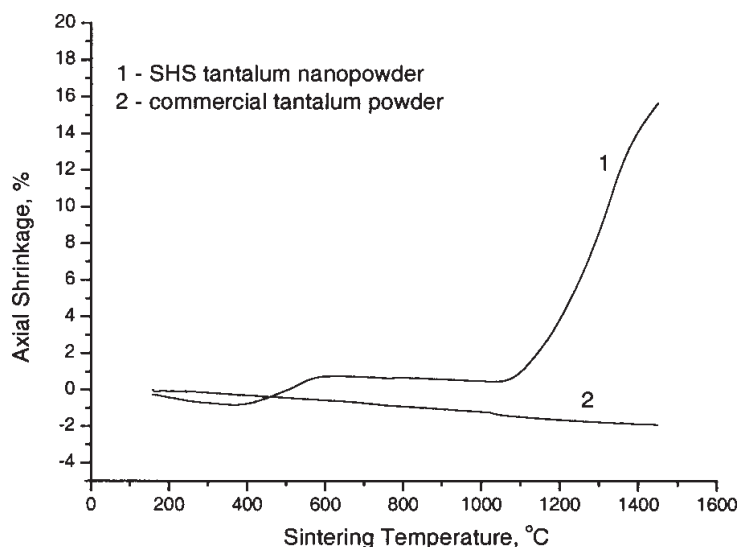


FIGURE 10 - Sinterability of Ta powders: (1) nano-powders prepared by SHS and (2) commercially available Ta powder (particle size  $\leq 10 \mu m$ ).

various applications from redox compounds/mixtures was performed by Patil *et al*<sup>24</sup>.

One of the most interesting methods for fabricating nano-powders developed at the Tomsk Research Center (Siberia, Russia) is fabricating fine powders of the diborides of IV group metals. This procedure involves the following stages: mixing a IV group metal with boron, pelleting, ignition, and synthesis in the combustion mode. The particle size can be controlled by introducing fluorides of lithium, potassium and sodium (or their mixture) into the charge (0.81-1.96 mol/mol end product). This method was applied to produce the nano-powder of  $TiB_2$  (87% particles below 100 nm in size)<sup>25</sup>.



Another achievement is the method for synthesis of fine silicon nitride from ferrosilicon nitrified by SHS-based technique. The nano-particles of silicon nitride are separated by washing with acid (30% particles below 100 nm in size).

A simple and economic approach to synthesis of transition metal nano-powders has been developed by Nersisyan *et al*<sup>26,27</sup>. It was shown that the nano-powders of Ti, Ta, Nb, W, Mo can be prepared upon reduction of transition metal oxides in melted salts of alkali or alkali-earth metals. During combustion, melted salt forms a protective layer around the primary metal particles thus preserving their nanostructure.

The optimal concentration of salt is 20-60 wt%. The salt can be either added to the green mixture (e.g., reduction of  $\text{Me}_x\text{O}_y$  with Mg) or it can appear during combustion (reduction of  $\text{Me}_x\text{O}_y$  with sodium in the presence of  $\text{NaN}_3$ ,  $\text{NaBH}_4$ , etc.). The average particle size is 20-50 nm while the content of oxygen, 0.5-0.6 wt.%.

As a rule, SHS-produced transition metal nanopowders exhibit good sinterability. Of particular interest is the sinterability of Ta nano-powder and an unusually high (87-90%) relative density at 1300-1350°C (Fig. 10)<sup>28</sup>. The commercially available Ta (particle size below 10  $\mu\text{m}$ ) does not exhibit any shrinkage in the above temperature range. W and Mo nano-powders were found to exhibit the same behavior during sintering.

Commercialization of SHS nano-powders is quite promising. Testing the developed production method by using an SHS technological reactor showed excellent prospects for large-scale production. Nowadays, a Ta capacitor made of SHS-produced Ta nano-powder is being tested at Samsung Electronics. The results will be coming soon.

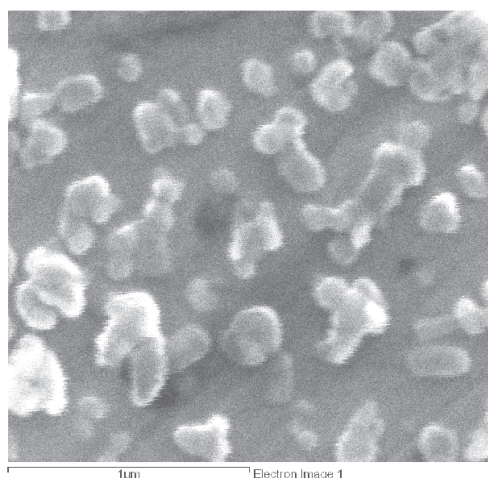


FIGURE 11 - AlN powder<sup>29</sup>.

The microstructure of the AlN powder fabricated by combustion of Al in  $\text{N}_2$  (at 60 atm) is presented in Fig. 11<sup>29</sup>.

The combustion product is the AlN powder consisting of slightly sintered agglomerates characterized by bimodal size distribution: 15 wt % particles below 100 nm, 75 wt % particles 2-10  $\mu\text{m}$  in size. This result may be explained by the AlN synthesis procedure when 18 wt. % of pure Al (20  $\mu\text{m}$ ) is added into the green mixture of SHS AlN (3-10  $\mu\text{m}$ ). The reaction product is nanosized AlN.

Results of works considered in this section prove that nanophased polycrystalline products can be fabricated by varying combustion conditions and/or introducing regulative additives into the green mixture. Application of appropriate postprocessing methods (such as chemical dispersion) will lead to nano-sized powders.

## 2.2. Mechanoactivated SHS

One of the first projects connecting SHS with mechanochemistry was devoted to synthesis of complex oxides from simple oxides involving mechanical treatment of green mixture<sup>30</sup>:



In Ref. 30, the green mixture was mechanoactivated in a planetary mill in an oxygen-free atmosphere. Combustion was found to exhibit a 8-10-fold increase in the burning velocity. However, the nano-structure of the combustion products has not been explored so far.

Meanwhile, combination of SHS with mechanical pretreatment is current interest. In this case, the pretreatment affects the burning velocity, combustion temperature, and disintegration of combustion product.

Nowadays, mechanical activation can be used for (1) initiating SHS in low-caloric systems and (2) diminishing the particle size in combustion products. Some consequences of MA are given below.

According to Ref. 31, superstoichiometric titanium carbide ( $\text{TiC}_{1.27}$ , or  $\text{Ti}_{0.79}\text{C}$ ) can be regarded as a highly defective Ti sublattice (because of the presence of Ti vacancies). The Ti grains (about 0.5  $\mu\text{m}$  in size) were found to contain the crystallites about 3 nm in their size. Probably, further mechanical or thermochemical treatment of the product can be expected to yield a nano-scale product.

The mechanoactivated synthesis of  $\beta$ -SiC from Si and C powders is described in Ref. 32. The degree of conversion was found to attain 100%, the grain size of homogeneous  $\beta$ -SiC attaining a value around 7 nm.

TiC with a particle size of 30 nm was synthesized in Ref. 33. The temperature of high-temperature deformation at hot pressing of the TiC nanopowder was found to be 500°C, which is lower than that of a regular one.

The same research group obtained nano-scale  $\text{TiB}_2$ <sup>34</sup>. The product microstructure and size distribution are presented in Figs. 12 and 13.

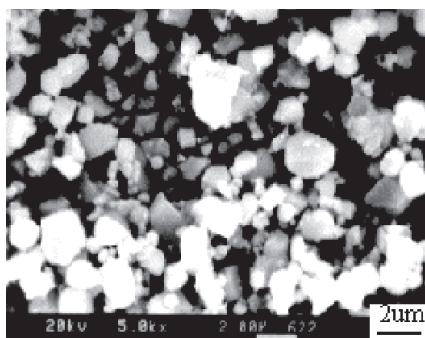


FIGURE 12 - Microstructure of  $\text{TiB}_2$ <sup>34</sup>.

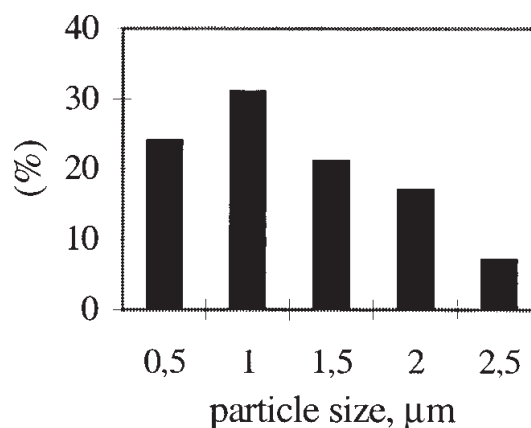


FIGURE 13 - Size distribution for  $\text{TiB}_2$ <sup>34</sup>.

According to Ref. 35, the Ti and Si powders with a particle size of 25-30  $\mu\text{m}$  and 44  $\mu\text{m}$ , respectively, were mixed (and milled) at various Ti/Si ratios in a ball mill. For the Si content of 34-60 at. %, the heat release was found to initiate thermal explosion. For lower contents of Si, slow reaction with product amorphisation takes place. The formed silicides had a particle size below 100 nm. The size of Ti and Si particles is defined by the duration of MA. During MA, the milled reagents transform into the grains of  $\text{TiSi}_2$ ,  $\text{Ti}_5\text{Si}_3$ ,  $\text{TiSi}$  and  $\text{Ti}_5\text{Si}_4$ . There is no  $\text{Ti}_5\text{Si}_4$  in the phase diagram, which implies that the compound has a non-equilibrium crystal lattice. Probably, a non-stoichiometric compound  $\text{TiSi}_{1-x}$  ( $x = 0.2$ ) has been synthesized in Ref. 35 but this has to be confirmed by structural analysis.

Mechanoactivated synthesis of some interesting compounds and alloys was carried out in Ref. 36-38, although the decisive role of SHS has not been analyzed.

Combination of SHS with MA of intermetallics (in Ni-Al, Ni-Si, Ni-Ge, and Ti-Ni systems) and oxides (in Ba-Zr(Ti,Hf,Mo,W,Al)-O, Ca-Mo-O, Sr-Mo-O, and Pb-Mo-O systems) is considered in Ref. 39. This approach was shown to be quite promising for practical implementation. Even a short-term MA of SHS product was found to yield uniform single-phase nano-scale powders (particle size about 10 nm) of complex oxides, nitrides, borides, carbides,

etc. It is concluded that metastable phases usually obtained by MA can be manufactured from equilibrium SHS intermetallides.

Fabrication of nanocomposite  $\text{TiB}_2\text{-TiAl}_3$  powders is described in Ref. 40. Thermal explosion was found to occur during mixing the reagents, which results in formation nanosized (25 nm)  $\text{TiB}_2$  grains.

The grain size as a function of MA time is given in Fig. 14. The grain size increases with increasing treatment time and exhibits a tendency to saturation. Being quite unusual, this result has to be explained. It seems that processes of disintegration and aggregation occur simultaneously, and the polycrystallite size is determined by relative contribution from these processes.

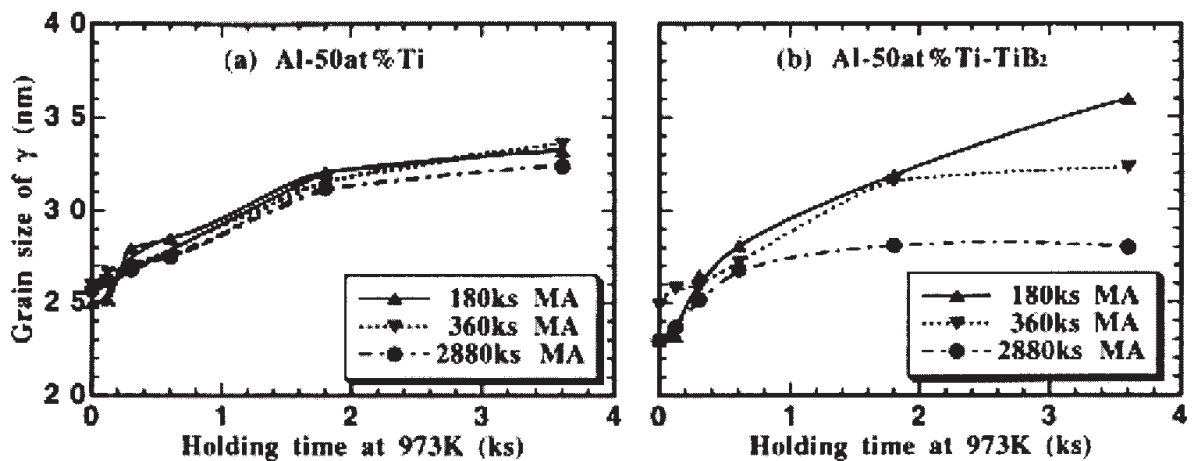


FIGURE 14 - Grain size as function of MA time for the  $\text{TiB}_2\text{-TiAl}_3$  system<sup>40</sup>.

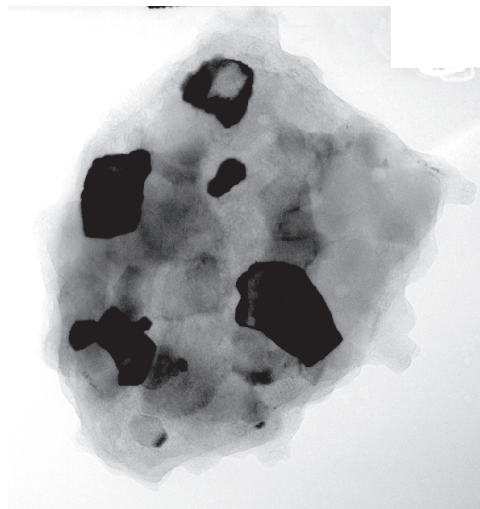


FIGURE 15 - TiC nanocrystallites observed by TEM<sup>41</sup>.

This assumption can be verified experimentally by analyzing the particle structure. It should be polycrystalline grains with the size decreasing from left to right along the curve.

Mechanoactivated powders were pelleted and subjected to the action of electric current. The formation of  $\text{TiB}_2$  was found to affect TiAl particle growth. Note that the Al-Ti system (50 wt % Ti) is more sensitive to MA.

Co-existence of coarse ( $>500$  nm) and nanosized (about 70 nm) TiC particles after MA of Ti and C powder mixture (in a ball mill for 3 h) is of especial interest<sup>41</sup> (Fig. 15).

### 2.3. Gas-phase SHS

Unlike combustion in condensed systems, combustion of gases has been thoroughly studied; however the lack of knowledge about SHS in gas mixtures is fairly noticeable. This can be explained by existing only a few gas systems which can burn to yield useful condensed products. The approaches applied for the studies were as follows:

- sodiumthermic reduction of chlorides in the gas phase with formation of simple and complex compounds,
- gas-phase reduction of fuel gases (hydrocarbons, silanes, boranes, etc.) yielding oxides
- chemical synthesis in flames forming independently on the synthesis reactions and playing a role of gas-phase “chemical furnace”.

The following devices are used for study of gas-phase combustion synthesis under severe conditions of high-temperature synthesis and synthesis of multiphase particles:

- flat premixed burner<sup>42-45</sup>;
- shock-wave reactor<sup>46</sup>;
- combustion vessel with laser ignition<sup>47</sup>;
- coflow burner<sup>48-52</sup>;
- hydrocarbon fuel/ $\text{O}_2$ /(Si precursor)<sup>53</sup>;
- volume combustion burner<sup>54-55</sup>, etc.

Various methods for synthesis of non-oxide, single-oxide, and mixed-oxide powders are classified and thoroughly analyzed in a comprehensive review on gas-phase combustion synthesis of particles<sup>56</sup>. Influence of various synthesis parameters (including electric field) on morphology and composition of resultant powders were found to determine a mode of nucleation and grain growth (homogeneous nucleation, agglomeration coalescence). However, aerosol reactors and CVD systems were not reviewed in the paper.



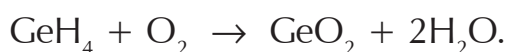




Another interesting example is synthesis of TiAl nano-particles (6 nm) in zero-gravity<sup>62</sup>. Various condensation modes and their influence on the product morphology were analyzed.

In Ref. 63, experiments with cool flames of silane ( $\text{SiH}_4$ ) and germane ( $\text{GeH}_4$ ) yielded Si, Ge,  $\text{SiO}_2$ ,  $\text{GeO}_2$  and  $\text{Si}_3\text{N}_4$  films and particles. Gas-phase combustion synthesis of ultrafine amorphous  $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{SiN}_x\text{C}_y$  particles and crystalline BN particles is described in Ref. 64.

As is known, condensation can be heterogeneous and homogeneous. In the former case, the nuclei of condensed phase form throughout the gas volume as a result of collisions of many product species, while in the latter case, product condensation takes place only on the surfaces contacting with the reacting gas. In the former case the product is obtained in the form of powders while in the latter one, in the form of films. The reaction parameters at which a switch between the product condensation modes takes place have been determined<sup>65</sup> for the following reaction (Fig. 17):



SHS of dielectric, protective and semiconducting films as well as nano-scale powders can be carried out at low temperatures and pressures. This can be regarded as a significant advantage of the method since at these conditions high density charges are eliminated from the surface that markedly improved quality of final semiconducting items.

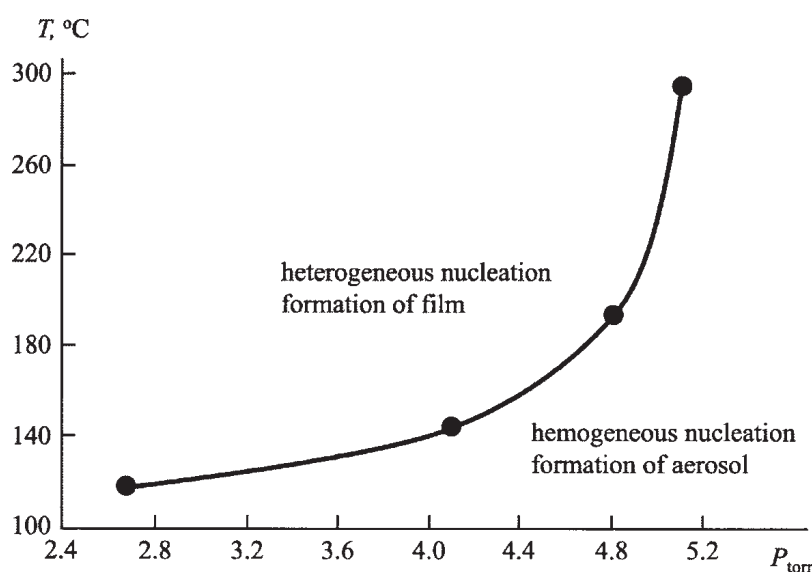


FIGURE 17 - Regions of homogeneous and heterogeneous condensation of  $\text{GeO}_2$ <sup>65</sup>.

This synthesis can be controlled by using common methods for controlling chain reactions without applying plasma or photochemical techniques.

However, in the papers on gas-phase SHS the presented information is mainly limited by description of fabricated products. The connection between combustion mechanism and condensation mode, hydrodynamic factors and combustion and structure formation parameters, gas flow mode (laminar or turbulent) and morphology and structure of product particles have not been analyzed so far.

For SHS in gas suspensions, the reagents used for infiltration combustion can be applied. However, due to markedly decreased density of heat release and poor heat exchange between the particles, combustion in such systems can hardly take place. That is why this kind of SHS proceeds largely through transferring particles into a gas phase (partly or completely) and combustion product condensation. As a rule, the size of particles formed in these processes is much lower than that of starting reagents.

An original approach to SHS in gas suspensions is proposed in Ref. 66. In this case, a cloud of metal particles is generated in the gas phase (oxygen, nitrogen, ammonia, etc.). Combustion in the cloud is initiated by electric spark and the combustion products are collected on a filter. This method was used to synthesize  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{FeO}$ ,  $\text{TiN}$ , and  $\text{ZrN}$  powders with a particle size of 10-100  $\mu\text{m}$ .

Similar results were obtained upon continuous combustion in a two-phase mixture<sup>67,68</sup>. The spherical  $\text{Al}_2\text{O}_3(\gamma)$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{ZrO}_2$  particles with extremely narrow size distribution (40 nm) were synthesized in a diffusion or homogeneous flame. The reagent particle size is below 10  $\mu\text{m}$ .

As mentioned above, pyrolysis of compounds in flames with formation of final products can also be regarded as gas-phase SHS. In this case, both reagents (introduced into the flame) and flame components can participate in the reaction or the flame can be chemically inert providing only heat and medium for the reaction. This method was applied to synthesize the following nanosized compounds:  $\text{TiAl}$ <sup>62</sup>,  $\text{Ti-W}$ <sup>69</sup>,  $\text{SiO}_2$ <sup>56, 70</sup>,  $\text{Si}_3\text{N}_4$ <sup>71</sup>,  $\text{TiB}_2$ <sup>9</sup>,  $\text{GaN}$ <sup>72</sup>,  $\text{Y}_2\text{O}_3\text{:Eu}$ <sup>73</sup>,  $\text{AlN}$ <sup>74</sup>.

## CONCLUSIONS

In this paper, a scientific discipline that appeared as a combination of two actively developing lines of research - nano-scale materials and SHS - has been considered and illustrated with some examples with special emphasis on production of nano-powders and ideology of appropriate R & D.

On our opinion, there are three stages of R & D in the field.

- (1) Synthesis of nano-powders. Here the main task objective is selection of a best synthetic approach. Fabrication of nano-scale powders was the final task in almost all considered papers.
- (2) Characterization of SHS-produced nano-powders. What differs SHS powders from similar materials produced by other techniques? What are new characteristics of SHS-produced powders?
- (3) Applied issues. What is the technical and economic efficiency of SHS for fabricating nano-scale materials? Where can be applied SHS-produced nano-powders? It is reasonable to organize an industrial-scale production of SHS nano-powders?

SHS community tends to go through these three stages and looks forward for obtaining promising results of their activity.

## REFERENCES

1. A.G. Merzhanov, I.P. Borovinskaya, *Dokl. Akad. Nauk SSSR* **204** (2) 366-369 (1972).
2. A.G. Merzhanov, in *Fizicheskaya khimiya: Sovremennye problemy* (Physical Chemistry: Current Problems), Ya.M. Kolotykin, Ed., Moscow: Khimiya, 1983, pp. 8-45.
3. I.P. Borovinskaya, in *Kontseptsiya razvitiya SVS kak oblasti nauchno-tekhnicheskogo progressa* (SHS: Concepts of Current R & D), A.G. Merzhanov, Ed., Chernogolovka: Territoriya, 2003, pp. 178-182.
4. R.G. Aivazyan, V.V. Azatyan, V.I. Kalachev, V.I. Rubtsov, *Fiz. Goreniya Vzryva* **30** (4) 85-91 (1994).
5. V.V. Azatyan, A.G. Merzhanov, in *Khimicheskaya fizika na rubezhe XXI veka* (Chemical Physics at the Edge of XXI Century), Ed., Moscow: Nauka, 1996, vol. 2, 74-88, pp. 13-20.
6. V.V. Azatyan, *Usp. Khim.* **68** (12) 1122 (1999).
7. E.I. Maksimov, A.G. Merzhanov, V.M. Shkiro, *Zh. Fiz. Khim.* **40** (2) 468-470 (1966).
8. A.G. Merzhanov, I.P. Borovinskaya, Yu.E. Volodin, *Dokl. Akad. Nauk SSSR* **206** (4) 905-908 (1972).
9. A.G. Merzhanov, *Combust. Sci. Technol.* **98** (4-6) 307-336 (1994).
10. A.G. Merzhanov, *Int. J. SHS* **4** (4) 323-350 (1995).
11. I.P. Borovinskaya, G.A. Vishnyakova, L.P. Savenkova, *Int. J. SHS* **1** (4) 560-565 (1992).
12. V.K. Prokudina T.V. Shestakova, I.P. Borovinskaya, et al, in *Problemy technologicheskogo goreniya* (Problems in Technological Combustion), A.G. Merzhanov, Ed. Chernogolovka, Chernogolovka, 1981, vol. 2, pp. 5-8.

13. V.V. Zakorzhevskii, I.P. Borovinskaya, N.V. Sachkova, *Neorg. Mater.* **38** (11) 1340-1350 (2002).
14. I.P. Borovinskaya, T.I. Ignat'eva, V.I. Vershinnikov, et al., *Neorg. Mater.* **39** 698 (2003).
15. L. Stobierski, Z. Wegrzyn, J. Lis, M. Bucko, *Int. J. SHS* **10** (2) 217-228 (2001).
16. D. Kata, J. Lis, R. Pampuch, L. Stobierski, *Int. J. SHS* **7** (4) 475-486 (1998).
17. H. Chen, Y. Cao, X. Xiang, J. Li, C.C. Ge, *J. Alloys Compounds* **325** (1-2) L1-L3 (2001).
18. R. Pampuch, *J. Eur. Ceram. Soc.* **19** (13-14), 2395-2404 (1999).
19. V.V. Zakorzhevsky, I.P. Borovinskaya, *Int. J. SHS* **9** (2) 171-191 2000.
20. A.P. Amosov, G.V. Bichurov, V.M. Erin, et al., in *SVS: Teoriya i praktika* (SHS: Theory and Practice), Å.Å. Sytshev, Ed., Chernogolovka: Territoriya, 2001, pp. 314-332.
21. A.P. Amosov, G.V. Bichurov, N.F. Bol'shova, V.M. Erin, et al., *Int. J. SHS* **1** (2) 239-245 (1992).
22. H.H. Nersisyan, V.N. Nikogosov, S.L. Kharatyan, A.G. Merzhanov, *Fiz. Goreniya Vzriva* **27** (6) 77-81 (1991).
23. A.K. Khanra, L.C. Pathak, S.K. Mishra, M.M. Godkhindi, *Mater. Lett.* **58** (5) 733-738 (2004).
24. T. Minami, K.C. Patil, *Mater. Phys. Mech.* **4** 134-137 (2001).
25. V.B. Balashov, A.I. Kirdyashkin, Yu.M. Maximov, I.R. Nazyrov, Russ. Patent 2 087 262, *Byull. Izobret.* (23) (1997).
26. H.H. Nersisyan, J.H. Lee, C.W. Won, *J. Mater. Res.* **17** (11) 2895-2864 (2002).
27. H.H. Nersisyan, J.H. Lee, C.W. Won, *Mater. Res. Bull.* **38** (7) 1155-1146 (2002).
28. H.H. Nersisyan, J.H. Lee, S.I. Lee, C.W. Won, *Combust. Flame*, in press.
29. V.V. Zakorzhevskii, *Cand. Sci. (Chem.) Dissertation*, ISMAN, 2004.
30. V.V. Aleksandrov, M.A. Korchagin, *Int. J. SHS* **1** (3) 417-420 (1992).
31. M. S. El-Eskandarany, *Met. Mater. Trans. A* **27**, 2374 (1996).
32. M.S. El-Eskandarany, K. Sumiyama, K. Suzuki, *J. Mater. Res.* **10** (3) 659-667 (1995).
33. W. Wang, Z. Fu, R. Yuan, *J. Ceram.* **2** (1) 73-75 (1998).
34. W. Wang, Z. Fu, R. Yuan, unpublished results.
35. S. Doppiu, M. Monagheddu, G. Cocco, F. Maglia, U. Anselmi-Tamburini, Z.A. Munir, *J. Mater. Res.* **16** (5) 1266-1279 (2001).
36. P. Nandi, P.P. Chattopadhyay, S.K. Pabi, I. Manna, *Mater. Phys. Mech.* **2** (4) 116-120 (2001).
37. L. He, E. Ma, *J. Mater. Res.* **11** (1) 71-80 (1997).
38. F.J. Gotor, M.D. Alcala, C. Real, J.M. Criado, *J. Mater. Res.* **27** (7) 1655-1663 (2002).

39. T. Grigor'eva, M. Korchagin, N. Lyakhov, *KONA* (20) 144-158 (2002).
40. K. Uenishi, T. Matsubara, M. Kambara, K. F. Kobayashi, *Scripta Mater.* **44** (8-9) 2093-2097 (2001).
41. E. Heian, N. Karnatak, D. Vrel, M.F. Beaufort, S. Dubois, *Abstr. VII Int. Symp. on SHS*, Cracow, Poland, 2003.
42. H.F. Calcote, W.A. Felder, D.G. Keil, O.B. Olson, *Proc. 23rd Symp. (Int.) on Combustion*, The Combustion Institute, Pittsburgh PA, 1990, pp. 1739-1744.
43. D.R. Hardesty, F.J. Weinberg, *Proc. 14th Symp. (Int.) on Combustion*, The Combustion Institute, Pittsburgh PA, 1973, pp. 907-918.
44. G.D. Ulrich, Â.À. Milnes, N.S. Subramanian, *Comb. Sci. Techol.* **14** 243 (1976).
45. Y. Xiong, S.E. Pratsinis, *J. Aerosol Sci.* **22** 637 (1991).
46. H.F. Calcote, W. Felder, *Proc. 24th Symp. (Int.) on Combustion*, The Combustion Institute, Pittsburgh PA, 1992, pp. 1869-1876.
47. I. Glassman, K.À. Davis, K. Brezinsky, *Proc. 24th Symp. (Int.) on Combustion*, The Combustion Institute, Pittsburgh PA, 1992, pp. 1877-1882.
48. R.L. Axelbaum, C.R. Lottes, J.I. Huertas, L.J. Rosen, *Proc. 26th Symp. (Int.) on Combustion*, The Combustion Institute, Pittsburgh PA, 1996, pp. 1891-1897.
49. D.P. Du Faux, R.L. Axelbaum, *Combust. Flame* **100** 350-358 (1995).
50. V. Revankar, A.Y. Zhao, V. Hlavacek, *Ind. Eng. Chem. Res.* **30** 2344 (1991).
51. M.R. Zachariah, S. Huzarewicz, *J. Mater. Res.* **6** (2) 264-269 (1991).
52. K. Ueyama, T. Ono, M. Matsukata, R. Oshima, *J. Chem. Vap. Dep.* **1**, 280 (1993).
53. B.W. Gerhold, K.E. Inkrott, *Combust. Flame* **100** (1-2) 144-152 (1995).
54. P.F. Miquel, J.L. Katz., *J. Mater. Res.* **9** (3) 746-754 (1994).
55. M.R. Zachariah, R.G. Joklik, *J. Appl. Phys.* **68**, 311 (1990).
56. M.S. Woodridge, *Progr. Energy Combust. Sci.* **24** 63-87 (1998).
57. N.F. Calcott, W.A. Felder, *Abstr. I Int. Symp. on SHS*, Alma-Ata, 1991, p. 38.
58. K.A. Davis, K. Brezinsky, I. Glassman, *Combust. Sci. Technol.* **77** 171-178 (1991).
59. R.L. Axelbaum, D.P. Du Faux, C.A. Frey, et al, *J. Mater. Res.* **11** (4) 948-954 (1996).
60. D.P. Du Faux, R.L. Axelbaum, *Combust. Flame* **100** (3) 350-358 (1995).
61. R.L. Axelbaum, J.I. Huertas, C.R. Lottes, et al, *Mater. Manufact. Processes* **11** (6) 1043-1053 (1996).
62. R.L. Axelbaum, B.H. Chao, *Proc. IV Int. Workshop on Microgravity Combustion*, 1997, Cleveland (USA), pp. 37-42.
63. V.V. Azatyan, R.G. Aivazyan, *Kinet. Katal.* **32** (6) 1287-1294 (1991).

64. Yu.M. Grigor'ev, A.G. Merzhanov, *Int. J. SHS* **1** (4) 600-639 (1992).
65. V.V. Azatyan, R.G. Aivazyan, A.G. Merzhanov, V.I. Rubtsov, *Kinet. Katal.* **35** (1) 30-37 (1994).
66. Ota K., Abe S. *Europ. Appl. O 151 4900 A2, Proir.: 09.02.84, JP 22463/84, 290584 JP 109108/84, Data of Publication of Application: 14.08.85, Bull.* 85/33.
67. N.D. Ageev, Ya.I. Vovchuk, S.V. Goroshin, *Fiz. Goreniya Vzryva* **26** (6) 54-62 (1990).
68. A.N. Zolotko, Yu.I. Vovchuk, N.I. Poletaev, et al., *Fiz. Goreniya Vzryva* **32** (3) 24 (1996).
69. R.L. Axelbaum, J.I. Huertas, C.R. Lottes, S.Y. Hariprasad, S.M.L. Sastry, *Mater. Manufact. Processes*, 11(6): 1043-1053 (1996).
70. I.S. Altman, D. Lee, J.D. Chung, et al, *Phys. Rev. B: Condens. Matter* **63** 161-202 (2001).
71. Y.-L. Li, Y. Liang, F. Zheng, et al, *J. Mater. Res.* **15** (4) 987-994 (2000).
72. Y.G. Cao, X.L. Chen, Y.C. Lan, Y.P. Xu, T. Xu, J.K. Liang, *J. Mater. Res.* 15 (2) 267-269 (2000)
73. Y.C. Kang, D.J. Seo, S.B. Park, H.D. Park, *Jpn. J. Appl. Phys. (Part I)* **40** (6A) 4083-4086 (2001).
74. C.C. Hwang, C.Y. Weng, W.C. Lee, S.L. Chung, *Int. J. SHS* **6** (4) 419-429 (1997).



## Discussion

**V. Vikulin:** Don't you think that SHS process is good for producing not only nano-powders but also nano-ceramics, because the processing time is short.

**A. Merzhanov:** It is possible, but in my lecture I discussed only about nanopowders but not nanoceramics.

**W. Rieger:** In 1968, in the laboratories of Lonza in Switzerland we made experiments on the formation of BN by reacting B with  $N_2$  in a fluidized bed. We found it very difficult to control the temperature. Can you inform about the use of fluidized bed synthesis for the SHS reaction principle and the way to control the temperature?

**A. Merzhanov:** Formation of BN in reaction of boron with nitrogen is a simple process. To carry it out it is necessary to compress nitrogen up to 6-8 kbar. The temperature may be controlled by microthermocouples. In our case, it was 2100-2400 K.

**P. Sajgalik:** What are the main tools to control the temperature and the reaction front velocity?

**A. Merzhanov:** There are two methods for temperature control: thermo-electrical (use of thin thermocouples when combustion temperature is less than 3000 K) and optical-spectral (for temperatures more than 3000 K). Besides, the temperature can be easily determined by thermodynamic calculation (in case of adiabatic terms of SHS).

**S. Baik:** In the process of BN synthesis from  $B_2O_3$  and Mg metal, can you use Al or Ti metal with  $B_2O_3$  to form  $(BN + Al_2O_3)$  or  $(BN + TiO_2)$ ?

**A. Merzhanov:** To carry out synthesis of ceramics  $BN + Al_2O_3$  and  $BN + TiO_2$  by means of SHS metallothermic reaction, the  $B_2O_3 + Al$  and  $B_2O_3 + Ti$  mixtures should be used. The process is carried out in nitrogen. Thus, we produced  $BN + Al_2O_3$  ceramics while there was no necessity to obtain  $BN + TiO_2$  ceramics.