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Chemical classes of the SHS processes and materials

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Abstract. The paper concerns chemical issues of self-propagating high temperature synthesis. Chemical classes of the SHS processes and products are considered. The results of research into SHS chemistry are discussed according to the classification suggested by the author: solid solutions of nonmetals in metals, binary compounds (carbides, borides, silicides, nitrides, hydrides, oxides, chalcogenides, etc.), chemical mechanism of formation in combustion mode, and intermediate products. Single - phase multicomponent SHS systems involving complex carbides, oxides, nitrides, carbonitrides, hydrocarbides, and hydronitrides are also treated. An extended class of the SHS products comprises complex heterogeneous mixtures of refractory inorganic compounds, as well as hard alloys. The reactions used for synthesizing SHS products of different classes are presented. The use of SHS for producing organic and polymer compounds was experimentally shown to be possible. Finally, the discussion of some issues related to the crystalline structure and particle size of SHS products is presented which is important for understanding the process itself, as well as for practical application of SHS compounds of different classes.

INTRODUCTION

Self-propagating high-temperature synthesis is associated with certain classes of chemical reactions which are characterized by exothermicity, high rates of interaction between reactants, and high temperatures. These features of SHS reactions to a certain extent determine those classes of chemical compounds which can be synthesized by SHS methods.In first turn they are refractory inorganic compounds of metals with non-metals, metals with metals, and non-metals with non-metals. Currently, more than five hundreds of simple and complex SHS products have been synthesized. They are carbides,borides, nitrides, silicides, oxides, hydrides, intermetallics, chalcogenides, and also composite materials from non-metallic ceramics, hard alloys, ets. [1,2,3].

To date,SHS method is successfully used to produce organic meterials [4,5], which is another manifestation of a high potential of the combustion synthesis.

SHS has been extensively developing when being used as main reactions between elements (metals and nonmetals of the III - VIII groups of the Periodic Table). This trend is currently most developed.

The use of interaction between two or several elements is commonly made when synthesizing powdered SHS products, porous and fully dense materials and parts from nonmetallic ceramics, and hard alloys.

An increasing role in SHS is played by the processes involving chemical compounds: oxides, hydrides, azides, salts, organic and inorganic compounds, polymers, etc. In contrast to elemental reactions the interaction between compounds in combustion mode is characterized by enhanced complexity of the synthesis reactions and features certain particularities. The reactions forming refractories from oxides commonly involve metal-reductants (Mg, Al, Zn, Ca, etc). Essentially, the process comprises two stages: conventional metallothermic process (reducing oxide) and chemical interaction between reduced metal and other reactants. SHS processes with the participation of oxide and metal-reductant were termed "SHS with reduction stage" and are being used to produce powdered composites, high-quality fine-grained powders of individual compounds [3,6,7], cast refractory compounds, materials, and coatings [8,9,10]

Table 1 Chemical reactions and main classes of SHS products.

Basic reactions in SHS	SHS products
Synthesis from elements	Carbides , borides, nitrides , silicides
Ti(Zr,Hf,Nb,Ta,Al...)+C(B,N_2,Si,H_2,S,P,O)	hydrides , oxides,
B(Si,P...) + N_2(C,P...)	intermetallics,
Ni(Ti,Nb,Mo,W...) + Al(Ni,Co,Fe,Ge...)	chalcogenides , single - phase solid
SHS with reduction stage	solutions , heterogeneous mixtures
$2MoO_3 + 4Al + C \longrightarrow Mo_2C + 2Al_2O_3$	hard alloys ,
$B_2O_3 + 3Mg + N_2 \longrightarrow 2BN + 3MgO$	inorganic compounds
$TiO_2 + B_2O_3 + 5Mg \longrightarrow TiB_2 + 5MgO$	for preparative
	chemistry ,
Synthesis involving compounds	organic compounds
$TiH_2 + 2B \longrightarrow TiB_2 + H_2$	
Ti(Zr,Ta,Si,B)+NH_3(NH_4N_3,NaN_3) $\longrightarrow$ TiN...	
$PbO + TiO_2 \longrightarrow PbTiO_3$	
$Ln_2O_3 + Ml_2O_2 + Cu \xrightarrow{oxidizer} LaMe_2Cu_3O_7$	
$ZrCo + H_2 \longrightarrow ZrCoH_3$	
Ti + C_2H_2 (CH_4,C_2H_4) $\longrightarrow$ TiC...	

Of great interest are reactions utilizing various chemical compounds as reactants [3,11,12,13] and phase synthesis within one system using phase transitions [14,15]. Chemical reactions employed in SHS and main classes of SHS products are given in Table 1.

To attain clear understanding of state-of-the-art in the research on SHS processes and products it is expedient to consider the following combustion-produced materials:

- single phase solid solutions of metals in nonmetals;
- binary compounds;
- single phase solid solutions based on two or several refractories;
- heterogeneous mixtures;
- organic compounds.

Single phase solid solutions of nonmetals in metals

Single phase solid solutions of nonmetals in metals are "lower" phases formed directly in the course of SHS. The conditions and mechanism of their formation have been extensively studied in combustion of porous titanium and zirconium samples in gasous nitrogen at pressures of 0,1 up to 500 MPa [16,17]. Theoretical consideration of the possibility of combustion between metals and nonmetals forming merely solid solutions has been carried out in [18].

The systems of Zr+N_2 and Ti+N_2 are those of most highly exothermic. Homogeneity regions of α-solid solutions of nitrogen in these metals are fairly large and attain compositions of $ZrN_{0,33}$ and $TiN_{0,27}$. Thermodynamic calculations and experiments have shown that SHS process in Zr+N_2 and Ti+N_2 systems is possible to occur at the expense of solid solution formation. The dependence of calculated adiabatic combustion temperature in Zr+N_2 system on nitrogen content in homogeneity region of solid solution is given in Fig.1; combustion temperatures are seen to be high. A necessary condition for the formation of single-phase solid solution of nitrogen in metals is the arrest of the reaction at the stage of solid solution formation. The further nitriding of the solid solution can be ceased in several ways.Most common ones are sample quenching and sharp gas drop immediatly after the passage of the combustion front. An efficient way is also to create conditions when after-burn (bulk after-nitriding of the samples heated in the combustion front) is unlikely to happen. In Zr+N_2 and Ti+N_2 systems such unfavorable contitions form spontaneously since the samples under combustion often become sintered or molten, especialy when nitrogen pressure is higher than 3 MPa, and there is no access for the gas into combustion zone.Other techniques eliminating the after-burning could be confining sample's lateral surface in a gas-tight jacket or implementing the combustion process in the mixture of metals with nitrides in a pure surface combustion mode which plays the role of "chemical furnace" to facilitate the products homogenization.

An important achievement in the studies of the direct combustion synthesis of solid solutions was the production of compositions with minimum nitrogen content ($MeN_{0,1}$-$MeN_{0,2}$) and synthesis of single-phase oversaturated solid solutions of $MeN_{0,34}$-$MeN_{0,45}$ composition, which have nitrogen content exceeding the values known from literature. This fact initiated the hypothesis of nitride formation in combustion mode, in contrast to commonly accepted mechanism of reaction diffusion through the product film, by means of saturating metal with nonmetal along with forming "oversaturated" solid solutions which then decompose to form solid solution of lower composition and nitride MeN_x [19]. In this case,the combustion rate was determined by the rate of dissolving non-metal in metal; at this stage the major heat release takes place. Generalizing these concepts of various metal-nonmetal systems one could assume that the systems with wide regions of homogeneity of solid solutions might burn, under certain conditions, involving the solid solution saturation step and without yielding any compounds. The systems with narrow regions of homogeneity of solid solutions under specific conditions (reaction mass melting, high pressures) can also produce solid solutions when burning with their subsequent decomposition or crystallization.

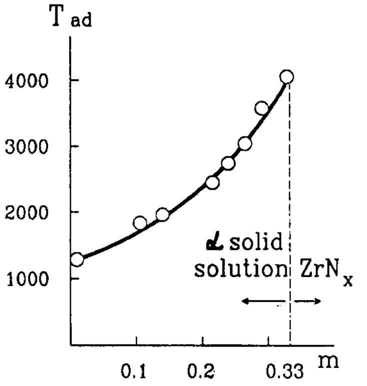


Fig.1. Combustion temperature vs. solid solution composition.

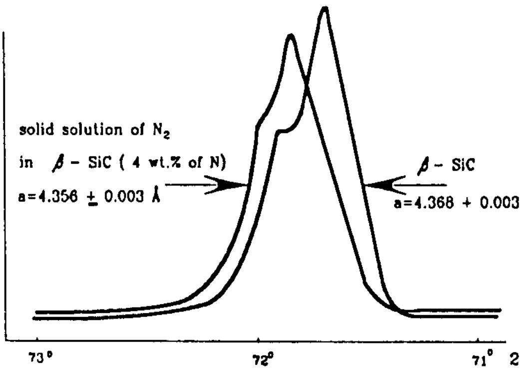


Fig.2. Formation of solid solution silicon carbide-nitrogen.

From this point of view the experiments on combustion between silicon and carbon in high-pressure gaseous nitrogen (up to 500 MPa) are of great interest. Providing such extreme conditions we could observe the formation of solid solution of nitrogen in silicon carbide. In Fig.2. are given parameters of the β-SiC lattice with nitrogen dissolved in it (N=4 wt %) as compared to parameters of pure β-SiC lattice.

Unusual results were also obtained when mixtures of boron and phosphorus combusted in high-pressure nitrogen atmosphere ($P_{N_2} \geq 300$ MPa). The synthesized single-phase product of general formula BPN_x is a solid solution of nitrogen in BP and have properties of superhard material [20].

Examples of such interaction including dissolving in solid-solid systems have been described by Vidavsky for Zr-C system [21] and by Itin and Bratchikov for SHS intermetalics, particularly Ti-Co system [22]. Aleksandrov and Boldyrev [23] and Holt with coworkers [24] performed direct observation of the dissolving stage during SHS product formation in Ni-Al and Ti-C systems by measuring the phase structure of the combustion wave with the use of synchrotron radiation. Currently, structure formation during SHS reactions is being intensively studied with the use of novel methods employed in structural macrokinetics. Of interest is a series of works by Merzhanov and Rogachev with coworkers [25,26] devoted to the studies on structural dynamics of chemical reactions and the formation of refractory compound microstructure in short-time high temperature processes. These investigations are carried out with the use of X-ray microanalysis, optical spectroscopy, Auger-spectroscopy, physical and mathematical modelling.

Shteinberg with coworkers obtained unique results on carbon dissolving in titanium in the course of the reaction between Ti and C under thermal explosion conditions. The authors thoroughly investigated the mechanism of this process and laws of structure formation.

As to the Me-N systems with complex state diagrams (e.g., Ta-N, Nb-N), which comprise solid solutions with narrow regions of homogeneity (in contrast to Zr-N and Ti-N), single phase solid solutions in these systems are also being formed during combustion. However, it is hard to isolate them and they only can be observed in quenched products, being located in layers adjacent to the combustion front, so-called "heating-up zones" [14].

Search for the conditions of direct synthesis of single phase solid solutions had intensified studies on crystal structure of combustion products and led to interesting results in this area, some of which this paper is going to dwell on. On the other hand, these studies make it possible to realize a deeper, more "intimate" mechanism of interaction between reactants in SHS mode which is, by far, not yet well understood.

BINARY COMPOUNDS. INTERMEDIATE PRODUCTS

Most extended studies are devoted to the problem of combustion synthesis of binary compounds of different classes. To date, practically all known refractory inorganic materials such as carbides, borides, nitrides, silicides, chalcogenides, and others have been prodused by SHS. Usually, the final products of synthesis are higher compounds, which frequently show better performance characteristics when they are used in different fields of technology.

As was shown in numerous papers, the formation of higher phases, however, occurs in a complex, multistep way through the formation of lower compounds: semicarbides, seminitrides, lower borides, silicides, etc. These phases can be prodused in SHS mode as individual end products under special conditions or isolated as intermediate compounds when the combustion reaction is arrested (for instance, products quenching).The other way of synthesizing lower phases within one system can be subsequent treatment of the SHS products (annealing, quenching) allowing phase transitions to occur. Finally, there exist interesting indirect evidences of the occurrence of these phases in SHS processes. To date, a great deal of studies on identifying and isolating lower phases have been carried out, so it is expedient to consider only some most characteristic works.

A convenient example for better comprehension of the mechanism of SHS product formation is combustion of porous, cold-pressed tantalum samples in gaseous nitrogen. The study of the combustion process in this system has been carried out in a wide pressure range (from 2 up to 300 MPa) using tantalum powder of different particle size (<10 μm, ≥40 μm) and of relative sample density, Δ, from 0.2 to 0.6. In addition, combustion product quenching in liquid nitrogen was performed immediately after the combustion front passage. In some cases tantalum powder was pressed into quarz cylinders. In a number of experiments additional heating or annealing of the combustion products was implemented [14, 28]. Generalized results of the experiments on synthesizing various phases in the Ta-N system are schematically presented in Fig.3.

Upon studying combustion mechanism of the $Ta+N_2$ system a couple of intriguing facts directly concerned with chemical transformations in the combustion front and after its passage were revealed. One of these facts is the occurrence of second combustion front when tantalum powder is burnt in quarz tubes which are sealed at the top end to eliminate gas supply through combustion products. When nitrogen was supplied only through initial tantalum powder towards the combustion front there appeared weakly luminous, first combustion front which was propagating at ever increasing velocity towards the end of the sample. Arriving at the lower end of the sample the front produced a flash, then the second combustion front arose, which was brighter than the first one and moved in the opposite direction with deceleration to a complete stop. X-ray analysis of quenched combustion products showed that during the first front passage a solid solution of nitrogen in tantalum and γ-Ta_2N are formed. In the layer where the second front stopped, the combustion product is that of triple-phase : in addition to solid solution and γ-Ta_2N there exists ε-TaN_{hex}. In the layers where the second front was displacing in a steady-state fashion the combustion product was that of single phase ε-TaN_{hex}.

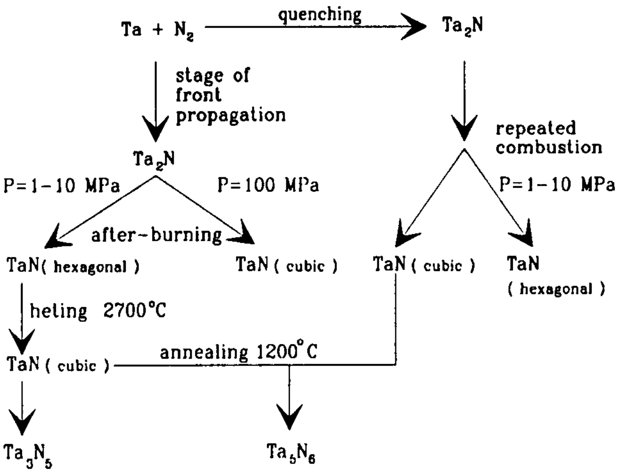


Fig.3. Combustion products formation in the system Ta-N.

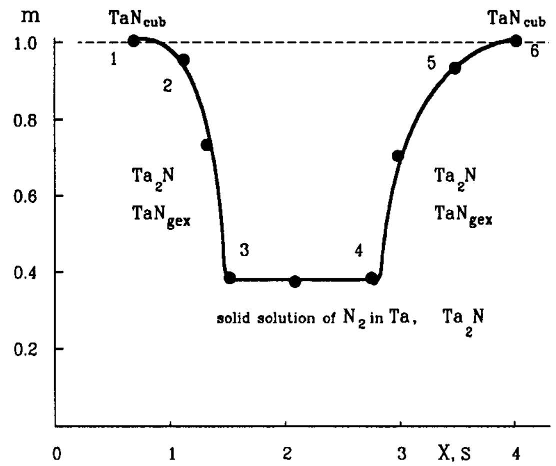


Fig.4. Nitrogen concentration profile along the specimen.

Two combustion fronts in Ta-N system have also been observed in experiments with tantalum powders pressed into quarz tubes (both ends were open to let the gas in). However, in this case the second front arose, the same as the first one, at the ignition spot and was proceeding in the same direction down the green mixture but with a time delay. In Fig.4 is given nitrogen concentration profile along the sample (M is an arbitrary unit; when M = 1 the composition is that of stoichiometric mononitride TaN). The phase composition of combustion products is given as well. It can be seen that complete conversion occurs at the ends of the burnt sample, whereas in the middle of the sample only solid solution of nitrogen in tantalum and γ-Ta_2N are formed. The analysis of numerous results obtained during the study of combustion processes in Ta + N_2 system revealed multistep character of the interaction between tantalum and nitrogen and determined optimum conditions for synthesizing any phase involved in SHS mode. The experiments showed that in the preheating zone adjacent to the combustion front nitrogen was practically always dissolved in tantalum forming solid solution. This step is exothermic, but as the heat evolved is not enough, the reaction zone propagation in the form of the combustion front is not self-sustained. The combustion front propagation is governed by thermal fluxes of strongly exothermic reaction of γ-Ta_2N formation. In the after-burn wave (bulk after-nitriding of the sample heated by the combustion front) the third exothermic step occurs - ε-TaN_{hex} is formed according to the following equation :

$$Ta_2N + 1/2\ N_2 = 2\ TaN + Q\ (J)$$

In the after-burn zone the forth step takes place: this is endothermic transition ε-$TaN_{hex} \longrightarrow \delta$-$TaN_{cub}$. δ-TaN_{cub} is thermodynamically stable only at high temperatures and can be retained after combustion due to very rapid cooling, in fact in quenching fashion.

Not less interesting example of chemical step-likeness in SHS processes with the formation of lower phase is the occurrence of metastable phase of ε-Ti_2N during titanium combustion in nitrogen atmosphere. The combustion process in this system was studied in our work [17,32], and also by Hisao, Miyamoto, and Koizumi [29] and Munir, Holt, and Davy [30,31].

American scientists carried out the works with the use of X-ray and metallographic analyses, as well as scanning electron microscopy of quenched combustion products which led to the conclusion that the combustion wave is propagating due to the formation of a thin TiN_{1-x}(x=0.01-0.06) layer and solid solution of nitrogen in titanium. They also obtained theoretical results concerning the formation of the nitride and nitrogen dissolving in titanium.

According to literature data, the phase of ε-Ti_2N is unstable and starts decomposing at temperatures exceeding 1000-1100°C. We first produced this phase when decomposing oversaturated solid nitrogen solutions in titanium of $TiN_{0.33}$-$TiN_{0.42}$ composition.

Besides, ε-Ti_2N phase was discovered in the quenched products of titanium combustion in nitrogen range of 300-450 MPa.

The following up studies by Karimov and Ehm with coworkes [32] dealt with combustion products of the Ti-N system. They used neutron diffractometer (λ=1.08 Å) which was installed at the thermal column of a neuclear reactor. In their experiments the specimens were undergoing heat treatment (homogenizing annealing) in the temperature range of 1500-1300° K and 1300-1600°K with quenching and subsequent annealing of the products after quenching.

It was found that ε-phase forms in the concentration range of $0.38 \le N/Ti \le 0.42$. The ε-T_2N_{1-x}($0.24 \ge x \ge 0.16$) phase is characterized by lower nitrogen content as compared to that of stoichiometric compound Ti_2N. The ordered tetragonal phase δ'-Ti_2N was found to form at 800°C on the base of metastable high-temperature cubic δ-phase. The homogeneity region is in the range of $0 \le x \le 0.1$. Based on the data obtained, a more precise diagram of the Ti-N system was suggested. A fragment of this diagram and phase composition of products after heat treatment are presented in Fig.5.

Specimen	1500–1300 K	1300–600 K	quenching 1700K	after (800K)
$TiN_{0.45}$	ε + δ	ε+δ+δ'	δ	δ'
$TiN_{0.42}$	ε	ε	ε	ε
$TiN_{0.40}$	ε	ε	ε	ε
$TiN_{0.38}$	ε	ε	ε	ε
$TiN_{0.33}$	α + ε	α + ε	α + ε	α+ε+δ

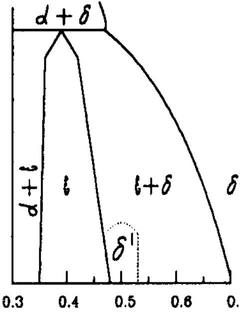


Fig.5. Oversaturated solid solution.

Table 2 Combustion product composition of Me-Si system at various Si/Me ratios.

Si/Me ratio in green mixture, at.%	Phase composition of combustion products
	Molybdenum-silicon system
1,0	$MoSi_2$, Mo_5Si_3, Mo, Mo_3Si
2,0	$MoSi_2$
2,4	$MoSi_2$, Si
	Titanium-silicon system
0,3	Ti_5Si_3, Ti
0,6	Ti_5Si_3
2,4	$TiSi_2$, TiSi, Si
	Zirconium-silicon system
0,4	Zr_2Si, Zr_5Si_3, Zr
2,0	$ZrSi_2$
2,4	$ZrSi_2$, Si

Systems with complex state diagrams such as Me-B, Me-Si, Me-S(Se), Me-Me' possess a wide range of intermediate combustion products. The lower phases in these systems can be produced without any use of additional techniques (particularly, combustion products quenching) but only varying process parameters such as initial constituents ratio, sample diameter and density, and reactant particle size. Any deviation from optimum initial constituents ratio and departure from adiabaticity conditions for the process in Me-Si systems result in occurrence of intermediate compounds in the combustion products [33]. The systems comprising silicon are more sensitive to variations in the combustion conditions than others. Combustion products composition for Mo-Si, Ti-Si, and Ta-Si systems at different initial metal/nonmetal ratios is given in Table 2.

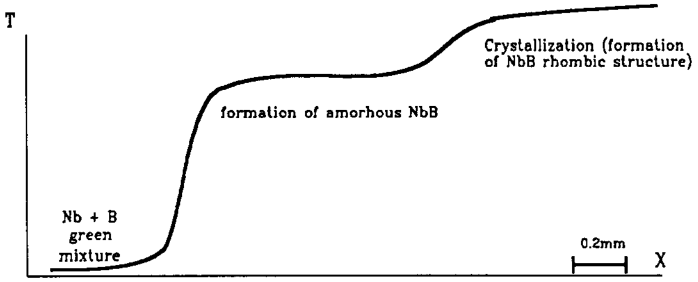
The method of producing various phases with the use of phase transition is relatively scanty as regarding its employment in SHS. Phase transitions can be observed in Ta-N system (Fig.3). As can be seen from this figure, tantalum burning in nitrogen does not lead to the formation of Ta_5N_{6-x}. This nitride forms as the result of δ-TaN_{cub} decomposition (with nitrogen content higher than in $TaN_{1.12}$) during annealing at temperatures exceeding 1200°C and exposure time not less than 0.5 h. Thus produced Ta_5N_{6-x} ($x=0.3\div0.5$) nitride proved to be stable in vacuum up to 2000°C. Merely at 2500°C and exposure time of 4 h this nitride transforms into ε-TaN_{hex} loosing some portion of nitrogen. Thus, tantalum nitride of Ta_5N_{6-x} composition is one of the most stable in Ta-N system. Ehm and Petrunin have used neutron diffraction analysis to show that this phase has hexagonal lattice with parameters a=5.16Å and c=10.27 Å.

Annealing δ-TaN_{cub} in ammonia at 800°C during 12 h led to the formation of Ta_3N_5 with characteristic red color, however, the transformation was incomplete: X-ray analysis showed some impurities of ε-TaN and δ-TaN.

Munir and Trambukis obtained Ti_5Si_3 by combustion synthesis and described phase transitions in Me-Si systems [15]. The combustion reaction was found to occur in the presence of liquid phase prior to which relatively weak solid-state processes take place. Using SEM and X-ray diffraction methods, the synthesis of Ti_5Si_3 was found to occur by the following scheme:

$$TiSi_2 \longrightarrow TiSi \longrightarrow Ti_5Si_4 \longrightarrow Ti_5Si_3$$

Of no less interest are indirect methods for identifying intermediate products in the course of SHS reaction, though they are not well developed yet. One of these methods is experimental measurement and analysis of profiles of the combustion temperature in accordance with the state diagrams of the systems under investigation. This trend is being intensively developed by Zenin in his works [34]. A hypothesis on stepped formation of final SHS products through forming lower phases and even amorphous products, being primary compounds, was suggested by Merzhanov [35] basing on the experimental data obtained by Zenin. This hypothesis is illustrated in Fig.6 for Nb-B system. The temperature profile of the combustion was obtained in Zenin's work by thermocouple method and then superimposed on the state diagram. Characteristic regions corresponding to the formation of various phases including those of primary amorphous products can be seen on the curve.



Combustion wave structure in the system Nb + B (A.A. Zenin)

Fig.6.
Hypothesis of the formation of intermediate amorhous compounds.

It should be noted that certain amorphous phases of the SHS products were identified and isolated in earlier works about which we will talk more when considering crystalline structures.

Unfortunately, practically no application was found by indirect method for identifying intermediate products by comparing the combustion rates of the reactant mixtures when introducing inert additives and in the presence of one constituent in excess which can be both an inert diluent and active reactant [36]. The comparison is carried out in coordinates: combustion rate - adiabatic combustion temperature. The method can be demonstrated for the Me-B systems.

In Me-B systems which according to the state diagram comprise not more than one boride (e.g., Hf-B system), the rate and temperature of combustion did not depend on the diluent origin, whereas in the system comprising several borides (Ti-B), if reactants were in excess, a marked increase in the combustion rate was observed due to additional heat release in exothermic reactions of intermediate phase formation. Experimental data processing in universal coordinates relating the combustion rate to the product composition made it possible to predict TiB phase formation in Ti-B system and ZrB_{12} in Zr-B system, the former of which was later isolated and the latter was identified on X-ray patterns.

COMPLEX MULTICOMPONENT SHS PRODUCTS

Complex multicomponent compounds and heterogeneous mixtures are of great importance among SHS products, particularly those obtained recently. A keen interest to complex compounds is understandable since they have a set of properties best suited for current needs. Examples of chemical reactions resulting in complex SHS products formation are given in Table 3.

Table 3 Synthesis of multicomponent products

Reactants	Type of reaction	Examples
Chemical elements	addition	$Ti + Si + 2C \longrightarrow TiC + SiC$ $Ti + C + Ni + Al \longrightarrow TiC + NiAl$
Oxides	Redox	$TiO_2 + Zr + C \longrightarrow TiC + ZrO_2$ $Ti + Mo + WO_3 + Al + C \longrightarrow TiC\text{-}WC\text{-}Mo_2C$
Alloys, Salts, refractory compounds	Decomposition Substitution	$Ba(NO_3)_2 + Ti \longrightarrow BaTiO_3$ $Ti + B_4C \longrightarrow TiC + 2TiB_2$ $FeTi + Ti + 4B \longrightarrow 2TiB_2 + Fe$
Mixtures with reactive fillers and gaseous reactants	Mixed	$3TiO_2 + 4Al + NaN_3 \longrightarrow TiN + 2Al_2O_3 + Na$ $3Cu + 2BaO_2 + 1/2\ Y_2O_3 \xrightarrow{O_2} YBa_2Cu_3O_7$

Multicomponent SHS systems can be classified into two large groups:

- single phase solid solutions of two or several refractory compounds;
- heterogeneous systems, including hard alloys.

Single phase solid solutions of compounds

Single phase solid solutions of compounds are in great abundance among SHS products on the following reasons. Firstly, many refractory compounds, being produced by SHS, have high, sometimes unrestricted mutual solubility due to relationship between their crystalline structures. Therefore, double, triple, and more complex carbides,nitrides, silicides, oxides, chalcogenides, and the like can be readily synthesized. Besides, some representatives of different classes possess good mutual solubility. All this results in the formation of multicomponent carbonitrides, hydrocarbides, hydronitrides, etc.

The second reason for wide use of SHS to synthesize complex compounds is a simplicity of this method allowing the process to occur in one step.

One, very characteristic, but unfortunately not widely known example is the use of SHS for producing carbonitrides of Nb and Zr with general formulae: $Nb_{0.3}Zr_{0.7}C_xN_{x-1}$; $Nb_{0.5}Zr_{0.5}C_xN_{1-x}$; $Nb_{0.7}Zr_{0.3}C_xN_{1-x}$. These single phase compounds were synthesized by combusting mixtures of Zr+Nb+C in gaseous or liquid nitrogen at various constituent ratios [37]. The influence of process parameters such as nitrogen pressure, diameter and density of the preforms, metal particle size, on chemical and phase composition of the products have been thoroughly studied, as well as carbonitride structures. To comprehend the mechanism of formation of complex compounds the quenching of the products was implemented at different stages of the process. Interesting results have been obtained, two of which are the most significant. Firstly, not only unknown untill recently carbonitrides of Nb-Zr had been synthesized, but also those to produce which by furnace method was impossible. Crystalline lattice parameters of some of them vs. consituents ratio are given in Fig.7. Secondly, quenching combustion products at different stages of the process allowed us to observe a great variety of reactants conversion into complex carbonitrides through the formation of intermediate solid solutions, depending on the combustion conditions they could be seminitrides and semicarbides, mononitrides and monocarbides. The determination of optimum conditions for combustion synthesis of complex carbonitrides of Nb-Zr of different composition has become an important practical result of this work.

Of the same type of work should be considered the studies concerned with carbonitrides of TiC-TiN and TaC-TaN [37]. In the latter case, continuous solid solutions based on TaN were

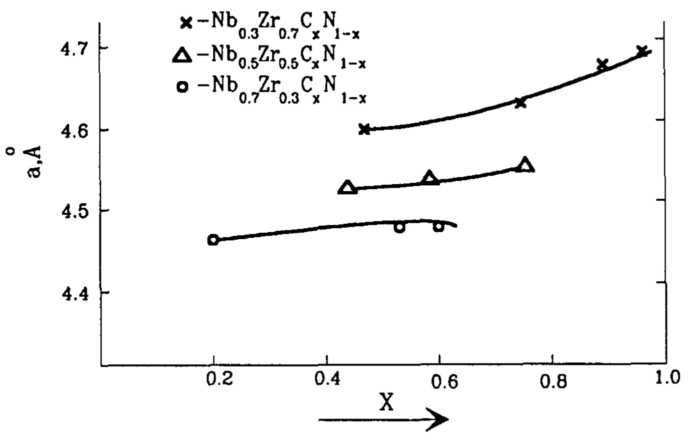


Fig.7. Single phase solid solutions of carbides with nitrides.

successfully produced for the first time. This became possible due to the formation of cubic TaN in SHS mode. An impressive example of the use of SHS for producing complex hydrocarbides and hydronitrides are the works by Dolukhanyan with coworkers. Of particular interest is the study on the combustion of the mixture of two metals (for instance, zirconium and niobium) in the atmosphere of two gas reactants - nitrogen and hydrogen [38]. It was shown that at certain ratios of partial pressures the presence of hydrogen retards the stage of bulk after-nitriding occurring after the combustion front passage and instead after-hydriding takes place resulting in the formation of metal hydronitrides. This method was used to synthesize quinticomponent single-phase hydronitrides of the following composition: $Zr_{0,9}Nb_{0,1}C_xN_{1-x}H_{0,19}$ - $Zr_{0,4}Nb_{0,6}C_xN_{1-x}H_{0,26}$.Some of their properties and crystalline lattice parameters have been determined. Important results have also been obtained when studying intermetallic combustion in hydrogen [39]. The combustion process parameters (particularly, the combustion temperature) turned to be crucial for the reaction path. Thus, during hydriding ZrCo at T_c=600-700 °C the following hydrogenolysis reaction takes place:

$$ZrCo + H_2 \longrightarrow ZrH_2 + Co.$$

Whereas at T_c=200-300 °C an intermetallic hydride is formed:

$$ZrCo+3/2H_2 \longrightarrow ZrCoH_3.$$

Of scientific and practical interest is the combustion synthesis of advanced ceramic materials - single-phase solid solutions, Si_3N_4-AlN-Al_2O_3 (sialon). Loryan with coworkers [40] found that SHS method can be used to synthesize various sialons with general formula $Me_x(Si;Al)_{12}(O;N)_{16}$ where Me is Y; Ca; Mg...,as well as polytypes of aluminum nitride. The phase diagram of Me-Si-Al-N system is shown in Fig.8.

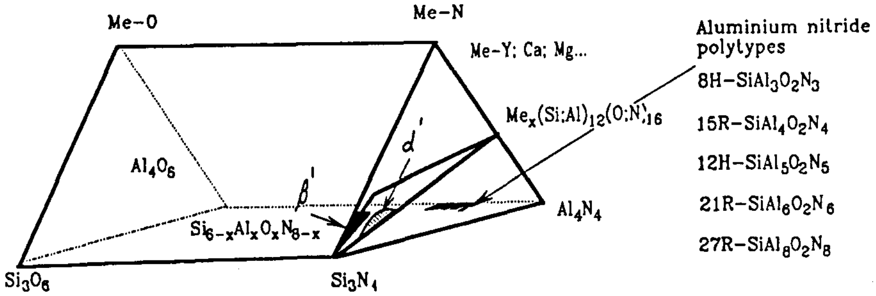


Fig.8. Phase diagram in the system Me-Si-Al-N.

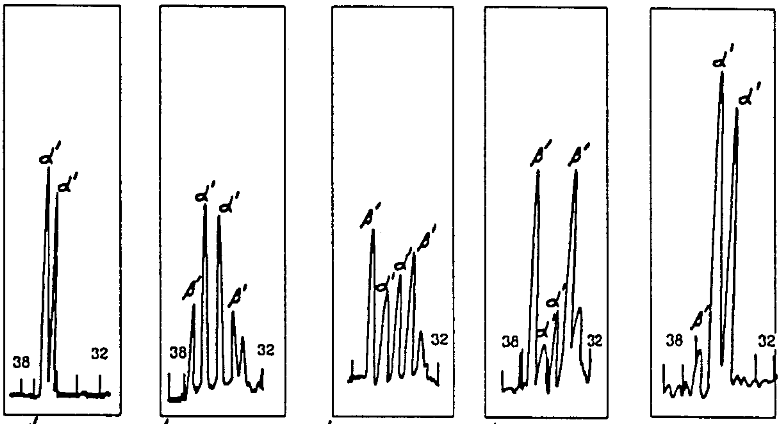
Importantly, sialons feature high homogeneity with the main phase content exceeding 95 %. As a unique result is considered the synthesis of α-and β - sialons depending on combustion conditions and initial mixture composition:

$$MeO + Si + Al + (\alpha,\beta\text{-}Si_3N_4) \xrightarrow{N_2} \alpha'\text{-sialon}$$

$$Si + Al_2O_3 + AlN \xrightarrow{N_2} \beta'\text{-sialon}$$

$$SiO_2 + Al + Si \xrightarrow{N_2} \beta'\text{-sialon}$$

The X-ray pattern of α' ⟶ β' transition vs. stabilizing additive content is given in Fig.9.



α' SIALON α' SIALON+5%Al_2O_3 α' SIALON+10%Al_2O_3 α' SIALON+15%Al_2O_3 α' SIALON+20%Al_2O_3

Fig.9. α' ⟶ β' phase transformations.

Recently, in the field of complex SHS products a tendency appeared to thoroughly investigate chemical mechanism of the process and its step-likeness. Modern equipment is being employed such as synchrotrons, high temperature X-ray installations in dynamic mode, thermal and mass-spectrometric analyses are carried out.

Nersesyan with coworkers were engaged in studies on the formation mechanism of lithium niobate in the combustion of Li_2O_2-Nb_2O_5-Nb mixture and superconducting ceramics Y_{123} in the combustion of Y_2O_3-BaO_2-Cu-O_2 system [41]. A fast-response automatic weigher specially designed for SHS studies was used in the experiments on lithium niobate formation [42]. The following steps of chemical transformation in niobate synthesis were experimentally determined:

$$Li_2O_2 \longrightarrow Li_2O + 1/2O_2$$

$$LiO_2 + Nb_2O_5 \longrightarrow 2LiNbO_3$$

$$3Li_2O + Nb_2O_5 \longrightarrow 2Li_3NbO_4$$

$$Li_3NbO_4 + Nb_2O_5 \longrightarrow 3LiNbO_3$$

$$LiNbO_3 + Nb_2O_5 \longrightarrow LiNb_3O_8$$

$$LiNb_3O_8 + Li_2O \longrightarrow 3LiNbO_3$$

$$5Li_2O_2 + 4Nb_2O_5 + 2Nb = 10LiNbO_3$$

There are some other works concerned with the consideration of the formation mechanism of complex oxide systems. Exothermic reactions employed in thermal batteries were studied by McCauley [43]:

$$Zr + (air) \longrightarrow ZrO_2 \quad Zr + BaCrO_4 + (air)$$

$$3Zr + 4BaCrO_4 \longrightarrow 3ZrO_2 + 4BaO + 2Cr_2O_3$$

$$3ZrO_2 + 3BaO \longrightarrow 3BaZrO_3$$

$$3Zr + 2BaCrO_4 \longrightarrow 3ZrO_2 + 2BaO + 2Cr$$

$$3ZrO_2 + 2BaO \longrightarrow 2BaZrO_3.$$

Worthy to be mentioned are very interesting and promising investigations by Pampuch and Stobirsky [44] concerned with the phase formation mechanism in Ti-C-Si system. The role played by liquid and gaseous phases in a specific mechanism of heterogeneous SHS reactions has been studied in this work. The formation of Ti_3SiC_2 phase was of great success.

Heterogeneous systems

High requirements to modern materials have brought about extensive studies on SHS producing heterogeneous systems which could be considered in the following sequence:

-heterogeneous mixtures of refractory compounds;
-hard and special alloys;
-gradient materials.

Because of great deal of work done in this area it is hard to present all results obtained, so we will dwell on some of them. It should be noted that it is the synthesis of heterogeneous systems where most wide range of various SHS methods are used, namely: powder synthesis, forced SHS densification, gas pressure SHS, SHS casting, SHS extrusion, and others. Respectively, of a great variety are also initial reactants (elements, compounds) and types of interaction between reactants. In Table 3 are given some examples of these reactions.

Heterogeneous mixtures of refractory compounds

The study of geterogeneous mixtures began from the works on combustion processes in elemental systems of Ti-B-C type [45]. An important achievement of this study is establishing chemical step-likeness of the process and the relation between products composition and combustion parameters. It was shown that the formation of final products - heterogeneous mixtures of Ti-TiB_2 - under certain conditions can occur through complex transformations with the participation of intermediate products: nonstoichiometric titanium carbides, titanium monoboride and subsequent transition $2TiB \xrightarrow{t^o} TiB_2 + Ti$.

Later on, heterogeneous system of TiC-TiB_2 was synthesized by us in the combustion reaction between B_4C and Ti mixtures under conditions of forced dencification. By varying initial reactants ratio and combustion conditions practically nonporous structures and eutectic alloys were obtained. The study of the combustion reactions: $2Ti+2B+C \rightarrow TiC+TiB_2$; $3Ti+B_4C \rightarrow TiC+2TiB_2$ and $Ti+Si+2C \rightarrow TiC+SiC$ was also carried out by Miyamoto, Koizumi [46], and others.

Odawara and Taneoka [47] studied in detail the combustion of Ti-Al-B mixtures at various constituents ratio. The combustion product structure was analyzed by X-ray diffraction and SEM methods. It was shown that the structure of final composite TiB_2-Al, particularly the grain size, depends on the constituents ratio. Fine-grained structure of the composite (<0.5 µm) is forming at the constituents ratio of $Ti+Al+4B$.

The formation of heterogeneous composite C-SiC in SHS mode has been implemented by Izawa and Miyai [48]. These authors managed to obtain macroscopically uniform C-SiC system by carrying out SHS reaction between carboneous material and molten silicon. The composite was composed of β-SiC 30 mol% and carbon 70 mol%. By using scanning and transmission electron microscopes it was shown that the pores of the initial carboneous material were filled with SiC.

Gas pressure SHS method has a great potential to synthesize heterogeneous ceramic materials in combustion mode. SHS process occurring at a high pressure of the gaseous reactant makes it possible to form in one step complex multicomponent heterogeneous systems using practically unlimited number of combinations of initial constituents: elements and compounds. Various types of reactions can be used as well: those are reactions of addition, substitution, compound decomposition, and with reduction stage. Recently, using gas pressure SHS reactions we managed to obtain a whole bunch of interesting heterogeneous systems in the form of powders, materials, and parts. These are BN-$SiO_2(MgO)$; BN-TiB_2; BN-SiC; BN-B_4C; AlN-TiB_2; Si_3N_4-SiC-TiN(C), sialon-SiC, etc. Many of them possess valuable electrophysical and thermochemical properties. In Table 4 are given some properties of ceramic material Si_3N_4-SiC-TiN(C) [49].

Table 4. Properties of SHS Black Ceramics of aSi_3N_4+ bSiN+ cTiN+ dC composition

Density, kg/m^3	$(3.05-3.40) * 10^3$
Porosity, %	< 1 - 15
Modulus of Elasticity, GPA	180-250
Rockwell Hardness, HRA	85-93
Vickers Hardness, GPa	6.1 -14.6
Flexural Strength, MPa, up to T ≅ 1500°C	300-650
Critical Stress Intensity Factor', MN/m^3	2.5 - 5.0
Thermal Conductivity in the temperature range of 873-1371 K, W/M*K	18 - 20
Thermal Stability (H_2O, 1250±10°C)	≅ 60 cycles

It should be mentioned that in one and the same system heterogeneous mixtures of different composition can be produced as the end products depending on initial reactants ratio and combustion conditions. In Fig.10 are represented X-ray patterns of combustion products of the Ti-B-N system obtained under different conditions, by Loryan et al., [50]. The formation of the TiB_2-AlN system has been studied by DeAngelis [51]. He employed the reaction $TiN+AlB_2 \longrightarrow TiB_2+AlN$. A preheating of the green mixture was carried out prior to exothermic reaction.

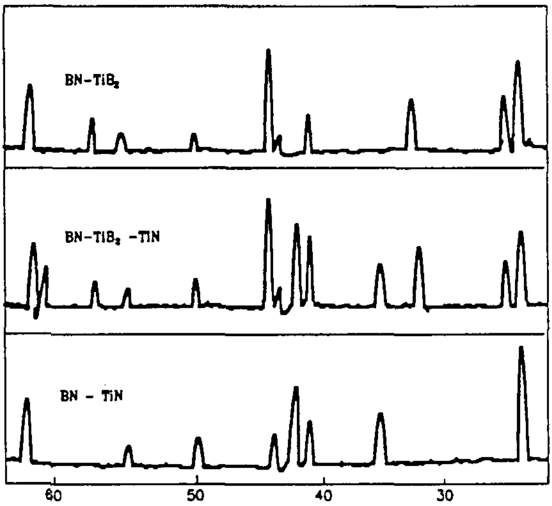


Fig.10.
Combustion products of Ti-B-N system.

As unusual heterogeneous systems can be considered mixtures of Zr/ZrC/ZrB_2 synthesized with the use of SHS by Zhenling et al. [52].

Worthy to be mentioned are the works of many authors concerned with producing the systems of refractory / intermetallics by various SHS methods. We consider some of them. A great deal of SHS reactions to form the systems with borides, carbides, and intermetallics were carried out by Dunmead, Holt, Kimgman, and Munir [53]. All final products both refractory carbides and borides and intermetallics (aluminides of Ni, Ti,Cu; nickelides of Ti, titanides of Fe and Co) are formed in the course of the combustion of elemental powder mixtures under pressure. The composites produced have high density and mechanical strength.

Ramers with coworkers [54] described exothermic reaction between Ti and Al powders with a SiC additive. They managed to obtain SiC-TiAl composite of high flexural strength.

High pressure SHS reactions in Ti-Ni-B system were employed by Sata with coworkers to produce composite materials of TiB_2-TiNi. Up to 95 mol % TiNi could form in the SHS process. TiB_2 had undermicron grain size if TiNi content exceeded 50 mol % .

Kaieda with coworkers conducted an interesting experiment on SHS bonding SiC whiskers with TiAl intermetallic. Metallographic study of the materials as well as X-ray diffraction and SEM analyses showed that SiC whiskers are uniformly distributed in TiAl powder and strongly bonded with SiC.

A wide range of heterogeneous mixtures of refractory compounds have been produced by SHS method with reduction stage. This method was successfully used to synthesize dozens of various compositions of refractory carbides, borides, nitrides, silicides with oxides of aluminum, magnesium, and other metals.

The major contribution to this field of powder SHS was made by Mamyan, Holt, Munir, Moore, Koizumi, Logan, Cutler, Miyamoto, Wojcicky [7, 53, 55, 56, 57, 61, 70].
The compositions of the heterogeneous mixtures produced and the range of initial reactants are permanently increasing in their variety, for instance, at the expense of using raw materials of complex composition. From this point of view great interest are the studies carried out by Mamyan et al., who synthesized complex heterogeneous mixtures of the following types: BaB_6-LaB_6-MgO-$MgCl_2$; LaB_6-CaB_6-MgO-$MgCl_2$; $MoSi_2$-Al_2O_3; BN-MgO; TiB_2-$B_{13}C_2$-Al_2O_3 [60].

The distinctive feature of these works is the use of various types of raw material from different regions of the Soviet Union and other countries in the SHS process, as well as large number of thermodynamic calculations of the combustion temperature and product composition allowing the optimum use of SHS conditions [6]. One of the diagram based on thermodynamic calculations for diatomite - Mg-N_2 with final products Si_3N_4+MgO, is given in Fig.11.

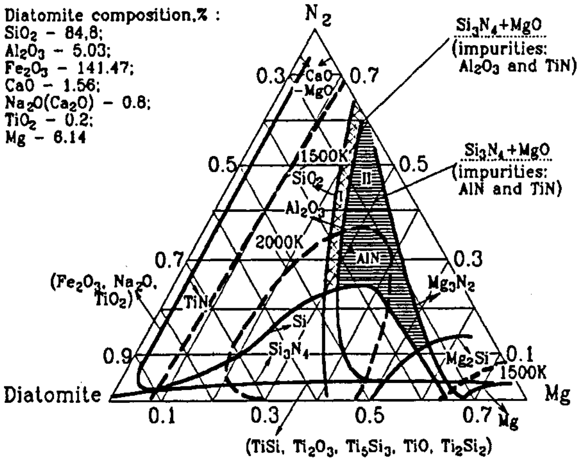


Fig.11.
SHS with reduction stage. Silicon nitride production from diatomite.

Among unique products obtained with the use of SHS with reduction stage are heterogeneous mixtures SiC-Y_2O_3, SiC-ZrO_2 synthesized by Pampuch, TiC-ZrO_2 and NiAl-Al_2O_3 - by Miyamoto with coworkers, (WC;Co)+Al_2O_3 compositions - by Wojcicky [60], ultrafine - powders in TiB_2-Al_2O_3 system - by Logan [57], materials based on TiC-Al_2O_3 - by Koizumi [55], some interesting compositions of $TiC_{0,5}TiN_{0,5}$-Al_2O_3, HfB_2-Al_2O_3 type - by Cutler [59], etc.

Not less important, numerous studies in the area of heterogeneous mixtures with oxides were accomplished in the framework of SHS casting trend. Major contribution in this field was made by Yukhvid with coworkers [8,9] and Odawara [10]. From chemical viewpoint, the studies carried out by Yukhvid feature greater variety of cast compositions with a refractory constituent such as carbide, boride, and silicide and Odawara obtained a wider range of cast materials based on oxide mixtures.

The starting mixtures used in SHS casting are known to be extremely exothermic and the combustion temperature can exceed 3500°C in some cases. According to Merzhanov [9] SHS casting comprises two major reaction types:

Type 1. Oxide-elemental type $3CrO_3+6Al+2C \longrightarrow Cr_3C_2+3Al_2O_3$

Type 2. Oxide type $MoO_3+B_2O_3+4Al \longrightarrow MoB_2+2Al_2O_3$

A specific role is played by thermite reactions known since long which occur without involving nonmetallic constituent forming refractory oxygen-free compound, for instance:

$$Fe_2O_3+2Al \longrightarrow 2Fe+Al_2O_3.$$

Cast SHS products comprise heterogeneous mixtures of refractory compounds with oxides (cast composites). Yukhvid with coworkers synthesized various types of such composites: powders, parts, and coatings [8]. Importantly, the refractory compound was uniformly mixed with the oxide of metal-reductant. Of major interest are the systems:$TiC-Cr_3C_2-Al_2O_3$; $VB-Al_2O_3$; $Cr_2O_3-Al_2O_3$; $Mo_2C-Al_2O_3-MgO$, and the like. Yukhvid with coworkers thoroughly intestigated the formation mechanism in cast systems, combustion laws and distinctive features of the composite synthesis; theoretical models of some processes employed in SHS with melts have been suggested.

As was mentioned above, a large contribution to producing cast materials with the use of SHS was made by Odawara [10,62]. Among composite materials obtained by this author the most interesting are $Al_2O_3-SiO_2-FeO$; $Al_2O_3-SiO_2-B_2O_3$; $Al_2O_3-ZrO_2$, and others. Initial reactants for synthesizing heterogeneous mixtures of oxides are very diverse:

$$Fe_2O_3-Al-Si \longrightarrow Al_2O_3-SiO_2-FeO$$
$$Fe_2O_3-Zr \longrightarrow Al_2O_3-ZrO_2$$
$$Fe_2O_3,Al,Mg,Si_3O_2 \longrightarrow Al_2O_3,SiO_2,FeO,MgO$$

Fe + thermite mixture (Al,Fe_2O_3,SiO_2), etc.

Heterogeneous SHS systems may be considered to involve an extended group of special and hard alloys based on refractory carbides, borides, nitrides, and the like, with binders such as Ni, Co, Fe, Ti, etc. This group also comprises gradient alloys which are currently of special interest. Special alloys such as master alloys of nitrided ferrovanadium, ferrochromium, ferromanganese, and others are of primary importance in the works by Maksimov et al, [63]. The initial reactants for producing desired materials are metallic alloys and the task is to retain needed alloy composition during combustion. Commonly, the combustion process is carried out in nitrogen atmosphere and the basic reaction can be as follows:

$$FeV+1/2\ N_2 \longrightarrow VN + Fe$$

Quite recently, Yukhvid with coworkers employed the wastes of metallurgy production to obtain ferroalloys by SHS method:

scale + Al chips + filler(Me chips, oxide waste) ⟶ ferroalloy + corrundum (Al_2O_3).

Some examples of this process:

$$\sum Fe_mO_n+Al \longrightarrow (Fe-Al)+Al_2O_3$$
$$\sum Fe_mO_n+Al+Ti \longrightarrow (Fe-Ti)+Al_2O_3$$
$$\sum Fe_m+Al+V_2O_5 \longrightarrow (Fe-V)+Al_2O_3$$

(used catalysts)

Interesting, unusual for SHS, alloys have been recently described by Moore [64]. These are aloys with general formula Ni-Ti-x (x=Fe,Pd). They can be obtained in SHS mode using the following reactions:

$$Ti(s)+Ni_{0,5-x}(s)+xPd(s) \longrightarrow TiNi_{0,5-x}Pd_x(l);$$
$$0,23 \leq x \leq 0,5.$$

The synthesis conditions for the alloys of different composition, and their microstructure and properties have been studied in detail. A thorough thermodymanic analysis has been carried out and it was shown that the value of $\Delta H^{o}_{f}/C_{p\;298}$ may play a crucial role in producing such materials.

Wang, Munir, and Holt [65] conducted experiments to produce Cu-(25-50)at.% Al alloys in thermal explosion mode. Using the methods of gamma-spectroscopy, DTA, and SEM, they studied solid-state diffusion processes and liquid phase formation which occurred prior to the basic combustion reaction.

The development of SHS chemistry of hard alloys based on refractory compounds with binders and dopants has been accomplished mainly due to so-called "direct synthesis" of materials and parts (SHS densification, SHS casting, SHS extrusion, gas pressure SHS, SHS-HIP). In this case, the range of materials is not diversified and, as a rule, involves tungsten-free or tungsten-dificient hard alloys. To get acquainted with chemical classes of SHS hard alloys we may consider several examples of compositions produced as compared to commercial counterparts. In first place a group of STIM (Russian acronym for synthetic hard tool material) alloys based on titanium carbides and borides should be mentioned [66]. Chemical composition of these alloys and some of their properties are given in Table 5. Two new alloys can be discerned: $TiC_{0,42-0,47}$ and TiB-Ti. The first one was devised by Ratnikov with coworkers [67] to be used as a material with enhanced ductility and impact strength. Further it was successfully employed for creating porous frameworks under superelastic ductility conditions. The material of TiB-Ti was suggested by Merzhanov [68] and then thoroughly studied by a group of researchers [69] to be used for devising thermostable alloy which found application as the basic material of large-size rollers for rolling non-ferrous metals (Cu, Al) in the works by Kvanin, and also for usage under sharp temperature drop conditions. As being very promising are considered hard alloy materials of the following compositions: $Ti\text{-}B_2\text{-}Cu$; $TiB_2\text{-}Al$; $TiB_2\text{-}Fe$; TiC-Ni(Mo,Cu); $Al_2O_3\text{-}Fe$, $(TiC\text{-}Al_2O_3)Fe$, $(WC+Al_2O_3)Co$, and the like.

Table 5. Hard alloys of STIM grade

Grade	Wear-resistant component	Metal binder	Grain size, μm	Hardness, HRA
STIM 1B/3	TiC, TiB_2	Cu	4-5	93,5
STIM 3B/3	$(Ti,Cr_x)\,C_y$	Ni	3-4	92,5
STIM 4	TiB	Ti	1-2	86
STIM 5	TiC_xN_{1-x} alloyed by Mo	Ni	1-2	92,0
Non-stoichiometric carbide	$TiC_{0.42-0.47}$	Ti	1-2	86-88

A significant number of recent works by the researchers from different countries [70,71,74] deal with the conditions for producing these alloys and structure formation in SHS mode, as well as their properties. It should be noted that researchers show a keen interest not only to alloys but also to the issues concerning kinetics and mechanism of the processes occurring in SHS. From this viewpoint, of interest are the works conducted by Levashov and Bogatov with coworkers [72,75] aimed at elucidating the formation machanism of alloys based on $TiC\text{-}Cr_3C_2Ni$ under conditions of SHS densification with ultrasound effect. The ultrasound effect was shown to significantly influence alloy microstructure, grain size, and to enhance performance characteristics of the material.

The study of kinetics of SHS process for producing Ti-C-Ni system was carried out by Dunmead and Holt with coworkers [53].

A special role is played by gradient hard alloys the attention to which is ever increasing. Sata with coworkers consider these materials as very promising to be employed in engines and aircrafts including supersonic jet planes. Sata et al.[74] carried out experiments on producing functionally gradient materials (FGM) with the use of HIP-SHS and employing impulse electromagnet effect. Among the systems used was that of TiB_2-Cu (metal-ceramics). The preparation of initial mixtures for FGM and hydrostatic pressing in the course of synthesis are computerized. The general reaction of FGM synthesis can be as follows:

$$Ti+2B+aTiB_2+XCu \longrightarrow (1+a)TiB_2+XCu.$$

Functionally gradient SHS materials based on Tic-Ni are described by Miyamoto et al, [71]. These authors are dealing with the issues of combustion sintering, microstructure formation, and reaction control.

A noticable role is played by gradient alloys in the investigations of researchers belonging to Merzhanov's school (Pityulin, Bogatov, Rogachev, Levashov, and others) [75]. In contrast to Japanese investigators, these authors mainly employ SHS densification method. A distinctive feature of this technique is a preliminary preparation of pressed alternating layers of reactant mixture and metal binder which after combustion transform into porous skeleton of a refractory compound impregnated with molten metal binder. Thus, alloys with properties changing over the bulk or materials with a preset gradient of binding metal concentration can be synthesized. The laws of structure formation of gradient materials in Ti-C-Ni and Ti-Cr-C-Ni systems in dependence on SHS parameters have been studied in detail. Two main types of the material have been described: with symmetric and asymmetric nickel concentration profile. The investegations resulted in two alloys SYGMA-1 and SYGMA-2 which have enhanced physicomechanical characteristics. Some strength characteristics of SYGMA-2 in comparison with commercial tungsten-containing hard alloy are given in Table 6.

Table 6. Some properties of Sygma-2 alloy

Alloy	Impact toughness, kgf m/cm	Hardness, HRA
SYGMA-2	1,3	90
WC-Co (8%)	0,35	87,5
WC-Co (20%)	0,48	84

In recent years, more organic compounds, among them polymers, showed up in the field of SHS. In the beginning, they were used as additives to SHS green mixtures with the aim to substitute one of the inorganic reactants and improve the conditions for combustion (e.g., to increase gas phase content). Major achievements in this area are due to the investigations carried out by Kharatyan with coworkers [76]. The carbides that they have obtained using polyethylene and other polymers as one of the reactants feature high dispersity and enhanced sinterability. in our experiments on synthesizing Si_3N_4, SiC, Si_3N_4-SiC we used as additives silicon-organic polymers and organic compounds which substantially influenced the crystal structure of the products, (Fig.13). We also managed to synthesize metal-containing polymer of -C-C-Zr-C-C-O- composition which was identified after the combustion of Zr+C mixtures in high presure CO_2 atmosphere [77]. This polymer features very high thermostability.

Of great interest are the studies carried out by Merzhanov and Klimchuk with coworkers [5] concerning the combustion synthesis of some organic compounds. The reactions of oxidizing hydroquinine into quinhydrone, forming dibrommalonic acid, and interaction between malonic acid and piperazine have been accomplished. The major laws of SHS were studied employing the reaction for piperazine malonate synthesis:

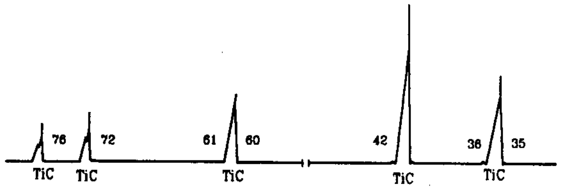
$$C_4H_{10}N_2+C_3H_4O_4 \longrightarrow C_7H_{14}N_2O_4.$$

The yield of the desired product was 100 %. The studies performed allow the development of innovative solid-state ("dry") technology for organic synthesis which may happen to be more efficient as compared to conventional processes.

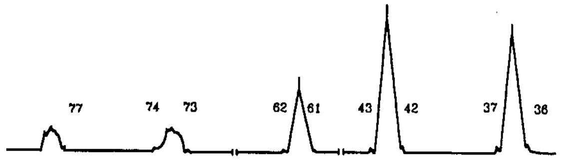
Considering chemical classes of SHS products, one cannot help mentioning their crystalline structure and particle size distribution.

CRYSTALLINE STRUCTURES OF SHS PRODUCTS

Of great importance in SHS research are efforts aimed at revealing the relationship between combustion conditions and the crystalline structure of materials produced. At least three crystalline structures typical for SHS products can be identified. Most of SHS compounds of different classes produced from powdered elemental reactants are polycrystals. Commonly, the products are in equilibrium state and have distinct, narrow characteristic peaks on X-ray patterns. Many of them can be considered as typical examples of equilibrium compounds. Nevertheless, under special or nonoptimum conditions of synthesis and, particularly, during cooling (natural or forced quenching), the forming of non-eqmulibrium products with blurred and broadened lines on X-ray patterns is observed. In Fig.12 are given examples of X-ray patterns of different type for titanium carbide, TiC.



Equilibrium

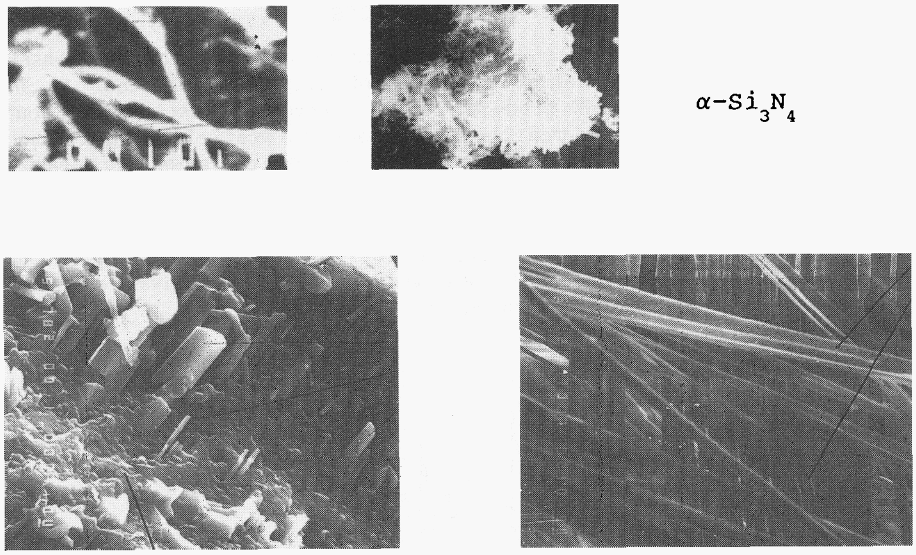


Non-equilibrium

Fig.12.
TiC X-ray pattern.

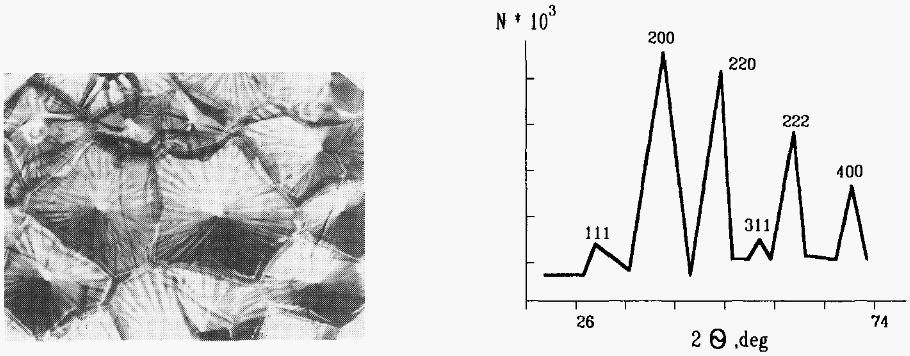
As it was said above, the primary step in SHS process is apparently formation of amorphous phases which later, depending on conditions (the rate and temperature of combustion and cooling, presence of crystallizers, etc.), aquire certain crystalline structures. So far, there are a few works in this area, but some experimental data on amorphous SHS products formation have been already obtained. Most frequently, the formation of amorphous phases was observed when non-metals (B,Si,P) were burnt in high-pressure nitrogen atmosphere (P_{N_2} = 300-800 MPa). Amorphous phase are fairly stable after the combustion and can be crystallized during heating or when they are kept at room temperature for extended period of time . Chemical analysis revealed that the composition of the amorphous products formed corresponds to that of stoichiometric nitrides, however, in some cases phases unknown from literature were obtained, particularly, pink-brownish boron nitride of $BN_{0,75}$ combustion [77]. After heating or extended exposure to room temperature amorphous stoichiometric compounds, as said above, were crystallized retaining their chemical composition. Amorphous SHS products formation was also observed by Mamyan during boron nitride synthesis from boron anhydride (SHS process with reducing stage). Amosov obtained amorphous products when synthesizing silicon nitride in azides presence. In our experiments amorphous silicon nitride was produced in the course of combustion between silicon powder and gaseous nitrogen in the presence of ammonium chloride. In these reactions amorphous silicon diimide was identified as an intermediate product which is known to be a network polymer. In our view this intermediate compound then transforms into SHS silicon nitride with a unique particle structure in the form of whiskers. Under various combustion conditions, silicon nitride powders with different particle structure (agglomerates, columnar crystals) have been obtained. The mechanism of their formation in SHS mode was thoroughly studied by Mukasyan with co-workers [78]. Different structures of SHS - Si_3N_4 powders are presented in Fig.13.

An important area in SHS research is single crystal synthesis. Investigations aimed at producing single crystals in combustion mode apparently have not been performed yet, though there are some evidences of such a possibility. Fairly large, up to 3μm, clear-cut single crystals of TiC have been obtained and thoroughly stydied by Prokudina with coworkers [79]. SHS-TiC single crystals formed during combustion of Ti+C mixtures in sealed reactors of 20 l capacity. Interesting experiments were carried out by Pityulin when he combusted tantalum powder in nitrogen atmosphere using chemical oven for heating-up the reactant mixture. Molten δ - TaN_{cub} with distinct grains has been synthesized (Fig.14).


α-Si_3N_4

β-Si_3N_4 β-Si_3N_4

Fig.13. SHS Si_3N_4 structure



TaN Structure (cub)

Cast TaN (cub)

Neutron Diffraction Pattern δ– $Ta_{0.83}N$ (cub)

Fig.14. TaN Structure (cub).

It should be noted that δ-TaN_{cub} has never been produced by conventional methods. We were first to synthesize this compound by burning tantalum in liquid nitrogen [82]. The structure of this compound was investigated by Shekhtman with the use of X-ray analysis. Later Ehm and Petrunin with coworkers [81] studied more thoroughly δ-TaN_{cub} using neutron diffraction method. Compositions with "superstoichiometric" nitrogen content ($TaN_{1,2}$) were given the priority in this study. Nitrogen atoms were shown to be located in octahedric interstitial sites; metal sublattice had defects. Consequently, more correct chemical formula of this nitride is δ-Ta_yN ($y<1$), which is different from that commonly used in literature, TaN_x ($x>1$). It should be mentioned that because of this particularity of its structure, δ-TaN_{cub} differs from other nitrides of transitional metals of IY-YI group of the Periodic Table which have cubic lattice of NaCl type. The vacancies in crystal lattice are possibly the cause of anomalously high values of microhardness of δ-TaN_{cub} (3200 kg/mm^2) as compared to that of other nitrides which never exceeds 2000 kg/mm^2.

Concerning the issue of producing single crystals of refractory compounds in SHS mode, our paper devoted to obtaining single crystals of WC should be mentioned. Fairly large, clear-cut crystals of this carbide were obtained by Yukhvid in experiments on forming cast refractory compounds with the use of strongly exothermic reactions. The synthesis of nonmetallic nitrides in SHS mode practically always yields some portion of combustion products in the form of single crystals growing from gaseous phase ("whiskers", columnar crystals, clear-cut crystals of different shape), Fig.13.

Not less important is the task of growing single crystals from powdered SHS products. SHS compounds proved to be very convenient raw material for growing single crystals of various classes. Most of powdered SHS compounds feature high purity. Particle size distribution of these compounds can be tailored to fit the requirments for better crystals growth.

One of the most impressive examples of how SHS products can be used of crystal growth on commercial scale is lithium niobate powder obtained by Nersesyan with coworkers [83]. Single crystals of lithium niobate grown from SHS charge feature high purity, perfect structure and good electrophysical properties. The same authors developed a method for synthesizing ultrapure powders of gadolinium molibdate from which high quality single crystals are being grown $Gd_2Mo_3O_{12}$.

Investigations aimed at selecting and using SHS products for growing single crystals are being conducted by Shteinberg and his coworkers [84]. They obtained and studied some of physical and chemical properties of SHS-TiB_2 and SHS-B_4C single crystals.

Particle size distribution of SHS products

To successfully employ SHS products, particle size distribution of combustion products is of significant importance. Two aspects of this issue should be taken into account: (1) particle size of the products produced directly by SHS and (2) product particle size which can be achieved by employing conventional and innovative methods of comminution.
Particle size of SHS products as was shown in the course of combustion mechanism studies in different systems, strongly depends on the process step at which these products are formed. Analysis of SHS products of different classes shows that the range of their particle size is very wide; it is expedient to classify products into several groups:

- coarse-grained with broad particle size distribution
- coarse-grained with narrow particle size distribution
- fine-grained as SHS produced
- fine-grained due to subsequent crushing, grinding, and special treatment.

Coarse-grained SHS products with particle size up to I mm and wide particle size distribution can be produced by using various technological types of SHS. These can be combustion products obtained from initial reactant containing powdered mixtures of elements with broad particle size distribution. In this case the condition for large particles to form is large reactive mass and extended cooling time.

A batch of coarse-grained powders (mainly abrasives) with different particle size is being manufactured by using mechanical grinding of compacted or cast SHS products and subsequent classification. Classification of powders is carried out in a fairly small range of particle size, commonly in accordance with abrasive specs requirements.

A very interesting task is fabricating fine-grained SHS products directly in combustion mode. Currently, investigations of structure formation in SHS process are being intensively conducted by Merzhanov, Rogachev with coworkers [25]. Earlier works on combustion products quenching and subsequent prolonged comminution show a possibility of formation of fine-grained SHS products with particle size ≤ 3 μm in the course of combustion reaction. Powders of SHS carbides, nitrides, borides, silicides with particle size range of 1-5 μm and 1-10 μm can be readily manufactured from oxide by SHS method with reduction step [7]. Usually, these powders have narrow particle size distribution. Recently, Logan [57] described fine-grained (~ 1 μm) powder of titanium diboride produced by this SHS method. There are examples of synthesizing fine-grained SHS products of different classes with the use of various compounds as starting reactants [12, 13], or by creating special conditions for the process to occur. To obtain fine powder of silicon nitride we used various organic materials as additives into starting mixtures. As it was said above, nitrides having interesting structures have been synthesized, among them β-Si_3N_4 with distinctly seen "columnar" crystals and, also, α-Si_3N_4 with particles of irregular shape and 0.2-0.5 μm in size.

Mechanical comminution of SHS products requires a special approach due to particularities in the structure of sintered bodies and agglomerates after combustion. We have started investigations in this area employing different types of grinders: ball, globe and vibrating mills, pneumocomminuters, attritors, etc. The smallest particle size currently achieved during milling is ranging from 1 to 3 μm. A promising technique for comminution of SHS products seem to be chemical treatment of combustion products the use of which allows the structure of individual particle to retain in contrast to the case when mechanical milling is employed [85].

Surface vs. chemical treatment time plot for Al powder is given in Fig.15. A picture of agglomerate with constituent particles "disclosed" in the course of the treatment is presented in Fig.16.

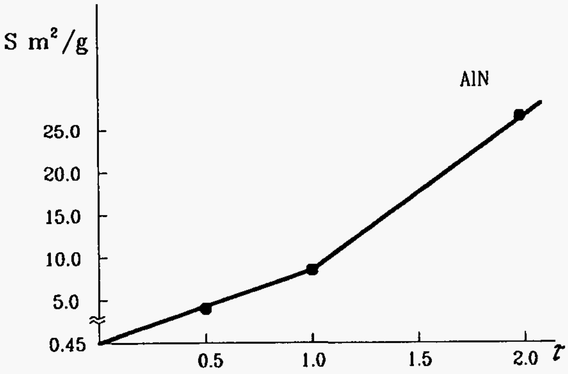


Fig.15.
Al powder specific surface vs. processing time.

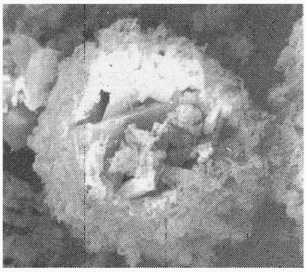


Fig.16.
Chemical treatment Si_3N_4.

Conclusion

Chemical classes of SHS processes and products are currently covering a whole branch of inorganic chemistry and metallurgy which is continuously extending. It turned out that combustion reactions can yield practically all known to date refractory and inorganic compounds. Some experiments, particularly, on the synthesis of new phases, amorphous products, and organic materials show that SHS method is far from reaching its limit and most interesting results are still ahead.

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