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Review Paper

History and Recent Developments in SHS

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Abstract: In a search for new patterns of combustion, I. P. Borovinskaya, V. M. Shkiro, and the author in 1967 made a scientific discovery that was later termed 'solid flame phenomenon'. The solid flame represents a special pattern of combustion when all of the compounds involved — starting, final, and possibly intermediate — are present in their solid state even at maximum combustion temperatures. It was also found that the products of solid flame represented valuable refractory compounds: carbides, borides, etc. This circumstance has lead to the development of a new production method for manufacturing refractory compounds, the self-propagating high-temperature synthesis (SHS). Since that time, a wealth of work was carried out in the Soviet Union and then in other countries (USA, Japan) which made SHS a leading branch of research and development. The fundamentals of SHS were formulated, a huge number of intended chemical syntheses were performed, original production methods and equipment were developed, medium-scale production was implemented into industry, and the basic concepts of SHS commercialization were formulated. From the solid-flame-driven method of synthesizing refractory compounds of limited potentiality, SHS became a powerful technology of inorganic materials, in which combustion of various compounds synthesized compounds and designs materials. The following items will be considered in the paper: (1) History of SHS: from a scientific discovery to producing materials; (2) SHS precursors (the theory and methodology of combustion, exothermic processes in the practice of pyrotechnics, metallurgy, and preparatory chemistry); (3) Some examples of the newest achievements in the field of SHS (structuring in SHS products, synthesis of complex compounds, growth of single crystals from SHS products, development of functionally gradient materials, the gas-phase SHS, in-line SHS production, etc.).

1 INTRODUCTION

As is known, the conventional methods of ceramics production are based on the classical processes of powder metallurgy — the sintering of chemically inert powders (components of ceramics) at high temperatures giving consolidated materials or articles. For these purposes, the other processes involving various pretreatment are being used in industrial engineering — hot uniaxial pressing, hot isostatic pressing in gasostats (HIP), plasmochemical synthesis and sputtering, gas-phase deposition (PVD and CVD), etc.

A common feature of these processes is the use of strong external heating to accelerate processing. As a result, the ceramic technologies are regarded as energy intensive ones.

During the past few years, an alternative approach based on the utilization of highly calorific charges and setting-up an autowave mode by a local initiation became popular. In this way, inorganic materials (including ceramics) can be synthesized due to the layer-by-layer self-heating to high temperatures at the expense of internal energy. The autowave propagation mode is ensured by heat transfer from hot combustion products to cold starting reactants. The process is characterized by a distinctly defined combustion front travelling through a charge and thus converting it to final products (chemical compounds, materials). These processes were termed Self-propagating High-temperature Synthesis (SHS).

In this communication, the state-of-the-art in the field, some most recent results, and the historical outlook on SHS as a new branch of R&D will be represented.

2 THE STATE-OF-THE-ART IN SHS

Much attention was paid to the R&D that ensured the development from the formulation of fundamentals to setting-up industrial production, including chemical syntheses and the development of new technologies, materials and instrumentation.

2.1 Fundamentals of SHS[1–4]

SHS as a kind of combustion belongs to the non-

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linear chemical phenomena with a varied degree of positive and negative feedback. As a result, the end product represents not only a consequence of combustion but also accounts for combustion. Such processes are classified as the technology-intensive ones — their practical application requires a deep insight into the mechanism of processes, otherwise it would be impossible to control the processes and to provide optimum processing conditions and high quality of products.

SHS investigations aim at elucidating the wave propagation patterns, the zone structure of a combustion wave, the chemical, physicochemical, and fluid dynamics phenomena in the wave, the heat balance in the system, the phase and structure transformations in combustion products. These studies are carried out using the modern methods of experimental diagnostics, combustion theory, kinetics, chemical thermodynamics, and high-temperature physical chemistry. The data of comprehensive studies allowed formulating the control means for burning velocity, temperature and degree of conversion; whereas the accumulated experience ensured reliable control of the composition, morphology, and structure of the end products.

The SHS studies gave rise to a new branch of fundamental research — structural macrokinetics.[2,4,12] This discipline treats the joint occurrence of structural and phase transitions, chemical reactions and heat/mass exchange with special attention to positive and negative feedback between them.

The SHS processes are most comprehensively studied for the powdered mixtures of metals (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, etc.) with nonmetals (B, C, Si, S); for the intermetallic mixtures of Ni, Co, Ti, Al, etc.; for the hybrid systems of the metal–gas type with H_2, N_2, O_2 as reactants, and for the metallothermic mixtures *metal oxide–nonmetal oxide (or nonmetal)–reducing metal (Al, Mg)*.

To date, the attention of researchers has focused on the multicomponent systems that offer a variety of transformation pathways in a combustion wave.

2.2 Chemical synthesis[4–7]

Chemical synthesis is a main designation of SHS. Combustion is carried out in a way that ensures obtaining an end product of a desired chemical and phase composition. In synthesizing chemical compounds, it is desirable to obtain a single-phase product of minimum contamination. This is achieved by a proper selection of a green mixture, by ensuring complete combustion and sufficient exposure at high temperatures.

By the SHS method, the following systems are being produced: binary compounds and solid solutions of chemical elements, solid solutions of binary compounds, multicomponent solid solutions and compounds, nonstoichiometric phases, high-temperature and high-pressure phases, etc.

Chemical synthesis is a fine art that requires not only a deep insight into the mechanism of SHS but also a good deal of intuition.

To date, about 500 various compounds have been synthesized by SHS: refractory compounds (borides, carbides, nitrides, silicides), oxides (tanthalates, niobates, ferrites, cuprates, etc.), intermetallics (aluminides, germanides, nickelides), chalcogenides (sulfides, selenides, tellurides), phosphides, hydrides, and some others. Their number has no principal limitation. A general trend in the field can be characterized by a gradual refusal to search for new synthetic capabilities of SHS in favor of specific purpose-oriented synthetic problems.

2.3 SHS Materials[2,7–10]

Chemical synthesis is closely related to the problem of developing new advanced materials. In this respect, SHS also demonstrates its capabilities, because the products obtained can acquire not only a desired composition but also structure, thus providing the control means for their physical and service parameters.

To date, about 100 projects have been developed for manufacturing the materials of varied designation. Among them are hard alloys, cutting materials, nitrided ferroalloys and alloying agents, advanced ceramics, refractories, heat resistant and temperature-strong intermetallics, light alloys, superconducting ceramics, solid lubricants, and many others.

On the basis of SHS, new advanced materials are being developed: composite powders, foam ceramics, ceramics containing no activators for sintering, anisotropic ceramics, and oxygen-free single crystals. Special attention is paid to the development of macroinhomogeneous structures, i.e. the materials with an intentionally organized inhomogeneous structure: coated materials, multilayered and functionally-gradient materials, composites, welded workpieces, etc.

2.4 SHS Technology[2,4,7,8,10]

The special capabilities of SHS best manifest themselves in the applications of SHS. Such outstanding features of SHS as the internal heat release and high burning velocity allow highly-productive and resource-saving manufacturing new high-quality materials to be suggested.

Table 1. SHS technological types

Technological type	Basic idea	End product
TT-1 Burning of green mixture	Burning of charge in sealed reactors or in air	Shapeless cakes, powders
TT-2 SHS sintering	Burning of shaped charge on a retention of shape and size	Porous and low-porous articles
TT-3 Forced SHS compaction	Burning of charge followed by product consolidation by uniaxial pressing, uniform compression, extrusion, rolling, forging and explosion	Compact non-porous materials and articles
TT-4 Technology of high-temperature SHS melts (SHS metallurgy)	Burning of highly calorific mixing yielding high-temperature melts in the bulk or on the surface	Ingots, cast articles, surfacing
TT-5 SHS welding	Burning of charge in a gap between workpieces upon external energy supply	Welded workpieces
TT-6 Gas-transport SHS technology	Burning of the mixtures containing gas-transport agents and parts to be surfaced	Coated parts, powders

To date, about 30 SHS production methods have been suggested. They can be classified in six technological types (TT) (Table 1). They differ in the composition and structure of a green mixture, in the burning conditions, in the composition and pressure of gaseous environment, in the type and intensity of external action, and in their morphology and destination of end products.

Two approaches are being used in SHS technology. The first of them is the production of not end but intermediate products, which are then used as raw materials in further processing. For instance, the powders are prepared from sintered cakes (TT-1) and ingots (TT-4); the cutting inserts, from consolidated blanks (TT-3), etc. The second approach is based on the direct (net-shape) production of finished articles, thus eliminating the intermediate stages and products (e.g. powders). In this way, the ceramic articles (TT-2), hard-alloy parts (TT-3), and cast tubes (TT-4) are being produced; in this case, synthesis, structuring, and shaping are carried out in a one-stage process.

The facilities of SHS technology are more simple than that used, e.g. in powder metallurgy (because heating elements are absent). Among SHS facilities, the universal reactors 20–30 litres in volume became most popular (SHS-20 and SHS-30). These reactors are used to manufacture the elemental, magnesiothermic, and aluminothermic powders, to perform SHS surfacing and SHS sintering. The list of SHS facilities available includes SHS cameras with thermovacuum treatment of samples, SHS gasostats of high pressure, special presses equipped with press dies of varied size and shape, nondestructive explosion vessels, SHS extruders and roll mills, equipment for SHS forging, centrifugal SHS machines, apparatuses for SHS welding, etc.

In spite of considerable progress in SHS technologies, their technical level should be regarded as the pilot-scale one. The productivity of SHS installation is sufficiently high. However, a new level of productivity can be attained upon further improvement in the instrumentation and setting-up the automated in-line production. Among the works in this direction, the Spanish–American–Russian 'Prometheus' Project should be mentioned. This project aims at setting up a modern SHS production line for powders on an industrial scale (F. Llorente, M. Werle, I. Borovinskaya).

Some SHS technologies have found their industrial applications. In Russia, the USA, and Japan, the SHS powders of inorganic compounds, nitrided ferroalloys, ceramic insulators, high-temperature heaters, shape memory alloy wire, cutting inserts, ferrite articles, etc., are produced on an industrial scale.

2.5 Technical and economic efficiency of SHS[8,11,12]

In view of actual penetration of SHS into industry and engineering, much attention is being paid to the studies on the efficiency of SHS. The following physical factors were found to define the efficiency of SHS: high temperature and high burning velocity (high degree of conversion and self-purification ensure high quality of products; high productivity), internal heat release (energy saving, the feasibility of dealing with large amounts of green mixture and producing large-scale articles, simplicity of installation), controlled cooling rate (autoannealing and autoquenching, controlling the material strength).

The technical efficiency of SHS is normally determined by comparing the service parameters of SHS products with those of conventionally obtained products taken as a prototype. Typically, the service parameters of SHS products are 3–5 times higher. For the SHS powders, their composition (chemical, phase, and granulometric) and the properties of end products (produced from powders) are compared with those of their furnace analogs.

Of great importance here are the technological factors, first of all, the economic factors. As a rule, a comparative analysis is attended by serious difficulties due to a lack of technological details (know-how).

An interesting analysis was carried out in Ref. 11 (see also Refs 8 and 12). Using the Russian experience in SHS production, the production cost for some SHS powders was calculated with due regard for the Western conditions (the cost of raw materials, labor cost, etc.). It was found to be lower than the world market prices of these products; this confirmed the high economic efficiency of SHS technologies. The ratio of the cost of SHS products to the world prices is 0·13–0·25 for the elemental powders (AlN, Si_3N_4); 0·25–0·35 for aluminothermic powders (Cr_3C_2); and 0·4–0·45 for magnesiothermic powders (TiB_2, BN).

None of the SHS productions can be set up without a thorough economic design.

3 SOME NEW DEVELOPMENTS

Now let us consider some new developments that may outline the directions of further research and development in the field of SHS.

3.1 Ultrafine and nanometric powders

For a long time, it was thought that only large particles (several microns and above) could be obtained by the SHS method, and accordingly, they were thought to be unsuitable for sintering. But it was found recently that by controlling structuring and improving the dispergation procedure for the primary SHS products (cakes, ingots), finely dispersed powders (0·1–1·0 μm) could be obtained.

A new method for processing the cakes of nonmetal nitrides — the so-called chemical dispergation — was suggested by Borovinskaya *et al.*[13] A cake of SHS product is placed in a liquid of special composition at some specified temperature. The defect layers at the crystallite boundaries are dissolved, whereas the crystallites are not. As a result, the cake disintegrates giving the single-crystalline particles of crystallite size.

As an example Fig. 1 presents the photographs of AiN particles. In one of them, a large (hollow) agglomerate particle obtained upon mechanical disintegration is shown; in the other, the particles prepared from the same cake by chemical dispergation. The homogeneity of particles and their small size (about 0·1 μm) should be emphasized.

By chemical dispergation, the other fine-grained powders were obtained at the Institute of Structural Macrokinetics (hereafter ISMAN). The maximum value of specific surface attained for other SHS powders is 14 m^2/g, 11·5 m^2/g, 11 m^2/g, and 8 m^2/g for BN, S_3N_4, SiC, and B_4C, respectively.

An attack on the size of SHS particles is being continued. Recently, Yuan and co-workers obtained nanometric NiAl crystallites (5–70 nm) by using the so-called mechanical alloying — an intensive mechanical treatment of green mixture (see Ref. 12).

Of interest is the reverse problem — an increase in the size of single-crystalline particles upon a decrease in the cooling rate for combustion products that enhances the extent of recrystallization. By this method, the single-crystalline particles of TiC, about 1 mm in size, were obtained.

Obtaining ultrafine and nanometric particles, as well as large single crystals, illustrates the possibility of controlling the SHS process in solving specific fine problems of materials science.

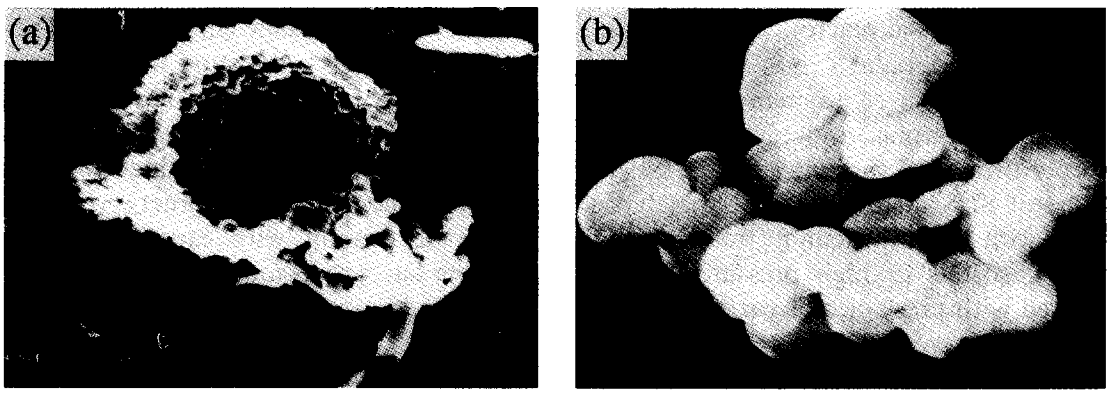

Fig. 1. Particles of SHS aluminium nitride. (a) Hollow agglomerate particle, grain size ~5 μm (partial disintegration). (b) Single-crystalline particles, grain size ~0·1 μm (complete disintegration).

3.2 Technology of SHS ferrites[14]

The synthesis of ferrites is yet one more SHS technology that has found its industrial application. These systems are interesting not only because of the practical importance but also in view of the complex mechanism of their formation, so that the synthesis of ferrites can be regarded as a test for the synthetic capabilities of SHS.

The SHS of ferrites is a complicated multistage process. The basic reaction is the oxidation of iron:

$$2Fe + 1{\cdot}5O_2 \rightarrow Fe_2O_3.$$

To synthesize a desired ferrite, iron oxide is added to iron powder together with other oxides. The overall reaction scheme may be represented in the form:

$$2\alpha Fe + (1-\alpha)Fe_2O_3 + \sum_{i=1}^{n} m_i(Me_2O_R) + 1{\cdot}5xO_2 \rightarrow$$

$$\rightarrow Fe_2O_3 \cdot \prod_{i=1}^{n} m_i(Me_2O_R)_i,$$

where R is the metal valence, m_i is the mole number for metal oxide, n is the number of functional metals that form ferrite, and α is the coefficient that governs the caloricity of the SHS process.

Sometimes, carbonates or nitrates are added instead of metal oxides. The SHS of ferrites is controlled by the penetration (spontaneous or forced) of oxygen from the environment.

To date, almost all of the known ferrites (barium, strontium, manganese, cobalt, bismuth, yttrium, etc.) were prepared by the SHS method. The most extensively studied is the SHS of nickel–zinc and manganese–zinc ferrites, as well as barium and strontium hexaferrites. Recently, the powder of MZ 2000 manganese–zinc ferrite was synthesized at ISMAN. By its physical and service parameters, the sintered articles of this powder do not deteriorate the best Japanese samples (initial susceptibility 2000 ± 200, the saturating flux 5030–5460 G at 15 kOe, coercive force 30–42 Oe, etc.).

As compared to the conventional ceramic technology, the SHS technology of ferrites is advantageous, because (i) small-scale highly productive reactors are being used instead of large furnaces and (ii) the stage of first firing (ferritization) is absent (due to high temperatures, ferritization occurs in the course of synthesis). Because ferritization is an energy- and time-consuming stage, the SHS method becomes more efficient.

Three SHS ferrites (NN 100, NN 600, and NM 600) are now produced on an industrial scale in Russia. In one of the Russian plants, an in-line production with a spatially fixed combustion front was put in action. The raw materials are continuously supplied to the input, whereas ferrites are taken out at the output. In this case, the productivity is directly determined by burning velocity and attains a value of about 1.5 thousand tons (at the three-shift operation).

Manufacturing ferrites is a good example of SHS applications in a large-scale production.

3.3 Large-scale hard-alloy articles

In the second half of the 1970s, a new method for manufacturing hard alloys was suggested (see, for example, Ref. 2). The method is based on SHS performed with multicomponent powdered mixtures in press dies: the combustion-synthesized hard-alloy structure (wear-resistant grain surrounded with metal binder) is densified to the non-porous state by applying pressure to a still hot product. By this method, new hard alloys of the STIM group were obtained, and a new production method for manufacturing cutting inserts, dies, and other low-scale parts was suggested.

During the past few years, a unique installation for SHS manufacturing (TT-3) large-scale hard-alloy articles has been developed at ISMAN.[15] It comprises a 2000 t press, large-scale press dies, initiation units, and a system for controlling current pressure, punch velocity, and temperature at different points of sample; therefore, the kinetic curves of combustion and densification can be readily recorded.

In these studies, the main problem is a proper choice of load (densification) pattern that would ensure a desired density of material. Because the experiments are expensive, it was difficult to do it empirically. On the other hand, a lack of the rheodynamic theory for these systems did not allow performing appropriate calculations. The solution to the problem was found by processing the kinetic curves of loading and densification; and as a result, the empiric equation for densification was derived:

$$\frac{d\Delta}{dt} = \varphi\,(T, \Delta, P-P_*).$$

This equation was used to determine the optimum conditions of densification. Here, Δ and T are the relative density and temperature of combustion product at moment t, respectively; P is pressure; and P_* the equilibrium pressure of pressing.

$$P_* = -a(1+bT)\Delta^m \ln(1-\Delta),$$

where it was found that a and b are constants of a given substance.

The densification occurs at $P > P_*$; at $P = P_*$, $\varphi = 0$ (Δ = const), the φ function acquires a complicated form.

This equation was used to optimize the structure of STIM-4 (the product of combustion in the system Ti + αB + alloying agent ($\alpha < 1$)). The material obtained exhibited high density ($\Delta > 0{\cdot}99$) and uniformity of composition and properties (hardness, strength) over the entire article.

The opportunity was also used to develop the materials of a new class — the so-called macrocomposites that represent the blocks of hard alloy in a metal matrix; these materials combine the properties of hard alloys with the ductility of metals.

By SHS, the following articles have been manufactured: hard-alloy disk-mirrors 600 mm in diameter; blanks for drawing dies, wear-resistant rings for dye dispergators, rolls for hot copper rolling — all 370 mm in diameter. The wear resistance of rolls was 2 times higher than that of H13 steel (USA). The rings and rolls are being commercialized in Russia.

The production of large-scale articles is a brilliant example of the unique capabilities of SHS.

3.4 Refractory and building ceramics[16–18]

This R&D avenue has sprung up recently, in the end of the 1980s – beginning of the 1990s. The special feature of these processes is that the combustion of metals (Al, Mg, etc.) is carried out in air or oxygen in the systems filled with inexpensive ingredients (sands, clays, solid wastes) or refractory compounds of special designation (oxides, borides, etc.). The basic reactions are versatile. As an example, let us consider the case of Al as a combustible.

The reaction scheme for aluminum oxidation with molecular oxygen has the form:

$$2\ \mathrm{Al} + 1{\cdot}5\mathrm{O_2} \rightarrow \mathrm{Al_2O_3}.$$

As a rule, the reaction which occurs is controlled by permeation.

Of considerable interest are the processes of the gasless oxidation of Al by higher oxides; upon partial reduction of oxides

$$\frac{2}{3}(n-1)R{\cdot}\mathrm{Al} + \mathrm{Me_2O}_{nR} \rightarrow \mathrm{Me_2O}R + \frac{(n-1)R}{3}\ \mathrm{Al_2O_3}$$

where R is the metal valence and $n > 1$.

The reaction involving both molecular and oxide oxygen became most popular:

$$\mathrm{Me_2O}_R + \frac{2R}{3}\ \mathrm{Al} \xrightarrow[\text{gasless stage}]{} 2\mathrm{Me} + \frac{R}{3}\ \mathrm{Al_2O_3}$$

$$\xrightarrow[\text{permeation-controlled stage}]{\mathrm{O_2}} \mathrm{Me_2O}_R + \frac{R}{3}\ \mathrm{Al_2O_3}$$

In the autowave process, an additional amount of metal oxide is formed. At high temperatures, these oxides ensure the formation of the end product of the desired composition and structure.

The technology of refractory and building ceramics is based on the experience acquired in conventional ceramic technology. The basic idea is fairly simple — some fraction of oxides from a conventional green mixture is substituted with metal elements that are further converted to oxides upon combustion. This allows one to convert the elements to oxides in the SHS mode, to refuse from furnaces, and to obtain a material of desired quality. In addition, SHS opens new horizons for the variation of the processing procedure and for the development of new materials.

The joint efforts of the Kazakh Institute for Combustion Problems and ISMAN resulted[16] in the development of a new class of refractory materials (Furnon trade mark). The Kazakh ores (chromite, dolomite, etc.) are being used as raw materials. These materials found their application in the maintenance and repair of firing kilns: the SHS green mixture is used as a masonry mortar. The SHS process carried out in a gap between refractory bricks ensures a high-quality joining (welding) between them. The experience acquired in Kazakhstan and Russia shows that the SHS refractories enhance the service life of kilns and furnaces by a factor of 2–3. According to the scheme adopted, the SHS green mixture is commercially available, with the SHS process being carried out by the customer.

A search for new SHS refractories is being continued. Recently, using magnesium as a combustible and magnesium compounds (nitrate, oxide) as fillers, a new highly porous (up to 70%) material with heat resistance 2500–2700°C was synthesized at the Kazakh Institute for Combustion Problems.

By the method of SHS sintering (TT-2), the production procedure was suggested at ISMAN[17] for manufacturing thin floor tiles (3–4 mm thick) of high strength and wear resistance. The optimum Al content in a green mixture was found to be 5 wt%. At lower Al content, the tiles were insufficiently strong; at higher ones, the cost of Al became higher than the cost of electric power consumed in furnace processing.

To date, the work on the development of building materials of varied mechanical and thermal characteristics, on the bulk strengthening of porous silicon-containing materials, and on the surface strengthening of chamotte, mullite–silica, etc., articles is in progress at ISMAN.[18]

The development of refractories and building materials represents an example of the successful penetration of SHS into new branches of industry and engineering.

4 ON THE HISTORY OF SHS

As SHS gradually demonstrated its scientific and practical significance, an increasing interest was displayed to its history, to the closely related processes described in the past. A rich collection of the Western papers devoted to the exothermic effects in synthesis was compiled by Hlavaček.[19] However, this collection cannot be regarded as an actual 'SHS history', because these results were obtained independently: the preceding events had no influence on the subsequent ones. The works cited in Ref. 19 did not result in the appearance of a new original research avenue in chemistry and technology, as well as in formulating an original ideology and methodology. Nevertheless, to know these works is interesting and instructive. Unfortunately, the related works of the Russian authors (in particular, those of N. N. Beketov — a founder of aluminothermy[20]) have not been mentioned in Ref. 19.

SHS differs from the processes described in Ref. 19 by a distinctly defined combustion front and the conditions of its travelling; by a deep insight into the interrelation between the processes and product characteristics, on one side, and the parameters of the 'green mixture–environment' system, on the other; and by the possibility of controlling the processes to optimize the synthesis conditions. Such an approach became possible only after the development of the modern combustion theory that established the nature and mechanism of self-propagating chemical reactions. No wonder that SHS has sprung up only in the 1960s of the 20th century and not earlier, in spite of the existence of its precursors.

A real history of SHS is closely related to the discovery of the so-called solid flame. In the 1960s, the studies on the mechanism of combustion in gasifying condensed systems — such as explosives, gun powders, and solid propellants — were carried out in Chernogolovka (near Moscow) at the Research Center of the USSR Academy of Sciences. At that time the role of gasification in combustion was vividly argued. To check one of the hypotheses, the authors[21] prepared the gasless iron–aluminum thermite diluted with alumina. After combustion, the sample retained its initial weight, because starting reactants and products remained in their condensed state during combustion. In contrast to gasifying systems, the gasless combustion was consistent with the predictions of the simplest combustion theory.

A search for new gasless systems has lead to a remarkable discovery (Merzhanov, Shkiro and Borovinskaya, 1967), later termed the solid flame (SF) phenomenon. The SF is a solid-state combustion when reactants and products remain in their solid state even at high combustion temperatures. Chemically inert powder of refractory metals (Nb, Ta, Mo, W, etc.) and nonmetals (B, C) served as reactants whereas the products represented refractory compounds (borides, carbides). It soon became clear that the SF is an efficient method for obtaining refractory materials; the method was termed Self-propagating High-temperature Synthesis (SHS).

It follows that the studies on the mechanism and theory of combustion in gasifying condensed systems, as well as the experience acquired in the combustion of thermites (that represent the low-gasifying compositions), played a key role in the build-up of SHS (Fig. 2).

Since that time (1967), SHS has been developed extensively and has now become an important avenue of R&D (Table 2).

Not repeating the table content, let us outline the following:

(1) SHS developed from simple to more complicated:

fundamentals of SHS: diagnostics of combustion → kinetics and thermodynamics → theory and mathematical modeling → optimization of synthesis → structural macrokinetics;

SHS technology: SHS powder technology → SHS sintering → forced SHS compaction → SHS surfacing;

SHS materials: homogeneous materials → heterogeneous, macrohomogeneous materials →macroinhomogeneous structures;

SHS raw materials: chemical elements → chemical compounds as control means and fillers →chemical compounds as reactants → mineral raw materials and industrial wastes.

(2) Theory and practice of SHS developed jointly and harmoniously, in close mutual interconnection.

(3) SHS penetration into technology and materials science was accompanied by an acute competition: new had to overcome strong resistance from old to win its own fields of application.

(4) Comprehensive SHS studies in the West

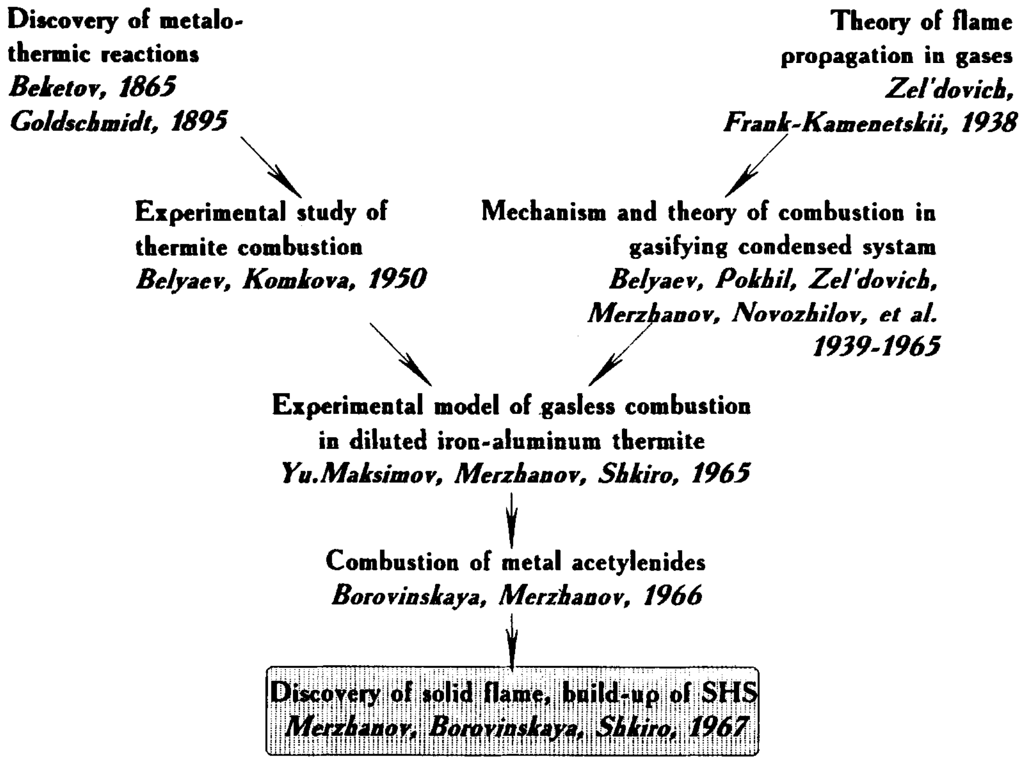

Fig. 2. Schematic diagram of SHS history: actual precursors.

Table 2. History of progress in SHS

Basic results	Directions of subsequent research. Principal investigators.
1. Primary concepts of combustion in SHS systems, *Merzhanov, Borovinskaya, Khaikin, 1968–72.*	Fundamentals of SHS: combustion mechanism and theory, mathematical modeling, kinetics and thermodynamics, structural macrokinetics. *Aldushin, Barzykin, Borovinskaya, Holt, Grigor'ev, Kharatyan, Mal'tsev, Matkowsky, Merzhanov, Munir, Novozhilov, Shkadinskii, Shkiro, Shteinberg, Zenin,* et al.
2. First syntheses and certification of SHS products (nitrides, carbides, borides, silicides). *Borovinskaya, 1969–71.*	Extension of the raw-material basis for SHS and of the classes of SHS products. *Boldyrev, Borovinskaya, Dolukhanyan, Itin, Kaieda, Yu. Maksimov, Mamyan, Moore, Naiborodenko, Nersesyan, Pampuch, Puszynsky, Yukhvid, Varma,* et al.
3. First installation for the pilot-scale production of SHS powders. *Borovinskaya, Ratnikov, Prokudina, Merzhanov, 1972.*	Improvement and further development of the technology of SHS powders. *Avakyan, Borovinskaya, Dolukhanyan, Yu. Maksimov, Mamyan, Makhonin, Nersesyan, Prokudina, Ratnikov, Yukhvid,* et al.
4. First applications of SHS products in abrasive pastes and powders. *Karyuk, Borovinskaya, 1973.*	Development of new SHS materials and articles. *Borovinskaya, Bunin, Kvanin, Koizumi, Ksandopulo, Levashov, Yu.Maksimov, Miyamoto, Moore, Ordan'yan, Pampuch, Pityulin, Sata, Sokolovsky, Wojcicki,* et al.
5. First experiments on the net-shape SHS production of materials and articles. *Merzhanov, Borovinskaya, Ratnikov, 1975.*	Fundamentals of SHS technology: forced SHS compaction, SHS sintering, SHS surfacing, SHS welding. *Bloshenko, Borovinskaya, Gordopolov, Kvanin, Koizumi, Meyers, Miyamoto, Odawara, Rabin, Rice, Stolin, Shteinberg, Shtessel, Yukhvid,* et al.
6. Initiation of SHS research in the US and Japan. *Holt, McCauley, Odawara, 1979–80.*	Worldwide development of SHS ● USA (*Hlavačhek, Holt, Logan, Matkowsky, Meyers, Munir, Moore, Niiler, Rabin, Rice, Spriggs, Thadhani, Wojcicki,* et al.) ● Japan (*Kaieda, Koizumi, Miyamoto, Odawara, Sata,* et al.) ● China (*Lai, Yuan,* et al.) ● Other countries (*Moya, Pampuch, Patil,* et al.)
7. First commercialization of SHS. Kirovakan Plant of High-Temperature Heaters. *Pogosyan, Sarkisyan, Dolukhanyan, Borovinskaya, Merzhanov, 1979.*	Setting-up SHS production in: ● the countries of former USSR (*Ksandopulo, Kuliev, Lebedev, Prozorov, Tarakhchan,* et al.) ● USA (*Blakely, Hida, Logan*) ● Japan (*Kaieda*)
8. International meetings Int. Symp. of Amer. Ceram. Soc., San Francisco, *1988. Holt, Munir.*	International Symposia on SHS. Alma-Ata, 1991; Honolulu, 1993. *Ksandopulo, Merzhanov, Spriggs,* et al.

were initiated at a ten-year delay and were stimulated by the Soviet works (in spite of the existence of works cited in Ref. 19). To date, SHS is a worldwide problem, being solved due to the joint efforts of research workers from numerous countries.

5 CONCLUSIONS

Research and development in the field of SHS is in progress. The principal research avenues concern the mechanism of combustion in multicomponent systems in a wave, mathematical modeling of non-one-dimensional unsteady processes, and structuring in combustion products. In technological applications, the net-shape production of SHS materials and articles (with an emphasis on the macroinhomogeneous structures) is being improved; the in-line production technologies are being developed; and a search for new applications is being continued. An important task is to compare different production methods for manufacturing the same materials and thus to determine the best applications for those or other technologies of inorganic materials.

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