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Self-propagating high-temperature synthesis of nanomaterials

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Abstract. The results of recent studies in the field of self-propagating high-temperature synthesis of nanosized materials are surveyed. The possibilities of the synthesis of nanomaterials in the combustion mode are demonstrated. Examples of applications of the self-propagating high-temperature synthesis for the preparation of nanopowders, films and compact materials are given. The bibliography includes 116 references.

I. Introduction

The self-propagating high-temperature synthesis (SHS) is an autowave process analogous to the propagation of a combustion wave.[1] In this process, a chemical reaction is localised in the combustion zone that spontaneously propagates over a chemically active medium. This process is actively exploited in the technology of inorganic materials: this makes it possible to produce powders, compact materials and workpieces as well as make coatings and weld component parts.[2]

The self-propagating high-temperature synthesis is effectively applied not only in technology but in a solution of various problems of modern materials science as well. Among such problems, the following may be mentioned: design of functionally graded materials,[3] single crystal growth,[4] development of gravity-sensitive processes,[5] realisation of chemical reactions under conditions of micro-gravity and zero gravity,[6, 7] mechanochemical treatment of reactants and reaction products,[8] thermochemical generation of electric and magnetic fields,[9] *etc*. As in the powder metallurgy, the particle size of reactants and reaction products plays a crucial role in the self-propagating high-temperature synthesis. In this respect, the SHS is closely interrelated with nanotechnology. Further reduction in the particle size is an urgent task since the size effects have a decisive influence on both the SHS process itself and properties of the resultant materials.

In the present review, the results of recent investigations in the field of SHS of nanosized materials are surveyed. Possibilities of its applications aimed at the preparation of nanopowders and films, compact materials with nanosized grains and pores are considered. Distinctive features of the SHS involving nanosized components (reactants, functional additives) are discussed.

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II. Formation of nanostructures in the processes of self-propagating high-temperature synthesis

The possibility of direct preparation of nanosized structures by SHS is not self-evident. Some specialists in materials science believe that SHS products are always large-grain structures due to high temperatures developed during combustion. In fact, conversion of initial reactants into final products as a result of SHS is a complicated multi-parameter process. Therefore, there are several ways to control it. Provided that the ways to adjust the required conditions are established, one may hope to succeed in the synthesis of nanostructured materials.

About one hundred papers devoted to the self-propagating high-temperature synthesis have been published over last few years. Most interesting of them are discussed below.

I P Borovinskaya suggested a concept[10] of further developments of investigations in the field of the SHS of nanomaterials, in which the formation of nanostructures is related to the combustion mechanism. The major types of such processes were considered including: solid flame combustion 'solid + solid' systems (including one of its modifications, *viz*., combustion with an interstitial molten layer); gas-phase SHS (*e.g*., chain flames, combustion of condensed systems with a gaseous interstitial zone); combustion of 'solid + gas' systems (*e.g*., filtration combustion, combustion of gaseous suspensions).

Let us analyse the potentials of these methods.[10]

In the case of a solid flame SHS process, the combustion reaction proceeds in the diffusion mode. As a result of a chemical reaction between two solid reactants, a continuous layer of solid products starts to grow on grains of one of the reactants, which separates the reactants. Thus, the total rate of the process is limited by the diffusion of the second component through the product layer. Since the change in the specific volume of grains of the starting reactants due to the formation of the product layer atop them is rather small, the size of the particles formed is similar to that of particles of the starting reactants. Owing to the high diffusion resistance of contacting areas of the particles, recrystallisation processes are virtually completely suppressed in such systems.

Thus, nanosized reactants have to be used in order to produce nanosized products by solid flame combustion processes.

In solid-state systems with an interstitial molten layer, the possibility of formation of nanocrystallites depends on the crystallisation and recrystallisation processes and thermal regimes of combustion and cooling of the product after the completion of the reaction.

Among synthetic methods allowing production of nanoparticles, the gas-phase SHS, *i.e.*, combustion of gases giving rise to a condensed product, is of particular importance. The reaction proceeds on nuclei that are formed by an agglomeration of primary particles of the product. The particles grow until the reactants are consumed. If the reaction mixture is allowed to rapidly expand, the process stops due to the fast artificial cooling (quenching) of the mixture. Using this technique, one may stop the particle growth at any required stage. A continuous combustion process with a continuous quenching of the mixture at a certain conversion level, which allows a control over the size of the particles formed, is readily realisable for gaseous mixtures.

Sedimentation of particles from a gaseous suspension gives rise to nanopowders that can be further used in various technological steps involving powder mixtures. The flame-cladding of powders (*i.e.*, their coating with a metal layer) is of particular interest. In particular, nanosized powders of titanium carbide coated with a nickel–molybdenum film, which can be used for production of hard alloys, have been prepared in this way.

Synthesis in the chain flames is one of the modifications of the gas flame SHS.[11] It involves the same processes as described above for the generic gas flame SHS but at a lower temperature. This allows preparation of thermally unstable products. Synthesis in the chain flames is most frequently applied to the preparation of nanosized oxides.[12, 13]

It has to be noted that heterogeneous condensation can also be carried out in flames. In order to make a coating (or deposit a film) on a workpiece, it is introduced into the suitable flame.

The chemical condensation combustion of condensed mixtures is of great interest. In this case, the reactants are brought to the gaseous state prior to the initiation of the reaction. If condensed products are formed exclusively or predominantly in the reaction, the gas-phase stage can even elude detection by researchers. This process is insufficiently explored to date. In the SHS processes that include a gas-phase stage of the chemical conversion, the formation of nanosized products is largely determined by conditions of the chemical condensation, which can be deliberately adjusted.

Unusual mechanisms of formation of nanoparticles are often observed for 'solid + gas' systems. In particular, the filtration combustion of porous solids (*e.g.*, powder bitstones or compacted blanks) or gaseous suspensions is worth mentioning.

The above qualitative analysis taken from the conceptual work [10] demonstrates that diverse physicochemical transformations are realised within the SHS processes, such as: chemical reactions, reaction diffusion, melting, dissolution, crystallisation, recrystallisation, evaporation, sublimation, dissociation, chemical condensation, *etc*. All these processes affect the crystal structure of the product formed. Generation and growth of nuclei are most important for the formation of nanoparticles. Therefore, if the problem of preparation of nanosized products by means of SHS is posed, special attention has to be paid to crystallisation, recrystallisation and chemical condensation.

III. Traditional processes of the self-propagating high-temperature synthesis

Let us first consider traditional SHS processes, which allow preparation of nanomaterials. They include the combustion processes in mixtures of powders and in solid + gas systems. Formally, the combustion involving nanosized powder reactants may also be classified as a traditional SHS process but studies in this field have begun only recently. Unfortunately, most authors report only the synthesis of nanomaterials by means of the SHS and do not analyse the mechanisms and kinetic features of their formation.

1. Preparation of nanomaterials based on powder mixtures

SHS processes involving powder mixtures are predominantly applied to the preparation of nanosized metal oxides and silicon carbide. For instance, nanocrystalline α-Al_2O_3 has been synthesised [14] from a mixture of powdered aluminium nitrate and urea. Heating followed by self-ignition of the mixture resulted in a melt from which a foamed α-Al_2O_3 structure was formed. After grinding the product, α-Al_2O_3 powder with the particle size of $\sim$ 100 nm was obtained.

An Al_2O_3–ZrO_2 solid solution has been synthesised [15] from a mixture of aluminium and zirconium nitrates (oxidants) with urea (combustible material). The process was conducted in the thermal explosion mode in the following sequence: heating of the mixture to 450–600 °C, melting, ignition and combustion. The resultant product composed of agglomerates with a size not exceeding 100 nm was ground, coated with BN, compacted and sintered at 1200 °C. The final product manifested high quality as regards its physicomechanical characteristics: relative density, 99%, the Vickers hardness, 4.45 GPa, crack resistance coefficient K_{1c}, 8.38 MPa $m^{1/2}$, the size of Al_2O_3 and ZrO_2 grains, less than 50 nm.

A technology of self-propagating high-temperature synthesis of β-SiC based on the direct heating of the green mixture has been developed.[16] The authors used an original means of heating, *viz*., the burner (flare) was moved along the sample with a velocity equal to that of the combustion front propagation. The size of the β-SiC grains produced was close to the nanorange (< 200 nm) and virtually independent of the particle size of the parent silicon.

Preparation of nanosized silicon carbide attracts a lot of attention. A direct synthesis of SiC has been accomplished [17] in the thermal explosion mode with microwave heating. The initial Si and C particles were of equal size ($\sim$ 43 μm). The silicon carbide powder produced was composed of needle-shaped particles with a diameter of 36–76 nm and length of 360–1500 nm.

In those cases where smaller Si and C particles were used, small fibres were produced. Note that in this process the combustion is initiated in the bulk of the sample and then propagates towards its surface in the SHS mode. This model is supported by conclusions of a theoretical investigation [18] into post-induction phenomena occurring in the course of a thermal explosion in 'porous reagent–reactive gas–solid product' systems.

A procedure for the preparation of an engineering ceramic according to the reaction:

$$TiO_2 + Al + C + ZrO_2 \xrightarrow[Ar]{SHS} Al_2O_3 + TiC + ZrO_2$$

has been described.[19] The reaction product was a mixture of crystalline TiC and ZrO_2 with amorphous Al_2O_3. The size of the TiC and ZrO_2 crystallites was *ca*. 20 nm. Crystallisation of Al_2O_3 from the amorphous phase occurs after completion of the chemical reaction. Note that although ZrO_2 is not involved in the reaction it undergoes structural transitions resulting in a decrease in its particle size from 10 μm to 20 nm.

The problem of what the chemical reactions or phase or structural transitions are that occur in the combustion wave during the SHS processes is of primary importance. Many phase and structural transformations of substances occur far beyond the combustion front when the chemical processes are already completed. This can lead to substantial changes in the microstructures of the combustion products. Figure 1 shows some typical examples of the dependence of the product grain size on the distance from the combustion front. The data presented suggest [20] that the recrystallisation processes leading to an increase in the grain size (by a factor of 10) [20] proceed actively in the system after completion of the chemical reactions in the combustion wave. Definitely, monitoring of the evolution of the microstructure is a

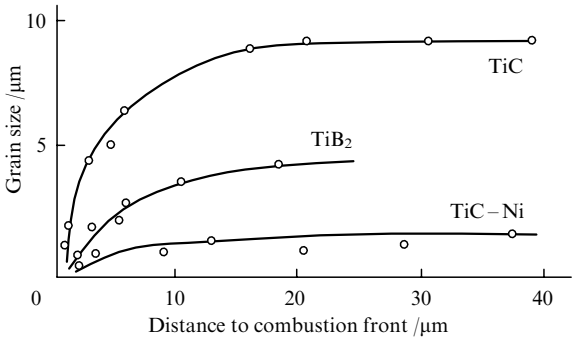


Figure 1. The dependence of sizes of TiC, TiB_2 and TiC – Ti grains on the distance from the combustion front.[20]

complicated task. Its solution requires dedicated techniques and high-resolution instruments.

2. Preparation of nanomaterials based on 'powder + gas' systems

An interesting two-stage synthesis of nanosized silicon carbide has been reported.[21] Its first stage involved combustion of a mixture of powdered Si and C (with an excess of Si) in a nitrogen atmosphere, which gives rise to Si_3N_4 and SiC. The second stage included a reburdening of the mixture produced with carbon (soot) followed by the carbothermal reduction of Si_3N_4 to Si and subsequent interaction of the latter with carbon. As a result of this two-stage process, the initial Si + C mixture is converted into nanosized SiC. Direct interaction of Si with C results in the formation of coarser particles. The chemical reaction may be represented as follows:

$$\mathrm{Si} + m\,\mathrm{C} \xrightarrow{\mathrm{N_2}} \frac{1-m}{3}\,\mathrm{Si_3N_4} + m\,\mathrm{SiC} + Q_1,$$

$$\frac{1-m}{3}\,\mathrm{Si_3N_4} + m\,\mathrm{SiC} + (1-m)\mathrm{C} + Q_2 \longrightarrow \mathrm{SiC} + \mathrm{N_2}\uparrow.$$

The scheme of structural changes occurring with the starting materials and intermediate products during the SHS is shown in Fig. 2.

A method of preparation of SiC – AlN powders (solid solutions) by means of combustion of mixtures of micrometer-sized powders of Al, C and AlN and a submicrometer powder of Si in a nitrogen atmosphere at a pressure of 4 atm has been suggested.[22] The authors used two routes, *viz*., synthesis in the thermal explosion mode and the propagating combustion wave mode. The SiC – AlN solid solutions prepared using both the filtration combustion and thermal explosion represented powders with the particle size smaller than 200 nm. The crystal structure of the SiC – AlN powder synthesised using the SHS showed disorder at the atomic level. In order to produce ceramics, the powdered SiC – AlN solid solutions were sintered. Such a thermal treatment led to the ordering of their crystal structures. The obtained engineering material possessed high mechanical properties, thermal and chemical stability.

Synthesis of filamentous silicon nitride with a particle diameter of 60 – 400 nm has been reported.[23] A silicon powder with the particle size of 0.5 – 2.0 μm doped with NH_4F and Al powder mixed with a β-Si_3N_4 powder (acting as a thinner) was used as the starting material. The reactants were mixed in the following proportions: $Si : Si_3N_4 : NH_4F : Al = 87 : 10 : 2 : 1$ (mass %). The combustion was conducted in a nitrogen atmosphere at a pressure of 100 atm. The authors emphasise the key role of NH_4F (it favours a decrease in the adiabatic combustion temperature and in the heat conductivity and accelerates the crystal growth) in the formation of β-Si_3N_4 nanofibres. The morphology of the silicon nitride microstructure is shown in Fig. 3. It is clearly seen that the crystals are either straight, stranded or wavy in shape.

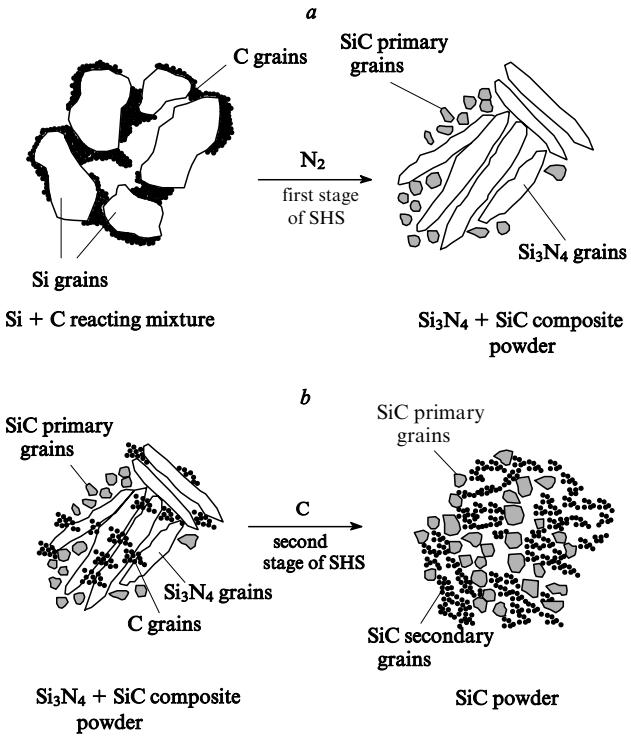


Figure 2. Morphological changes occurring in the course of the SHS of silicon carbide from powdered Si and C in a nitrogen atmosphere; (*a*) the stage of formation of the SHS products, Si_3N_4 + SiC; (*b*) the stage of SiC formation.

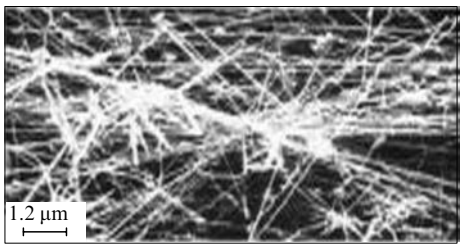


Figure 3. The morphology of silicon nitride microstructure.[23]

Two schemes for the preparation of nanosized β-Si_3N_4 – β-SiC materials by means of the solid-state chemical synthesis (*a*) and in the SHS mode (*b*) [24] are shown in Fig. 4.

Self-propagating high-temperature synthesis of various hydrogen-containing substances [25, 26] including nanosized hydride powders has been accomplished as a part of a systematic investigation into the combustion processes of metals and alloys in a hydrogen atmosphere. Unfortunately, the mechanism of formation of the nanopowders was not discussed.

The preparation of nanosized boron nitride powders in the SHS mode can be carried out in three ways according to the following reactions:[27]

(1) synthesis from elements

$$\mathrm{B} \xrightarrow{\mathrm{N_2}} \mathrm{BN},$$

(2) synthesis involving boron oxide

$$\mathrm{B} + \alpha\text{-}\mathrm{B_2O_3} \xrightarrow{\mathrm{N_2}} m\,\mathrm{BN} + n\,\mathrm{B_2O_3} + \mathrm{O_2}\uparrow,$$

(3) synthesis from B_2O_3 including a stage of magnesiothermic reduction

$$\mathrm{B_2O_3} + 3\,\mathrm{Mg} \xrightarrow{\mathrm{N_2}} 2\,\mathrm{BN} + 3\,\mathrm{MgO}$$

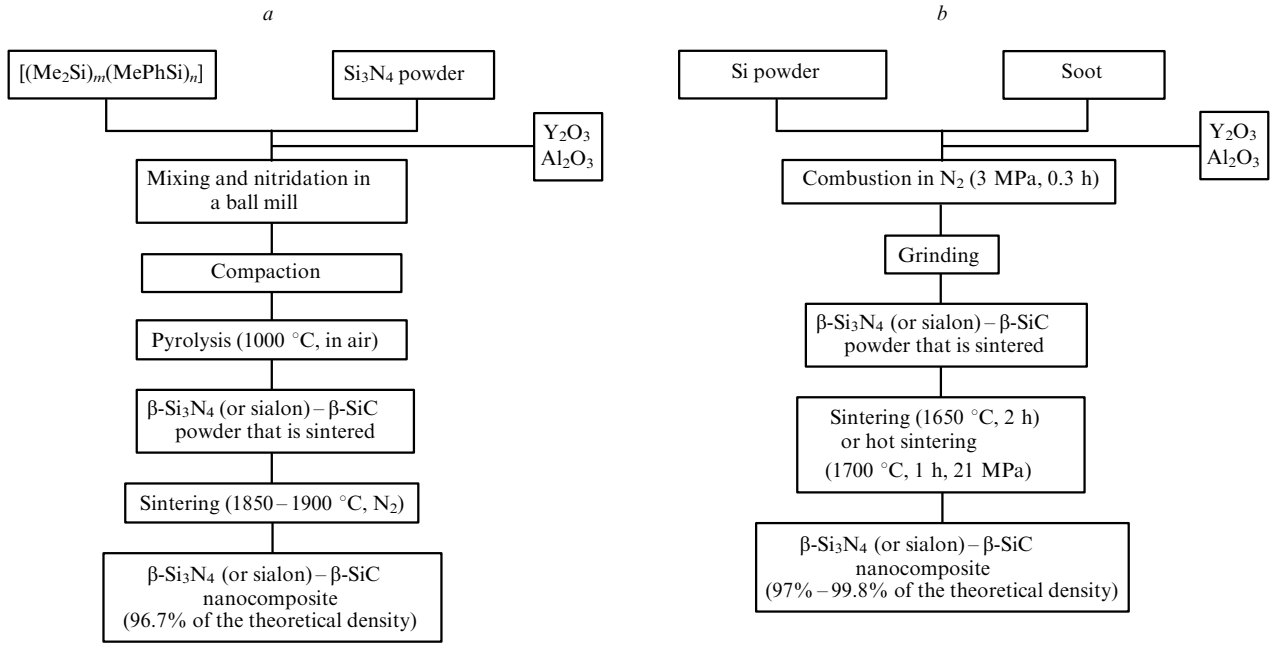


Figure 4. Two schemes of the preparation of Si_3N_4 – SiC nanocomposites from powders;[24] (*a*) chemical pathway, (*b*) in the SHS mode.

In all the cases, the products represented BN crystallites with a size of 100 – 200 nm combined in larger agglomerates.

In order to produce nanosized particles, it was necessary that the combustion product (semi-finished material) underwent further mechanical and thermochemical processing using acids and alkalies under drastic (for the dissolution of MgO) or mild (for the preparation of nanocrystalline samples through the chemical dispersion) conditions. The shape and size of BN particles were determined and the specific surface areas of both semi-finished material and the final product were calculated. Table 1 summarises the major characteristics of BN prepared by different methods.

The mechanical processing of the semi-finished material did not result in complete disintegration of the crystallites and thus the final product represented a powder containing agglomerated particles with different specific surface areas. Subsequent thermochemical treatment (chemical dispersion †) resulted in further disintegration of crystallites and in an increase in the specific surface area of the product. Fully disintegrated powders were obtained only from semi-products prepared by magnesiothermic reduction of B_2O_3. Such powders were composed of pure crystallites with a size of 100 – 200 nm. The specific surface area of the final product amounted to ~ 60 m^2 g^{-1}. The effectiveness of the above approach to the preparation of nanosized particles depends on whether crystallite formation process during the SHS can be controlled.

The microstructures of a boron nitride powder produced in the SHS mode before and after the chemical dispersion are shown in Fig. 5.[27]

† The chemical dispersion is one of the modifications of the thermochemical treatment of a product,[28] which leads to dissolution of boundary (typically, defective) layers of crystallites and to removal of contaminations, whereupon the crystallites themselves are not dissolved. As a result of such a treatment, a polycrystalline product is disintegrated into single-crystalline particles.

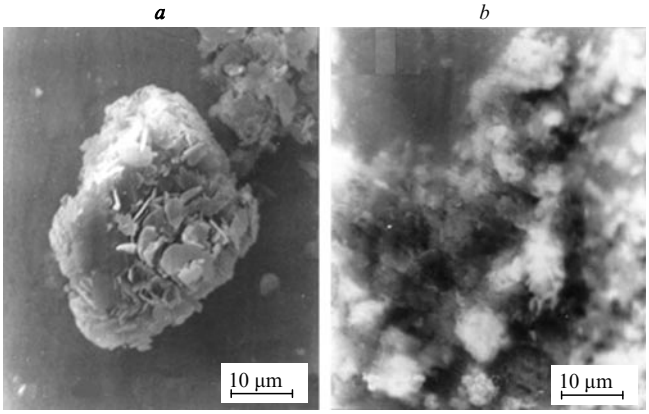


Figure 5. The microstructure of a BN powder;[27] (*a*) agglomerated hollow particles of powdered boron nitride taken from the SHS product, (*b*) single-crystalline BN formed as a result of the chemical dispersion.

Table 1. Self-propagating high-temperature synthesis of fine BN powders.[24]

Powdered reactants	Intermediate product	Method for the isolation of the final product	Specific surface area /m^2 g^{-1}	
			of intermediate product	of target product
B	Polycrystalline BN cake	chemical dispersion	~6	10 – 12
$B + B_2O_3$	BN + B_2O_3 cake	treatment with water, chemical dispersion	4.5 – 5.5	8.5 – 12.0
$B_2O_3 + 3$ Mg	BN + MgO cake	chemical enrichment, chemical dispersion	3.0 – 10.5	9.5 – 60.0

IV. Gas-phase self-propagating high-temperature synthesis

Despite the fact that the combustion of gases is fairly well investigated (in contrast to the combustion of condensed systems), the gas-phase SHS has not been sufficiently explored to date. This is because there are only a few known gaseous systems that can undergo combustion to form condensed products. In particular, three processes have been studied:

(1) sodiothermic reduction of chlorides in the gas phase giving rise to chemical elements or compounds;

(2) gas-phase oxidation of combustible gases (hydrocarbons, silanes, boranes, *etc.*) with the formation of respective oxides;

(3) chemical reactions in independently generated flames that played a role of gas-phase 'chemical furnaces'.

1. Self-propagating high-temperature synthesis including a stage of sodiothermic reduction of chlorides

A remarkable feature of the sodiothermic reduction of chlorides is the formation of water-soluble NaCl as a by-product of the SHS. Therefore, the isolation of the target product from the reaction mixture faces no problems in contrast to that in the cases of magneso- or aluminothermy.

For the first time, the process of the sodiothermic reduction of chlorides by means of the gas flame combustion has been applied to the preparation of powders of reduced silicon and silicon and titanium nitrides [29, 30] using gaseous silicon and titanium chlorides as reactants and sodium or sodium–potassium vapour as the reducing agent. Other examples of syntheses of nanosized products through the SHS including a stage of sodiothermic reduction may be found elsewhere.[31–33] In particular, a gas-phase combustion of $TiCl_4$ and BCl_3 in sodium vapour yielded a titanium diboride powder, which represented agglomerates with a size of 20–100 nm composed of spherical TiB_2 particles with the diameter of less than 15 nm (after vacuum sublimation and annealing at 1000 °C) (Fig. 6).[31]

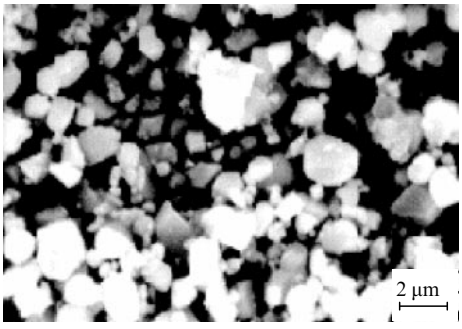


Figure 6. Nanoparticles of titanium diboride.[31]

An interesting example of preparation of a nanosized TiAl powder (~ 6 nm) under conditions of zero gravity, which favoured the formation of a stable air suspension has been reported.[34] Different condensation modes and their influence on the morphology of the particles formed were considered.

2. Gas-phase oxidation of combustible gases

Self-propagating high-temperature synthesis of particles and films of Si, Ge, SiO_2, GeO_2, Si_3N_4 by means of oxidation and pyrolysis of silane or germane [11, 35, 36] as well as gas-phase synthesis of ultradispersed amorphous powders of SiC, Si_3N_4, SiN_xC_y and of crystalline BN in the combustion mode [37] have been reported. The main advantage of this method for the production of insulating, protective and semiconductive films or nanosized powders is the possibility of performing the synthesis at relatively low temperatures and pressures, which allows one to avoid high charge densities on surfaces of the films, which greatly enhances the quality of the semiconducting products.

The chain character of the SHS processes makes it possible to apply a variety of well-established techniques developed for chain processes for their control without recourse to plasmochemistry or photochemistry. In particular, small amounts of suitable additives can be used to promote (*e.g.*, hydrazine) or, *vice versa,* inhibit (*e.g.*, olefins) the SHS. In most cases, the application of plasmochemistry is undesirable since the charged species formed in the plasma increase the surface charge density and thus deteriorate the product quality. Additionally, surface defects are developed under the action of flame or light.

Unfortunately, it is information on the products obtained that is normally given in publications devoted to the gas-phase SHS, whereas a discussion of relations of the combustion mechanism with the condensation processes and the effects of hydrodynamic factors on the combustion and the structure formation is lacking. A dependence of the morphology of the particles formed on the gas flow regime (laminar *vs.* turbulent) and its change upon a flow crisis have also eluded exploration.

To date, the gas-phase SHS has been studied only on a few case systems since gas mixtures forming solid products and having a relatively large thermal effect upon combustion are scarce. Further progress of this method can be connected with the utilisation of additional heating sources (*e.g.*, recuperative heating of reactants, plasma-induced heating, electrogas heating, *etc.*).

Realisation of the SHS using gaseous suspensions as reactants is highly problematic due to low heat evolution and poor heat exchange between particles. In this case, preliminary partial or complete gasification of reacting particles followed by a condensation of the combustion product is typically applied. The particles formed in such processes are usually substantially smaller than those of the starting reactants.

An original version of gaseous suspension SHS has been suggested.[38] In order to initiate the SHS, it is necessary to generate a cloud of metal particles in an atmosphere of a gas (oxygen, nitrogen, ammonia or another gas), which is subsequently ignited by a spark discharge. After completion of the reaction, the products are collected on a filter. Powders of Al_2O_3, MgO, SiO_2, TiO_2, ZrO_2, FeO, TiN and ZrN with the particle size of 10–100 μm were synthesised by this method.

Similar results concerning the preparation of nearly monodisperse spherical particles of γ-Al_2O_3, Fe_2O_3, Fe_3O_4, ZrO_2 with the size of ~40 nm have been reported.[39, 40] Fine metal particles with the size not exceeding 10 μm dispersed in a gas phase were taken as the starting reactants. The combustion process was induced by a diffusion or homogeneous flare.

3. Syntheses in flames

Pyrolysis of substances in flames may also be regarded as a modification of the gas-phase SHS. In this case, both the substances that are introduced into the flame and the chemical components of the flame itself can be involved in the synthesis, the reactions involving the flame components may differ from those involving the external components introduced to the flame (the formation of the target product). In those cases where the flame is chemically inert, it may be considered as a gas-phase 'chemical furnace' that only provides high temperature. Using this approach, it was possible to synthesise the following nanosized substances: TiAl,[41] Ti-W,[42] SiO_2,[42, 43] Si_3N_4,[44] TiB_2,[31] GaN,[45] Y_2O_3–Eu [46] and AlN.[47] For instance, SiO_2 nanopowders were prepared from an SiH_4–H_2–O_2–Ar gas mixture using a hybrid gas burner.[42] Adjustments of combustion conditions (*e.g.*, the stoichiometric composition of the fuel gas for the burner) made it possible to produce particles with the sizes ranging from 6–8 nm (at high oxygen concentration) to 18–20 nm (at low oxygen concentration).

V. Stimulated self-propagating high-temperature synthesis

It is well known that the SHS process can easily be subjected to external stimulation. The simplest and most common means is thermal action. Owing to a thermal energy transfer to the original mixture or the combustion zone, the temperature and combustion rate can be deliberately increased and thus the composition and characteristics of the combustion products can be affected.

Joule heating by passing electric current through the burden is one the simplest ways of such an energy input. Typically, two types of Joule heating are used in experiments, *viz*., the contact heating, which results in bulk self-heating of the whole sample turning into the thermal explosion (the so-called electrothermal explosion, ETE), and local heating leading to a local ignition and formation of a combustion wave.

The former method was first suggested by Knyazik *et al*.[48] in the mid 1980's. It was further developed and applied to the study of heat liberation kinetics of high-temperature (> 3000 °C) and fast reactions in heterogeneous condensed systems (*e.g*., Ti – C, Ti – B, Ta – C, Ni – Al, *etc*.).[49 – 51]

The latter method referred to as field-activated SHS was elaborated by Munir in the late 1990's.[52] It is used to enhance the completeness of the combustion in the solid flame SHS processes.

Several attempts to produce nanostructured materials making use of the thermal action on the combustion products have been undertaken.[20, 53, 54] In particular, quenching of a burning Ti + 2B mixture allowed production of TiB_2 grains with different sizes depending on the combustion front position.[53] The grain growth proceeded very fast resulting in a size change by one order of magnitude (see Fig. 1).

1. Mechanochemical self-propagating high-temperature synthesis

The SHS of nanosized materials can most efficiently be influenced by mechanical actions. These include mechanical treatment of a burden, mechanical action on a burning sample and mechanical treatment of products. All three methods give interesting results.

Mechanical activation of reactants before the initiation of the SHS process is a very important stage. This increases the reactivities of the particles that are treated due to an increase in the defect concentration and/or the reaction area (due to a decrease in the particle size). Therefore, the mechanical activation prepares the particles for the active involvement in the reaction. Its maximum effect is observed in the case of 'ideal' [55] solid flame SHS processes. For the liquid-phase SHS, such an effect can be either weak or even totally absent.

The mechanical activation can influence the velocity and conditions of the combustion front propagation (macrokinetic effect) as well as the shape and size of the crystallites and porosity of the structure (structural effect).

A control over processes of the wave propagation and of the structure formation in the product is a challenging task. To date, only the problems of the initiation of the SHS in weakly exothermic systems and of a decrease in the size of crystallites of the combustion products have been resolved.

Several examples of the influence of the mechanical activation on the course of the SHS are given below.

Preparation of titanium carbide with the composition $Ti_{44}C_{56}$ from a mixture of powdered Ti and C has been described.[56] Prior to the initiation of the SHS process, Ti and C powders were mechanically activated in a ball mill. The titanium carbide particles produced represented polycrystals with the size of ~ 0.5 μm composed of crystallites with the size of ~ 3 nm. It is very likely that subsequent mechanical or thermochemical processing of the product can result in a powder containing true nanosized particles. Note that the product can be formulated as $TiC_{1.27}$ or $Ti_{0.79}C$, which corresponds to carbon overstoichiometry. Therefore, the Ti sublattice of the product should have numerous defects (vacancies). This result is new in principle, which requires, in our opinion, a careful verification.

A mechanochemical synthesis of β-SiC starting from powdered Si and C has been accomplished.[57] It was shown that mixing of the starting reactants in a ball mill resulted in the full conversion of Si and C to β-SiC (100% degree of conversion). The product formed had a homogeneous structure with the grain size of ~ 7 nm.

A titanium carbide powder with the particle size of 30 nm has been produced by pressure-assisted sintering.[58] The deformation temperature of the resulted nanosized powder is 500 °C lower than the conventional temperature. The same authors reported a synthesis of nanostructured TiB_2.[59] The microstructure of the product and the particle size distribution therein are shown in Figs 7 and 8, respectively.

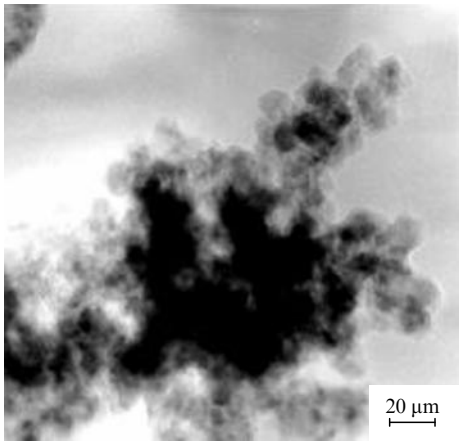


Figure 7. The microstructure of TiB_2.[59]

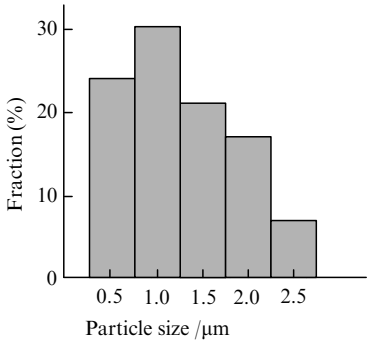


Figure 8. Size distribution of TiB_2 particles.[59]

Grinding of combustion products is an efficient way to produce nanosized particles. For instance, mixing and ball milling of powdered silicon and titanium with the particle sizes of 25 – 30 μm and 44 μm, respectively, yielded a series of silicides $TiSi_x$ (where x is defined by the ratio of the reactants) with a particle size less than 100 nm.[60] In cases of high Si content in the reaction mixture (34 at.% – 60 at.%), the reaction proceeds in the thermal explosion mode. During the mechanical activation, disintegration of the reactants occurs, which is accompanied by formation of grains of products with the following compositions: $Ti_{33.4}Si_{66.6}$, $Ti_{62.5}Si_{37.5}$,$Ti_{50}Si_{50}$ and $Ti_{55.6}Si_{44.4}$. For lower silicon contents, the components interact slowly giving an amorphous product. This process is especially interesting since it provides an example of a control over the final structure of the target powders.

Syntheses of various compounds (*e.g*., TiN) and alloys (*e.g*., Fe – Al – Cr) using mechanical activation have been described.[61 – 63] Unfortunately, the thermal patterns of the proc-

esses (*i.e.*, emergence of heating centres, thermal explosion, flame propagation, *etc.*) were not analysed.

The mechanical activation was shown[64] to have a great potential for the self-propagating high-temperature synthesis of metal alloys (*e.g.*, Ni–Al, Ni–Si, Ni–Ge, Ti–Ni) and oxides [*e.g.*, Ba–Zr(Ti, Hf, Mo, W, Al)–O, Ca–Mo–O, Sr–Mo–O, Pb–Mo–O, *etc.*]. The influence of the mechanical activation of both the reactants and the products was carefully studied and the industrial applicability of the technique was convincingly demonstrated. It was noted that even brief mechanical activation allows production of homogeneous monophasic nanosized powders of complex oxides, nitrides, borides, carbides, and so on with a particle size of ~ 10 nm. It was concluded that metastable phases normally formed as a result of the mechanical activation can be produced from equilibrium intermetallide products of the SHS as well.

A dedicated study aimed at the preparation of nanosized composite powders in the system TiB_2-TiAl_3 starting from powdered Ti, Al and TiB_2 has been conducted.[65] Prior to the SHS, the powder mixtures containing Al–50 at.% Ti and Al–25 at.% Ti–10 vol.% TiB_2 were first activated mechanically in a ball mill and then heated at the rate of 0.33 K s^{-1} and maintained *in vacuo* at various temperatures. After that, flashing and compaction of the mechanical mixtures *in vacuo* were followed by their heating to the sintering temperature. The microstructures of the final products TiB_2-TiAl_3 are shown in Fig. 9. Nanosized grains of TiB_2 (25 nm) are well-resolved in the microphotography (see Fig. 9 *b*).

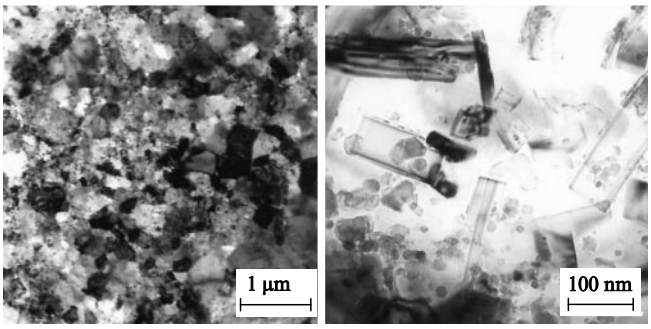


Figure 9. The microstructure of TiB_2-TiAl_3 nanocomposites;[65] (*a*) $TiAl_3$ grain, (*b*) TiB_2 grain.

The dependence of the size of the product grains on the duration of the mechanical treatment is plotted in Fig. 10 for the two systems, *viz.*, Al–50 at.% Ti (*a*) and Al–25 at.% Ti–10 vol.% TiB_2 (*b*). It is clearly seen that in the case of the Ti–Al system (see Fig. 10 *a*), prolonged mechanical treatment leads only to an insignificant increase in the grain size apparently approaching saturation, whereas in the Ti–Al–TiB_2 system (see Fig. 10 *b*), the grains become noticeably smaller after longer treatments under conditions of the isothermal storage at 973 K. Therefore, the effect of the addition of TiB_2 on the growth of $TiAl_3-TiB_2$ grains is revealed.

2. Gravity and shock-wave actions on the SHS products

In order to control the grain structure of materials, one can take advantage of gravity, which can lead to both the increase and decrease in the grain size of the combustion products.

The influence of the load factors on the microstructure has recently been demonstrated[66] for a $TiC-Cr_3C_2-Ni-Mo$ composite material (*i.e.*, a complex titanium–chromium oxide with a nickel–molybdenum binder) prepared by SHS from a powdered mixture of titanium, chromium, nickel and molybdenum oxides with aluminium and carbon (as soot or graphite). The grain size of

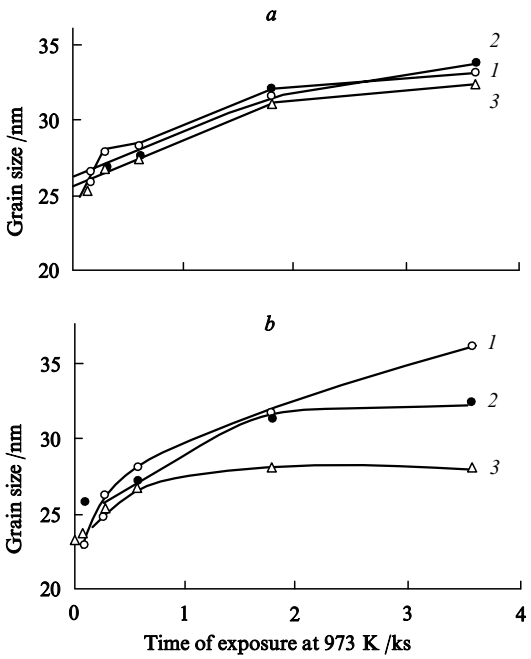


Figure 10. Grain size *vs.* duration of the mechanochemical treatment dependences for two systems: Al–50 at.% (Ti) (*a*) and Al–50 at.% Ti–TiB_2 (*b*).[65]
Duration of mechanical activation /ks: (*1*) 180, (*2*) 360, (*3*) 2880.

the solid product formed is plotted in Fig. 11 as a function of the load factor applied. It was established that this affects not only the microstructure but also the combustion rate and temperature along with the phase and chemical composition of the product. For instance, on going from the load factor of 10 g to 500 g, the content of bound carbon in the material was either increased 1.5-fold (if soot was taken as a reactant) or, *vice versa*, decreased more than two-fold (if coarse-grain graphite was used). This is explained by the gravity-assisted segregation of the reactants in the combustion wave under the action of the load factor.

The formation of unusual structures upon combustion of a NiO–Ni–Al system has been reported.[67] This experiment was conducted aboard the space station 'Mir' under microgravity conditions. As a result of the zero gravity, the molten intermetallide combustion product NiAl was deposited as large drops onto the surface of the oxide phase Al_2O_3 giving rise to mushroom-shaped crystallites (Fig. 12).

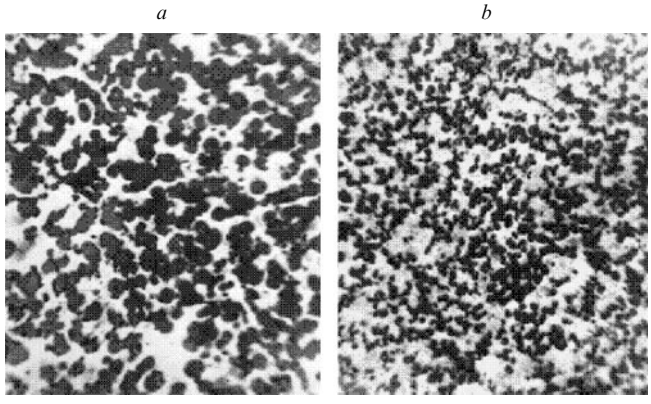


Figure 11. Effects of the load factor on the microstructure of the $TiC-Cr_3C_2$ + Ni–Mo system.[66]
(*a*) load factor of 100 g, (*b*) load factor of 1000 g.

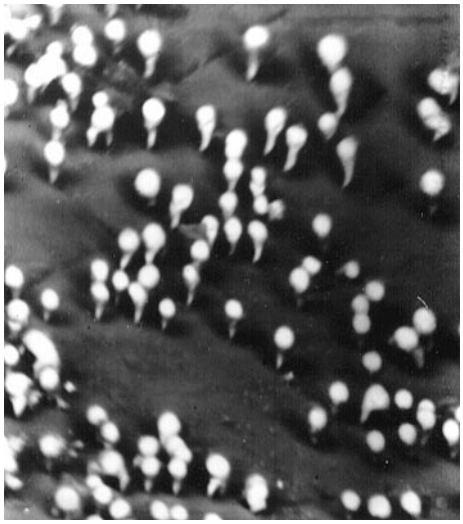


Figure 12. The formation of the NiAl intermetallide phase on the surface of the Al_2O_3 oxide phase under conditions of the zero gravity.[67]

A shock wave can be applied to reactants in the course of the SHS or to reaction products after its completion as an alternative means of the mechanical activation. The effects of shock waves on reactants at a certain stage of the process are different depending on the shock wave amplitude, loading diagram and characteristics of heat dissipation. All other parameters being the same, an increase in the pressure first leads to compaction and deformation of reactants (no chemical reactions are yet initiated). Upon further increase in the pressure, the concentration of structural defects is increased and an intense intermixing and heating of the reactants occurs, which leads to the initiation of the chemical reaction. Shear strains present in the shock wave front disintegrate the product so that only very fine particles are formed. A control over the heavily strained state of the matter that develops upon the shock-wave action would make it possible to deliberately change the chemical composition thus producing materials with preset characteristics at lower energy consumption.

Shock-wave compaction of titanium carbide prepared by the SHS has been reported.[68]

An attempt has been undertaken [69] to combine the SHS with the shock-wave load in the synthesis of titanium carbide. The size of the product grains produced in this experiment did not exceed 1 μm. The authors asserted that titanium carbide prepared in this way manifested improved mechanical properties. Such an approach has also been applied to syntheses of other carbides,[68–71] intermetallides [72, 73] and silicides.[74–79] However, according to the data reported, no nanostructures could be obtained upon the direct shock wave action on a sample during the SHS. Therefore, grinding of the final product remains the most suitable solution of the problem.

3. Self-propagating high-temperature synthesis in electric and magnetic fields

The effects of the electric and magnetic fields on the course of the SHS have been studied. In particular, in the SHS of tantalum carbide, the starting powders of Ta and C were mechanically activated and simultaneously subjected to the electric field.[80]

$$\text{Ta (45 μm)} + \text{C (13 nm)} \longrightarrow \text{TaC (30–50 nm)}.$$

This solid-phase system (neither solid reactants nor the products melt during the SHS) is characterised by a linear increase in the combustion rate and temperature with an increase in the electric field strength. The degree of conversion can be increased (*i.e.*, the underburning degree can be reduced) using Joule heating. It was found that two types of particles (*viz.*, rounded and

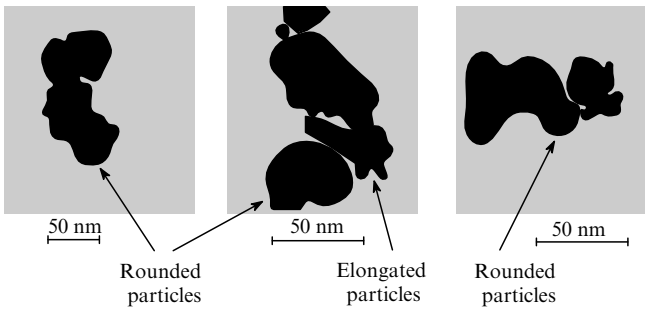


Figure 13. The microstructure of nanosized TaC particles as a function of the electric field strength.[80]
E /V cm^{-1}: 6.92 (*a*), 14.61 (*b*), 30.33 (*c*).

elongated, Fig. 13 *a*, *b*) are formed as a result of the SHS. Presumably, the particles tend to acquire a rounded shape at stronger electric fields. The composition of the product is also affected by the electric field strength. Indeed, the final product is composed of Ta_2C and TaC particles when the synthesis is performed at weak electric fields whereas only TaC particles are found at strong fields.

A procedure for the preparation of nanosized $MoSi_2$ by SHS combined with the mechanical activation and the electric field action has been described.[81] For the synthesis of molybdenum disilicide, a mixture of Mo and Si powders was used:

$$\text{Mo (150 μm)} + \text{Si (45 μm)} \longrightarrow \text{MoSi}_2\text{ (68–75 nm)}.$$

First, the Mo and Si powders were mechanically activated, then compacted, subjected to the electric field and ignited. The mechanical mixtures (Mo + Si) represented agglomerates with the sizes ranging from 0.2 to 200 μm composed of nanosized crystallites of molybdenum and silicon. According to powder X-ray diffraction data, the molybdenum and silicon particles had the sizes of 54 nm and 34 nm, respectively (note that the size of Mo crystallites varies in the range from 5 to 100 nm). The authors compared structures of the $MoSi_2$ products prepared by two routes, *viz.*, by combining the SHS with the mechanical activation (MASHS) and a complex approach involving mechanical activation, SHS and action of the electric current of up to 1500 A (MAFAPAS, Fig. 14). In the former case, the size of $MoSi_2$ grains reached 45 nm whilst in the latter case, 73 nm.

Yet another $MoSi_2$ synthesis has been reported.[82] In this work, the influence of the mechanical and electric activation on the formation of a dense $MoSi_2$ ceramics was elucidated. Finer Mo powders (3–7 μm) were taken for the synthesis. Prior to the SHS initiation, the reactants were mechanically activated in a

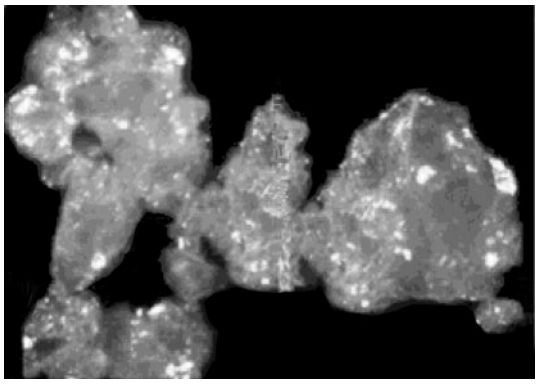


Figure 14. Nanocrystalline $MoSi_2$ produced from Mo and Si powders using the mechanical activation and electric field action.

planetary ball mill, compacted and then subjected to the electric field. The size of crystallites in the dense ceramics produced was ~ 20 nm.

The method applied to the preparation of the starting powders for this SHS process is worth a special note. The Mo and Si powders were ground in separate planetary ball mills. The size of the molybdenum particles decreased from 3–7 μm down to 20–110 nm depending on the milling conditions. With an increase in the duration of the mechanical treatment and in the electric field strength, the grain size decreased. This technique is of potential use in the technology of nanopowders.

The SHS method combined with mechanical activation of reactants has been utilised for the preparation of a composite based on $TiAl_3$ with Al_2O_3 inclusions.[83] Sintering of Ti and Al powders was conducted on a support, through which electric current passed. The growth of grains during sintering was decelerated by the presence of Al_2O_3 particles. The composite material produced had the grain size of ~ 10 nm. The authors noted that a decrease in the particle size resulted in the enhancement of the composite mechanical properties.

Synthesis of an AlN–SiC composite from powdered α-Si_3N_4, Al and C has been described.[84]

$$\alpha\text{-}Si_3N_4\,(0.5\ \mu m) + Al\,(7\ \mu m) + C\,(10\ \mu m) \longrightarrow$$

$$\longrightarrow AlN - SiC\ (< 100\ nm).$$

The synthesis included the following steps (Fig. 15): compaction of the starting Si_3N_4, Al and C powders, formation of blanks for the SHS process, induction heating followed by the thermal explosion turning into the SHS. As a result, a solid solution of AlN–SiC in Si_3N_4–Al–C was produced.

The authors analysed the mechanism of the formation of the AlN–SiC solid solution as a function of the electric field strength. They found that dissolution of silicon nitride in molten aluminium occurs in the first stage and only after that nitridation of aluminium starts. The reaction proceeds in the temperature range from 600 °C (melting point of aluminium) to 1400 °C.

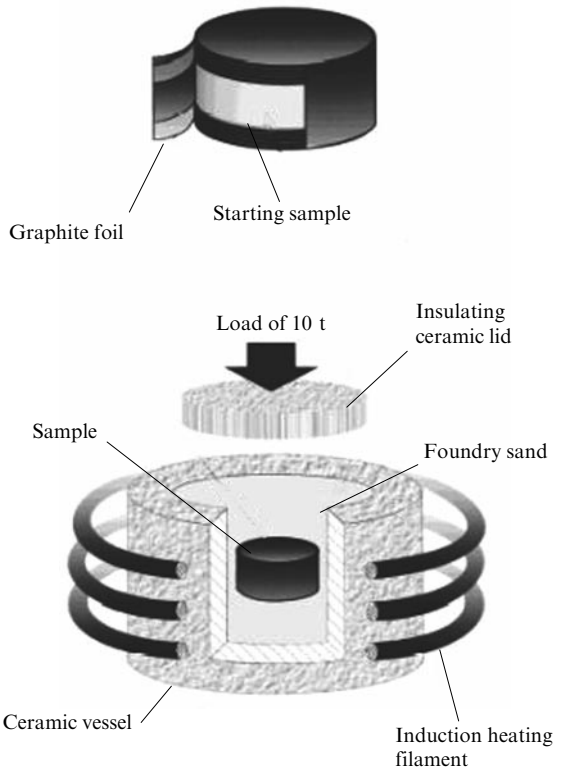


Figure 15. Experimental setup for the SHS of a solid solution of AlN – SiC in Si_3N_4–Al–C.[84]

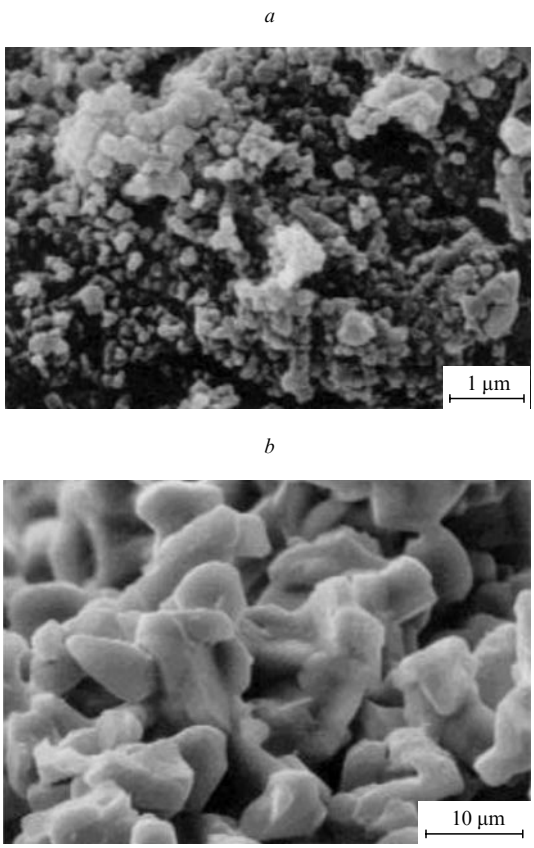


Figure 16. The microstructures of two solid solutions of AlN–SiC in Si_3N_4–Al–C produced at 1750 °C (*a*) and heated to 1850 °C (*b*).[84]

It is noteworthy that the microstructure of the product varies substantially depending on the annealing temperature of the product. The microstructures of solid solutions produced at temperatures of 1750 °C and 1850 °C are shown in Figs 16 *a* and 16 *b*, respectively. The authors did not perform a precise determination of the particle size, but, in their opinion, particles smaller than 100 nm were present in the solid solution.

The efficiency of the mechanical activation in the synthesis of nanosized powders by the SHS has recently been demonstrated [85] in the preparation of nanocrystalline $NbAl_3$ powders. The process was implemented in two steps: the mechanical activation of the starting Nb and Al powders was followed by the SHS. The powders were ground in a mill, compacted and then the SHS was initiated *in vacuo*. It is of note that agglomerates as large as 100 μm were present in the burden after the mechanical activation, which however disappeared after the completion of the SHS. The combustion product contained $NbAl_3$ particles with a size of ~ 60 nm.

Studies devoted to the preparation and compaction of iron powders have recently been reviewed.[86] The authors discuss features of the microwave-induced ‡ syntheses of iron powders and classify diverse methods of the preparation of nanocrystalline iron powders and of ceramic nanopowders (Table 2). They note that all the preparative techniques (except for that based on the microwave technique) are characterised by low performance. Additionally, not all of the techniques allow preparation of powders with the uniform size distribution. The authors conclude

‡ The microwave-induced synthesis can be considered as a modification of the SHS since it involves a stage of a self-propagating reaction that is initiated after ignition of the burden.

Table 2. The methods for the synthesis of ceramic nanopowders.[86]

Method of synthesis	Products
Mechanical activation in ball mills	Fe, Co, Ni, NiAl, TiAl, FeSn
Synthesis under laser irradiation	AlN, MnO_2, TiO_2, Ti
Condensation from a gas-phase	Fe, MgO, Cu, TiO_2
Sputtering deposition	Al, Cu, Mn
Chemical deposition	SiC, $BaTiO_3$, W–Cu, Mo–Cu
Plasma induction	Fe, AlN, Cu, metal borides, nitrides and carbides
Microwave plasma	Fe, Co, Mo, Ni, TiO_2, ZrO_2,Al_2O_3

that the microwave-induced synthesis of powders is the most cost-efficient method for the preparation of powders with the particle size of 10–15 nm.

Methods for the preparation of nanosized niobium aluminide using SHS preceded by the mechanical activation of the burden have been surveyed recently.[87] Different modes of the mechanical activation as applied to the synthesis of iron aluminides by the SHS have been considered.[88] The following scheme of the technological process was suggested: preparation of a mixture in a ball mill, formation of cylindrical blanks for the SHS, combustion of the blanks with the online monitoring by means of synchrotron radiation. The results of this monitoring are summarised in Table 3. It was found that the mechanical treatment of the initial mixture reduces the ignition temperature by more than 100 °C.

Table 3. Powder X-ray diffraction data on the phase composition of different cross-sections of an iron aluminide sample prepared by the SHS.[88]

Probing depth /mm	Phases revealed	Crystallite size /nm
0 (surface of the sample)	FeAl, Fe_2O_3, Fe_2Al_5	–
0.5	FeAl, Fe_2O_3	25
1.5	FeAl	40
2.5	FeAl	35
3.5	FeAl	25
4.5	FeAl	35
5.0 (back side of the sample)	FeAl, Fe_2O_3, Fe_2Al_5	–

The SHS of titanium nitride upon grinding of titanium in a ball mill in a nitrogen atmosphere has been investigated.[63] During the process, the system ignited, *i.e.*, a local thermal explosion occurred, which gave rise to a propagating combustion wave. The authors assume that there is a critical size of titanium particles (80 Å), just below which the system is ignited. Selected results of this study are given in Fig. 17 and Table 4.

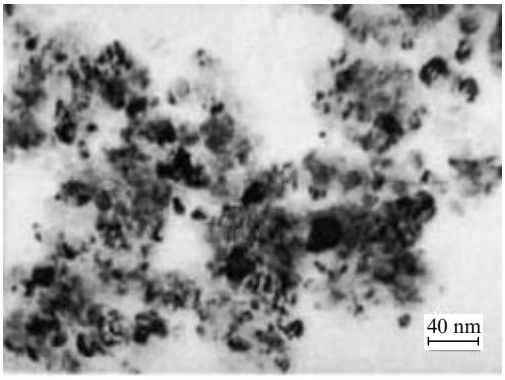


Figure 17. The microstructure of a titanium powder mechanically activated for 492 min.[63]

Table 4. The influence of the duration of mechanical activation on the nitrogen content and on the titanium and titanium nitride crystallite sizes in the sample.[63]

Duration of the mechanical activation /min	c_N (at.%)	d_{101} Ti /Å	d_{200} TiN /Å
Pressure of 11 Bar			
0	–	810	–
31	5.9	166	–
60	9.4	113	76
77	13.5	87	76
85	16.1	84	76
94	43.5	–	155
129	43.7	–	96
240	48.5	–	88
Pressure of 1.5 Bar			
0	–	810	–
60	5.8	134	–
91	9.9	89	76
131	24.0	80	75
152	40.3	–	78
185	42.2	–	84
256	43.9	–	77
492	50	–	76

Therefore, the mechanical activation is one of the most important processes in the technology of nanoparticles. The majority of numerous studies performed in this field confirm the great potential of various methods of activating the SHS aimed at the preparation of nanomaterials (as regards both powdered and compact products).[88–92]

4. Self-propagating high-temperature synthesis in thin films and in systems with nanosized reactants

The self-propagating high-temperature synthesis in thin films and in systems with nanosized reactants is a very new direction within the SHS.[93–97] Multilayer nanofilms built up of hundreds or thousands of alternating layers (each having a thickness of 1–100 nm) are very promising for the design of novel materials and coatings. They often exhibit unique properties. In particular, the hardness of a multilayer film can substantially exceed that of a single layer approaching the hardness of diamond. As has been established quite recently, autowave processes analogous to the gas-free combustion can be initiated in some multilayer films.[98] The velocity of the wave propagation can in such cases reach a few meters per second. To date, self-sustained reaction waves have been observed for several films composed of hundreds of alternating nanolayers, such as Al/Monel 400 (see Ref. 98) and Nb/Si.[99]

Previously, the gas-free combustion has been detected in layered systems built up of alternating Ni and Al foils with the thicknesses of 50 μm.[94] Combustion waves have also been observed in two-layer films prepared by electrochemical deposition [100] or vacuum deposition of a metal vapour.[97] In those films, the layer thickness was in the range from 0.1 to 200 μm.

The gas-free combustion in multilayer Ti/Al films has been studied [95] with the emphasis put on the elucidation of the structure formation in the reaction products (Fig. 18). A previously unknown effect of an inheritance of the preferable crystallographic orientation of the reactants by the gas-free combustion products was revealed.

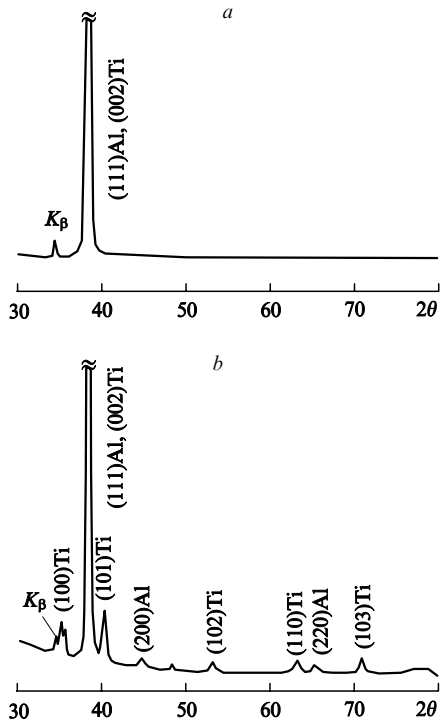


Figure 18. Powder diffraction patterns of the initial multilayer foil (*a*) and of the synthesis product (*b*).
Planes of the close packings of atoms in the initial foil and in the product are parallel to the sample surface.[95]

Combustion of films composed of 150 layers of titanium and aluminium (with the thickness of a single layer of 100 nm and the total thickness of 15 μm) in the SHS mode results in the formation of nanosized two-phase product containing TiAl and Ti_3Al.

First attempts to apply the SHS in thin films with a gradient composition have been undertaken [101] to solve the problem of hardening of composite armors (which is of military significance) (Fig. 19).

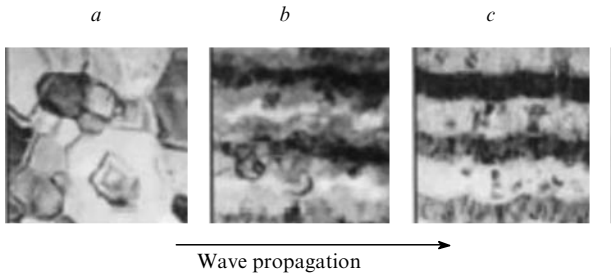


Figure 19. Microphotographs of the evolution of multilayer nanofoils during the SHS
Foils after the reaction (*a*), at the moment of the reaction (*b*), before the reaction (*c*).

The current status of investigations in the field of preparation of multi-component nanostructured thin (~1 nm) films has recently been reviewed.[102]

Nevertheless, it is the SHS using nanosized reactants that found most widespread applications in the synthesis of nanosized products. Primarily, this is due to the simplicity of the approach. Essentially, this implies that the reactants, on the one hand, serve as crystallisation centres and, on the other hand, suppress growth of the product grains.

The influence of the electric field on the morphology of products has been discussed [80] for a case reaction of Ta with C giving rise to TaC particles.[80] The use of a nanosized carbon powder (13 nm) allowed the authors to obtain tantalum carbide with the particle size of 30–50 nm.

Similar results have been reported for syntheses of Al_2O_3–TiAl–Ti_3Al composites [103] as well as of other inorganic powders doped with nanosized particles (ZrO_2, Al_2O_3, W, WC, NbC, *etc.*).[104,105]

The formation of nanosized particles as combustion products have also been confirmed in a series of SHS processes [19, 26, 80, 103, 105, 106] utilising nanosized reactants (*e.g.*, Y_2O_3, ZrO_2, TiO_2, C, *etc.*) (Table 5).

Table 5. Examples of nanosized materials produced by the SHS using nanosized reagents.

Product	Particle size /nm	Ref.
ZrO_2	8–12	106
Ti–H, Zr–H, Ti–N–H, Zr–N–H, Ti–Zr–N–H	<50	26
Al_2O_3–TiC–ZrO_2	10–20	19
(Ti, Cr)C–Ni	500–1500	105
Al_2O_3–TiAl–Ti_3Al	<100	103
TaC	30–50	80

Sol–gel processes and precipitation from solutions are further examples of the use of nanosized reactants for the synthesis of nanomaterials. Essentially, these processes imply conversion of a liquid into a gel (as a result of hydrolysis coupled with polycondensation) and further to a glass, monolithic composite, powder or thin coating (as a result of heating or combustion at relatively low temperatures). The sol–gel technology has several drawbacks related to the high costs of starting materials and to the large shrinkage of gels upon drying and sintering.

Synthesis of a widespread dielectric, $BaTiO_3$, from different precursors, such as BaO_2, $Ba(NO_3)_2$ and $Ba(OAc)_2$, using carbohydrazide, glycine or citric acid as a combustible material has been described in a recent review.[107] The combustion reaction was conducted in the presence of titanyl nitrate. Yet another review [108] lists nanocrystalline oxides (with the particle size of 10–35 nm) prepared by combustion of aqueous solutions containing metal and ammonium nitrates and redox mixtures.

Among chemical processes exploited for the preparation of nanomaterials, the self-propagating low-temperature synthesis is worth a special note. It is realised most easily in gas-releasing systems. For instance, titanyl hydrazinecarboxylate $TiO(N_2H_3COO)_2 \cdot 2H_2O$ undergoes an autocatalytic exothermic decomposition upon heating in air up to 300 °C, which proceeds in the combustion mode and is accompanied by liberation of large amounts of gases, *i.e.*, N_2, CO_2, H_2O. As a result of the reaction, a nanosized TiO_2 powder (8 nm) is formed, which is characterised by high free surface area (110 $m^2\ g^{-1}$). The formation of TiO_2 is described by the following equation:

$$TiO(N_2H_3COO)_2 \cdot 2H_2O \longrightarrow TiO_2 + 2N_2 + 2CO_2 + 5H_2O.$$

The SHS can also be realised in stages of condensation, coagulation and drying of the final product. Different modifications of these techniques are considered elsewhere.[109, 110]

VI. Conclusion

The self-propagating high-temperature synthesis of nanosized materials is a relatively new research field. Its active development was stimulated by a common enthusiasm regarding nanomaterials. Summarising the results discussed in this review, we conclude that the SHS is indeed an efficient route giving rise to nanosized

materials despite high temperatures of the process that typically favour growth of crystallites. Among factors beneficial for the formation of nanosized particles in combustion products, the following are of primary importance: utilisation of nanosized reactants; multitude of nuclei actuating the crystallisation (or condensation) of reaction products; control over the rate of cooling of combustion products; the action of crystallisation, recrystallisation and chemical condensation processes on the SHS; self-limitation of the crystallite growth in multiphase combustion products.

Potential applications of various types of the SHS aimed at the preparation of nanomaterials have not been equally explored. The area most studied is the mechanochemical SHS whereas the gas-phase SHS is the least investigated.

It is the experimental conditions leading to the formation of nanomaterials that attracted major attention of researchers. At the same time, specific properties of SHS-materials and advantages of their practical use are insufficiently represented in the scientific literature (though it is also true for nanomaterials produced by other methods).[111,112] Enhancements of properties of nanomaterials synthesised by the SHS (first of all, as regards their high inclination to sintering and compaction) has been documented by only a few researchers.[113–116] The mechanism and kinetic characteristics of the formation of nanomaterials by the SHS remain virtually unexplored. A quest for the most efficient ways to control the structure formation in combustion products along with investigations into the structure–property relations for the substances produced are promising directions of prospective studies.

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