Reviews

Fundamentals, achievements, and perspectives for development of solid-flame combustion*

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The review is devoted to the problem of self-propagating high-temperature synthesis (SHS). The fundamentals of SHS are briefly considered, the most promising results of the experimental diagnostics and modeling of SHS processes are presented, new nonlinear phenomena and the data of thermodynamic calculations, as well as kinetic and macrokinetic studies are discussed. The main types of the SHS technology and their application for the preparation of new compounds, materials, and items along with technical and economical effectiveness are considered. New directions and perspectives of SHS are discussed.

Key words: combustion, self-propagating high-temperature synthesis; experimental diagnostics; mathematical modeling; energy-saving technologies, production.

Introduction

In 1967, Borovinskaya, Shkiro, and the author[1] studied experimental models of combustion in condensed systems and discovered a process during which all substances (starting, final, and sometimes intermediate) exist in the solid state even at very high combustion temperatures. Later this phenomenon was called solid flame (SF) or solid combustion. Solid flame was first discovered in mixtures of titanium and boron powders, whose interaction was performed in an autowave mode as a running wave of the oxygen-free combustion in an inert atmosphere to form titanium monoboride as the combustion product.

The photograph of this combustion (Fig. 1) distinctly shows the main stages of the process:

— initiation (ignition);
— propagation of the front separating a mixture of the initial reagents from the incandescent combustion product;
— cooling of final product.

A similar situation is observed for all systems of this type. The appearance of the solid flame resembles the combustion of thermites,[2,3] but differs in the chemistry and macrokinetics and, as has been elucidated in further studies, in the possibility of practical use.

The phenomenon of SF has aroused tremendous scientific interest. First, it was unclear how slow solid-phase reactions, which, in addition, result in the formation of solid products,* can occur in such fast modes as combustion. It was precisely this circumstance

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* These are so-called autoretarding reactions, during which the layer of the solid product formed separates the reagents and prevents their further interaction.

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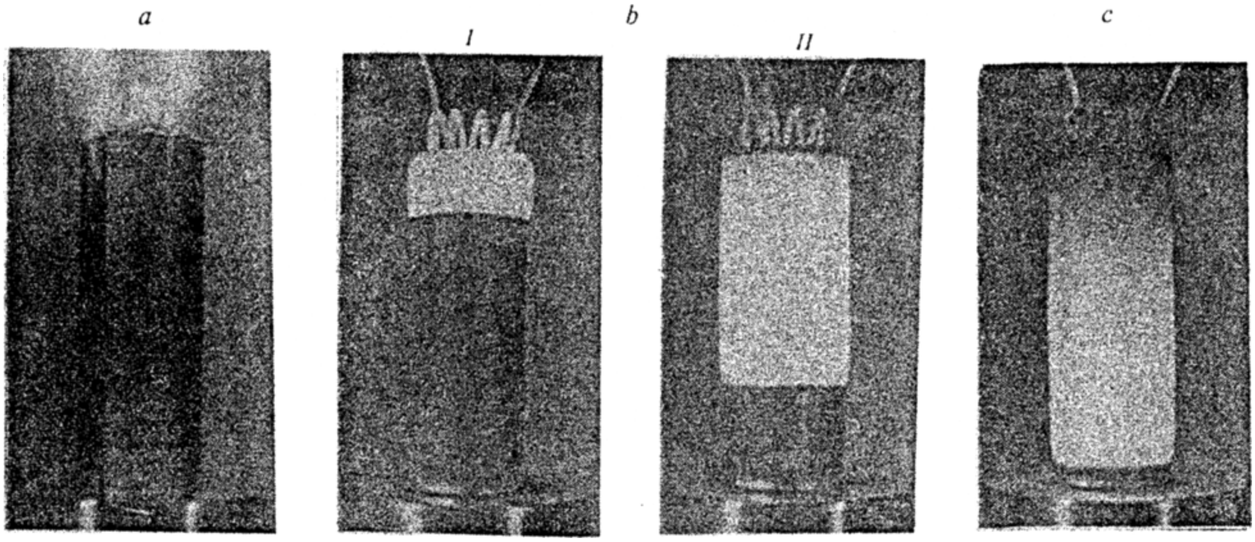

Fig 1. Frames of the SHS process (combustion of the cylindrical sample molded from a mixture of titanium and boron powders); *a*, ignition of the initial sample, $t = 0$ s; *b*, propagation of the combustion front, $t = 0.1$ (*I*) and 2.7 (*II*) s; and *c*, cooling of the burnt sample, $t = 4$ s.

which made it possible to license the phenomenon of SF as a scientific discovery under the title "Phenomenon of the wave localization of autoretarding solid-phase reactions".[4]

Not only unusual combustion processes, but also their products were of interest. Depending on the choice of reagents, they were refractory compounds: borides, carbides, silicides, and other substances, as well as multicomponent materials, for which the known methods of synthesis were energy-consuming and low-efficient. A new method of their preparation appeared, which was called the self-propagating high-temperature synthesis (SHS).[1,5]

Specific features of SHS are evident and attractive: no energy consumption for the achievement of high temperatures, high rates of synthesis, and the simplicity (or absence) of special equipment.

The self-propagating high-temperature synthesis, which appeared at the interfaces between the theory and practice of combustion, on the one hand, and between the chemistry and technology of materials, on the other hand, served as a "springboard" for new ingenious directions of studies, one of which is the structural macrokinetics involving phase and structural transformations in the sphere of direct and inverse relations between chemical reactions and transfer processes.[6—9]

Interest in the discovery (in SF as a phenomenon and in SHS as a method of synthesis) favored the fast development of these studies. Scientific, technological, material-science, and industrial fundamentals of SHS have been developed during recent years. First, the work was carried out at the Branch of the Institute of Chemical Physics in Chernogolovka (Academy of Sciences of the USSR) and then in different scientific centers in our country and abroad.

This review is an attempt to look at SHS as a scientific discipline, to tell how this large, fast-developing scientific technical field has grown from the scientific discovery mentioned.

Primary SHS: results and ideas

In the first experiments[5,10,11] we studied reactions of direct synthesis from elements to form refractory compounds, which occur *via* the scheme

$$R^1 + R^2 \rightarrow P + Q,$$

where R^1 = Ti, Zr, Hf, Nb, and Ta; R^2 = B, C, N_2, and Si; P is the product (borides, carbides, nitrides, and silicides), and Q is the heat effect of the reaction.

It was clear from the very beginning that SHS is a thermal process, and the possibility of autowave processes of the combustion type in SHS systems is caused by the heat release in the chemical interaction of reagents ($Q > 0$) and its transfer from hot to cool layers of the substance. The aforementioned refractory compounds have high binding energies between atoms, and their synthesis from elements is accompanied by the release of a large amount of heat. Due to this specific feature, they became perfect experimental models for studying SHS.

A simple task was posed in the first experiments: to study the dependences of the front propagation velocity and some other easily measured parameters of combustion as well as the composition (chemical and phase) of the final products of combustion on various parameters: the particle size of the reagent, density, the initial temperature and diameter of the sample, the composition of the charge, the nature and concentration of

Table 1. Main parameters of the SHS process

Initial system		Process	
Parameter	Value	Parameter	Value
Size of particles, r/μ:		Burning velocity, U/cm s^{-1}	0.1—20
metals	5—100	Combustion temperature, T_{max}/K	2300—3800
nonmetals	0.1		
Relative density of samples, Δ	0.3—0.6	Rate of heating of the substance in the wave, ω/deg s^{-1}	10^3—10^6
Size of samples:		Power of ignition,	
diameter, d/mm	5—20		
length, l/mm	(2—5)d	q_{ign}/cal cm^{-2} s^{-1}	10—200
Initial temperature, T_0/°C	25—400	Delay of ignition, t_{ign}/s	0.2—1.2
Pressure of gas, p/atm	1—150	Ignition temperature, T_{ign}/K	800—1200

controlling additives and diluents, and the pressure and nature of the surrounding gas. Special experiments on checking these or other ideas and theoretical studies were also performed.[12,13] The experience obtained in studying combustion of gasifying condensed systems, propellants, explosives, and rocket fuels (see, *e.g.*, Refs. 14—18) had a great effect on the methodology of the investigations. The typical values of parameters that characterize conditions of SHS and the process itself are presented in Table 1.*

The rather high level of dispersity of the reagents should be emphasized: it is difficult to perform SHS in coarse-powdered systems.

Attention has been drawn to the possibility of obtaining high burning velocities, combustion temperatures, and heating rates in the wave, which are not typical of combustion in heterogeneous condensed systems. This made it possible to regard SHS as an extreme chemical process.

The systems and processes studied were divided into two groups. The first includes mixtures of R^1 and R^2 powders. In these systems, combustion occurs without participation of the gaseous medium (in vacuum or in an inert gas) and does not result in the gasification of reactants. It is the so-called gasless combustion.

The second group contained hybrid systems, in which R^1 is a metal powder as a filling or molded sample, and R^2 is a gas. At rather low pressures of the gas, its content in pores of the sample is small, and the self-propagating (frontal) process can occur only due to the spontaneous infiltration of the gas from the environment to the combustion front. In this case, the combustion front acts as a "pump",[10] which injects the gaseous reagent from the surrounding medium into pores. This variety of the SHS process, which was discovered for combustion of pelleted Ti samples in nitrogen,[10] was named infiltration combustion. It is of interest that the idea about the possibility of autowave processes in similar hybrid systems appeared after the chemical analysis of central layers of the products formed in the combustion of titanium and boron mixtures in nitrogen,* which revealed a great amount of bound nitrogen.

The studies of gasless and infiltration combustion processes have led to the following important results.

1. The burning velocity can substantially depend on parameters and vary as much as a factor of 10—15 in the same system. The parameters which exert the strongest effect are the particle size (heterogeneity scale) and the concentration composition of the charge. The types of dependences of the burning velocity on parameters are classified in one of the works of the author,[19] and some experimental data are generalized by Rice.[20]

2. There are combustion limits related to heat losses from the combustion zone to the surrounding medium. The values of critical diameters of sample, below which the combustion does not propagate, are usually low (several millimeters or less).

3. A steady combustion mode, at which all points of the front move with the same time-independent velocity can lose its stability upon the variation in parameters. When the stability is lost, the propagation process is not ceased, but gains unusual, previously unknown forms:

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* In particular cases, some values can be beyond the range of the values presented in Table 1.

* In the first experiments on SHS, it was mistakenly assumed that nitrogen is an inert gas.

thermal autooscillations of the front, spinning waves, and thermal turbulence (see p. 10).[21]

4. The macrostructure of the products of gasless combustion, as a rule, is uniform: the composition of the substance is almost the same in all points of the bulk of the products. For infiltration processes, the situation is more complicated and depends on the ratio of the characteristic times of infiltration to the chemical reaction in the wave. Limiting cases are possible when the combustion wave propagates in layers as in the gasless systems (in this case, the macrostructure is uniform), and only surface layers of the sample burn out, while the sample bulk remains unreacted (in this case, the graded macrostructure forms).

5. The chemical homogeneity of the microstructure is related to the complete transformation of the reactive system. For SHS processes, strong underburning of reagents is possible, especially in the case of coarse particles of the reagent and short times of the heat relaxation of the combustion products. The factor that prevents completeness of the transformation is the low relative density of samples for gasless processes and, by contrast, the high density for infiltration processes. A strong incompleteness of the transformation in the combustion zone can result in such unusual phenomena as the existence of two stationary fronts which move one after another, the repeated combustion in an partially burnt sample, or the reflection of the front from the plane surface of the sample as it moves to the opposite direction.

The homogeneity of the microstructure of the products by phase composition (the formation of monophase products) often depends on the correlation of conditions of the process with the phase diagram of the system.

Understanding of the aforementioned regularities revealed during the primary studies of SHS resulted in the creation of methods for controlling the rate, temperature, and completeness of combustion as well as the composition and structure of the products. The synthesis of monophase refractory compounds (borides, carbides, nitrides, and silicides) with a low content of admixtures of unreacted elements, the synthesis of off-stoichiometric carbides and borides with ordered supermolecular structures, and the preparation of solid solutions of metals and nonmetals as well as binary refractory compounds in the same process can be presented as examples.[22] The cubic modification of tantalum nitride was first synthesized in the bulk (not in the film) by the SHS method.[23,24] There were interesting experiments on the combustion of boron in liquid nitrogen in sealed vessels to form small amounts of borazon, a cubic modification of boron nitride.[22]

An important success in primary studies of SHS processes was the understanding of the main mechanism of the propagation of purely solid flames, which seemed intriguing when this phenomenon was discovered. It was not difficult to establish that the long time of reacting of particles in the combustion wave determined by diffusion processes in the solid state obviously contradicted the observed burning velocities. The situation was aggravated by the fact that the interaction of reagents occurred with a strong retardation due to the formation of the product as a barrier layer between them. Therefore, it was unclear from the viewpoint of the classical theory of combustion how SF can propagate.

Detailed purposeful studies made it possible to answer this question. Various factors characterizing solid and gas flames are presented in Fig. 2. For combustion of gases, the kinetic retardation of the reaction associated with burning out of the initial substance is low, and the process is determined by the strong heat acceleration of the reaction. As a consequence, the combustion front is formed at an almost complete transformation of reagents in a narrow (compared to the preflame zone) zone adjacent to the combustion products. The velocity of the front propagation (U) is determined by the maximum combustion temperature ($T_{\max}$), which can be calculated from thermodynamic concepts. These classical ideas were developed by Zel'dovich and Frank-Kamenetskii.[25]

In solid flames, the kinetic retardation is strong due to peculiar laws of the interaction of elements (diffusional reaction) and is comparable with the thermal self-acceleration of the reaction. As a result, they compete in the combustion wave. This leads to the fact that the burning velocity is determined by the incomplete conversion ($\eta_* < 1$) and is related to some intermediate temperature T_*, which is lower than $T_{\max}$. The parameters determining the burning velocity cannot be thermodynamically calculated and are determined from some additional macrokinetic condition. These processes are characterized by an anomalously broad reaction zone, whose frontal part only affects the propagation of the front. A considerable portion of the substance can react in the afterburning mode. Obviously, similar processes are possible only for high exothermic reactions, which develop high temperatures. Thus, the specific features of the solid combustion are caused by high values of the heat effect of the reaction and difficulties in the achievement of completeness of the heat release.[26,27]

The primary studies of SHS processes performed by the author and co-workers[22,28—31] played an important role in the development of SHS as a unique and promising scientific direction.

Subsequently, interest in SHS and the problems of investigation were considerably growth. Successes were achieved in the development of methods for experimental diagnostics and mathematical modeling of SHS, independent kinetic and thermodynamical studies at high temperatures, and in the enlargement of the raw material and material-scientific basis of SHS. The latter made it possible to advance considerably from studying the mechanism of the combustion to the development of the technology and industrial production of materials.

The main features of the modern SHS will be considered below.

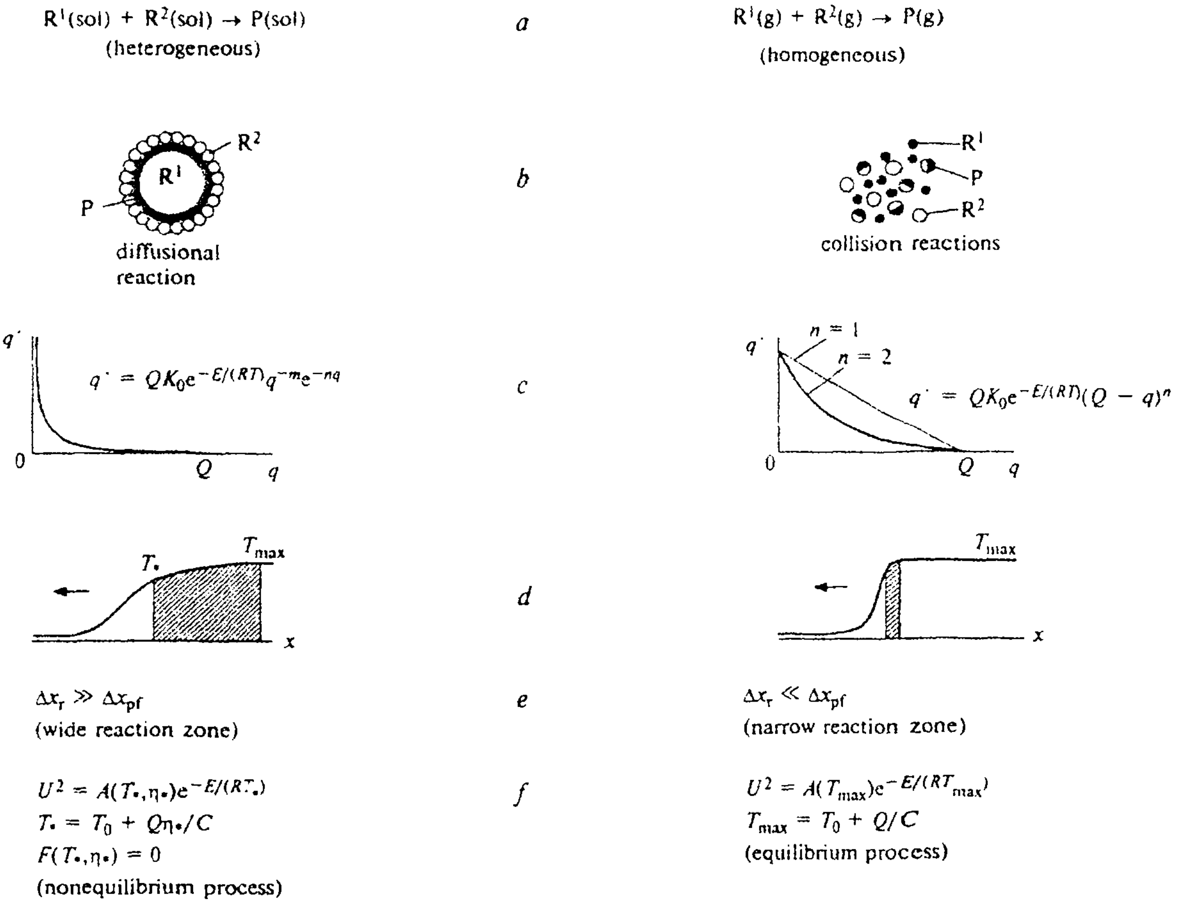

Fig. 2. Representation of the nature of solid flames: *a*, scheme of the reaction (the structure of the initial system; *b*, model of the reaction; *c*, law of heat release (q is the amount of released heat, $q/Q = \eta$ is the conversion of reagents, E is the activation energy); *d*, the structure (temperature profile) of the wave (the reaction zone is hatched, x is the linear coordination, along which the combustion wave propagates); *e*, the ratio of zones (Δx_r is the width of the reaction zone, Δx_{pf} is the width of the preflame zone); *f*, rate (U) of the flame propagation (C is the heat capacity).

Experimental diagnostics and theoretical studies of steady SHS processes

The diagnostic studies, whose purpose was the determination of the mechanism of SHS in each particular case, played an important role in the development of the SHS problem. The majority of these studies was performed for steady modes of combustion.

These works made it possible to reveal three levels of diagnostics.[32]

The *first level* is based on phenomenological approach. The experiments are restricted to measurements of easily observed parameters of SHS (for example, limits of the front propagation and loss of stability, the combustion velocity, and the composition of the final products) for various parameters of the system. It is precisely the phenomenological approach that prevails in the primary studies of SHS described previously.

The phenomenological studies showed that the burning velocity (and often the composition of the combus-

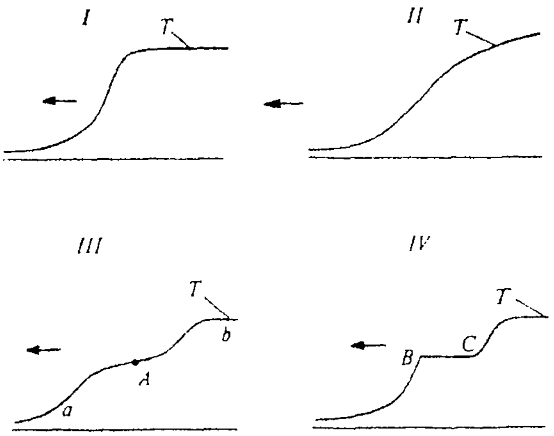

Fig. 3. Elementary types of temperature profiles in the wave: *I*, classical profile; *II*, solid-flame profile; *III*, staged reaction (*a*, the first and *b*, the second stages, *A* is the inflection point); *IV*, phase transition (isothermal plateau *BC* corresponds to the phase transition).

tion products as well) are complicated functions of parameters. Their explanation by theoretical models makes it possible to obtain indirect information on the mechanism of SHS for these or other classes of systems.

Thermal probing of the combustion wave (measurement of temperature profiles in the wave) is related to the *second level* of diagnostics. This is usually carried out by inertialess microthermocouple or optical spectral methods.[33,34]

The diagnostic studies of the second level showed that the combustion wave in SHS systems is rather long and has a fine structure, and various effects accompanying combustion can be monitored on the temperature profile as breakdowns, bendings, and isothermal surface areas. The elementary types of temperature profiles are presented in Fig. 3, and the temperature profile of combustion of a mixture of titanium and silicon powders, which is typical of many systems with a complicated phase diagram, is presented in Fig. 4 as an example.

The *third level* of diagnostics is associated with the direct study of the dynamics of phase and structural transformations in SHS processes. The first two levels are typical of all autowave combustion processes, while the third level is inherent to SHS only. In this case, the diagnostics is aimed at understanding the dynamics and the mechanism of the phase and structure formation in the final products of the combustion. Changes in the phase composition and structure of the substance in SHS processes are studied by time-resolved X-ray diffraction analysis and quenching of the burning sample followed by the layer-by-layer chemical analysis of the substance.

The continuous detection of the phase composition of the substance in the wave requires the fast-responce procedures of X-ray measurements. The author suggested to use the synchrotron radiation[35] for these purposes. This idea was successfully realized by Aleksandrov, Boldyrev, and co-workers[36] and was developed in the

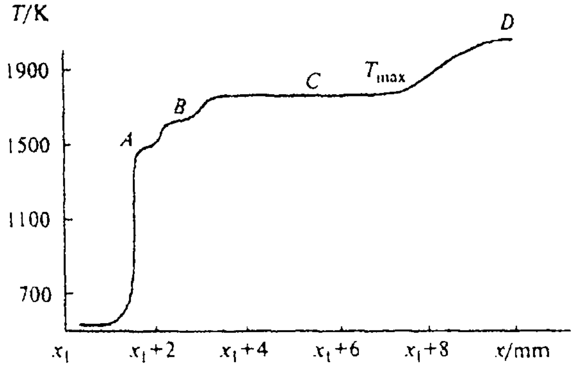

Fig. 4. Temperature profile in the combustion wave of the 5 Ti + 3 Si system: *A* and *B* formation of intermediate products Ti_3Si and Ti_5Si_4; *C*, melting of the intermediate product $TiSi_2$; and *D*, formation of the final product Ti_5Si_3.

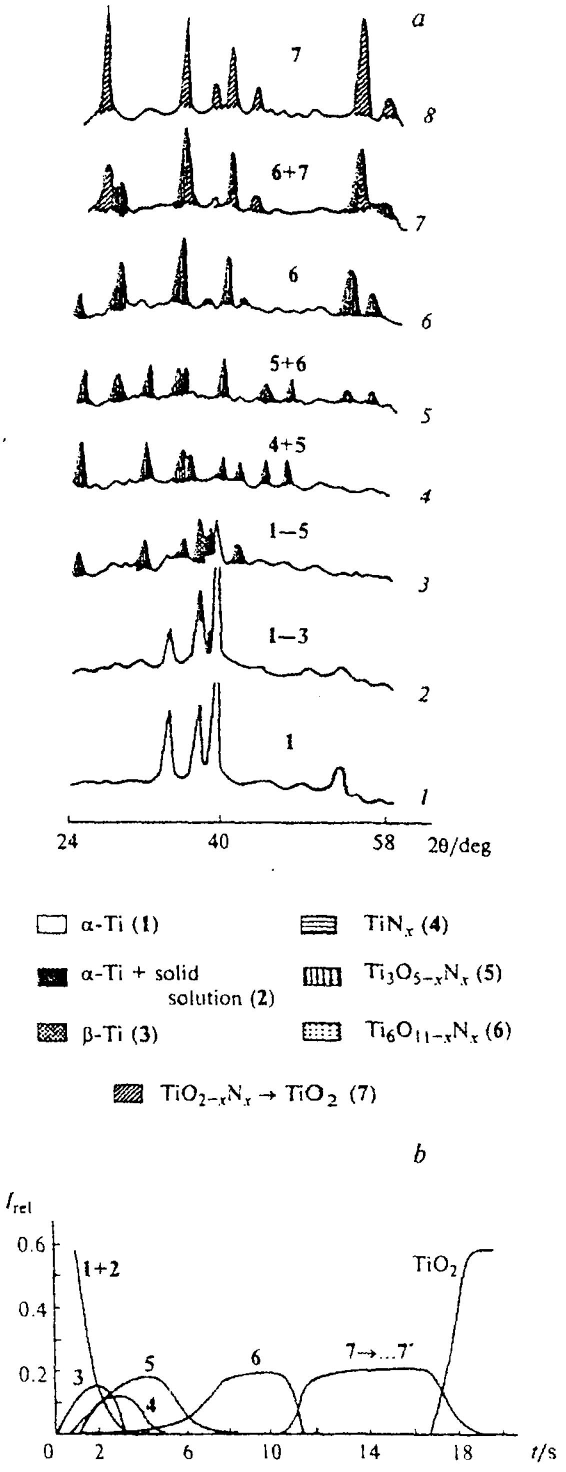

Fig. 5. Combustion of titanium in air. *a*. Dynamic diffraction patterns; **1**—**7**, different individual phases alternating in the SHS processes; curves *1*—*8*: 0 (*1*), 1 (*2*), 2 (*3*), 3 (*4*), 5 (*5*), 7 (*6*), 10 (*7*), and 11 (*8*) s from the beginning of the experiment. *b*. Kinetics of the change in the phase composition in the wave.

works of American researchers.[37] The idea of the experiment is simple. An X-ray beam is focused on some point of the surface of the sample, against which the combustion wave is running. The diffraction pattern is recorded almost without inertia: the time of outfitting diffraction patterns is equal only to 0.01—0.05 s, which is considerably shorter than the time of presence of the substance in the wave even for fast SHS processes. Thus, the process can be characterized by a family of diffraction patterns detected from different points of the wave (but from the same point of the sample). The processing of these diffraction patterns makes it possible to plot the profiles of the initial, intermediate, and final phases in the wave and to study the kinetics of a change in the phase composition of the substance during SHS.

However, synchrotron measurements are difficult and expensive, which does not allow one to perform detailed and wide studies of phase transformations during the SHS processes. Recently, a laboratory setup based on the usual X-ray diffractometer has been created, which makes it possible to solve the same problems as for the use of the synchrotron radiation.[38] The kinetics of a change in the phase composition during SHS processes in the Ni + Al; Ti + C; 5 Ti + 3 Si; Nb + N_2; Ti + N_2; Ti + air, and other systems were studied using this setup.[39] The overall view of phase transformations for the combustion of titanium in air is very rich.[39,40] The time-resolved diffraction patterns and their kinetic processing are presented in Fig. 5. It is of interest that the primary stage of the interaction of titanium and air in the combustion wave is the formation of titanium nitride, and the final product (rutile) forms due to its oxidation *via* many hydroxynitride phases.

However, the time-resolved X-ray analysis makes it possible to obtain information from the surface layers of the sample. The extrapolation of the results to the deep layers requires an understanding of the macrokinetic picture of SHS.

The analysis of quenched samples is used to obtain both local (in any microvolume) and averaged (in layers parallel to the planar front of the combustion) information. The main problem is to establish the correspondence between the values measured by this method and the values that take place in the combustion wave *in situ*. Therefore, the quenching rate is an important parameter of the method.

In the first experiments,[22] the burning sample was quenched by liquid argon.* The cooling rate was about 10^2 deg s^{-1}. Then a new unconventional procedure was suggested.[41] A sample from the SHS charge was placed in a spherical gap in a copper wedge. The combustion front propagates from the base to the vertex of the wedge. As the front moves, the diameter of the sample decreases, heat losses to the copper block increase, and the extinguishment occurs at some distance from the vertex. The cooling rate near the extinguished front is estimated as 10^3 deg s^{-1}.

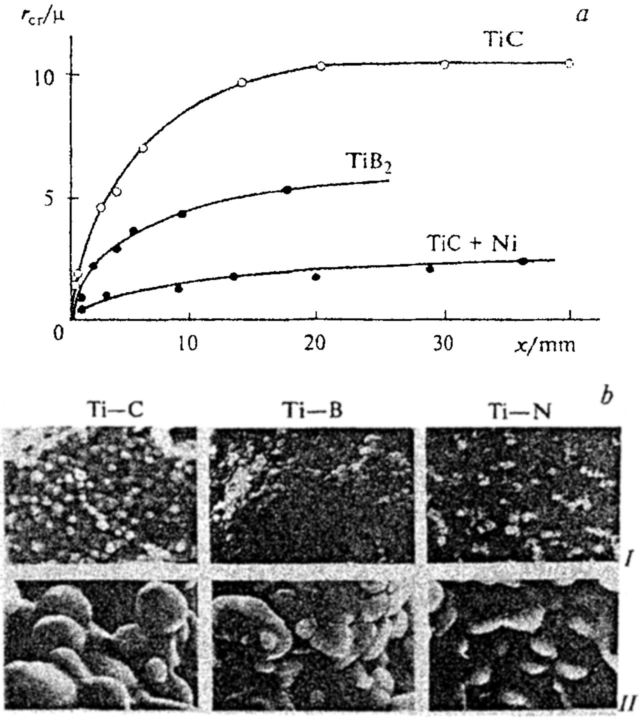

Fig. 6. Recrystallization of the product in SHS processes; profiles of sizes of crystallites r_{cr} (*a*) and photomicrographs of structures (*b*): *I*, combustion zone; *II*, final product.

The most interesting results using the quenching procedure were obtained in the study of the dynamics of the formation of the grain structure in combustion products. The dependence of sizes of a grain of the product on the distance to the front for several compounds and a microphotograph of the combustion product are presented in Fig. 6.[7] A strong recrystallization growth of grains after the completion of chemical processes is distinctly seen (the increase in sizes of particles can be up to tenfold).

The comparison of the data on the formation of the phase composition of the combustion products obtained using both procedures of the third level testify to the good agreement between the results obtained.

The theoretical studies of SHS persue the same purposes as the experimental diagnostics. However, they are characterized by a more general statement: for classes of systems and processes, but not for individual objects. The basic system of equations which describes the steady combustion of SHS systems comprises classical one-dimensional equations of the flame propagation, which take into account heat losses for kinetic functions of the autoretardation type:[12,42—44]

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* In some cases of quenching with liquid nitrogen, the sample is not extinguished but flames up with a greater activity, which initiated the development of SHS processes with liquid nitrogen as the reagent.

— *equation of heat conduction*

$$\lambda \cdot \mathrm{d}^2T/\mathrm{d}x^2 + c\rho U \cdot \mathrm{d}T/\mathrm{d}x + Qk_0 e^{-E/(RT)}\varphi(\eta) -$$
$$- (2\alpha/R_0)(T - T_0) = 0,$$

— *kinetic equation*

$$-U\mathrm{d}\eta/\mathrm{d}x + k_0 e^{-E/(RT)}\varphi(\eta) = 0,$$

— *boundary conditions*

$$x = -\infty,\ T = T_0,\ \eta = 0\ (\mathrm{d}T/\mathrm{d}x = \mathrm{d}\eta/\mathrm{d}x = 0);$$

$$x = +\infty,\ \mathrm{d}T/\mathrm{d}x = \mathrm{d}\eta/\mathrm{d}x = 0;$$

$$\varphi(\eta) = \eta^{-m}e^{-n\eta},$$

where k_0 is the pre-exponential factor, λ is the thermal conductivity of the substance, c is the specific heat, ρ is the density, α is the effective coefficient of heat transfer to the surrounding medium, and R_0 is the radius of the cylindrical sample.

The solution of this system, which is the simplest in the SHS theory, made it possible to discover the main features of the solid combustion (see p. 1): to determine the structure of the combustion wave (temperature and conversion profiles in the wave), to calculate the burning velocity and establish its relationship with the structure of the wave (with parameters of the problem), and to determine combustion limits which appear due to heat losses. For the description of the infiltration combustion, this system is supplemented by equations which express the nonisothermal infiltration transfer of the gas to pores of the solid substance.[13,45,46]

The steady-state theory of combustion of SHS systems was developed by taking into account various accompanying physicochemical processes, which was expressed as the introduction of additional terms and/or equations in the system mentioned above.

The most important result of the experimental diagnostics and theoretical studies is the development of concepts about two limiting mechanisms of SHS processes: equilibrium and nonequilibrium.

For the equilibrium mechanism, SHS processes of the phase and structure formation of the final products occur simultaneously with the chemical reaction. The reagents interact *via* the mechanism of diffusional reaction, the reaction product forms at the interface of contact of the reagents and can have a multilayered (according to the phase diagram) structure. By the state of the product, it is a local equilibrium process. It is difficult to obtain this limiting mechanism in a pure form. Its features can be seen in solid flames at very low propagation velocities.

For the nonequilibrium SHS mechanism, products in the metastable state form in the combustion wave, for example, in the form of an amorphous substance, melt, or oversaturated solid or liquid solutions; their transformation to the final products occurs far behind the combustion front in the so-called zone of structure formation and exerts no effect (unlike the equilibrium case) on the burning velocity. The intermediate phase of the substance identified in the phase diagram cannot be obtained in nonequilibrium SHS processes. The nonequilibrium mechanism is characteristic of very fast SHS processes.

The equilibrium approach named the Khaikin—Merzhanov—Aldushin mechanism was first used in 1972—1973 [12,42] and was popular in early studies of SHS processes. The nonequilibrium approach is associated with the name of Borovinskaya,[47] who, studying the combustion of chemical elements in nitrogen, discovered oversaturated solid solutions of nitrogen as intermediates and came up with the idea about the possibility of the formation of metastable combustion products. Both mechanisms were further specified and formulated more distinctly.[6,48]

An interesting method for diagnostics of the SHS mechanism[8] is based on the determination of the value

$$\xi_0 = Ux_0/a,$$

where x_0 is the distance from the combustion front to some point characterizing a fast growth of the phase of the final product in the wave (according to the data of time-resolved X-ray diffraction analysis) and a is the thermal diffusivity of the substance. When $\xi_0 \approx 1$ (*i.e.*, if its order of magnitude is equal to that of the dimensionless width of the combustion zone), the equilibrium mechanism takes place; if $\xi_0 \gg 1$, the nonequilibrium mechanism occurs. The kinetic curves of the phase formation in some systems using the ξ coordinate[9] are presented in Fig. 7. Both the limiting cases of the equilibrium and nonequilibrium mechanisms and the intermediate case are shown.

The notions about the SHS mechanism were developed by the formulation of ideas about the primary and secondary structure formation (the structure primarily originates in the combustion wave and develops far behind the front), about the equilibrium-nonequilibrium mechanism (the process is equilibrium with respect to the intermediate and nonequilibrium with respect to the final product), and about different rates of the development of different structural components (phase compo-

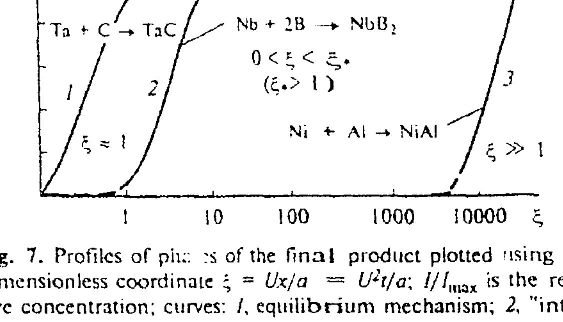


Fig. 7. Profiles of phases of the final product plotted using the dimensionless coordinate $\xi = Ux/a = U^2t/a$; I/I_{max} is the relative concentration; curves: *1*, equilibrium mechanism; *2*, "intermediate" mechanism; and *3*, nonequilibrium mechanism.

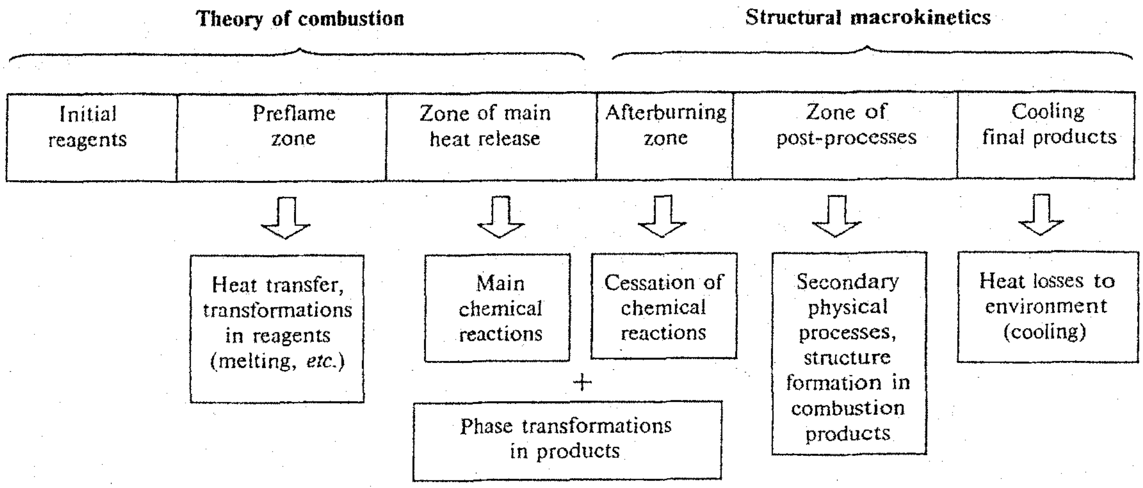


Fig. 8. Generalized zone structure of the wave in SHS processes.

sition, crystal lattice, grain structure, and others).[7–9] These concepts made it possible to express the essence of SHS by the formula[49]

$$\boxed{\text{SHS}} = \boxed{\text{combustion}} + \boxed{\text{structure formation}}$$

and to suggest the generalized structure of the wave in SHS processes (Fig. 8). In SHS processes, the destruction of the initial structure of reagents, which is typical of all combustion processes of condensed systems, is ceased by the formation of the structure of the products. Diversity physicochemical transformations behind the front is a characteristic feature of SHS and the subject of studies of the structural macrokinetics.

Speaking about experimental and theoretical studies of SHS, two more important results should be mentioned. The first of them is the discovery of the so-called phenomenon of capillary spreading (see Refs. 50 and 51 as well as review 52), which is observed in mixtures of coarse particles of "low-melting" metals with fine powders of nonmetals (for example, powders of titanium and/or zirconium with carbon and/or boron). In the preflame zone, where chemical reactions do not yet occur, metal particles are melted, and the melt wets nonmetal particles and spreads over their surface due to capillary forces. This results in a considerable homogenization of the charge, and the scale of heterogeneity decreases consideradly (by several orders of magnitude), which strongly accelerates the reaction and increases the burning velocity. Photographs of the charge and the combustion product are presented in Fig. 9 as an illustration of the phenomenon of capillary spreading. The experiments were carried out with large spherical titanium particles. The combustion product contains cavities (see Fig. 9, *b*), the sites occupied previously by titanium particles. The phenomenon of capillary spreading played an important role in understanding the nature of high burning velocities in the condensed phase.

Another result concerns the discovery of the superadiabatic effect. Studying the problem on the combustion of the SHS systems accompanied by infiltration (injection of the gaseous reagent through porous combustion products) with account for the interphase heat exchange, Aldushin and Seplyarskii[53] discovered that at certain temperatures the maximum temperature (T_{max}) in the wave can increase considerably the thermodynamic temperature calculated under the assumption of the absence of heat exchange between the gas and particles (T_{ad}). This effect can be easily explained: the gaseous reagent passing through hot combustion products is heated and transfers the heat to the combustion zone, additionally heating the reagents. The superadiabatic effect in the form of temperature profiles with and without account for the interphase heat exchange is schematically presented in Fig. 10. The superadiabatic effect is of great significance. This effect makes it possible to carry out SHS processes in weakly exothermic systems and to perform efficient quenching of products; an inert gas can be used instead of the gaseous reagent as a heat carrier (for gasless combus-

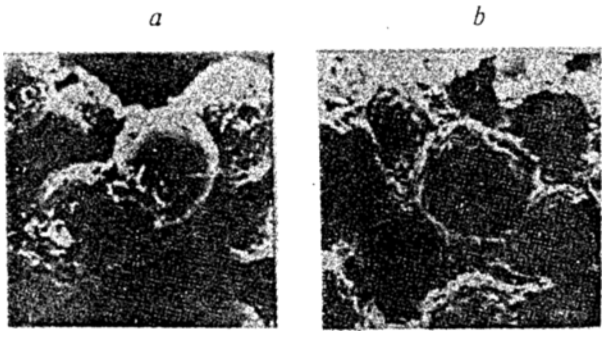


Fig. 9. Phenomena of capillary spreading; combustion of the Ti + C mixture (r_{Ti} = 100—200 μ, $r_C \approx 0.1$ μ); *a*, initial mixture; *b*, combustion product (TiC).

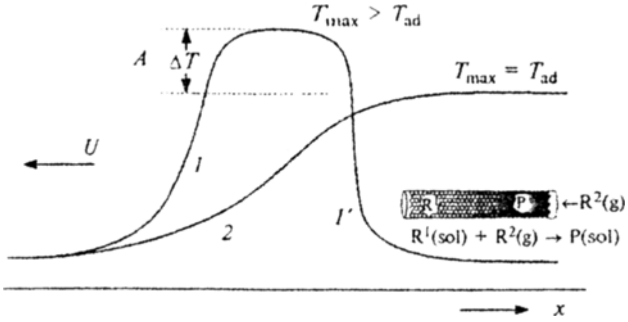


Fig. 10. Combustion with the accompanying infiltration of the reagent with (*1*) and without account (*2*) for the interphase heat exchange (*1′*, quenching of the product). Superadiabatic effect: *A*, zone of superadiabatic heating.

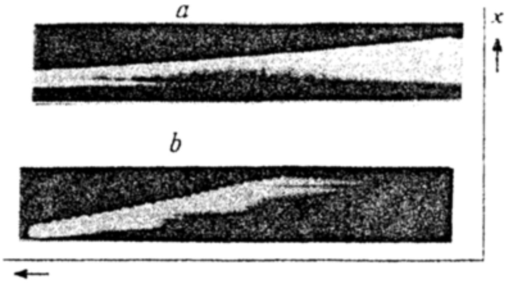


Fig. 11. Photoregistrograms of steady (*a*) and autooscillation (*b*) combustion.

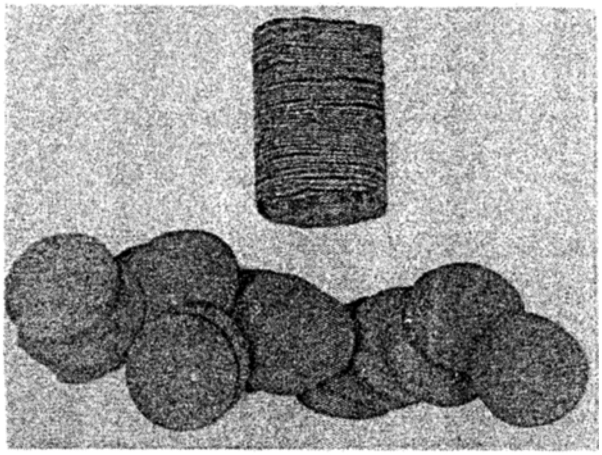


Fig. 12. Photograph of the HfC sample obtained in the autooscillation mode of combustion.

tion). The superadiabatic effect found use in the nonstationary heterogeneous catalysis[54] and reprocessing of solid waste and low-calorie sorts of coal.[55]

SHS as an object of nonlinear dynamics

It was found in the study of the SHS mechanism that it is an excellent object for studies in the area of nonlinear dynamics, in which, as is known, nonlinear relationships (direct and reverse) between various processes and nonlinear phenomena appearing due to these relations are studied. Induction processes with critical phenomena, the plurality of states and modes at the same parameters of the system with hysteresis effects, autowaves, autooscillations of the rate of chemical reactions, and others are well known in the nonlinear dynamics. Combustion is one of the most studied processes in the nonlinear dynamics. Such phenomena as thermal and chain explosions, ignition, and flame propagation became classical objects of studies. The SHS process is no exception. The studies of this process made a substantial contribution to the nonlinear dynamics and enriched it with new phenomena. Let us consider some of them.

Linear autooscillations of the combustion front. In these modes, the combustion front propagates nonstationarily. The values of the instant linear propagation velocity (combustion rates) oscillate around some average value. There is a stability limit, which separates steady and autooscillation modes. Far from the limit, the oscillations become relaxation and consist of alternating depressions and deflagrations. The layer of reagents is heated from hot combustion products during the depression, while it burns out rapidly during the deflagration. The typical photoregistrograms (photoscanning of combustion on the film moving across the propagation front) of the steady and autooscillation combustion are presented in Fig. 11. The autooscillations of the front appear on the photoregistrogram as ripples. A product with a layered structure is often formed during the autooscillation combustion, and it breaks down to planar tablets, whose number is equal to the number of pulses (autooscillations) (Fig. 12). The autooscillation combustion was predicted theoretically[56] and then observed experimentally.[21]

Spinning waves. This is a very unusual mode of combustion, for which the chemical reaction is localized not in a planar layer, but in a hot spot moving along the screw trajectory on the lateral face of the sample, *i.e.*, across the direction of wave propagation. The main direction of the spinning hot spot motion is formed during the ignition and determined by fluctuation factors. The spinning combustion was observed for the combustion of hafnium in nitrogen.[21] The subsequent frames of the combustion are presented in Fig. 13. It can be seen that the hot spot appears from the invisible side of the sample, moves across the front propagation, and disappears again. The spinning mode of the gasless combustion[57] and the planar spinning (on the planar surface for point ignition)[58] were obtained in further studies. A mathematical model of the spinning combustion based on the solution of the system of gasless combustion in the two-dimensional statement (combustion of the cylindrical shell) was suggested.[59] The temperature field in the sample during the spinning combustion in some moment t_1 and the lines of the spinning combustion front obtained by the calculation according to this model[59] are presented in Fig. 14. A hot spot, whose temperature is higher than that of the combustion products, is seen on the leading edge of the combustion front.

The autooscillation and spinning combustion processes were first considered as different phenomena, and only after theoretical studies it did become clear that they are different manifestations of the heat instability of the same process and are related to the combustion of the heated layer (preflame zone) of the combustion wave in longitudinal (autooscillations) and transversal (spinning) directions due to the loss of stability of the steady mode in longitudinal and transversal perturbations.[26]

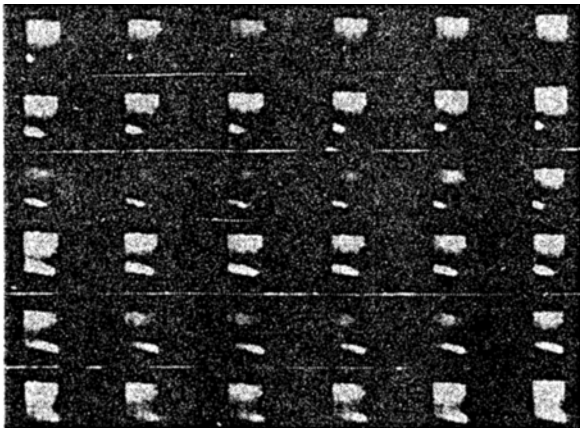


Fig. 13. Frames of spinning combustion of hafnium in nitrogen (sequence of the frames: from right to left, from top to bottom).

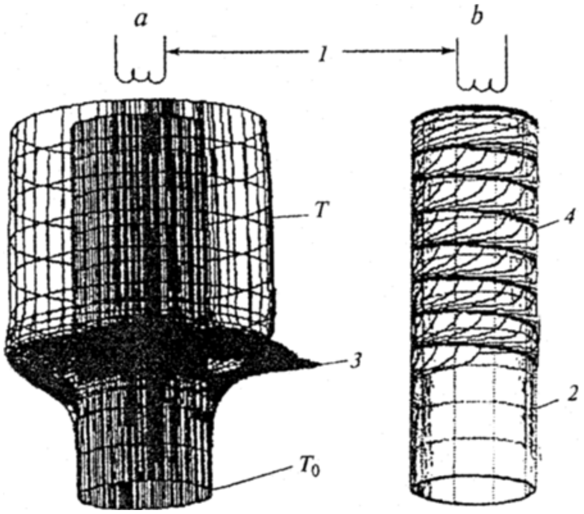
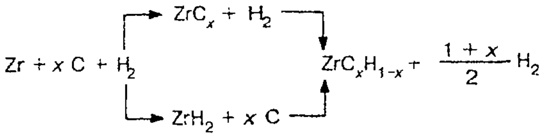


Fig. 14. Temperature field in the sample for spinning combustion in some moment (*a*) and lines of the front of spinning combustion (*b*) (computer calculation): *1*, ignition device; *2*, cylindrical sample; *3*, spinning hot spot; *4*, spinning trajectory; T_0 is the initial temperature; T is temperature (plotted in the radial direction).

Nonuniqueness of steady-state modes of the flame propagation. The studies of SHS processes showed that the steady mode of the flame propagation, which is established after ignition, is not always the same for the same parameters of the system. Different modes depending on the conditions of ignition can take place in complicated systems, in which competing processes occur. The possibility of the coexistence of two steady-state modes was found: the high-temperature (for intense ignition) and low-temperature (for mild ignition) modes. The coexistence of two modes takes place only in a certain region of parameters, and outside this region both modes degenerate into one.

The possibility of nonunique modes was predicted theoretically, when the scheme of combustion with two parallel exothermic reactions[60] was considered, and then it was confirmed experimentally in the study of SHS processes in metal—solid nonmetal—hydrogen systems.[61,62] The dependences of the burning velocity and combustion temperature of a mixture of zirconium and carbon black on the gas pressure (hydrogen) are presented in Fig. 15. The process occurs in accordance with Scheme 1.

Scheme 1



It can be seen from Fig. 15 that there are two branches on the curves of the dependences of U and T_{max} on p_{H_2}, which reflect two routes of formation of the final products, and the interval of p_{H_2}, in which two branches (modes) coexist. It should be noted that the second reaction in the second route is kinetically retarded and does not occur in the combustion wave. Therefore, the nonuniqueness is also typical of the combustion product: either ZrC or ZrH_2 forms.

The nonuniqueness of modes of the steady flame propagation was observed in further studies for other kinetic and heat mechanisms. The problem about the possibility of nonunique modes of combustion is basic, because the theorem on the existence and uniqueness of the steady mode of the flame propagation was proved in terms of the classical theory for kinetic models of simple reactions, and these concepts became commonly accepted.

The analysis and computer calculation by the equations describing autooscillations, spinning, and nonuniqueness are the subject of independent studies that

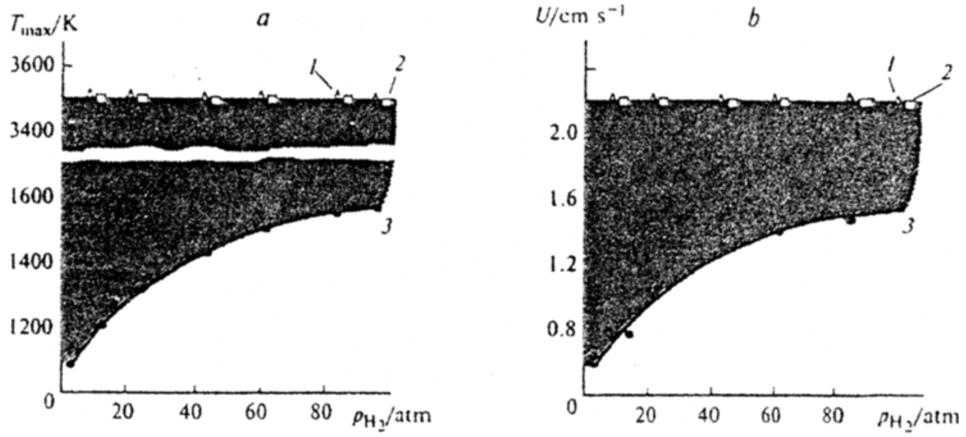


Fig. 15. Dependence of the temperature (*a*) and the burning velocity (*b*) of the Zr + C system on the hydrogen pressure; ignition by the mixtures: Ti + 2 B (*1*), 3300 K; Mo + 2 Si (*2*), 2000 K; Ti + H_2 (3), 1300 K.

are outside the scope of the SHS problem. It is noteworthy that spining waves were also found in processes of frontal polymerization due to SHS.[63]

In our opinion, the interest in nonlinear phenomena found in SHS is associated with the fact that attention was given, in essence, for the first time, to the "square" interaction of elementary manifestations of nonlinear relationships (autowaves + unstable modes, autowaves + nonuniqueness). Studies of complicated manifestations of nonlinear relationships are being developed. Recently, phenomena with a "triple" interaction of elementary nonlinearities (autowaves + nonuniqueness + unstable modes) have been observed experimentally.[64]

Thermodynamics and kinetics

It is difficult to imagine the problem of SHS without thermodynamic and kinetic studies. The main purpose of thermodynamic studies is to perform calculations which make it possible to determine the temperature T_{max} and the equilibrium composition of combustion products under adiabatic conditions of the SHS process.

In one of our works,[65] we suggested the simplest procedure of calculation of T_{max} under the assumption that the composition of combustion products is known (specified). This procedure was good for binary systems. A comparison of the calculated and experimental values of T_{max} for some systems is presented in Table 2. This comparison is evidence of the fairly good agreement of the data.[66] It is of interest that for one of the systems studied (Nb + 2 B), the experimentally measured combustion temperature (2700 K) turned out to be higher than the thermodynamically calculated value (2400 K).[66] Further, using special experiments, it was shown that this disagreement is related to the mistaken value of the heat of formation of NbB_2 given in the reference literature.

It should be emphasized that a necessary condition for a successful comparison procedure is to provide the adiabaticity of the process in experiments.

Table 2. Adiabatic temperature of combustion (T_{max})

Reaction	*d*/mm	M.p.(P) /K	T_{max}/K	
			calculation	experimental
Ti + 2 B → TiB_2	20	3190	3190	3190
2 Ta + C → Ta_2C	20	3770	2600	2550
Ta + C → TaC	20	4270	2700	2550
Nb + C → NbC	20	3750	2800	2650
Ni + Al → NiAl	20	1910	1910	1910
Co + Al → CoAl	20	1900	1900	1880
Nb + 2 Si → $NbSi_2$	20	2420	1900	1880
Mo + 2 Si → $MoSi_2$	20, 30	2360	1900	1920
Ti + 2 Si → $TiSi_2$	20	2470	1800	1770
5 Ti + 3 Si → Ti_5Si_3	30, 40	2390	2390	2350

At the Institute of Structural Macrokinetics of the Russian Academy of Sciences, using the known calculation procedure of specific impulse propellants and computer program, which took into account the laws of conservation, the condition for minimization of the thermodynamic potential, and the phase rule, for the calculation of not only temperatures, but also equilibrium compositions of combustion products, were developed. Almost all binary systems which are of interest from the viewpoint of SHS and for which thermodynamic functions are known (Scheme 2)[8], as well as several multicomponent systems, were calculated. The data base of the thermodynamic calculations is included in the computer reference book ISMAN-THERMO.[67]

The application of methods for thermodynamic calculations for multicomponent systems is very important and becomes a powerful method for the preliminary analysis of SHS processes. The triple diagram of the combustion products in the TiO_2—B_2O_3—Mg system is presented as an example in Fig. 16.[68] The optimum region, in which the target product TiB_2 and the single (inevitable) by-product MgO form, is hatched. There are undesirable by-products in other regions, and it is

Scheme 2

Groups	H	B	C	N	O	F	Al	Si	P	S	Cl	Ti	Fe	Br	I	Si	Te
I (Li, Na, K)	●	○	◑	◑	●	●	◑	○	○	◑	●	○	○	●	●	○	○
II (Be, Mg, Ca, Si, Ba)	●	◑	●	●	●	●	◑	◑	◑	●	●	○	○	●	●	○	○
III (B, Al)	●	●	●	●	●	●	●	○	○	●	●	●	●	●	●	◑	◑
IV (Si, Ti, Zr, Hf)	◑	●	●	●	●	●	◑	●	◑	●	●	○	○	●	●	◑	◑
V (V, Nb, Ta, Sb)	○	●	●	●	●	●	◑	●	◑	●	●	○	◑	●	●	○	○
VI (Cr, Mo, W)	◑	●	●	●	●	●	○	●	○	●	●	○	◑	●	●	○	○
VII (Mn)	●	●	●	●	●	●	○	●	●	●	●	○	○	○	○	●	●
VIII (Fe, Co, Ni)	◑	●	●	●	●	●	●	●	●	●	●	●	○	○	○	●	●
Lanthanides	◑	●	◑	◑	●	○	◑	◑	○	○	○	○	○	○	○	○	○
Actinides (U)	○	●	●	●	●	●	●	●	○	●	●	○	●	○	○	○	○

Designations: ● — calculated for almost all compounds; ◑ — incomplete calculations; ○ — no calculation data available.

inexpedient to perform SHS processes in these regions. It is of interest that the stoichiometric point corresponding to the overall reaction

$$TiO_2 + B_2O_3 + 5\ Mg \rightarrow TiB_2 + 5\ MgO,$$

is outside the optimum region due to side reactions. This additionally confirms the importance of the thermodynamic calculations.

Direct calorimetric measurements are also related to the thermodynamics of SHS processes. The results of measurements of heat effects of SHS processes using the specially developed SHS-calorimeter are presented in one of our works.[69] Processing of these data with corrections calculated by the results of chemical analysis of condensed products and the gas phase formed due to the degasification of admixtures makes it possible to determine the heats of formation of the compounds synthesized with a satisfactory accuracy (see also review 19).

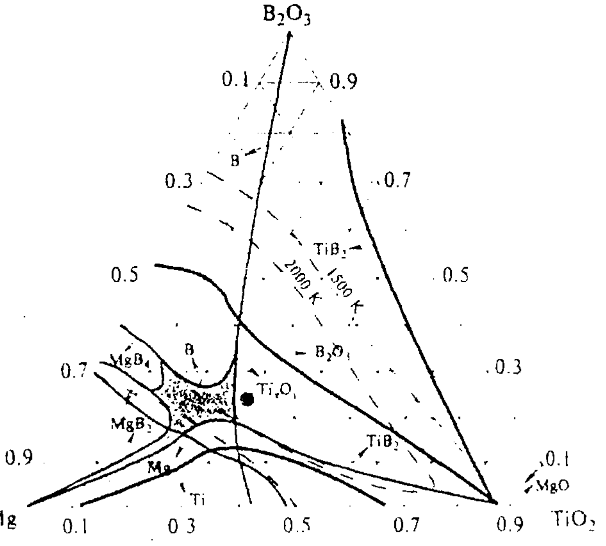


Fig. 16. Phase diagram for the TiO_2—B_2O_3—Mg system.

Using kinetic studies, one can obtain information on regularities of the heat release at the high temperatures characteristic of combustion waves. These kinetic studies are associated with great methodical difficulties precisely due to the high temperatures in the experiments. Some success was achieved in two directions.

1. Processing of thermograms of combustion and electrothermal explosion by the simplest theoretical models.[34,70] This approach gives indirect kinetic information on the process studied and makes it possible to estimate reliably the level of heat release. However, the kinetic interpretation of the results obtained is rough and sometimes ambiguous.

2. Direct kinetic measurements in model metal—gas systems, which are carried out using a specially developed electrothermograph.[71] The idea of the operation of this instrument is simple. A metallic filament, which is one of the reagents, is heated by an electric current and interacts with a gaseous reagent to release the heat. The temperature of the filament is maintained constant during the whole experiment by a controlling system (optical or electric). The measurement of the electric power due to the preliminary thermophysical calibration of the instrument makes it possible to calculate easily the rate of chemical heat release and its change. The process is carried out at different temperatures of the filament. Processing of the experimental data makes it possible to determine the kinetic equation and the values of its constants taking into account the value of the reaction surface. Thermal measurements are supplemented by quenching of the filament (by switching-off the current) and metallographic analysis of cross-sectional slides. The kinetics of the high-temperature interaction of titanium, zirconium, niobium, tantalum, and other metals with nitrogen, hydrogen, and oxygen as well as with complex gases (silane, hydrocarbons, and others) were studied by the electrothermographic method (see, *e.g.*, Refs. 72 and 73).

The kinetic curves on the heat release and the growth of nitride layers during nitriding of tantalum and at temperatures up to 3000 °C (!) are presented in Fig. 17

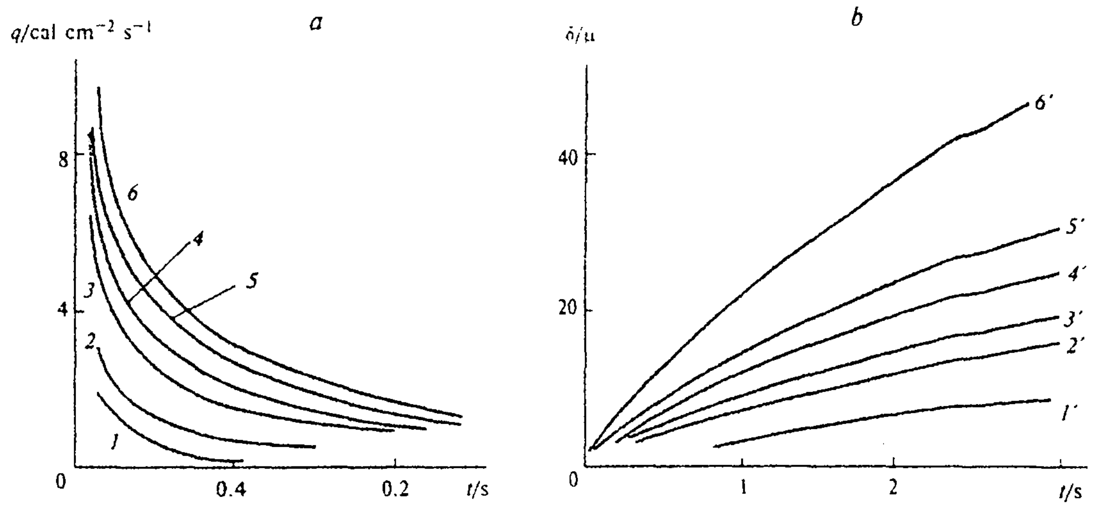


Fig. 17. Dependences of the rate of heat release (q') at 2210 (*1*), 2300 (*2*), 2610 (*3*), 2700 (*4*), 2860 (*5*), and 2970 (*6*) °C (*a*), thickness of the nitride film (δ) at 2420 (*1'*), 2570 (*2'*), 2650 (*3'*), 2750 (*4'*), 2840 (*5'*), and 2930 (*6'*) °C (*b*) on time in the reaction of nitriding of tantalum.

as an example.[74] The kinetic equation of heat release describing the interaction of tantalum with nitrogen corresponds to the normal parabolic law:

$$q' = K/q,$$

where K is the rate constant of the heat release and q is the amount of heat released to the moment t during nitriding of tantalum.

Combustion chemistry and chemical synthesis

The main goal of SHS is chemical synthesis. Therefore, special attention was always given to the chemical part of the research. The following typical problems were solved:
— selection of chemical objects for SHS and raw materials, provision of the exothermicity of processes;
— establishment of a relationship between products of the synthesis and conditions of combustion;
— study of the chemical mechanism of combustion reactions, elucidation of intermediate products and stages;
— study of the mechanism of self-purification from admixtures, control of the doped composition of products;
— complete certification of the final products of the synthesis obtained under optimum conditions.

Presently, more than 500 reactions and products have been studied to one extent or another in the area of SHS. Let us present the main types of SHS reactions.[22,47,75–79]

Synthesis from elements:

$Ti + C \rightarrow TiC$,

$Zr + 2\,B \rightarrow ZrB_2$,

$Mo + 2\,Si \rightarrow MoSi_2$,

$3\,Si + 2\,N_2 \rightarrow Si_3N_4$,

$Ti + H_2 \rightarrow TiH_2$,

$Nb + 2\,S \rightarrow NbS_2$,

$Al + P \rightarrow AlP$.

Synthesis involving compounds as reagents:

$Ti + TiH_2 + 4\,B \rightarrow 2\,TiB_2 + H_2$,

$3\,B + NaN_3 + HCl \rightarrow 3\,BN + NaCl + 1/2\,H_2$,

$FeV + 1/2\,N_2 \rightarrow VN + Fe$.

Synthesis with the reductive stage (metallothermal SHS):

$TiO_2 + B_2O_3 + 5\,Mg \rightarrow TiB_2 + 5\,MgO$,

$B_2O_3 + 3\,Mg + N_2 \rightarrow 2\,BN + 3\,MgO$,

$Cr_2O_3 + CrO_3 + 4\,Al + 2\,C \rightarrow Cr_3C_2 + 2\,Al_2O_3$,

$WO_3 + 2\,Al + C \rightarrow WC + Al_2O_3$.

Synthesis of complex oxides:

$Ti + 2\,BaO_2 + TiO_2 \rightarrow 2\,BaTiO_3$,

$Nb + 1/2\,Nb_2O_5 + Li_2O_2 \xrightarrow{O_2} 2\,NbLiO_3$.

It should be mentioned that the multiparametric conditions of the synthesis with the choice of optimum modes make it possible to obtain high-quality substances and materials. As a rule, SHS products are characterized by a high content of the main (desired) phase and a low concentration of unreacted reagents and impurity oxygen.[75] The most popular products are presented below.

Chemical compounds:
- refractory compounds (borides, carbides, nitrides, silicides);
- intermetallides (aluminides, germanides, nickelides, *etc.*);
- chalcogenides (sulfides, selenides, tellurides);
- hydrides of metals and intermetallides;
- phosphides;
- oxides (niobates, tantalates, titanates, cuprates, ferrites, *etc.*);
- organic and organoelement compounds.

Solid solutions of binary compounds:
- carbonitrides;
- carbohydrides;
- nitrohydrides.

Materials:
- hard alloys (refractory compound + metallic binder Fe, Ni, Co);
- mineraloceramics (refractory compound + oxides Al_2O_3, MgO, ZrO_2);
- heterogeneous ceramics (carboboride, boridonitride);
- nitrided ferroalloys (nitride + iron);
- composites (ceramics + metallic matrix, ceramics + polymeric matrix, intermetallides + ceramic matrix).

As has been already mentioned, in the primary SHS, the reactions of the direct synthesis from elements forming refractory compounds were the objects of studies. Further, the list of raw materials for SHS and the assortment of products of the synthesis were continuously widened. Metal and nonmetal oxides, metal-reducing agents, hydrides, sometimes chlorides and fluorides, alloys, oxygen-free compounds with low binding energy between the elements, hydrocarbons, azotocarbons, mineral raw materials, and industrial waste are presently used for the synthesis.

Many results interesting from the synthetic viewpoint were obtained: off-stoichiometric and superstoichiometric phases of transition metal compounds with the ordered nonmetallic sublattice, multicomponent monophase solid solutions of binary compounds, amorphous compounds, metastable phases, and others (see reviews 22, 27). Metastable monophase boron carbonitride,[80] the possibility of the synthesis of which was studied for many years, has recently been synthesized for the first time. Thermodynamic predictions of the possibility of manufacturing solid cyanogen β-C_3N_4 by the SHS method is of interest.[81]

The synthetic potential of SHS has attracted the attention of crystal chemists. Many neutronographic studies of SHS products were performed (see, for example, Refs. 82—84).

The establishment of the relationship between the chemical and phase composition with combustion conditions (charge + surrounding medium) has already become a routine procedure of studies (first diagnostic level). It has been shown that for systems with a simple phase diagram the chemical and phase composition of SHS products depends slightly on the combustion conditions. In these cases, it is very easy to synthesize the compounds. For multiphase systems, this dependence is substantial, and the search for optimum conditions of the synthesis is difficult and requires detailed knowledge of the chemical mechanism of SHS processes. Therefore, the chemistry of combustion studying the mechanism of reactions in the combustion wave with the elucidation of intermediate products and stages became an important direction in SHS investigations.

The first interesting result was obtained as early as in 1975,[24] when it was shown that for the combustion of tantalum in nitrogen the burning velocity is determined by the formation of an intermediate product, tantalum seminitride (Ta_2N), while the phase of the final product, tantalum mononitride (TaN), is formed in the afterburning mode. When the process is carried out at low pressures of nitrogen (tens of atm), the hexagonal modification of TaN is formed, and the cubic modification is formed at higher pressures. When tantalum—liquid nitrogen mixtures burnt, the intermediate stages did not play the leading role, and the formation of tantalum mononitride (cubic modification) became the main stage of the process.

Diagnostic methods of the second and third levels (see p. 6) play an important role in the combustion chemistry. Some data on revealing intermediate products and stages are presented in the reviews.[8,9,77,79]

Let us consider an example emphasizing the significance of studies of the chemical mechanism of SHS for the synthesis of yttrium-barium cuprate, a popular ceramic superconductor. It is an unstable compound. The region of homogeneity with respect to oxygen, in which superconducting properties are manifested, is very narrow, and the slightest loss of oxygen results in the disappearance of the superconductivity. For the solution of this problem, an ingenious reaction was suggested[85,86]

$$3\ Cu + 2\ BaO_2 + 1/2\ Y_2O_3 \xrightarrow{O_2} YBa_2Cu_3O_{7-x},$$

whose overall exothermicity (and, hence, the possibility of occurrence in the SHS mode) provided the oxidation of copper by internal (BaO_2) and external (O_2) oxygen. To obtain a high-quality result, detailed studies of the mechanism were performed using quenching and dynamic X-ray diffraction methods. This made it possible to study the dynamics of chemical and phase transformations in the wave and to plot kinetic curves for the initial reagents and intermediate and final products. As a result, the following mechanism of the SHS reaction was suggested:

$$2\ Cu + O_2 \rightarrow Cu_2O + 1/2\ O_2 \rightarrow 2\ CuO,$$

$$BaO_2 \rightarrow BaO + 1/2\ O_2,$$

$$\{BaO + BaO_2\}_{melt} + 2\ Cu_2O \rightarrow 2\ BaCu_2O_2,$$

$$\{BaO + BaO_2\}_{melt} + 2\ CuO \rightarrow 2\ BaCuO_2,$$

$$2\ BaCu_2O_2 + CuO + 1/2\ Y_2O_3 \rightarrow YBa_2Cu_3O_{6+\delta} + Cu_2O,$$

$$2\ BaCuO_2 + CuO \rightarrow BaCu_2O_2 + 1/2\ O_2,$$

$$2\ BaCuO_2 + CuO + 1/2\ Y_2O_3 \rightarrow YBa_2Cu_3O_{6+\delta}(\text{tetra}),$$

$$YBa_2Cu_3O_{6+\delta}(\text{tetra}) \xrightarrow{O_2} YBa_2Cu_3O_{7-x}(\text{ortho}).$$

Table 3. Parameters of yttrium-barium cuprate $YBa_2Cu_3O_{7-x}$

Technology (producer)	Trade mark	Content of oxygen, $7-x$	T_{cr}/K*	Y_{123} (%)**	Main admixtures	r_{av}/μ
Furnace powder (American companies)	SC5-5	6.92	93.5	98	CuO	40.0
	SC5-P	6.87	93.5	~99	CuO	8.2
	SC5-6.5	6.88	90.5	97	$BaCuO_2$	6.8
	SC5-7	6.85	92.5	99	CuO	5.7
	CHS A-1203	6.85	92.0	~99	$BaCuO_2$	3.0
	SSC 03-0065	6.89	92.0	~99	—	6.5
SHS powders (ISMAN)	SHS-J1	6.90	92.0	97	CuO	9.0
	SHS-J2	6.92	93.5	~99	—	8.0

* Critical temperature of the transition to the superconducting state.

** Content of the orthorhombic phase.

Let us call attention to the last reaction. This is a phase transition of the nonsuperconducting tetragonal (tetra) modification of yttrium-barium cuprate to the superconducting orthorhombic (ortho) modification in the presence of oxygen. The reaction occurs far beyond the combustion front, and its completeness provides the superconducting properties of the SHS product. The superconductor, which was highly appreciated by specialists, was synthesized in the SHS mode taking into account the mechanism presented above. A comparison of the quality of the SHS products with yttrium-barium cuprates produced by American companies[86] is presented in Table 3.

Works aimed at the improvement of the doped composition (self-purification from admixtures[87] and development of the theory[88,89]), studies of the solubility of SHS products and specific features of chemical analysis of SHS products,[90] the chemical treatment of the final products (effect of chemical dispersion[91]), and others played an important role in chemical investigations of SHS.

SHS technologies and materials

The simplest chemical problem, the synthesis of products of specified chemical and phase compositions, was considered in the previous section. The SHS method makes it possible to solve other, more complicated problems: the direct synthesis of materials with account of additional requirements to their structure and the direct synthesis (however, to a lesser extent) of items with certain shapes, sizes, and assumed properties. In the former case, the item obtained is the direct combustion product, *i.e.*, chemical bonds and the structure of the material, and the shape formation, mechanical and other properties of an item are formed in a single SHS process. For the solution of these problems, more than 30 technological varieties of SHS were developed, which were united in six main technological types (see Refs. 6, 8, 9, 78, 92—96). Let us consider briefly their substantial features.

Chemical synthesis. The process is performed in sealed SHS reactors or in open air. The products look like shapeless cakes. They can be directly used as preparations and semifinished products (for example, nitrided ferroalloys) or reprocessed to powders using mechanical and/or chemical methods. The latter is the most typical procedure in the SHS technology. The SHS synthesis is used for the production of more than 50 items with different dispersities: for sintering and hot molding of products by the powder metallurgy methods, gasothermal (plasma and detonation) deposition of coatings, and for use as abrasives and backfillings. The most popular SHS powders are TiC, TiN, TiC—TiN, TiB_2, TiC + TiB_2, TiH_2, AlN, α- and β-Si_3N_4, BN, SiC, B_4C, $MoSi_2$, NiAl, TiNi, and others.

SHS sintering. In this case, and item of a specified shape is preliminarily prepared from the charge, and the SHS process is carried out in such a way that the shape and size of the item would be retained. Two varieties of the process are most popular: the synthesis of nitride ceramics at high pressures and synthesis of carbide, boride, silicide, and intermetallide materials *in vacuo* with the preliminary thermal treatment of a charge. The products of SHS sintering are usually porous, but their stability is anomalously high due to the formation of carcass structures, which are not typical of materials of the powder metallurgy. This method is used for preparing high-temperature thermal and electroinsulators of BN, frictional couples from a new ceramic SHS material, "black ceramics," ceramic filters for purification of gases and liquids (including drinking water), preparations of TiC_x for metal infiltration and reprocessing under conditions of superplasticity, *etc.*

Forced SHS compaction. The SHS process is performed in a special molds, and a hot combustion product, which had no time to cool, is compacted to the poreless state. The variants differ by the methods of mechanical action. The uniaxial molding is most popular. The all-round compression of the process (HIP-process), extrusion, rolling, explosion, and forging (a dynamic action, whose intensity is intermediate between those of impact waves and static molding) are also used. The greatest success was achieved in the use of these methods for obtaining preparations and items of solid alloys. A series of new types of hard alloys of the STIM group (synthetic instrumental materials) with different combinations of hardness and strength was created. They formed the basis for the technology of cutting plates (STIM-5), rollers for rolling copper (STIM-4), and plates with an increased impact viscosity (STIM-2 and others). A variant of the SHS molding technology for the preparation of large-sized items of solid alloys (with characteristic size of 0.5 m and greater) was developed. A new type of materials was suggested: macrocomposites. Successes were achieved in the preparation of intermetallic and composite targets for magnetotronic deposition. At the present time, a special direction of research is the creation of functionally graded (*i.e.*, with nonuniformity of the composition specified beforehand) materials.

SHS metallurgy (technology of high-temperature SHS melts). For these purposes, a high-calorie charge (aluminothermal mixtures) is used, and the temperatures developed in the combustion of this charge are higher than the combustion temperatures of the products. The product is formed as a melt, to which the known metallurgical procedures are applied: crystallization of ingots, mold casting, surfacing, centrifugal casting, *etc.* In aluminothermal mixtures, combustion products are not monophase, and the phase separation (the heavy phase settles down, and the light phase floats up) occurs in the high-temperature melt due to gravitation forces. The structure of the product depends on the completeness of the separation: either graded or macrouniform structure for the complete and incomplete phase separation and also for the complete absence, respectively. The most popular are cast powders, objects with solid-alloyed facings, and metallo- and mineral-ceramic pipes consisting of metallic and ceramic phases (two-layered or macrouniform). The most popular metallic phases are carbides, borides, chromium, tungsten, molybdenum, and niobium silicides; the most popular ceramic phase is aluminum oxide. The technology is unique, because it makes it possible to cast refractory materials at 3000—3500 °C.

SHS welding. The SHS process is carried out in a gap between two objects to be a permanent joint. The conditions are selected in such a way that a melt, whose properties are close to the objects welded, would form. This is achieved by an individual selection of the charge and its preliminary heating (usually joule heating). The SHS process serves as the source of the high temperature, and the SHS product is used as the welding material. The SHS welding is applied for joining objects made of refractory metals and materials, such as niobium, tungsten, molybdenum, tantalum, graphite, and others. Sometimes a high strength of a weld can be achieved which is even higher than that of welded materials.

Gas-transport SHS technology. This is based on the introduction of special gas-transport additives in the charge, such as, *e.g.*, iodine. Due to their presence in the combustion wave, gaseous compounds (transferring agents for reagents) first appear and then decompose. As a result, in SHS processes a small portion of the final product forms *via* an intermediate gas phase. The use of this SHS process turned out to be most efficient in the deposition of coatings on objects preliminarily placed in a charge. The typical width of gas-transport coatings is 10—100 μ. The technologies of deposition of chromium or chromium boride coatings on steel objects and of titanium nitride on solid alloys have been developed. Objects to be covered include jig bushes, knives, drills, cutting plates, and others. The process is also efficient for the high-temperature protection of graphite.

All six technological types of SHS technologies are constructed according to a single principle. The generalized scheme of SHS technologies (Fig. 18) includes three traditional parts: preparation of the raw material, synthesis, and reprocessing of the product. The main specific feature is that the main stage is carried out in the SHS mode. The SHS technologies differ in types of initial raw material, structure of charges, types of chemical reactions and processes, internal actions, morphology of products and methods of their treatment (reprocessing), and design of the final products. Photographs of some SHS products are presented in Fig. 19 as an example.

SHS is not only a new technology for the preparation of known materials, but also offers the possibility of creating new types of materials, agglomerate, composite, and nanocrystalline powders, whiskers free and fibers, oxygenless ceramics containing no caking activators, anisotropic oxide ceramics, functionally graded materials, oxygenless single crystals, and others.[96,97]

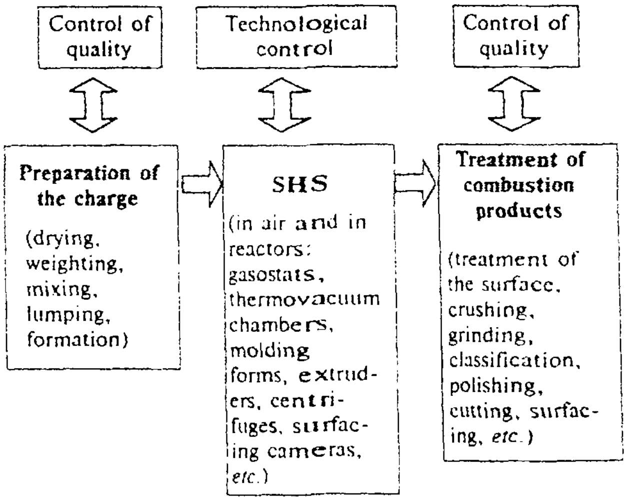


Fig. 18. Generalized scheme of the SHS technology.

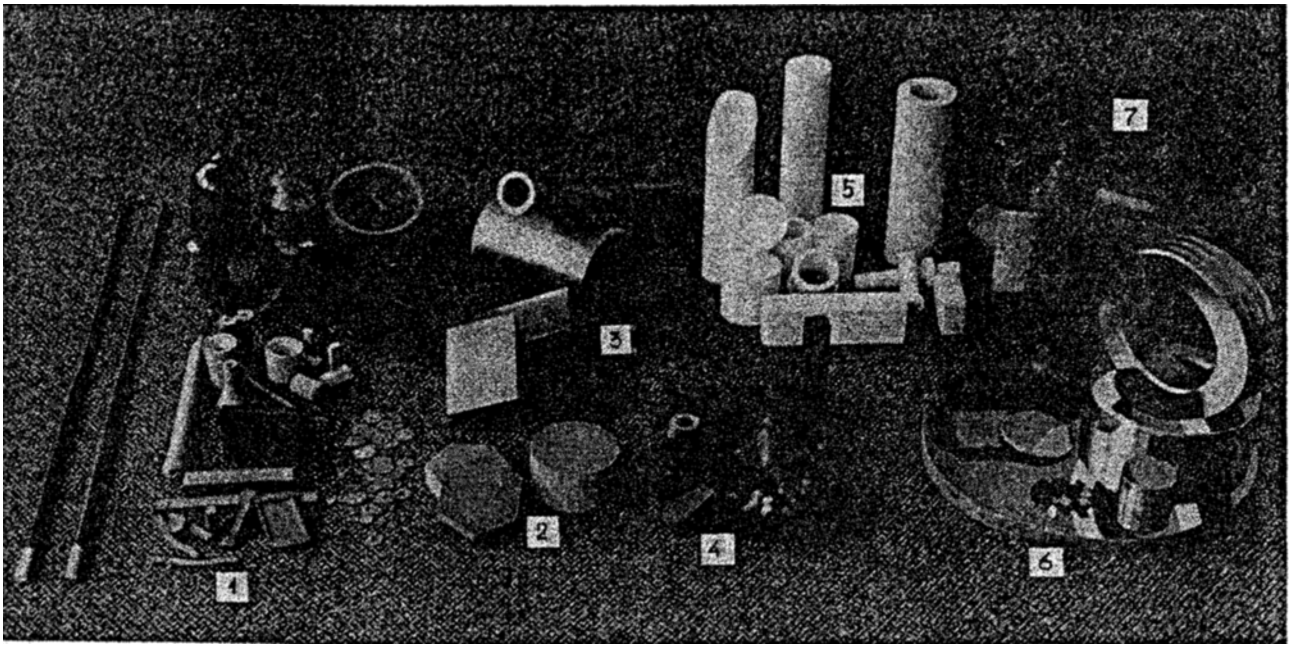


Fig. 19. SHS products: *1*, items of SHS powders, *2*, ceramic honeycomb structures; *3*, casted SHS items; *4*, "black" ceramics; *5*, items of BN; *6*, items of hard alloys; and *7*, refractory materials.

Production, application, and effectiveness of SHS products

Many SHS technologies and products are of great practical interest. In 1990, the real volume of SHS products was several thousand tons. For example, titanium carbide powders produced by the Experimental Plant of Powder Metallurgy (Baku) were used for the production of abrasive pastes (Poltava), which were used in more than a thousand plants in the Ukraine and Russia. Ceramic insulators (Kuibyshev) were applied in furnaces of directed crystallization in enterprises of the aircraft industry, and molybdenum disilicide was produced at the Kirovakan Plant of High-Temperature Heating Devices for domestic use (by the way, this plant was the first to implement the SHS technology). Unfortunately, the disintegration of the USSR and the economic situation had a negative effect on the condition and development of the SHS industry.

Against this background, we should mention a recent new application of the SHS technology. Experts of the Institute of Structural Macrokinetics of the Russian Academy of Sciences and the Kuznetsk Plant of Instruments and Ferrites developed the industrial SHS technology for ferrite powders production. Its basic idea is simple and interesting: in the traditional mixture of oxides from which ferrites are obtained in furnace processes, a portion of iron oxide is replaced by iron powder, and it is used as a fuel for the organization of SHS, *i.e.*, the following reaction is performed:

$$\alpha\mathrm{Fe} + (1-\alpha)\mathrm{Fe_2O_3} + \sum_{i=1}^{k}\beta_i(\mathrm{Me}_m\mathrm{O}_n)_i \xrightarrow{\mathrm{O_2}}$$

$$\rightarrow \mathrm{Fe_2O_3}\cdot\prod_{i=1}^{k}\beta_i(\mathrm{Me}_m\mathrm{O}_n)_i,$$

where α and β_i are coefficients.

The main chemical stages of the process are the oxidation of iron and the interaction of oxides to form ferrite. When the technology was finished, the minimum α value was selected which provided the self-propagating mode and satisfactory quality of the product. The technology is based on an industrial SHS reactor, in which the charge is continuously injected and the products are continuously brought out. Its production is equal to 1.5 thousand tons of ferrites a year. This continuous reactor is the first one used in the practice of SHS.

All previous SHS productions should be characterized as pilot and pilot-plant. Only the technology of SHS-ferrites made it possible to create the first large-tonnage SHS production.[98]

Not only products of SHS manufacturing have begun to be applied in the technique, but experimental lots of many SHS materials have been recommended in the solution of these or other technical problems. Some types of SHS production and the areas of their application are presented below.

Mechanical engineering:

— abrasive powders and pastes based on refractory compounds (including magnetoabrasive compounds);

— abrasive instrument of coarse compacted powders;

— items of pink corundum;
— hard alloys obtained from SHS powders, items of STIM group alloys: cutting plates, draw plates, molding instrument, rollings, and impact-resistant plates;
— ceramic powders for powder metallurgy;
— construction objects of black ceramics;
— electrodes for welding, electric-arc deposition of coatings, and electric-spark alloying;
— objects with wear-resistant coatings;
— welded graphite items.

Metallurgy:

— ingots of refractory materials;
— nitrided ferroalloys;
— refractory materials;
— tuyere for blast furnaces;
— crucibles for fusing nonferrous metals;
— boats for vacuum metallization.

Chemistry and the chemical industry:

— luminophores;
— technical boron;
— boron-containing refractory compounds;
— phosphides and phosphide-based fumigants;
— pigments;
— filters for purification of liquids and gases;
— pipes with inner corrosion-resistant coatings;
— catalysts (Ni-Raney, catalytic elements for after-burning of exhaust, and others).

Electrical engineering and the electronics industry:

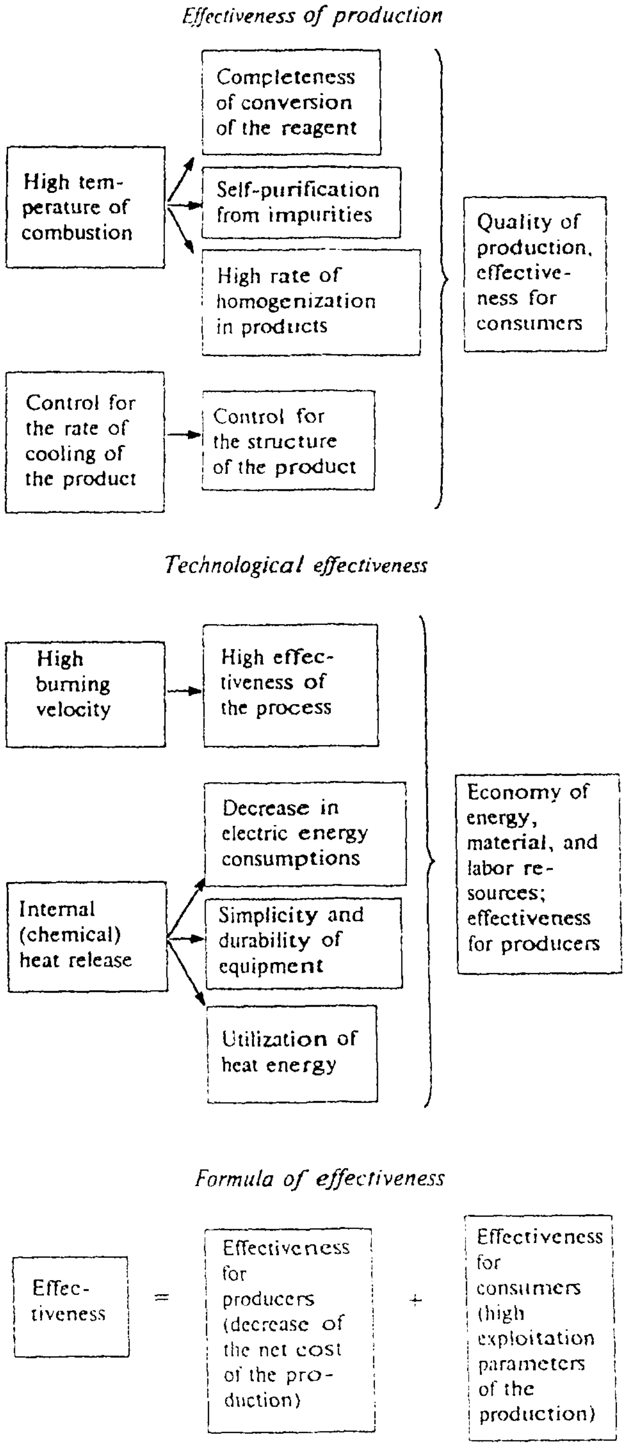
— high-temperature heating elements;
— items of electroconducting solid lubricants;
— incandescent filaments with protective coatings;
— oxide raw material for growing single crystals (niobates, tantalates, molybdates, others);
— superconducting ceramics (cuprates);
— ferrites;
— hermetic glue "Elastosil";
— plates of aluminum nitride for depositing coatings of silicon oxide on thermally unstable substrates.

Other areas:

— floor and wall slabs (building-material industry), high-temperature electric insulators for furnaces of directed crystallization (aircraft industry), implants for osseous operations from materials with shape memory (medical industry), and others.

An important problem for the introduction of a new technology is its effectiveness. At first glance, this is evident for SHS and is related to the specific physical features of the process and its unique features (Scheme 3). The high temperature and rate of the process, the use of the cheaper chemical energy instead of electric energy, and the simplicity and durability of the equipment predetermine both the technical and economical efficiency of SHS and endow it with the features of a resource-saving technology. However, there are some circumstances that make this difficult. For example, the high temperature facilitates recrystallization processes in products, which results in the growth of grains and a decrease in the strength of the material. Special measures are used to control this process (for example, fast cooling followed by quenching at a lower temperature or doping of functional additives). However, the main difficulty is the following. More expensive and scarce charges than in traditional processes are often used for the organization of SHS processes. In addition, the production of these "combustible" reagents

Scheme 3



requires a greater energy consumption than the production of normal charge compositions. Therefore, in the opinion of some opponents, the SHS technology cannot be considered to be energy-saving. However, experience refutes these arguments.

First, let us mention the technical efficiency, which is determined by the high physical and exploitation properties of SHS products.[99] For example, nitrided ferroalloys differ from their furnace-made analogs by a higher content of nitrogen and a higher efficiency for nitriding steels. Nitride SHS powders differ by a higher content of the main product and a low concentration of doped oxygen. Cutting plates of STIM-5 differ by a greater stability in cutting and a more universal character, *etc.* Ceramic SHS insulators provide a considerable increase in the period of continuous furnace operaion for directed crystallization, composite powders based on complex carbides, and large hard-alloyed rolls having no industrial analogs, *etc.*

The economical effectiveness of SHS is evident, for example, for the production of hydrides or some nitrides from the same raw materials as in the furnace technologies. This is also related to processes of the direct preparation of materials and items by the SHS method, which replaces multiple furnace heating in the preparation of the final production and some others. The technological parameters of three types of industries of aluminum nitride powder — SHS, furnace, and plasmochemical (according to the data of pilot productions of the former USSR) — are compared in Table 4 (see Ref. 100). As can be seen, the SHS technologies exceed alternative processes by almost all parameters. SHS powders of AlN are twice as cheap as furnace powders and they are four times cheaper than plasmochemical powders.

Interesting results were published in one recent work.[101] The net cost of the production of some SHS powders in different countries was determined taking into account the specific cost of resources (material, energy, and labor) customary in these countries. The net cost calculated was compared with the world prices of this production under the assumption that the quality of the production was the same. The results presented in Table 5 indicate the high profitableness of the production of SHS products, especially in countries with a low level of payment. The calculations on the complete power savings, the results of which have been recently published,[102] are also of interest. Let us present two examples. The synthesis of titanium carbide powders by the furnace method ($TiO_2 + 3\ C \rightarrow TiC + 2\ CO\uparrow$) requires 35 kW h kg^{-1} (according to the data of one of the plants of the former USSR). Similar parameters for two SHS methods are 2 and 3 kW h kg^{-1} for elemental ($Ti + C \rightarrow TiC$) and magnesium-thermal ($TiO_2 + 2\ Mg + C \rightarrow TiC + 2\ MgO$) methods, respectively. The main energy consumptions in the traditional technology are related to furnace heating, and in the SHS technology they are associated with reprocessing of the product after combustion (in the first case, mechanical treatment, and in the second case, chemical metallurgical treatment). Evidently, energy-savings is great in the production of TiC by the SHS method. However, let us take into account that energy consumptions for the preparation of metals used in the SHS technology are equal to ~11 kW h kg^{-1} for Ti and ~16 kW h kg^{-1} for Mg. It follows from elementary calculations that the SHS technology is energy-saving even taking into account the additional consumptions of the electric energy for the preparation of the raw material. The savings in electric energy is ~24 kW h kg^{-1} for the elemental SHS method and ~19 kW h kg^{-1} for the magnesium-thermal method. When the heat released during SHS is used, the savings in electric energy is more considerable (it was not taken into account in the calculations).

Table 4. Industrial parameters of SHS processes, furnace synthesis (FS), and plasmochemical synthesis (PCS)

Parameter	SHS	FS	PCS
Consumption of the raw material:			
aluminum/kg kg^{-1}	0.7	0.9	1.5
nitrogen/m^3 kg^{-1}	0.9	1.65	12.3
Consumptions of electric energy/kW h kg^{-1}	0.5	31	150
Labor consumptions (rel. unit)	1	1.4	3.5
Number of technological stages	8	18	5
Effectiveness/kg h^{-1}	4.0	1.0	0.75
Time of the technological stage/h	0.6	2.5	0.5
Net cost of powder (rel. unit)	1	2	4

Similar data can be presented for other processes. For example, the production of the manganese-zinc ferrite powder[*] is characterized by the following parameters: the consumptions of electric energy in the furnace and SHS technologies are 12 and 0.04 kW h kg^{-1}, respectively, and those required for reprocessing to the powder are 1 and 1.2 kW h kg^{-1}. The consumption of the electric energy for the production of the iron powder is equal to ~1 kW h kg^{-1}. The savings in electric energy in the plant is equal to 11.76 kW h kg^{-1}, and the power savings is equal to 11.57 kW h kg^{-1}. Thus, in SHS technologies, a possible increase in the price of the raw material is excessively compensated by the low consumptions for production, and the energy consumptions for the preparation of "combustible" reagents (metals) are compensated by the optimum thermal mode of the synthesis.

The experience of the studies and practical application of SHS processes made it possible to develop the

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[*] Furnace process:

$$Fe_2O_3 + 0.73\ MnO + 0.27\ ZnO \rightarrow Mn_{0.73}Zn_{0.27}Fe_2O_4;$$

SHS process:

$$0.8\ Fe + 0.6\ Fe_2O_3 + 0.73\ MnO + 0.27\ ZnO \rightarrow$$
$$\rightarrow Mn_{0.73}Zn_{0.27}Fe_2O_4.$$

Table 5. Economical effectiveness of production of SHS powders

Powder	Ratio of the price of the product to the world price in different countries				
	Russia	USA	Korea	China	India
Elemental powders:					
aluminum nitride	0.10—0.12	0.16—0.20	0.13—0.15	0.10—0.13	0.10—0.12
silicon nitride	0.15—0.18	0.27—0.30			
Ingots of chromium carbide	0.15—0.22			0.25—0.29	
Composite of the titanium—chromium carbide composition with the nickel binder	0.10—0.12				
Powders obtained by magnesium-thermal method:					
titanium diboride	0.20—0.25			0.39—0.41	
boron nitride	0.20—0.25	0.75—0.80		0.28—0.31	0.31—0.33
Ferrites	0.25—0.30			0.45—0.47	

scheme of the shortest transition from the primary synthetic idea to the production of one or another SHS product (Fig. 20).

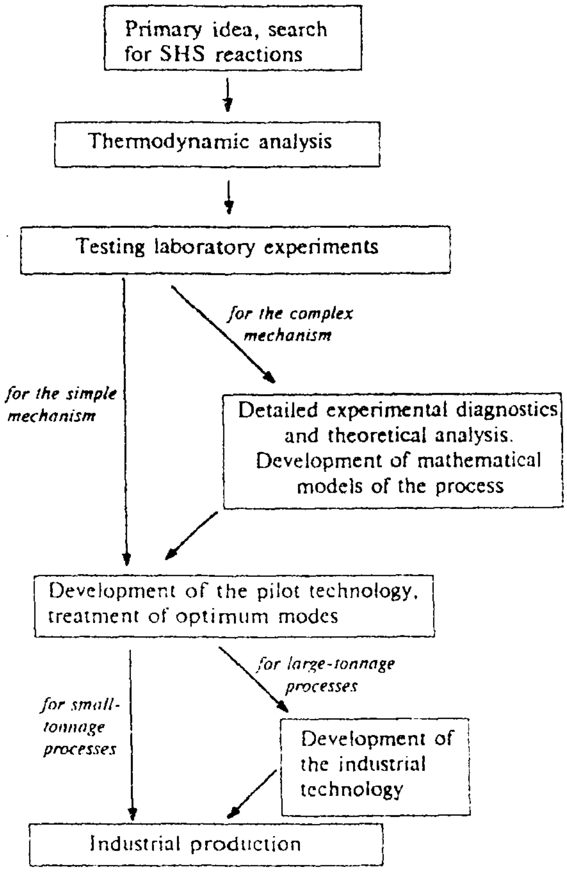

Fig. 20. Scheme of the transition from the primary idea to the industrial production of SHS products.

Organization of the work in our country

As has been mentioned, SHS processes were discovered in 1967 by researchers of the Department of Macroscopic Kinetics of the Branch of the Institute of Chemical Physics of the Academy of Sciences of the USSR in Chernogolovka, and the work was performed only in this Department for the first few years. Under the influence of the primary results reported at the II All-Union Symposium on Combustion and Explosion in 1969, research groups appeared in Tomsk and Erevan and began to collaborate actively with the scientists of the Institute of Chemical Physics in Chernogolovka in studying SHS processes. Then such groups appeared in Moscow, Alma-Ata, and other cities of the country. All-Union workshops on the theory and practice of SHS processes and All-Union conferences on technological combustion, in which not only researchers of SHS, but also scientists from interdisciplinary areas of science and engineering participated, were initiated by scientists from Chernogolovka.

In 1972 in Chernogolovka, the first pilot production of SHS products was created on the basis of a unique technological setup, and active relations with material scientists were formed. Interesting research groups for material science studies of SHS appeared in Kiev, Moscow, and Izhevsk. The first industrial units appeared in Kirovakan, Baku, and Erevan.

In 1979, the Council of Ministers of the USSR issued a Decree directed toward acceleration of the development and industrial management of this technology, the Scientific Council on the theory and practice of SHS processes was created, and then the Interdisciplinary Scientific Technical Complex (ISTC) "Thermosynthesis" was organized with the Institute of Macrokinetics of the Academy of Sciences of the USSR as the leading organization and regional scientific technical SHS centers in Tbilisi, Kuibyshev, and Alma-Ata, the Branch of the Institute of Structural Macrokinetics in Tomsk, and the Scientific Educational SHS Center MISIS—ISMAN. The ISTC "Thermosynthesis" performed many scientific studies and oversaw scientific technical developments (more than 100) on the creation of new technological processes, materials, and equipment; several new technological processes were prepared for introduction in industry and partially realized under industrial conditions.

Worldwide development of SHS

For a long time, domestic specialists worked alone in the area of SHS: similar work was not performed abroad, because SHS processes were assumed to be not promising for practical use. SHS has advanced to the world arena only since the beginning of the eighties.

In the U.S., the initiators of the work were J. W. McCauley[103] from the Research Center of the U.S. Army and J. B. Holt[104] from Lawrence Livermore National Laboratory. In our opinion, the review "Self-Propagating High-Temperature Synthesis as the Soviet Method for Preparation of Ceramic Materials" [105] played an important role for the origin of work on SHS abroad. At the present time, the U.S. is the second leading country after Russia in the volume of investigations in this area. American scientists contributed to the development of such directions in the SHS area as SHS using layered (foil) systems, SHS processes in electric fields and microwave actions, chaotization of the combustion of SHS systems, three-dimensional computation, the development of composite powders and materials, the creation of new variants of the force SHS compactization, and gas-phase SHS processes.[106—117] American researchers accept the pioneering and leading role of the Soviet (Russian) SHS school,[118] but, to attach a more ingenious character to their studies, they often use another name instead of SHS: "Combustion synthesis", which, in our opinion, does not reflect the essence of SHS processes exactly enough (for a terminological discussion, see Ref. 119).

The Japanese SHS school differs from the American school in the direction of application. This school developed functionally graded materials for the aerospace technique,[120,121] created technological methods for the combination of SHS with isostatic molding, SHS + HIP,[122] constructed a large-sized pipe for geophysical studies by centrifugal SHS-casting,[123] grew oxideless refractory single crystals from SHS products,[124] and produced wire with shape memory from the SHS titanium nickelide.[125]

Recently, Chinese scientists have been very active in the area of SHS. The schools of Beijing and Wuhan Universities can be distinguished among the Chinese research centers in this field. The main direction of the work in China is to create new materials. SHS research groups in India, Italy, Finland, Poland, Yugoslavia, and other countries are also actively working.

Presently, the worldwide development of SHS is a typical subject of international meetings. Beginning in 1991, international symposia on self-propagating high-temperature synthesis have been held (Alma-Ata, 1991; Honolulu, 1993; and Wuhan, 1995). The next symposium should be held in October, 1997 in Toledo (Spain). Special sessions (sections) on SHS have been organized in many conferences on combustion, pyrotechnics, metallurgy, and materials science.

It is difficult to overestimate the significance of the "International Journal on Self-Propagating High-Temperature Synthesis", published since 1992 (Allerton Press, New York).

In recent years, scientists from different countries have begun to cooperate. The most significant international project is the Spanish-American-Russian Project "Prometheus",[126] aimed at the creation of the industrial technology of some SHS powders, which would be adapted to Western industrial conditions.

Modern structure of the SHS area and prospects for further research

As a result of studies and the application of SHS processes and products for many years, the infrastructure of this area of scientific technical progress has been formed (Fig. 21). Two directions related to the macrokinetic and chemicotechnological grounds of SHS have been most developed. The third direction has been developed more weakly, but has become stronger. This direction is related to the ideology and methodology of the industrial development of SHS. In a recent work,[9] the author tried to consider the ten most promising directions of studies which would determine the area in the nearest future.

Let us discuss some promising problems. First let us consider chemical classes of the systems in which SHS processes occur. As has been shown above, these are mainly the systems that form inorganic materials (especially refractory materials), in which the efficiency of SHS is most significant due to the high temperatures necessary for the synthesis. However, there are many other inorganic systems with exothermic interaction of components, in which SHS processes either were not performed or have been poorly studied (for example, the mixtures forming semiconducting compounds). Systems of organic substances are of special interest from the point of view of broadening studies of objects. Examples of SHS processes in mixtures of powders of organic compounds are already known.[127—129] The organization of autowave processes in liquid-phase organic systems (solutions), which are the typical reaction medium in organic chemistry, is of basic interest. In this case, a new macrokinetic problem appears along with the chemical problem, namely, the interaction of the autowave process with the convective motion of the liquid. It is noteworthy that organic objects are convenient models for studying general problems of the SHS mechanism,

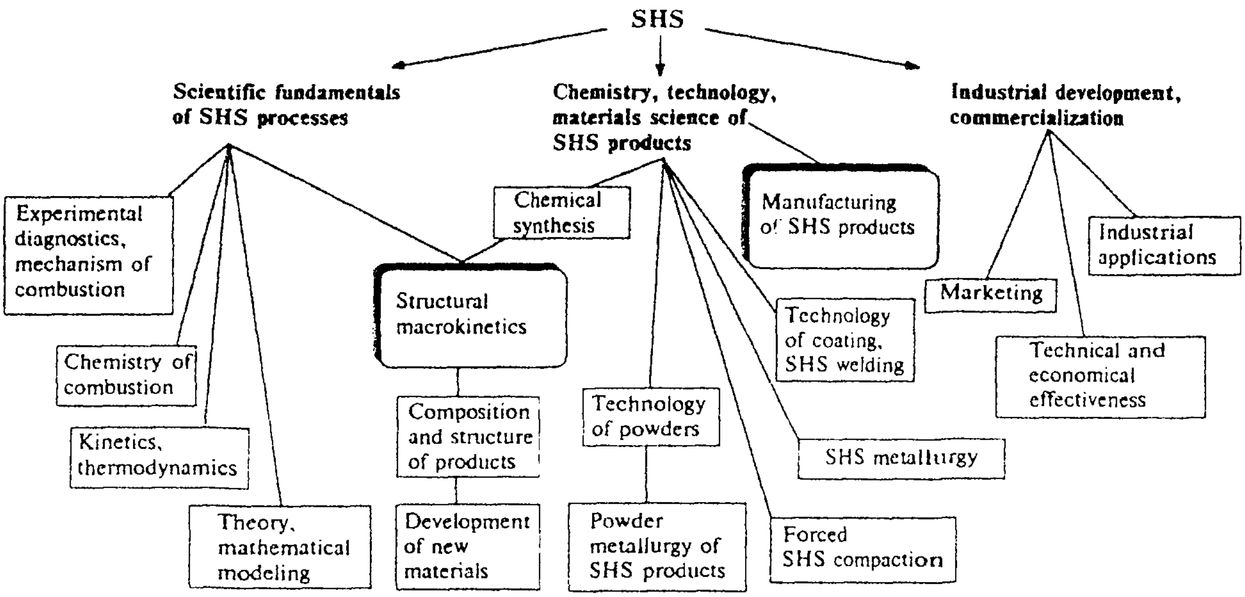

Fig. 21. Modem infrastructure of SHS as a scientific technical area.

because the low temperature of the processes, small rates of the front, and broad zones of transformation make it possible to use diagnostic methods of studies, including ESR, ^{1}H NMR, *etc.*, more widely.

It is promising to organize gas-phase SHS processes which make it possible to obtain products of combustion as fine particles or thin films (see, *e.g.*, Ref. 52). The choice of systems capable of burning and forming valuable products is the main problem, because systems which are interesting from the viewpoint of the synthesis are usually low-caloric. Therefore, future achievements should be associated with the additional supply of energy (using, for example, electric burners). In essence, there should be processes intermediate between combustion and plasma. Of course, branched chain processes of the chemical condensation type (for example, chain silane flame) are also very promising.

Among the new processes, we should mention the search for the detonation SHS process in which the energy responsible for the wave propagation is transferred not due to the heat conductivity (as in the normal SHS process), but by the impact compression. In the early studies of SHS in the experiments of Borovinskaya and then Adadurov, it was observed that the combustion of mixtures of boron powders with liquid nitrogen can transform to detonation. However, these studies were not developed. Now a purposeful interest in detonation SHS processes has emerged.[130]

Many unsolved problems arise when normal SHS charges are used. For example, SHS processes in systems with nanometric particles of reagents and with colloidal-type charges have not been studied at all, although qualitatively new structures of synthesized materials can be expected in these cases.

Particular problems of the combustion mechanism continue to evoke interest: the organization of perfect solid flames and contactless combustion of solid reagents,[26] the study of heterogeneous and unstable processes, and the solution of two- and three-dimensional problems of the combustion theory (see reviews 8, 9).

Recently, interest in the effect of gravitation forces and microgravitation conditions on SHS has increased due to active cosmic experiments.[131]

Many things should be done in the area of the structural macrokinetics of SHS processes; despite the successes achieved, it is in the very beginning of its development. In essence, only the ideology and methodology of the structural macrokinetics have been developed, the fundamental methodical procedures (dynamic X-ray diffraction analysis, quenching) have been created, and their efficiency has been illustrated. The development of this direction will allow one to create scientific grounds for the creation of materials of new generations.

In the SHS technology, the creation of new types of powders, monophase and multiphase (composite), of complex composition, and nanocrystalline, as well as whiskers and fibers, evokes great interest. In the powder metallurgy, only simple powders for sintering and hot molding are produced, while the chemical and morphological variety which can be provided by the SHS method is weakly used.

The studies in the field of the development (design) of functionally heterogeneous materials, graded and multilayered, including materials with coatings, are also very promising. Experiments have shown a high effectiveness of heterogeneous modes of combustion and methods for controlling them.[132] It seems very intriguing to produce chemically nonequilibrium materials, *i.e.*, materials whose composition and structure are formed finally under conditions of their exploitation due to post-reaction and additional energy release. This problem is related to controlling the incompleteness of the combustion and the formation of strength properties of the products formed. But the main problem is understanding what nonequilibrium materials are required and for what purposes.

The technology of the direct preparation of items by the SHS method followed by the minimum mechanical treatment is considered by many specialists as revolutionary. Indeed, what can be simpler and better than to kindle and immediately obtain an item? However, there are only several examples of successful solutions. Theoretically substantiated methods which make it possible to find optimum methods and modes of compaction products have not been developed. Mechanisms of the structure formation under conditions of force actions have been poorly studied. The relationship between studies performed and the theory and practice of the superplasticity of materials is not yet developed. The use of metallurgical methods are insufficiently efficient. Complex problems of the shape formation have not been solved. Only after similar works can the SHS technology of the direct preparation of items be considered to be revolutionary.

The combination of SHS with mechanochemical synthesis, *i.e.*, SHS processes under conditions of strong shift deformation in the charge and products, is interesting. It is clear that this will make it possible to intensify the synthesis and, applied to the powder technology, to increase noticeably the dispersity of the final products. It will be very fruitful to create an apparatus in which mixing of reagents, SHS processes, and grinding of products occur simultaneously, in one technological stage. Purely scientific studies of the effects of shear deformations on the burning velocity and the structure of products are also of interest.

As for the large-tonnage technology of SHS products (such as ferrites, ferroalloys, refractory materials, and others), we should emphasize the necessity of creating basically continuous SHS processes with the utilization of the released heat by its conversion to electric power. In this case, the known energetic technological approaches and the creation of small SHS electric stations should be discussed.

* * *

It is impossible to cover all of the interesting results and works in terms of this review. Therefore, the author tried to show the SHS area in the dynamics of its development, and some of the results presented served only as an illustration.

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