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Combustion and explosion processes in physical chemistry and technology of inorganic materials †

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Abstract. This review is the first attempt to generalise, in a descriptive-conceptual form, material-synthesising and material-affecting combustion and explosion processes and relevant physicochemical, technological and materials science problems with special emphasis on their practical (technological and industrial) applications. The bibliography includes 127 references.

I. Introduction

Combustion and explosion are physicochemical processes where transformations of substances are accompanied by intense release of energy and exchange of heat and mass with the environment. These processes, which have been known since ancient times, have made a significant contribution to the technological progress and ensured high level of development of modern civilisation. Combustion and explosion processes can be implemented in miscellaneous media, *viz.,* gaseous, condensed and multiphase (homogeneous, heterogeneous, organic, inorganic, *etc*.) and are therefore widely spread in nature and technology.

Combustion and explosion processes have both common and distinctive features. Common to both processes are high energy and nonlinearity, while distinctive features include the nature of their effects, self-propagation mechanisms, characteristic time scales and approaches to their theoretical description (Table 1).

It is noteworthy that common features prevail over distinctions. It is not therefore surprising that studies in the field of combustion and explosion are being developed in the framework of a single problem as can be judged from the establishment of the Integrated Scientific Council on Combustion and Explosion at the Presidium of the Russian Academy of Sciences, the journal 'Combustion, Explosion and Shock Waves', joint symposia on combustion and explosion, *etc*.

Combustion and explosion processes are described in terms of a specially developed scientific methodology based on the analysis of feedforwards and feedbacks of exothermic reactions and transport processes. This methodology was used for the description of numerous specific phenomena and effects typical of these processes. It is the existence of a particular scientific methodology that allowed consideration of combustion and explosion as an independent area of knowledge.

The place of the combustion and explosion science in the family of related scientific disciplines some of which are concerned with the studies of chemical reactions, while others deal with transport processes, is shown in Fig. 1.

As regards the uniqueness of the scientific methodology and the range of their practical applications, combustion and explosion processes are unrivalled. Some areas of practical applications of these processes are shown in Fig. 2.

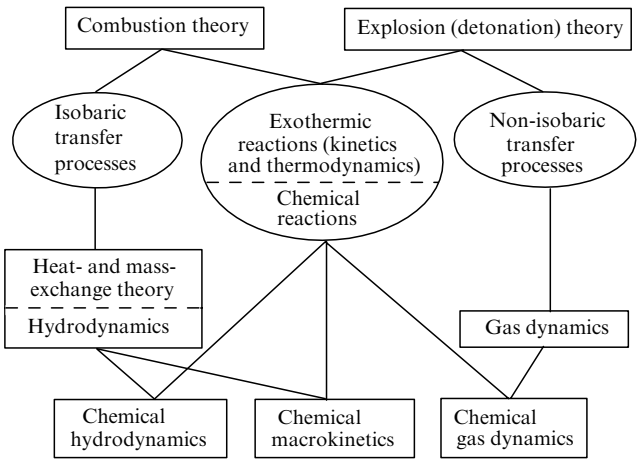


Figure 1. The position of combustion and explosion science in the family of related scientific disciplines.

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Table 1. Some common and distinctive features of combustion and explosion processes.

Process	Nature of effect	Mechanism of self-propagation	Characteristic time scale	Areas of knowledge used for theoretical description of the process
Combustion	heat	heat transmission, diffusion	milliseconds and more	chemical kinetics + theory of heat and mass exchange
Explosion	gas-dynamic	shock compression	microseconds	chemical thermodynamics + gas dynamics

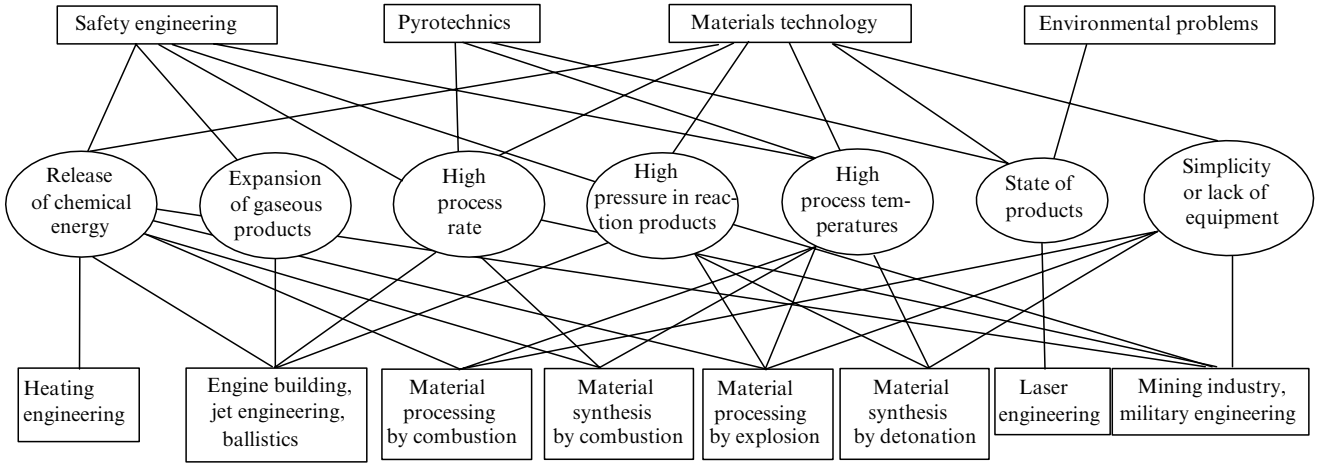


Figure 2. Practical applications of combustion and explosion processes.

A tremendous contribution to the chemistry of combustion and explosion has been made by Soviet (Russian) scientific schools.

— The school of N N Semenov laid the foundations of the modern theory of combustion and explosion. Its brilliant representatives Ya B Zeldovich, D A Frank-Kamenetsky, A F Belyaev, *etc*., have won international recognition for their studies in the field of combustion and explosion.[1–6]

— The schools of M A Lavrent'ev and M A Sadovsky developed the gas-dynamic principles of the explosion theory and substantiated the practical aspects of detonation effects (*e.g*., surface shots, material processing by explosion, *etc*.) on various substances.

— The schools of B P Zhukov and V S Shpak worked out problems of combustion of solid propellants.

Solid flame combustion (SFC) and self-propagating high-temperature synthesis (SHS) have been developed especially intensively. Studies in these areas were initiated and developed for a long time only in the USSR; however, researches and developments in the field of SHS are currently under way in 47 countries as can be judged from the ever increasing number of publications (totalling $\sim$ 10 000 at a rate of about 2 articles per day). The largest research centres dealing with in-depth studies of SHS are situated in Russia [Institute of Structural Macrokinetics and Materials Science of the Russian Academy of Sciences (ISMAN), SHS Research-and-Educational Centre of the Moscow Institute of Steel and Alloys and ISMAN, Department of Structural Macrokinetics of the Tomsk Research Centre of the Siberian Branch of the Russian Academy of Sciences, Samara State Technological University, Altai State Technological University], USA (University of Notre Dame, Northwestern University, University of California at Davis, Colorado School of Mines), Japan (Ryukoku University, Osaka University, Tokyo Institute of Technology), China (Wuhan University, Beijing University of Science and Technology, Harbin Institute of Technology), France (Montpellier University) and Israel (Israeli Institute of Technology). A significant contribution to SHS has been made by specialised international symposia and the 'International Journal of Self-Propagating High-Temperature Synthesis'.

This review considers only those combustion and explosion processes which are aimed at the development of materials with predetermined properties, namely, the synthesis of novel materials or imparting novel properties to the existing materials by virtue of their processing. The former approach entails material-synthesising combustion and detonation processes, while the latter is confined to material processing.

In considering miscellaneous material-synthesising processes, special attention will be given to combustion and explosion products as subjects for the synthesis and mechanisms of transformation of the starting elements in combustion and detonation waves (chemical reactions, phase transitions, structure formation of final products, *etc*.) and theoretical aspects of combustion and explosion. The main emphasis in the analysis of material processing will be laid on processing of materials by combustion and explosion, effects of high temperatures and high pressures on materials and interactions of processed materials with the green mixture.

II. Material-synthesising technological combustion and explosion processes

Material-synthesising processes include:

— classical technologies, *e.g*., blast-furnace processes, out-of-furnace metallothermy, incomplete combustion of hydrocarbons, *etc*.;

— self-propagating high-termperature synthesis (primary and advanced SHS);

— processes carried out in shock and detonation waves.

1. Classical processes. Out-of-furnace metallothermy

Some examples of classical processes aimed at the preparation of novel materials by combustion and explosion are given in Table 2. Although these technologies are out of date and are being

Table 2. Classical processes of industrial combustion.

Process	Combustion regime	Raw materials	Final product
Blast furnace process	filtration	coke, ore, additives, air	cast iron
Out-of-furnace metallothermy	liquid flame	ground ore or metal oxides	ferroalloys and reinforcers or reduced metals
Combustion of rich hydrocarbon–air mixtures	condensation	gaseous or liquid hydrocarbons, air	industrial carbon (soot)

developed at a very slow pace, they still find application as industrially useful processes.

Out-of-furnace metallothermy,[7] *i.e.*, a redox process carried out in powder mixtures of metal oxides and reducing metals in a combustion mode, is one of the most well-developed and well-studied classical processes. It was first implemented by N N Beketov and, later, by V M Goldschmidt as early as the 19th century; however, the first theoretical combustion research into metallothermic compositions (thermites) were carried out by A F Belyaev and L D Komkova as late as 1950.[8] The fundamental of out-of-furnace metallothermy has been detailed in the well-known book.[7]

The chemical scheme of an out-of-furnace metallothermic process can be presented as follows:

$$M_mO_n + \frac{nm'}{n'}M' \longrightarrow mM + \frac{n}{n'}M'_{m'}O_{n'} + Q,$$

where M_mO_n is the oxide of the metal to be reduced, M' is the reducing metal and Q is the heat of combustion. If the heat of combustion is high, the combustion proceeds in a wave mode. Al (aluminothermy), Mg (magnesiothermy), Ca (calciothermy) and Si (silicothermy) are generally used as reducing metals. Out-of-furnace metallothermy is used for joining metals and alloys. The most significant achievements have been attained in the production of ferroalloy ingots, hardeners and rare metals.

Special attention in the development of out-of-furnace metallothermic processes should be given to aggregate states of the final and by-products. A chart of the aggregate states of two combustion products [a reduced metal (P_1) and a reducing metal oxide (P_2)], which is based on thermodynamic calculations, is shown in Fig. 3.‡ The two coordinates, $T_{ad}/T_m(P_1)$ and $T_{ad}/T_m(P_2)$, reflect the correlation between the combustion and melting temperatures of the reduced metal and the reducing metal oxide. Here, T_{ad} is the adiabatic combustion temperature of the metallothermic mixture; $T_m(P_1)$ and $T_m(P_2)$ are the melting temperatures of the reduced metal and the reducing metal oxide, respectively.

There are four adiabatic combustion zones differing in the aggregate states of a metal to be reduced and a reducing metal, *viz*., zone *I*, solid metal and solid oxide; zone *II,* solid metal and liquid oxide; zone *III,* liquid metal and liquid oxide and zone *IV,* liquid metal and solid oxide. As can be seen from Fig. 3, the theoretical points are localised in all the four zones.

Of particular interest is zone *III* where a heterogeneous molten mass consisting of liquid metal oxide and drops of a liquid metal is formed. The drops sediment in the gravitational field of the Earth to produce an ingot. Such a phase separation allows easy isolation of the final product.

The combustion temperatures of the aforementioned systems depend on the pressure of an external gas, which suppresses

‡ Calculations performed by I S Gordopolov, A G Merzhanov and V I Yukhvid (ISMAN).

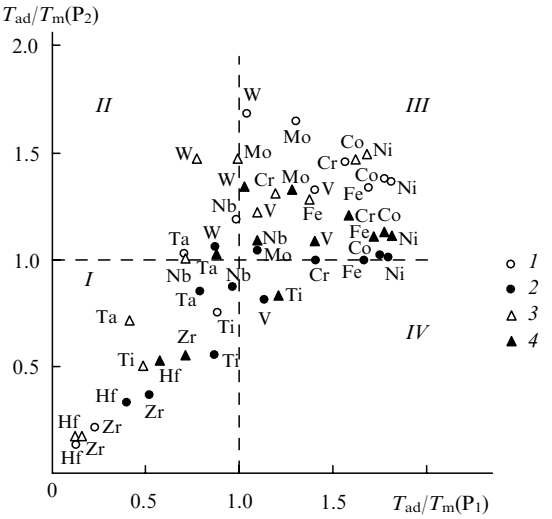


Figure 3. Aggregate states of combustion products prepared by out-of-furnace metallothermy. The pressure of the ambient gas is 0.1 MPa. Reducing metal: (*1*) aluminium, (*2*) magnesium, (*3*) silicon, (*4*) calcium. For description of zones *I*–*IV* see text.

gasification in the combustion. The dependences of the combustion temperatures on the gas pressure for some metallothermic systems are shown in Fig. 4.

Contamination of final products with reducing metals is the main disadvantage of out-of-furnace metallothermy.

Reduction of impurity content in the out-of-furnace ingots is a difficult task. Studies aimed at governing the chemical composition of Nb ingots prepared by aluminothermic reduction of Nb_2O_5 in the presence of Mg have been undertaken at ISMAN. In these studies green mixtures with the variable compositions and densities and variations of external gas pressures and of gravitational effects were used as the most modern methods for controlling the composition. The purest specimen of niobium obtained by this method contained 1.6 mass % Al, 0.04 mass % Mg and 0.74 mass % O. These results corroborate the conclusion by Yelyutin[9] that out-of-furnace metallothermy and refinement can be used for the preparation of pure metals.

Recently, Freidin *et al.*[10] have developed a method for the synthesis and refinement of molten products in a single technological step. To this end, a refining additive was mixed with a small

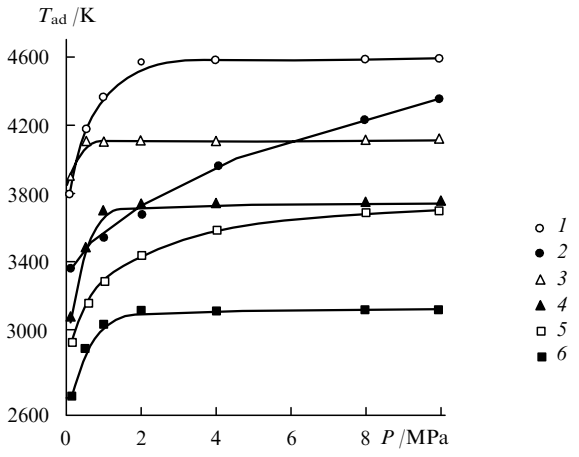


Figure 4. Dependence of combustion temperatures of various metallothermic compositions on ambient gas pressure (P).
(*1*) $MoO_3 + 2\,Al$, (*2*) $CrO_3 + 2\,Al$, (*3*) $WO_3 + 2\,Al$, (*4*) $V_2O_5 + 5\,Ca$, (*5*) $2\,WO_3 + 3\,Si$, (*6*) $Ta_2O_5 + 5\,Mg$.

portion of the green mixture and placed under the bulk of the green mixture which gradually converted into a melt. The melt passed through the layer with the refining additive thus undergoing purification and crystallised. The ingots thus prepared contained lesser amounts of impurities. This approach proved to be especially efficient in the aluminothermic synthesis of phosphide copper [11] and high-purity iron (total content of impurities did not exceed 0.01%). The feasibility of this approach in the synthesis of a broad range of metallothermic products presents interest. The most recent achievements in this area have been documented.[12, 13]

2. Solid-flame combustion and self-propagating high-temperature synthesis

Solid-flame combustion (SFC) is a self-sustained chemical wave process which yields fully or predominantly solid products (materials). The following types of SFC are known:

— gasless (solid-phase, liquid-phase, multiphase) combustion;

— infiltration combustion (with spontaneous or forced infiltration);

— condensation combustion (*e.g.*, of gases and condensed systems).

The phenomenon of SFC was discovered by Merzhanov *et al.*[14] and registered in the USSR Register of State Inventions and Discoveries under No. 287 in 1967. It was found that slow self-inhibited solid-phase reactions may be concentrated in definite zones following local initiation and proceed thereafter at fast rates commensurate with the propagation rate of the combustion wave. This unique phenomenon and the products formed immediately evoked keen interest from investigators. This discovery was preceded by studies on 'ignition' of metallothermic mixtures (Beketov and Goldschmidt, around 1900) and combustion of thermites (Belyaev and Komkova, 1950) [8] and copper acetylenide (Borovinskaya and Merzhanov, 1966) [§] and by development of a gasless combustion model (Maksimov, Merzhanov and Shkiro, 1965).[15] However, none of SFC processes could be implemented without a thorough knowledge of modern combustion theory.

Titanium monoboride was the first compound prepared by SFC.

$$\mathrm{Ti\ (solid)} + \mathrm{B\ (solid)} \longrightarrow \mathrm{TiB\ (solid)} + Q.$$

The snapshots illustrating the formation of TiB from solid elements are shown in Fig. 5 which has become widely popular. These frames depict the main stages of the combustion process, *i.e.*, initiation (ignition), propagation of the combustion front and cooling of the solid product. Depending on the operational conditions, the solid formed may represent a substance, a material or an end product.

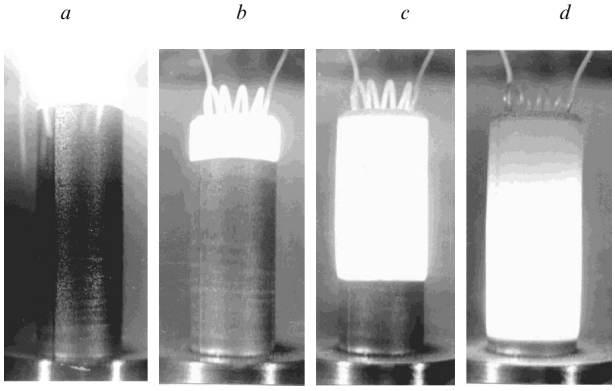


Figure 5. Frames of an SHS process;
(*a*) initiation ($t = 0$), (*b*, *c*) propagation of the combustion front [$t = 0.1$ s (*b*) and 2.7 s (*c*)], (*d*) cooling ($t = 4$ s).

The synthesis of compounds by SFC has got the name of self-propagating high-temperature synthesis (SHS). SHS is used for obtaining chemical compounds with predetermined compositions, structures and properties.

SHS is usually subdivided into primary and advanced SHS. This classification reflects the rapid progress in this area, which has changed the very concept of this synthesis.

Under primary SHS is understood the combustion of 'solid + solid' and 'solid + gas' systems and the formation of high-melting (refractory) materials (carbides, borides, nitrides, silicides, *etc.*) by direct synthesis, *i.e.*, based on the exclusive use of chemical elements as the starting reactants. Advanced SHS includes all possible combustion modes and yields valuable solid products and materials.

The fundamental tasks of primary SHS are as follows:

— studies of regularities and mechanisms of combustion;

— mathematical simulation of combustion;

— establishment of a relationship between the product composition and operational conditions (combustion);

— optimisation of operational conditions for the preparation of single-phase compounds.

3. Primary SHS

Although the build-up period of primary SHS was relatively short (1967 – 1972), it was marked for fundamental discoveries.[16 – 21]

First, the nature of solid-flame combustion was elucidated. Until that time, it was unclear how slow solid-phase reactions leading to solid products could occur in fast regimes, such as combustion. To rationalise this phenomenon, one had to abandon the equilibrium flame propagation theory proposed by Ya B Zeldovich and D A Frank-Kamenetsky.[22] According to this theory, the width of the reaction zone in the combustion wave is much narrower than that of the foreflame zone and can often be neglected.¶

However, in the solid-flame processes the reaction zone is significantly wider than that of the foreflame zone due to strong self-inhibition of the combustion reaction † (the non-equilibrium theory). Moreover, the reaction zone may even involve the afterburning subzone, which does not influence wave velocity. The concept of broad reaction zones [19] has subsequently become very popular. In terms of the non-equilibrium flame propagation theory, the SFC wave has a multizone structure and comprises three main zones, *viz.*, the preheating (preflame) zone ($T_0 - T_\mathrm{f}$), the zone where the major heat is evolved, which determines the combustion rate ($T_\mathrm{f} - T_*$) and the afterburning zone ($T_* - T_\mathrm{r}$). Here, T_0 is the initial temperature, T_f is the temperature of the combustion front separating the preheating zone and the reaction zone (the inflection point on the temperature curve) and T_* is the temperature determining the combustion rate (Fig. 6). These fundamental concepts underlie the novel, non-equilibrium flame propagation theory.[23]

According to this theory, the wave velocity U in broad zones is determined by the temperature T_* ($T_\mathrm{f} < T_* < T_\mathrm{ad}$) which reflects the incompleteness of conversion of the substance ($\eta_* < 1$)

$$U^2 = A\frac{T_*^2}{\eta_*}\exp\left(-\frac{E_\mathrm{a}}{RT_*}\right),$$

where A is the value determined by the reaction rate and heat transfer constants, η_* is the degree of conversion at temperature T_* and E_a is the activation energy.

§ Annual report of the United Institute of Chemical Physics of the Academy of Sciences of the USSR (Chernogolovka, 1966).

¶ This concept has been used in nearly all theoretical studies on flame propagation.

† The term 'self-inhibition' implies that the rate of combustion decreases drastically as the substances are burnt out. In the case of classical processes of flame propagation in gases, this effect is small.

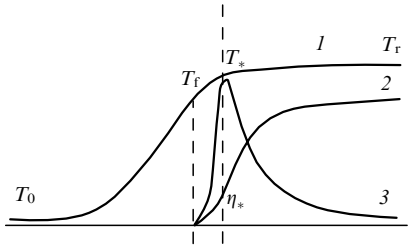


Figure 6. A schematic diagram of the structure of a solid-flame combustion wave (*1*), depth of conversion (*2*) and heat release rate in combustion (*3*).

Yet another important result is related to the elucidation of the infiltration combustion mechanism of 'solid — one-component gas' systems. Here it is necessary to distinguish between the gas inside and outside pores of a sample (internal and external reactants). At relatively low pressures, the propagation of the combustion wave is provided by infiltration of the external gas through the pores of the solid sample. Studies of combustion of zirconium in nitrogen [17] have established two limiting modes: the layer-by-layer mode (Fig. 7 *a*) and the surface (Fig. 7 *b*) mode. The interconversion of these two processes has been studied (Fig. 7 *c*). It was shown that the combustion mode is unambiguously described by the criterion π equal to the ratio of the characteristic times of infiltration (t_f) and the reaction occurring in the wave (t_r):

$$\pi = \frac{t_f}{t_r} \sim \frac{Ud}{P_0},$$

where d is the diameter of the sample and P_0 is the pressure of the ambient gas.

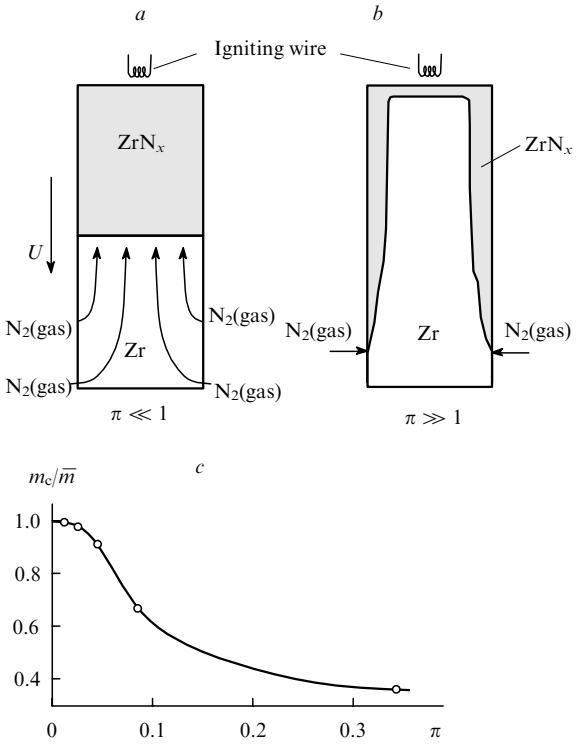


Figure 7. Layer-by-layer (*a*) and surface combustion (*b*) in 'porous solid – gas' systems and some regularities of their interconversions (*c*); m_c, nitrogen content in the centre of the sample, $\overline{m}$, average nitrogen content in the sample.

The infiltration (surface) combustion mode meets the criterion $\pi \gg 1$. In this case, the reaction is fast and the gas has no time to penetrate inside the sample; therefore, the combustion occurs only in the surface layers. The kinetic (layer-by-layer) combustion mode meets the criterion $\pi \ll 1$.

The development of infiltration concepts has provided a clue to uniform combustion of hybrid systems. The very first results in this area have stimulated numerous experimental and theoretical studies which culminated in the development of a general theory of infiltration combustion.[24]

Yet another important event is the discovery of combustion spin waves.[18] Under certain conditions, flame propagation occurs in an unstable mode, as a result of which the combustion centre begins to move along the sample by a spiral path rather than as a flat layer. A non-steady-state two-dimensional flame propagation model has been developed in order to elucidate the nature of this phenomenon.[25,26] The frames (*a*) and computer simulation (*b*) of spin combustion are shown in Fig. 8. As can be seen (Fig. 8 *a*), the combustion centre appears from the rear of the sample, moves in the lateral direction and disappears. The computer version was obtained after solution of the simplest two-dimensional non-steady-state problem of a transition to the post-ignition flame propagation mode:

$$\begin{cases} c\rho\dfrac{\partial T}{\partial t} = \lambda\left(\dfrac{\partial^2 T}{\partial x^2} + \dfrac{1}{x^2}\dfrac{\partial^2 T}{\partial \varphi^2}\right) \rho Q \dfrac{\partial \eta}{\partial t} - \alpha_t (T - T_0) \\ \dfrac{\partial \eta}{\partial t} = k_0 (1 - \eta) \exp\left(-\dfrac{E_a}{RT}\right) \end{cases}$$

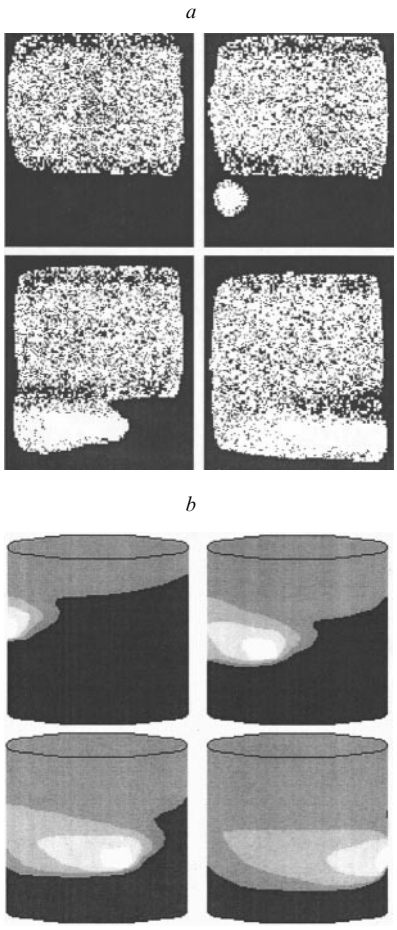


Figure 8. Snapshots of spin combustion of hafnium in a nitrogen – argon mixture (*a*) and visualisation of solutions of equations describing the spin waves (*b*).

Table 3. Examples of compounds prepared by primary SHS.

Compound	Metal content (mass %)		Non-metal content (mass %)		Lattice type	Unit cell parameters /Å	Micro-hardness /kg mm^{-2}
	total	free	total	free			
Titanium carbide	80.0	$<10^{-3}$	19.8	9×10^{-2}	cubic NaCl	$a = 4.323$	2900
Zirconium carbide	88.2	$<10^{-3}$	11.4	$<10^{-2}$	"	$a = 4.686$	3040
Niobium nitride	86.9	$<10^{-3}$	13.0	–	"	$a = 4.385$	1670
Titanium nitride	77.6	$<10^{-3}$	21.4	–	"	$a = 4.240$	1800
Tantalum nitride	91.8	–	7.5	–	"	$a = 4.323$	3200
Boron nitride	43.8 [a]	0.2 [a]	55.7	–	hexagonal	$a = 3.331$, $c = 3.518$	–
Titanium diboride	68.6	–	31.0	10^{-1}	"	$a = 2.619$, $c = 3.230$	3500
Hafnium diboride	89.0	–	10.7	$<10^{-2}$	"	$a = 3.134$, $c = 3.467$	2890

[a] Boron content is indicated.

with the following initial and boundary conditions:

$$t = 0,\ x > 0:\ T = T_0,\ \eta = 0,$$

$$t > 0,\ x = 0:\begin{cases} T = T_{\rm ign}, \text{ at } t \leqslant t_{\rm ign} \\ \dfrac{\partial T}{\partial x} = 0, \text{ at } t > t_{\rm ign}\ , \end{cases}$$

$$t > 0,\ x = x_0:\ \frac{\partial T}{\partial x} = 0\ .$$

Here, c, ρ and λ are the heat capacity, density and heat conductivity of the sample, respectively; x and φ are the integral and angular coordinates; Q, E_a and k_0 are the thermal effect, activation energy and a preexponential factor, respectively; α_t is the heat exchange coefficient and $T_{\rm ign}$ and $t_{\rm ign}$ are the ignition temperature and the delay time, respectively.

An analysis of the calculated dependences $T(x,t)$ and $\eta(x,t)$ and the instantaneous linear combustion rate $\mathrm{d}x/\mathrm{d}t$ at the point $(\partial\eta/\partial t)_{\max}$ has shown that, depending on the parameters, the post-ignition process occurs in either a steady-state combustion mode or a spin, self-oscillating or chaotic (non-steady-state) mode. It should be noted that all the three unstable combustion modes, *viz*., self-oscillating, spin and chaotic, can be realised in the same system for different parameters of the green mixture and under different operational conditions.

The discovery of spin waves gave impetus to the appearance of a huge number of publications and the spin wave has become a very popular subject of investigation in nonlinear dynamics.

However, the main result in the first stage of SHS development was associated with the synthesis of novel materials. A simple methodological scheme has been developed which included:

(*a*) elucidation of parameters determining the chemical and phase compositions of combustion products;

(*b*) analysis of their relationships;

(*c*) optimisation of conditions for the synthesis of homogeneous products.

Some examples of compounds obtained by SHS in the early stages of development of the method [16] are given in Table 3.

As can be seen, SHS enables the synthesis of chemical compounds of very high quality. This circumstance has played a crucial role in the development of the SHS method as a whole.

Self-propagating high-temperature synthesis is a multiparametric process which is controlled by many mechanisms. This means that its optimisation presents a problem, but once optimum conditions have been established, one can obtain products exceeding in quality the products prepared with the use of low-parametric processes, *e.g*., furnace synthesis.

Hence, primary SHS is a bright chapter in the history of solid-flame combustion.

4. Advanced SHS

A significant advance in the field of SHS has been made in the past 35 years after the discovery of the phenomenon of solid flame. These achievements include:

— considerable expansion of the raw material base for SHS, *i.e*., the range of compounds applicable for SHS;

— further development of combustion chemistry, structural macrokinetics, nonlinear dynamics, three-dimensional simulation;

— elucidation of effects of physical fields on SHS;

— development of technologies and facilities (equipment) for SHS;

— calculation of technological and economic efficiencies of SHS;

— synthesis of various valuable SHS products;

— pilot-plant and large-scale production of SHS products;

— commercialisation and marketing;

— a search for novel SHS processes.

Here we outline only some general trends in the development of SHS and refer all those who are interested in this branch of chemistry to some recent reviews [27–46] and papers.[47—51]

The infrastructure of advanced SHS is shown in Fig. 9. It comprises three main areas where SHS studies are under way. However, these investigations differ in their intensities. Thus the fundamental principles of SHS are rather well-developed, while industrialisation and commercialisation aspects of SHS are the least explored. This is not surprising, since SHS has been following the route from science to technology.

5. Transformations in shock and detonation waves

Studies of chemical and physicochemical transformations of substances in shock and detonation waves under the action of waves with inherent high pressures, high temperatures and shear deformations are important areas of research which have considerable technological significance.

Two types of processes initiated by shock and detonation waves are shown in Fig. 10. In the former case, the necessary conditions for the transformation of a substance are generated by external factors; in the latter case, they are created by self-propagating detonation processes.

Both types of processes are used for the preparation of superstrong materials (*e.g*., cutting diamonds and wurtzite-like BN).[52–54] Studies of transformations of substances in shock and detonation waves have posed the question about their localisation: in the wave proper (over microseconds) or after passage of the wave front (*e.g*., at residual temperatures 300–500 °C). Studies of transformations of various systems, *e.g*., Al + Fe_2O_3, Sn + S, Sn + Te, Al + S, Zr + 2 S, *etc*., in shock waves carried out by S S Batsanov [55] have shown that in these systems the synthesis occurs directly in the shock wave and is over within 10^{-7}–10^{-6} s.

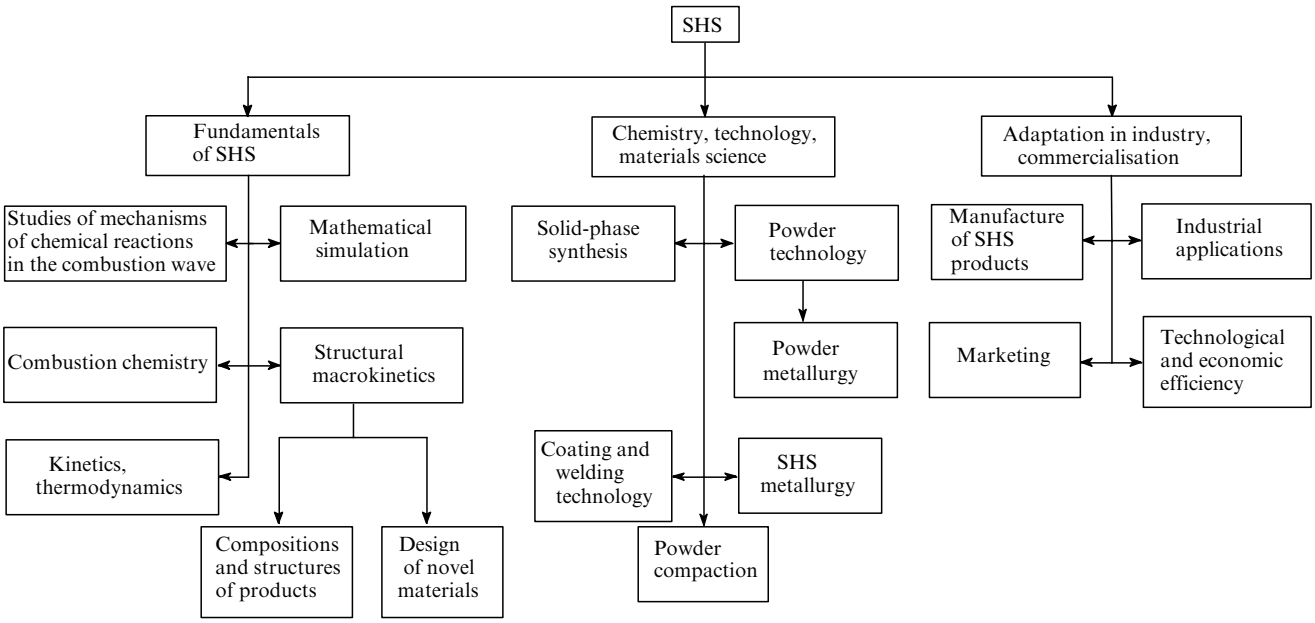


Figure 9. The infrastructure of SHS.

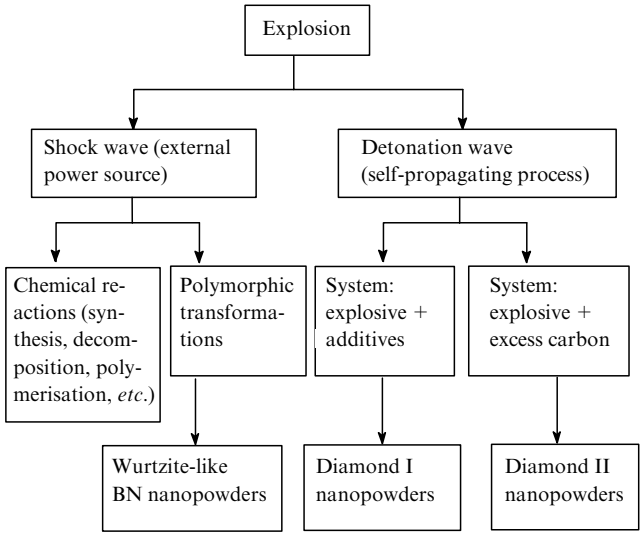


Figure 10. Chemical synthesis and physicochemical conversions in shock and detonation waves.

Numerous papers devoted to transformations of substances in shock waves have been published. For specialists in detonation techniques, their practical implementation presents no problem. The simplest approach consists in mixing of a tested substance or a sample with an 'explosive', formation of a blasting charge and initiation of explosion in a blasting chamber. An analysis of solid particles gathered after detonation gives some information about the explosion-induced transformations.[56]

Transformation of substances in the detonation wave is a new trend in the chemistry of combustion and explosion. In this case, we deal with shock-driven SHS where self-propagation of the wave is initiated by shock compression rather than heat transmission. Obviously, such processes can be realised only if transformation of substances is accompanied by an increase in the volume, *e.g.*, due to concomitant evolution of gas. This can be achieved by adding gas-evolving inert additives to the green mixture. This technological approach is used for the preparation of a broad range of SHS products.

Apparently, SHS was first discovered by I P Borovinskaya [21] at the dawn of SHS studies, more exactly, in experiments with combustion of a boron powder in liquid nitrogen in a sealed vessel. If nitrogen was taken in excess, SHS was accompanied by explosion. Interestingly, all the vessels split in two in the same place. This finding led the author to conclude that combustion passes into explosion. Later, special experiments aimed at initiating detonation confirmed the possibility of detonation in such systems. Unfortunately, at that and subsequent times these works did not receive proper attention.

Some new data on SHS in shock and detonation waves have been described.[57, 58]

6. On thermal explosion

The interest in thermal explosion as a technological process for the synthesis of novel inorganic materials has increased considerably in recent years.[59, 60] Whereas the combustion wave is initiated in some particular locus artificially, in thermal explosion the external source warms up the whole mass of the green mixture and ignition occurs spontaneously as a result of self-acceleration of the reaction. Where and how such ignition occurs and how transformation of substances proceeds under conditions of thermal explosion are these questions critical for conducting SHS syntheses.

Critical conditions and induction period are the most important characteristics of thermal explosion. Critical conditions are those in which the reaction passes from a slow (non-isothermic) mode to a detonation mode; the induction period is the explosion delay time. In other words, investigators are interested in whether and when the explosion takes place. Such a statement of the problem is aimed at the solution of safety problems.

The use of thermal explosion for the preparation of materials has posed some new questions: how does explosion develop in the post-induction period? what are the transformation modes? how does explosion affect thermal and concentration quasi-homogeneities? And so on.

The first explicit answers to these questions were given in a theoretical paper devoted to SHS.[61] We studied thermal explosion in both induction and post-induction periods up to complete conversion of the reactants. It was concluded that the process depends essentially on the ratio of internal heat transfer and external heat emission, the so-called Bio criterion (*Bi*)

$$Bi = \frac{\alpha r}{\lambda},$$

where α is the heat emission coefficient from the surface of a sample, r is the characteristic size of the sample and λ is the thermal conductivity of the green mixture.

At nearly all values of Bi (with the exception of the ideal case where $Bi = 0$), the temperature and concentration fields in the sample are nonuniform. Ignition takes place at a point where the temperature in the induction period is the highest and is accompanied by rapid elevation of temperature. The reaction spreads further from the spontaneous ignition site in the form of a combustion wave causing layer-by-layer transformation of the reacting charge into the reaction product.

There are two modes of combustion wave propagation. One of them is characterised by higher values of Bi and consists in the transmission of heat from high-temperature products to initial reactants by a classical flame propagation mechanism. In the other mode, the process is controlled by the temperature gradient generated in the induction period. In the latter case, the wave propagation is apparent being unrelated to the heat transfer mechanism and is initiated by sequential (layer-by-layer) adiabatic self-ignition of the green mixture. The second mode is realised at very low Bi values ($Bi \ll 1$).

Theoretical studies [62–64] are devoted to a detailed analysis of the nature and mechanisms of thermal explosion in the post-induction period. The results of these studies correlate with the aforementioned concepts which have considerable methodological significance. In current literature, thermal explosion was often opposed to SHS under the *a priori* assumption that thermal explosion represents three-dimensional combustion of the green mixture. It was found, however, that at $Bi \neq 0$ thermal explosion comprises a stage corresponding to the self-propagating process involving up to 80% of the reacting green mixture. After publication of the work,[48] two SHS modes came to be argued: artificial initiation of SHS and spontaneous (although local) initiation.

Until recently, there have been no experiments aimed at the application of thermal explosion to material-forming processes. The ideas developed in theoretical studies have long remained unclaimed which can be attributed to the difficulties in the implementation of SHS because of significant fluctuations in temperature, temperature gradients and characteristic time scales in a single technological process. Notwithstanding, recently such publications did appear (for a review see Ref. 60). It was shown that the synthesis of materials by thermal explosion is more applicable to those reactions that are not sufficiently exothermic where local ignition fails to induce further propagation of the combustion wave due to heat losses.

It was shown [65, 66] that thermal explosion in specially designed moulds and SHS compaction of the reaction product gives useful (from the standpoint of materials science) results.

Unfortunately, all the works aimed at the synthesis of materials by thermal explosion are carried out with no relation to macrokinetic concepts and studies which leads to a significant impoverishment of experimental data.

III. Material-affecting combustion and detonation processes

Processing of materials by combustion includes all kinds of flame coating: gas-thermal spraying (gas flames), aluminothermic welding ('liquid' flames), induction welding (microwave-induced thermal explosion) and condensation coating (chain flames). This category also includes remelting of reject or waste intermetallic articles and welding of components by electrothermal explosion.

In combustion and explosion processes, processable material is loaded into the reaction chamber together with the green mixture. The position of the green mixture relative to the processable material can be different: (1) the processable material is inside the green mixture; (2) the processable material and the green mixture are spatially apart but are in contact with one another and (3) the processable material and the green mixture are spatially apart and do not contact.

1. Material-affecting combustion

Combustion-induced material-affecting is carried out at high temperatures generated upon burning of the charge.

Aluminothermic welding, *i.e.*, coating of moulded hard alloys onto flat steel surfaces, is the most popular procedure.[27] The principle of this method is very simple and consists of the following. A layer of an aluminothermic green mixture able to form a 'hard' alloy is applied onto a steel plate (Fig. 11 *a*). After combustion of the mixture, a heterogeneous melt consisting of the 'hard' alloy and liquid alumina is formed on the surface of the plate. Under the action of gravitational forces, the melt stratifies in such a way that the lower layer adjacent to the steel base consists of the hard alloy and the upper layer consists of alumina. The latter performs an accessory function by protecting the hard alloy from oxidation by atmospheric oxygen. Thermal and chemical interactions of the 'hard' alloy with the steel plate result in a broad gradient intermediate layer (Fig. 11 *b*). After crystallisation of all layers, the oxide layer peels off leaving a steel part coated with the hard alloy.

The distribution of concentrations of chemical elements and microhardness as a function of the distance from the alloy (the molten layer) to the base are shown in Figs 12 and 13. The

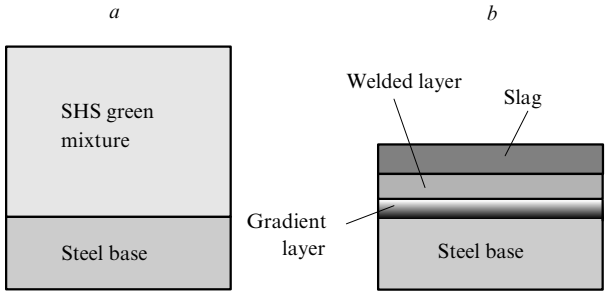


Figure 11. Application of a moulded coating onto a steel base (SHS welding);
(*a*) prior to processing by combustion, (*b*) after processing.

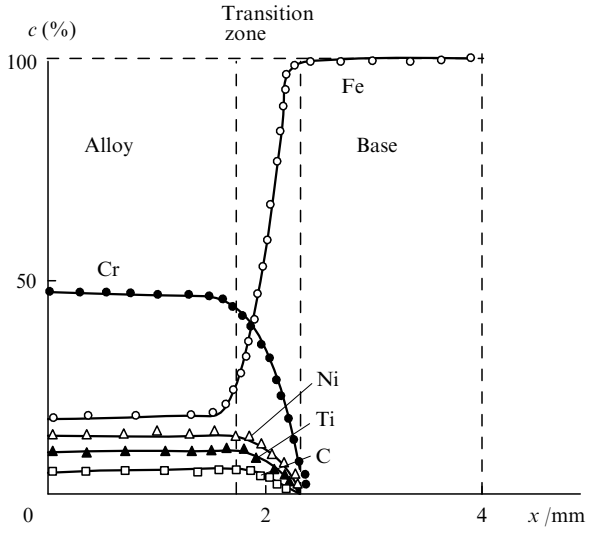


Figure 12. Distribution of chemical elements in a layer welded onto a steel plate (x is the layer height). Composition of the green mixture: TiO_2 + CrO_3 + NiO + Al.

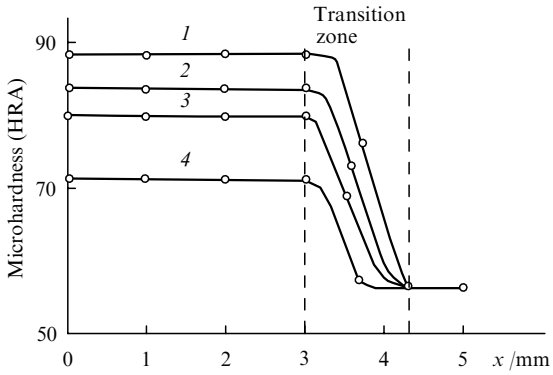


Figure 13. Distribution of microhardness according to Rockwell, the hardness scale A (HRA) in a welded layer.
The starting mixture: (*1*) Cr–Ti–C–B–Ni, (*2*) Cr–Ti–C–Ni, (*3*) Cr–C–Ni, (*4*) Cr–C–Fe.

presence of a distinct, broad (from 0.5 to 1.5 mm) intermediate zone is an obvious advantage of SHS welding, since it eliminates adhesion owing to the high degree of binding between the coating and the base.

Aluminothermic welding allows application of relatively 'thick' (> 0.5 mm) layers. Thinner layers are coated by induction SHS welding. This process is technologically similar to that described above, except that the charge layer is smaller and the process is implemented in a high-frequency electromagnetic field.[67] Numerous green mixture compositions aimed at the solution of miscellaneous practical tasks have been developed.

Electrothermal welding is yet another example of a material-affecting SHS.[68–70] In this process, the conducting green mixture (welding compound) composed of chemical elements is loaded into a gap between the parts to be welded which also play the role of electrodes. When electric current is passed through the electrodes, the green mixture is heated to self-ignition. The parameters are chosen so that the thermal-explosion product is formed in the melt. This interacts with the submolten layers of the parts to be welded and forms a fairly strong welding joint after crystallisation. The strength of the welding joint can be increased, if the melt is extruded from the gap prior to crystallisation with a simultaneous decrease in its thickness.

This approach was used for welding refractory parts of Nb, Ta, W, Mo and C to one another and between themselves. One of the most recent developments is welding of a hard alloy BK8 to the 40X steel.[70] A micrograph of a thin section of the welding joint is shown in Fig. 14. The Zr + Ni green mixture was used as the welding material.

The Zr + Ni green mixture ensures high strength of the welding joint: the break occurs in the hard alloy but not in the joint. Such a high breaking strength cannot be provided by conventional brass plating.

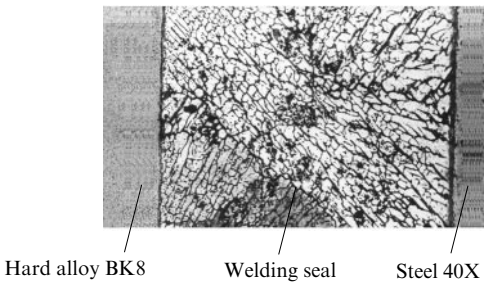


Figure 14. SHS welding. A micrograph of a longitudinal section of the solid alloy BK8 and the steel 40X.

Characteristics of the welding joints produced by SHS and traditional fusion are given in the table below.

Welding material	Flexural strength /MPa	Fracture surface
Ti + Ni	400–600 (welding)	welding joint
Zr + Ni	600–800 (welding)	hard alloy
Brass plating	200 (soldering)	welding joint

SHS welding is used for thermal bonding of refractory materials where conventional electric welding is of little effect.

2. Material-affecting explosion

A crucial role in material-affecting explosion is played by detonation energy which produces high pressure. Under the impact of high pressure, the processable material undergoes plastic deformation. Simultaneous action of pressure and temperature on the the processable material induces physicochemical transformations.

All detonation effects on processable materials are subdivided into mechanical and structural. The former includes crushing, dispersion (brittle fracture), pressing, calibration, punching and cutting (plastic destruction); the latter includes reinforcement of metals (workhardening), compaction of metal powders (controlled structure formation) and welding (bonding) of metals.

Explosion-induced welding is the most popular and technologically efficient procedure. A welding scheme of two plates is shown in Fig. 15. After welding, the flat surfaces of both plates acquire a wave-like shape. Pictures of typical welding joins are shown in Fig. 16. Interestingly, the cross-sections of welding joins of homogeneous metals manifest a purely sinusoidal shape (Fig. 16 *a*), whereas the S-shape of the welding joins of heteroge-

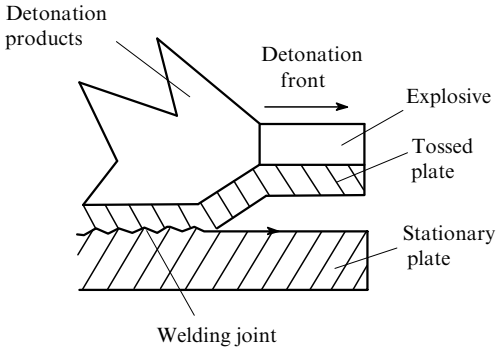


Figure 15. A schematic representation of detonation-driven welding.

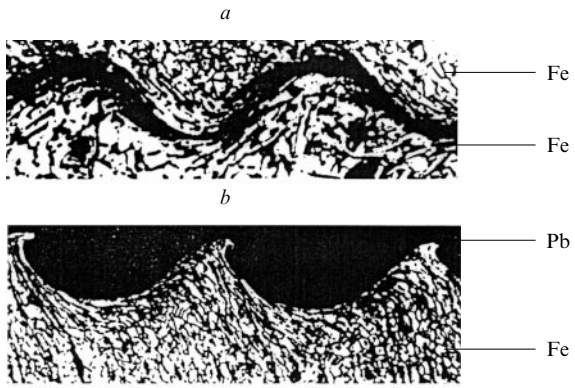


Figure 16. The sinuous structure of a welding joint obtained by detonation welding of the same (*a*) and different (*b*) metals.

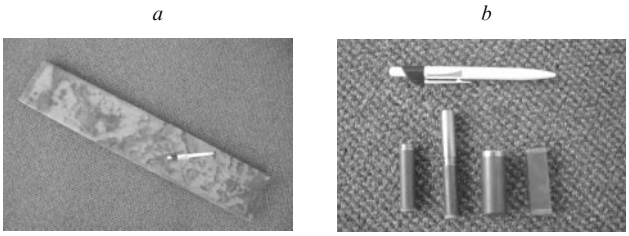


Figure 17. Some items prepared by detonation-driven welding: (*a*) thermobimetal, (*b*) trimetallic electrodes for a spectrograph.



Figure 18. Detonation cutting: cumulative charges (*a*) and slit items (*b*).

neous (or, more exactly, heterodense) metals is distorted due to the appearance of higher harmonics, which change the wave profile. This phenomenon was described in detail by Gordopolov.[71] Wave formation is a useful process, since it increases the strength of the welding joint.

Pictures of some items prepared by explosion-induced welding are shown in Fig. 17.‡ The most common practical task relates to the production of bimetallic rolled stock from billets obtained by explosion-induced welding.

Cutting of metals by explosion is also a highly efficient process. It is opposite to welding and is based on the use of cumulative jet streams generated by cumulative green mixtures. Significant progress in this field has been attained by a research team headed by V V Kalashnikov at the Samara State Technological University.[72] Photographs of cumulative charges and items processed by this technology are shown in Fig. 18. Detonation is also used for cutting metals with thicknesses of 1 cm and more.

IV. Combustion and explosion in physical chemistry of inorganic materials

The physicochemical aspects of combustion and explosion science are sufficiently well-studied as can be evidenced from numerous publications (particularly, those devoted to combustion)§ which have made a significant contribution to the development of high-temperature physical chemistry.

However, the boundaries of combustion and explosion as an independent trend of research in physical chemistry have not been adequately outlined. It remains to note that the science of combustion and explosion studies chemical and physicochemical transformations which occur spontaneously (after initiation) under non-isobaric and/or non-isothermal conditions, in a non-steady-state mode, have low characteristic times and yield (exclusively or predominantly) solid products.

The latter circumstance is of particular importance, since this review is devoted to materials.

‡ These pictures were made by Yu A Gordopolov in 1978, they were presented in a Report of the United Institute of Chemical Physics of the Academy of Sciences of the USSR.

§ A more prominent role in the explosion theory is ascribed to gas-dynamic factors.

Let us consider briefly some recent trends in physical chemistry of inorganic materials related to combustion and explosion processes.

1. On the chemistry of combustion and explosion

Study of the chemical mechanisms is one of the main areas of research in combustion and explosion science, which is sometimes referred to as the chemistry of combustion and explosion. Its main goals are as follows:

— determination of intermediate and final stages in combustion and detonation waves;

— development of methods for the isolation of intermediate products;

— characterisation of final products and its relationship to operational regimes.

Let us consider the formation of yttrium–barium cuprate possessing superconducting properties in a combustion wave as an example. This synthesis is a very 'capricious' process, since the final compound is thermally unstable, easily loses oxygen and, as a consequence, its superconducting properties. Traditionally, it is prepared by furnace synthesis using the reaction:

$$3\,CuO + 2\,BaO + 0.5\,Y_2O_3 + Q \longrightarrow YBa_2Cu_3O_{7-x}\,.$$

It was recommended[73] to perform this synthesis from a mixture containing copper, barium peroxide and yttrium oxide powders.

$$3\,Cu + 2\,BaO_2 + 0.5\,Y_2O_3 \xrightarrow{O_2} YBa_2Cu_3O_{7-x} + Q.$$

Although combustion of this mixture is easily initiated, the preparation of a high-quality product demands optimisation of conditions of synthesis. To meet this goal, the mechanism of this reaction in the combustion wave was studied. The formation and consumption of intermediate products and the formation of the final product were studied using different techniques. The reaction mechanism is as follows:[74]

$$BaO_2(\text{solid}) \longrightarrow BaO_2(\text{liquid}) \longleftrightarrow BaO(\text{liquid}) + 0.5\,O_2,$$

$$2\,Cu \xrightarrow{0.5\,O_2} Cu_2O \xrightarrow{0.5\,O_2} 2\,CuO,$$

$$(BaO_2 + BaO)_{\text{liquid}} + Cu_2O \longrightarrow BaCu_2O_2,$$

$$(BaO_2 + BaO)_{\text{liquid}} + CuO \longrightarrow BaCuO_2,$$

$$BaCuO_2 + CuO \xrightarrow{O_2} BaCu_2O_2 + 0.5\,O_2,$$

$$2\,BaCu_2O_2 + CuO + 0.5\,Y_2O_3 \longrightarrow YBa_2Cu_3O_{6+\delta} + Cu_2O,$$

$$2\,BaCuO_2 + CuO + 0.5\,Y_2O_3 \xrightarrow{O_2} YBa_2Cu_3O_{6+\delta},$$

$$YBa_2Cu_3O_{6+\delta} \xrightarrow{O_2} YBa_2Cu_3O_{7-x}.$$

The final stage represents a phase transition from a non-superconducting tetragonal phase to the superconducting orthorhombic phase with an insignificant overoxidation of the cuprate formed. The knowledge of this mechanism has made it possible to develop a technology for synthesising of a high-quality product with remarkable superconducting properties.[74] Some characteristics of $YBa_2Cu_3O_{7-x}$ powders synthesised in the combustion wave (grade SHS samples) and by furnace synthesis (other samples) are given in Table 4 (see Ref. 75). A comparative study of these powders was carried out by the US company 'Super Conco'. As can be seen from the Table, the SHS-J2 powder prepared by SHS is by far the best.

2. Kinetics of chemical reactions at high temperatures

Whereas the knowledge of chemical mechanisms of reactions occurring in a combustion wave helps control the quality of final products, kinetic studies are necessary for elucidation of mechanisms of self-propagation of the combustion wave. In the latter case, the main interest is focused on the kinetics of heat evolution.

Table 4. Comparative characteristics of powders of the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ prepared by the furnace method and SHS.

Sample	Content of oxygen [a] (a.u.)	Transition temperature /K	Y_{123} orthorhombic phase content (%)	Main impurities	Average particle size /μm
SC5-S	6.92	93.5	98	CuO	40.0
SC-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
CPS A-1203	6.85	92.0	99	$BaCuO_2$	3.0
SSC 03-0065	6.89	92.0	99	–	6.5
SHS-J1	6.90	92.0	97	CuO	9.0
SHS-J2	6.92	93.5	99	–	8.0

[a] Oxygen content was determined by iodometry.

It should be noted that the kinetic aspects of explosion science are not sufficiently developed (here, thermodynamic and gas-dynamic interests 'dominate'). In contrast, in combustion science these aspects constitute an independent and well-developed area of research. Direct kinetic studies are hardly possible due to high reaction rates and high temperatures; therefore, kinetic information is derived from the very combustion experiments using indirect methods. Determination of effective activation energy, E_{eff} (see Refs 76 and 77) using the formula:

$$U^2 = AT_{\text{ad}}^2 \exp\left(-\frac{E_{\text{eff}}}{RT_{\text{ad}}}\right)$$

is an example of such an approach.

A method for processing temperature profiles in the combustion wave aimed at determination of the heat evolution rate $\dot{q}$ (dq/dt) as a function of the temperature T and the amount of evolved heat q, has been developed.[78] It is reduced to the solution of the kinetic equation:

$$\dot{\eta} = \mathrm{f}(T, \eta), \eta = \frac{q}{Q},$$

where $\dot{\eta}$ is the reaction rate. Correct determination of the initial stages of transformations of various substances by this method is difficult: it provides reliable kinetic information only at more advanced stages of the conversion. Nevertheless, direct kinetic studies of chemical reactions in the temperature range close to that of the combustion wave were carried out for one class of reactions, *viz*., high-temperature reactions of metals with gases. The method in question represents electrothermography for kinetic studies.[79, 80]

The principle of the method is simple and well-known. A system of two reactants, *viz*., a thin filament made of the tested metal and a gas, is considered. The metal filament is heated by electric current and thus plays the role of a reactant and a high temperature source. The advantage of this method [79, 80] is that it employs an optical or electrical monitoring system and heat evolution compensation for maintaining the constant temperature of the filament by attenuation of the electrical power. This procedure allows recording time dependences of heat evolution rates at different constant temperatures. The process can easily be stopped by switching off the current (the cooling is complete within fractions of a second); the kinetics of growth of diffused layers is deduced from metallographic analysis of filament sections. The electrographic method was used to study the kinetics of reaction of some transition metals (Groups IV and V of the Periodic Table) with nitrogen, oxygen, hydrogen, silane and some hydrocarbons.

The dependences of heat evolution rates on the growth time and the width of the tantalum nitride film (product) for the reaction of tantalum with nitrogen are shown in Figs 19 and 20.[81, 82] An analysis of experimental results revealed that this process is described by a kinetic equation:

$$\dot{q} = 8.6 \times 10^{-2} \exp\left(-\frac{40\,800}{R}\right) q^{-1} \text{ (kcal}^2 \text{ cm}^{-4} \text{ s}^{-1}\text{)},$$

which reflects the parabolic oxidation law. Note that these results were obtained in a high-temperature range [2210 – 2970 °C(!)].

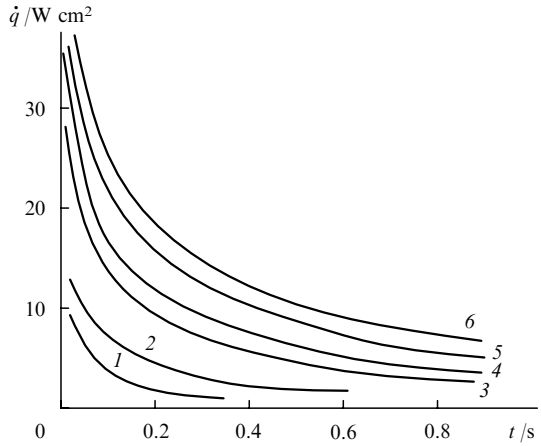


Figure 19. Kinetics of heat evolution in the high-temperature nitrogenation of tantalum.
T /°C: (*1*) 2210, (*2*) 2300, (*3*) 2610, (*4*) 2700, (*5*) 2850, (*6*) 2970.

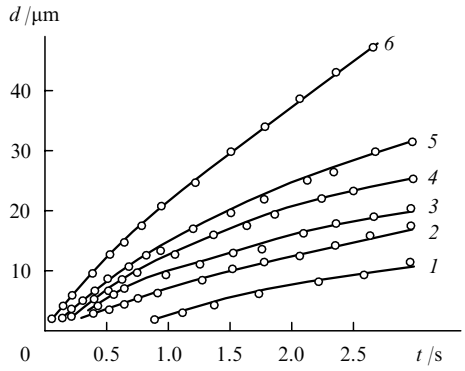


Figure 20. Kinetics of product layer growth (d) during high-temperature nitrogenation of tantalum.
T /°C: (*1*) 2420, (*2*) 2570, (*3*) 2650, (*4*) 2750, (*5*) 2840, (*6*) 2930.

Interesting studies of reactions of metals with complex gases (hydrocarbons, silane, *etc*.) have been carried out by Kharatyan *et al*.[83–85] In these multistep processes, decomposition of the gas on the surface of the filament and the formation of a solid film (carbon, silicon) were followed by the interaction of the latter with the metal by a diffusion mechanism.

3. Thermochemistry and thermodynamic calculations

An important line of investigations includes quauntitation of the amount of heat evolved during reactions of chemical elements in a combustion mode. These data enable easy determination of the heats of formation of various compounds with allowance for incomplete burning and impurities. The heats of formation of some high-melting materials prepared by SHS (carbides, silicides, borides) have been determined.[86] Direct measurement of heats of formation in a combustion mode gives more accurate results than the conventional method based on combustion of tested substances and the starting reactants in oxygen or fluorine. In the classical method, the values of the heats of formation represent a small difference of large numbers, which is a potential source of errors.

For carbides and silicides, which are readily burnt in oxygen or fluorine, the scatter in the values of heats of formation obtained by different authors is small. The values of the heats of formation obtained by direct measurement of the amount of the heat evolved in SHS are in good agreement with the literature data.

Borides are more stable compounds and their combustion is often incomplete, hence the scatter in the values of heats of formation cited in the literature. For these compounds, the direct measurements are more important in principle. The heats of formation of titanium-, zirconium-, hafnium- and other metal borides obtained by both methods are listed in Table 5.

Table 5. Heats of formation of metal borides.

Reaction	Heat of formation /kcal mol^{-1}	
	SHS	classical method [a]
Ti + B ⟶ TiB	40.0 ± 0.8	38
Ti + 2B ⟶ TiB_2	71.5 ± 1.4	63.6; 66.8; 70.07; 77.4
Zr + 2B ⟶ ZrB_2	66.7 ± 1.3	63.1; 72.0; 73.0; 77.0
Hf + 2B ⟶ HfB_2	62.6 ± 1.2	74.2; 80.0
Nb + 2B ⟶ NbB_2	52.7 ± 1.0	41.9; 49.7
Ta + B ⟶ TaB	38.6 ± 0.8	–
Ta + 2B ⟶ TaB_2	47.5 ± 1.0	46.3; 50.0; 52.0
Mo + B ⟶ MoB	26.9 ± 0.5	16.7

[a] Published data.

An important role in thermodynamic studies is ascribed to calculations of adiabatic temperatures and equilibrium compositions of combustion and detonation products. However, in the case of detonation processes such calculations are complicated due to the lack of reliable information about equations of state at high pressures and temperatures. As regards combustion and especially SHS, these processes are sufficiently well documented. There are two approaches to thermodynamic calculations.

In the first (approximate) approach, combustion temperature is determined under the assumption that the compositions of the products are known.[44] The calculations are made according to the equation:

$$\int_{T_0}^{T_{ad}} c(T)\mathrm{d}T = \left(Q - \sum_{i=0}^{n} L_{ph}^{i}\right) - \mu_{ph} L_{ph}\,,$$

where c is the thermal capacity of the product, Q is the heat of formation at T_0, L_{ph}^{i} are the heats of phase transitions at $T_{ph}^{i} < T_{ad}$, n is the number of phase transitions at $T_0 < T_{ph} < T_{ad}$, L_{ph} and μ_{ph} are the heats of phase transitions and the content of the high-temperature phase in the combustion product at $T_{ph} = t_{ad}$, respectively. At $T_{ph} > T_{ad}$ $\mu_{ph} = 0$, at $T_{ph} < T_{ad}$ $\mu_{ph} = 1$.

This method was used [87] for the calculation of T_{ad} for many self-propagating high-temperature reactions which yield a single product. The data obtained shed more light on the combustion mechanisms of many specific systems.

In the general case, the calculations are performed using a complete procedure which allows simultaneous determination of T_{ad} and equilibrium compositions of reaction products at T_{ad}. Originally, this approach was used in combustion studies of propellants, but after some modifications it was extended to material-synthesising combustion processes.

The first calculation of this kind was performed for direct synthesis of iron from iron oxide by reduction with methane.[88] A three-dimensional diagram of the combustion products is shown in Fig. 21 (the hatched area corresponds to the formation of reduced iron as a single condensed product).

Numerous thermodynamic calculations have now been performed. A special ISMAN-TERMO programme and a database

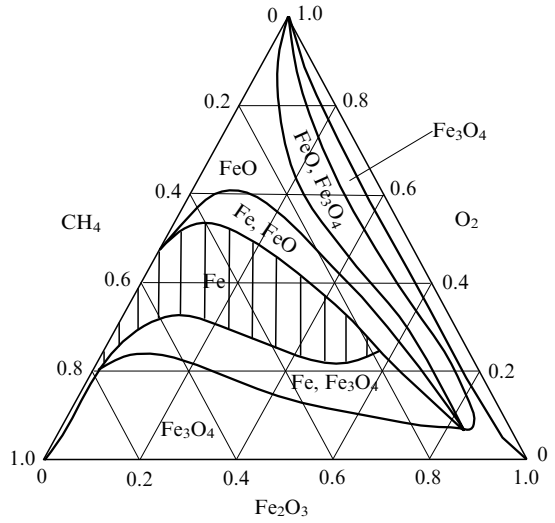


Figure 21. A triple diagram of combustion products in the Fe_2O_3 + CH_4 + O_2 system.

of adiabatic combustion temperatures of binary and ternary systems have been developed by the researchers of ISMAN.

4. Physicochemical effects in the mechanisms of combustion and detonation

Material-synthesising combustion and explosion are associated with evolution and transfer of heat (combustion) or a release of energy and shock-driven compression (detonation). As a rule, these processes are accompanied by various (mostly, physicochemical) effects and involve phase transitions. Their analysis falls also under the scope of physical chemistry of inorganic materials.

Let us consider several examples. Combustion of powder mixtures of low-melting metals (Ti, Zr) with more refractory non-metals (C, B) is accompanied by a very important effect termed 'capillary spreading'.[89] The mechanism of this effect is as follows. Prior to reaction with a non-metal in the precombustion zone, the metal reactant melts and spreads over the surface of refractory non-metal particles. Since the sizes of carbon and boron particles are usually 2–3 orders of magnitude smaller than those of the metal particles, the above-mentioned process results in spontaneous homogenisation of the green mixture, which increases the reaction rate and, correspondingly, the combustion rate. The experimental values of the combustion rates of the Ti + C systems are 10–15 cm s^{-1}. Such high rates for processes occurring in the condensed phase can be attributed exclusively to a significant increase in the reactivity of the green mixture.

Phase transitions (*e.g.*, melting) have a significant effect on the structure of the combustion wave. The temperature profile of the combustion wave is distorted due to phase transitions, these induce the appearance of isothermal plateaus on the temperature curve and a shift of the combustion zone, which determines the wave velocity, from the high- to the low-temperature zone (see, *e.g.*, Ref. 23).

Let us consider another example of a detonation process associated with physicochemical transformations in shock waves. After investigators of detonation have learnt to preserve the integrity of samples exposed to the shock wave, their attention came to be focused on the nature of changes caused by detonation. First of all, they posed themselves the question: where do phase transitions take place: in the shock wave proper (for an order of microseconds) or after passage of the wave at high residual temperatures? An answer to this question came after successful attempts to record the shock adiabat (the compression curve). The distortions in the smooth curve (shock adiabat) testified to physicochemical transformations in the shock wave. The shock

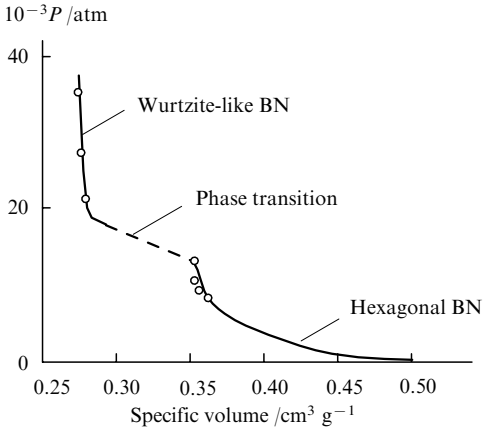


Figure 22. A shock adiabat of boron nitride.

adiabat for boron nitride shown in Fig. 22[90] provides an illustrative example of a phase transition from the hexagonal phase of BN to the wurtzite-like phase at increasing pressures.

At present, shock adiabats have been established for a broad range of compounds and are used for elucidation of shock compression mechanisms.

V. On the theory and mathematical simulation

Theoretical studies into material-synthesising combustion and detonation processes were largely concentrated on solid-flame combustion and made use of classical approaches developed in the flame propagation theory by Ya B Zeldovich for gases and further extended with account of formation of solid products (see, *e.g.*, Refs 6 and 35 and references cited therein). High thermal capacities, possible phase transitions of solid products and solid reactants and the lack of diffusion-driven transfer of products are the main factors responsible for the immense complexity of flame propagation modes.

Let us consider some key aspects.

As a rule, the information on the structure and velocity of the combustion wave is obtained through the solution of the simplest steady-state flame propagation equations:

$$\lambda\frac{\mathrm{d}^2T}{\mathrm{d}x^2}-c\rho U\frac{\mathrm{d}T}{\mathrm{d}x}+Q\rho\varphi(T,\eta)=0$$

(heat conduction equation),

$$U\frac{\mathrm{d}\eta}{\mathrm{d}x}=\varphi(T,\eta)$$

(kinetics equation)

where x is the linear coordinate of the combustion wave and $\varphi(T,\eta)$ is the kinetic function for the boundary conditions:

$$x=-\infty,\ T=T_0,\ \eta=0$$

and

$$x=+\infty,\ \frac{\mathrm{d}T}{\mathrm{d}x}=\frac{\mathrm{d}\eta}{\mathrm{d}x}=0.$$

The linear transfer of the reaction product was neglected in the solution of these equations; material-synthesising processes (*i.e.*, solid-phase reactions yielding solid products) were described by the 'non-classical' kinetic functions $\varphi(\eta)$.¶ The following kinetic functions were employed in the very first theoretical studies:[6,19]

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

where m and n are the constants.

More advanced theoretical studies took into account various features of evolution and transmission of heat in different systems, such as melting and formation of molten layers, transfer of mass and heat by infiltration after impregnation of initial porous green mixtures with the melt, multistep character of reactions, *etc.*[91–93]

Description of flame propagation processes in hybrid 'porous body – gas' systems is a more complicated task. At relatively low gas pressures, solid reactants do not contact with one another and the transformation of the solid demands the delivery of a gaseous reactant to the combustion zone. Usually, this situation is analysed for one-component gases which are fully consumed upon reaction. This assumption suggests that their transport proceeds in a purely infiltration mode (if another gas is present, allowance is made for diffusion).

Numerous studies on filtration combustion modes have been carried out. One-dimensional filtration was found to occur in cylindrical samples with gas-impermeable lateral surfaces and open edges. The results of one-dimensional combustion studies have been generalised.[94] A theoretical analysis of more complex filtration regimes, *e.g.*, combustion with lateral filtration leading to limiting surface and layer-by-layer modes and high-pressure combustion, has been carried out.[95,96]

Of substantial interest are material-synthesising combustion implemented in non-steady-state modes (in unstable regions, in particular). Studies by Ya B Zeldovich have shown that the enthalpies of condensed systems in combustion waves exceed those of the starting reactants (at initial temperatures) or final products (at combustion temperatures) which are equal. The excess of enthalpy is the reason for the instability of the wave propagation. In the case of gas-releasing systems, such as explosives, instability leads to extinction of the process. Owing to their high thermal capacity, the condensed products prevent extinction and wave propagation continues, however, in a complex or abnormal mode. The existence of one-, two- and three-dimensional non-steady-state modes reflects the complex nature of spatiotemporal instability.

In the case of one-dimensional instability, the smooth (nearly flat) combustion front characteristic of steady-state modes is preserved, and only time instability is observed. In this case, we deal with the so-called self-oscillations where the instantaneous value of the combustion front velocity fluctuates around a certain mean value (the so-called harmonic or relaxation oscillations, Fig. 23). Figure 23 shows curves for the time changes in the instantaneous front velocity in dimensionless coordinates for different limiting stability loss values (α_{st}).

A novel mode of combustion has been established in model studies of two-dimensional instability of a hollow cylinder with account of temperature distribution and degree of conversion along the height and circumference of the cylinder with no allowance for the radial direction.[18] Here we deal with the aforementioned spin wave where the reaction is concentrated in a centre moving along the sample by a spiral path. After a certain period of time, the velocity of the centre becomes constant indicating spatial instability, but temporal stability remains. Such regimes are usually described within the framework of a thin cylindrical shell model with allowance for longitudinal and tangential (angular) heat exchange components.

¶ The classical kinetic functions for the reactions of the nth-order appears as $\varphi(\eta)=(1-\eta)^n$.

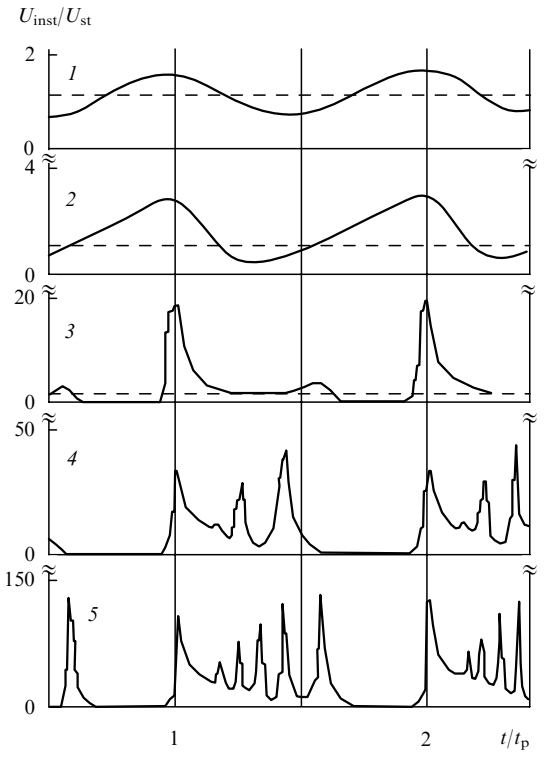


Figure 23. Self-oscillations of the front velocity as a manifestation of one-dimensional instability (U_{inst} and U_{st} are instantaneous and steady-state combustion velocities, respectively).
The structure of pulses at different deviations from the stability limit $\alpha_{st} = 0.99$ (*1*) , 0.94 (*2*), 0.82 (*3*), 0.64 (*4*), 0.50 (*5*).

Three-dimensional waves are generated in solid cylindrical samples under the action of a radial heat-exchange component. Such waves propagate in diverse modes which depend upon:

$$\alpha_{st} = \left(9.1\frac{c\rho T_{ad}}{Q} - 2.5\right)\frac{RT_{ad}}{E}$$

and

$$r = r_0\left[\frac{Q}{c}\,\frac{E}{RT_{ad}^2}\,\frac{kT_{ad}}{a}\right]^{1/2}.$$

The former parameter corresponds to the stability loss limit (the smaller α_{st} the greater the instability), while the latter represents a dimensionless radius of a cylinder, *i.e.,* the ratio of the cylinder radius to the characteristic width of the narrow reaction zone. The smaller α_{st} and the larger r the more complex the instability pattern. Some novel three-dimensional non-steady-state combustion modes, *viz*., spin waves with self-oscillations of the centre velocities, intermittent spin waves with temperature fluctuations, multipoint periodic waves with recurrent non-steady-state temperature and concentration fields and chaotic waves, have been described.[97–101] Studies of heat losses to the environment have established several novel regimes of combustion wave propagation described by paraboloid-type functions.

Interestingly, all these previously unknown regimes are described by a classical system of equations which is physico-chemically the simplest, *viz*., by the heat conduction equation in the cylindrical coordinates:

$$c\rho\frac{\partial T}{\partial t} = \lambda\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{1}{r^2}\frac{\partial^2 T}{\partial \varphi^2} + \frac{\partial^2 T}{\partial h^2}\right) + \rho Q\frac{\partial \eta}{\partial t}$$

and the kinetics equation:

$$\frac{\partial \eta}{\partial t} = \begin{cases} k_0(1-\eta)\exp\left(-\dfrac{E}{RT}\right) & \text{for } \eta < 1, \\ 0 & \text{for } \eta \geqslant 1, \end{cases}$$

where r, φ and h are the spatial coordinates (r is the radial, φ is the angular and h is the longitudinal axes of the cylinder) supplemented by the following boundary conditions:

$$t = 0\text{: } T = T_0,\ \eta = 0;$$

$$t > 0\text{: } r = r_0,\ \frac{\partial T}{\partial r} = -\alpha_t(T - T_0);$$

$$h = 0\text{: } \frac{\partial T}{\partial h} = 0;$$

$$h = h_0\text{: } \begin{cases} T = T_{ign} & \text{for } t \leqslant t_{ign}, \\ \dfrac{\partial T}{\partial h} = 0 & \text{for } t > t_{ign}, \end{cases}$$

where T_0 is the ambient temperature and the initial temperature of the sample; T_{ign} is the ignition temperature; α_t is the heat-transfer coefficient from the surface to the environment; r_0 and h_0 are the radius and the height of the cylinder, respectively, and t_{ign} is the duration of the initiating pulse.

The structure of a combustion front for a chaotic regime is shown in Fig. 24.

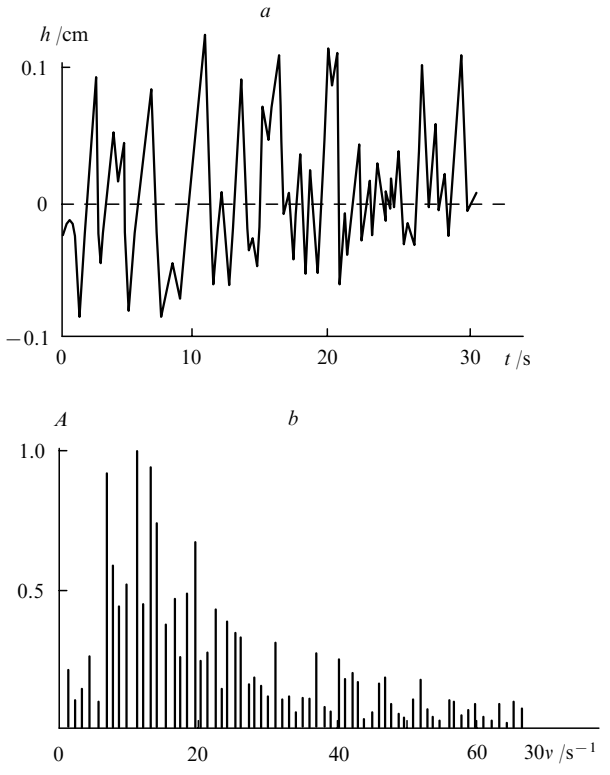


Figure 24. An example of a chaotic combustion regime in the Cr_2O_3 + Al + Al_2O system (*h,* lead of screw thread; *A,* amplitude);
(*a*) vibrations of the front coordinate relative to the average value, (*b*) amplitude – frequency spectrum.

All of the foregoing discussions related to processes occurring in mixed systems (powder mixtures). A more complex, but less explored instability pattern is observed in hybrid 'porous sample – gas' systems.

Unstable self-excited waves generated in various material-synthesising processes have become an attractive subject of

investigations in nonlinear dynamics. Investigators are contemplating the problem of making these processes more practicable.

VI. Materials science of combustion and explosion products

This important trend of research has a number of specific features, since the conditions of material-synthesising combustion and explosion differ dramatically from those used in ordinary processes, which cannot but reflect on the structures and properties of the final products.

Studies in the field of materials science develop along four main lines (chemical, physical, technical and theoretical).

The chemical materials science studies mechanisms of chemical and structural transformations in the combustion wave, dynamics of formation of the final structures of reaction products and their individual components (phase, crystalline, granular, porous, *etc.*), chemical properties of the reaction products (chemical analysis) and their relationship with conditions and parameters of the corresponding processes. Physical properties of materials and physical material processing fall under the scope of physical materials science. Technological materials science is concerned with the study of operational characteristics and applications of combustion and explosion products in different branches of science and technology. Theoretical materials science deals with structural and macrokinetic simulation and analysis of physical (equilibrium or non-equilibrium) states of reaction products in relation to thermal regimes.

The problem of equilibrium and non-equilibrium character of combustion and explosion products is very interesting and widely debatable. Peremptory and often erroneous judgements exist that the products formed are of non-equilibrium character, since the underlying processes are non-equilibrium. The incorrectness of this statement is due to the ambiguity of its solution, which depends on the criterion S:

$$S = \frac{t_{st}}{t_{tr}},$$

where t_{st} is the characteristic time of structure formation and t_{tr} is the characteristic product cooling time. If $S \ll 1$, the cooling period is long and the product undergoes self-annealing under long-term action of high temperatures, which leads to the formation of an equilibrium product. Synthesis in SHS reactors where the cooling time is 1–1.5 h and structural relaxation is complete is an example of a process for the preparation of equilibrium products.

At $S \gg 1$, the cooling time is short and self-quenching † takes place. In this case, non-equilibrium products are formed instead of equilibrium ones.

The structure of the product in the remaining broad intermediate variability domain of parameter S may be very complex.‡ For example, the equilibrium can be reached for one parameter, *e.g.*, chemical composition of the products, but cannot be reached for other parameters, *e.g.*, crystal phase structure.

Let us consider an interesting example. In 1970, I P Borovinskaya came to obtain an unexpected result in an attempt to synthesise boron nitride by combusting boron in nitrogen under high pressures ($\sim$ 300 MPa).[21] In one of these experiments, the tube broke and rapid release of pressure resulted in hardening of the burnt product. The sample of boron nitride thus obtained appeared to be amorphous. These studies have demonstrated the possibility of obtaining both non-equilibrium and amorphous products by hardening.

† Quenching is a rapid (10^3–10^4 deg s^{-1}) cooling of a sample and is usually implemented in two modes: in liquid nitrogen and in massive brass blocks for wedge-shaped samples.

‡ The term 'structure' is very broad and polysemantic. It entails chemical structure, phase state, grain size (in the case of granular structures), *etc.*

Rogachev *et al.*[102, 103] have described an original procedure for hardening of combustion products using a large copper block with a wedge-shaped cavity filled with a green mixture. Combustion was initiated at the wide base of the wedge and gradually spread deeper into the narrow channel. Increasing heat losses caused the flame to fade at some distance from the wedge base. Layer-by-layer analysis of combustion products made it possible to draw the dependences of chemical and phase compositions, grain size and other reaction parameters as a function of the combustion coordinate, *i.e.*, the distance from the combustion front. These dependences provide indirect (with some errors connected with the hardening time) information about the processes occurring in the combustion zone.

The picture of a combustion process carried out in a wedge-shaped cavity and the micrographs of the granular structures of the samples formed at different distances x from the wedge base are shown in Fig. 25. Figure 26 illustrates the dependence of the mean grain size on the combustion coordinate for TiC, TiB_2, *etc.* Based on the results obtained, it was concluded that after termination of chemical reactions occurring in the combustion wave the system undergoes intense recrystallisation as a result of which the size of the grains increases. The particles formed in the combustion zone have submicron and micron sizes which may increase by orders of magnitude in the course of recrystallisation. This hardening method provides a key to control over the granular structure and, correspondingly, the properties of the materials synthesised.

Studies of dynamics of phase transitions (polymorphous transformations) in the combustion wave are yet another impor-

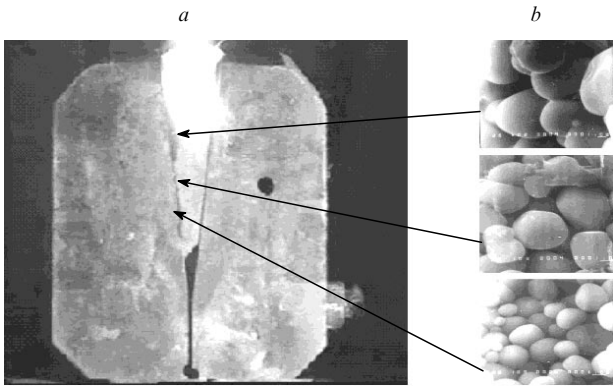


Figure 25. Combustion in a wedge-shaped gap: a picture (*a*) and micrographs of product structures taken at different distances from the combustion front (*b*).

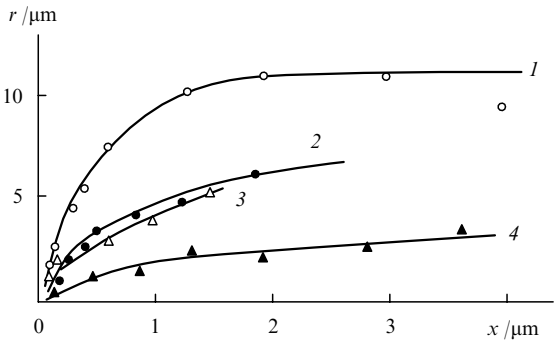


Figure 26. Distribution of grain sizes (r) of combustion products behind the combustion wave front (x is the distance behind the front) for processes of formation of TiC (*1*), TiB_2 (*2*), Ti_5Si_3 (*3*) and TiC + 20%Ni (*4*).

tant line of research. This required the development of novel techniques for the control over dynamics of phase transitions in all stages: from starting reactants to final products. In addition to hardening, these methods include dynamic X-ray phase analysis based on synchrotron radiation, standard analyses using X-ray tubes and other techniques. The principle of X-ray phase analysis is very simple. The X-ray beam is directed at a definite point on the lateral surface of the sample which is usually flat. When the combustion wave reaches this point, X-ray photographs are taken at definite intervals of time. X-Ray patterns allow the analysis of dynamics of phase transitions and, particularly, of the dynamics of formation of the final products.

Practical implementation of this technique requires the use of X-ray beams of high intensity and rapid shooting of X-ray patterns. The use of synchrotron radiation is the most appropriate to this end. The pioneering studies in this area were carried out on a synchrotron of the Institute for Nuclear Research of the Siberian Branch of the Russian Academy of Sciences by a research team headed by V V Boldyrev.[104] An Ni + Al system used in this study was subsequently employed in other model studies.[105, 106] A schematic representation of this experiment is shown in Fig. 27; the first dynamic phase formation curves are depicted in Fig. 28.

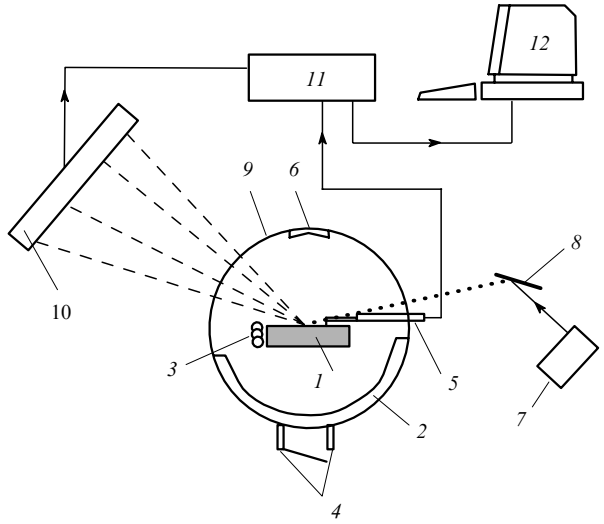


Figure 27. Dynamic X-ray analysis of SHS;
(*1*) sample, (*2*) reaction chamber, (*3*) igniting wire, (*4*) gas inlet and outlet (He), (*5*) thermocouple, (*6*) quartz window, (*7*) X-ray tube, (*8*) monochromator, (*9*) beryllium window, (*10*) linear detector, (*11*) interface unit, (*12*) computer.

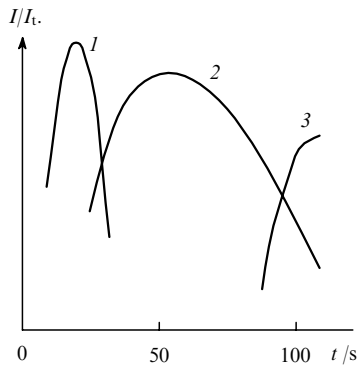


Figure 28. First dynamic curves of phase formation obtained in combustion in the Ni + Al system (*I* is the intensity of radiation);
(*1* and *2*) intermediate phases, (*3*) final product.

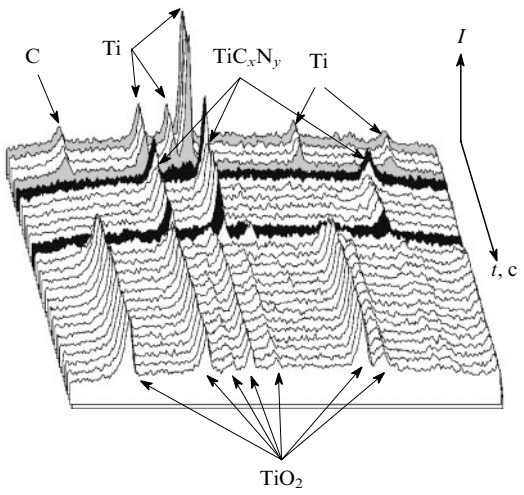


Figure 29. A series of dynamic patterns obtained in the combustion of the Ti–C system in air.[109]

A simpler design of a laboratory-scale X-ray diffraction analysis on an ordinary diffractometer supplied with a special detector was developed in further studies.[107, 108] A set of dynamic X-ray patterns obtained by this method is shown in Fig. 29 (see Ref. 109). Their processing made it possible to draw the concentration profiles of the combustion wave (patterns).

Interesting patterns were obtained in the studies of combustion of a titanium powder in air (Fig. 30).[110] These diagrams clearly demonstrate that the metal reacts with nitrogen rather than with oxygen to afford an intermediate nitride which undergoes subsequent oxidation to yield titanium oxide (TiO_2) as the final product.

$$\mathrm{Ti} \longrightarrow \mathrm{TiN}_x \longrightarrow \mathrm{Ti_2O_{5-x}N}_x \longrightarrow \mathrm{Ti_6O_{11-x}N}_x \longrightarrow$$
$$\longrightarrow \mathrm{TiO_{2-x}} \longrightarrow \mathrm{TiO_2\ (rutile)}.$$

A method for processing patterns was proposed, which provides information about the mechanism of phase formation in the combustion wave.[30] The dynamic phase transformation curves are treated in the $y-\xi$ coordinates, where y is the completeness of phase formation and ξ is the dimensionless spatial coordinate:

$$\xi = \frac{U^2 t}{a},$$

where a is the thermoconductivity of the substance.

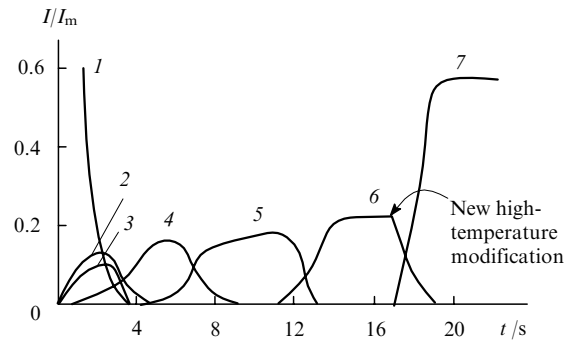


Figure 30. X-Ray phase diagrams obtained in the combustion of a titanium powder in air;
(*1*) α-Ti + solid solution, (*2*) β-Ti, (*3*) TiN_x, (*4*) $Ti_3O_{5-x}N_x$, (*5*) $Ti_6O_{11-x}N_x$, (*6*) TiO_{2-x}, (*7*) TiO_2 (rutile).

If $0 < \xi < 1$, the structure formation follows the Khaikin–Aldushin–Merzhanov equilibrium mechanism where chemical reactions and structure formation occur simultaneously. At $\xi \gg 1$, the process follows the Borovinskaya non-equilibrium mechanism, *i.e.*, the final product is formed at a sufficiently large distance from the combustion front due to decomposition of unstable intermediate products formed in the combustion wave.[6, 19, 27] An example of this process is given in Fig. 31.

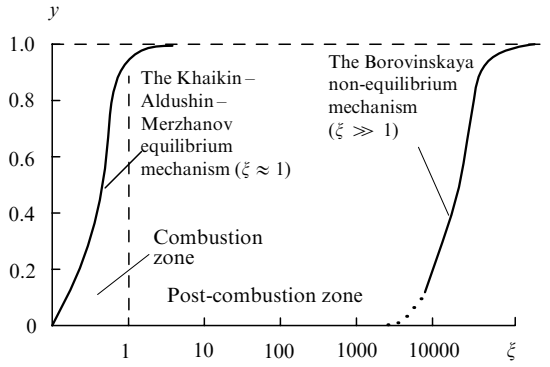


Figure 31. On the mechanism of structure formation in combustion processes.

To some extent, synchrotron and diffractometric methods are complementary. The former is more suitable for the study of fast burning systems, while the latter is more applicable to slowly burning systems. However, none of these methods allows identification of the initial stages of phase transitions. Therefore, increasing measurement sensitivity is a currently central methodological task.

A recently published paper [111] describes the use of the synchrotron method for obtaining information about processes occurring in the detonation wave.

Numerous papers are devoted to a comparison of miscellaneous characteristics of combustion and detonation products to those prepared by conventional methods. This is important from both the scientific and practical point of view, especially for SHS products, because here, like in no other field, their competitiveness with respect to products prepared by conventional methods had to be argued. Some characteristics of AlN powders prepared by SHS and sintered materials therefrom in comparison with particulate materials prepared by furnace synthesis are given in Table 6. Aluminium nitride is a very popular ceramic material which is widely employed in electronics for preparation of microchip boards where quality requirements are especially high. As can be seen from Table 6, the quality of the SHS product exceeds that of the furnace-made analogues in the content of fixed nitrogen and admixed oxygen, but the content of admixed iron in the former is higher. Sintered SHS materials prepared from AlN are also distinguished for high quality.

The next example is related to the synthesis of diamonds. In Table 7, specifications of diamonds prepared by two detonation methods are compared to those synthesised under static conditions at high pressures and temperatures. Diamonds prepared by the three methods differ in grain size (from nanosizes to millimetres) and hence in application fields. All artificial diamonds complement each other rather than compete.

Table 6. Comparative analysis of AlN powders obtained by SHS and by furnace synthesis.

Method	Sample brand [a]	Manufacturer (country)	Impurities (mass %)			Specific surface S /m^2 g^{-1}	Mean diameter (d_{50}) /μm	Characteristics of sintered powders		
			N [b]	O	Fe			λ /W K^{-1} m^{-1}	strength /MPa	electric strengh /kW m^{-1}
SHS	SHS-T	ISMAN (RF)	31.5–32.5	1.2–1.5	0.1–0.2	–	–	–	–	–
	SHS-C	ISMAN (RF)	33.5–33.8	0.5–0.8	0.06–0.1	0.6–0.8	< 15	–	–	–
	SHS-G	ISMAN (RF)	33.3–33.5	0.7–1.0	0.06–0.1	2.5–3.5	1.0–1.4	160–190	370–390	> 20
Furnace	–	RPC 'Reaktiv-Elektron' (RF)	31.0–32.6	0.4–2.9	0.3	–	–	–	–	9.6
	AlNeL®	ART (USA)	33.0	1.0	< 0.01 (see [c])	2.0–5.0	–	200	–	10
	CER-ALLOY	Ceradyne (Great Britain)	–	–	–	–	–	120–170	207–280	–
	Grade F	Tokuyama Soda (Japan)	33.6	0.9	0.001	3.2–3.5	1.5	170 ± 10	350	> 20

[a] Designations: SHS-T, technical grade; SHS-C, pure, conglomerates; SHS-G, pure, ground; [b] stoichiometric content is 34.19 mass %; [c] ppm.

Table 7. Specification of artificial diamonds.

Method for synthesis	Mechanism of formation	Size of crystal grains	Areas of application	Authors
Statical at high pressures and temperatures	phase transition of graphite into diamond in the presence of catalysts	< 5 mm	jewelry, boring/stone-working instrument, polishing tools	V N Bakul', L F Vereshchagin
Detonation-I	phase transition of graphite into diamond in a mixture of an explosive with graphite	0.01–5.00 μm	composite materials with metal/elastomer templates	O N Breusov, A N Dremin *et al.*
Detonation-II	formation of diamond from carbon present in the explosive	2–4 nm	superfinish polishing, motor oil additives	G V Sakovich, V M Titov *et al.*

The two detonation methods differ in principle. In one of them, carbon particles are incorporated into the explosive green mixture and diamonds are formed in the detonation wave. In another approach, explosives containing excess carbon (with respect to oxygen balance) are used without additives. Excess carbon atoms are condensed in the detonation wave into small (nanodimensional) particles. Such diamonds virtually represent condensed products of an explosion-induced chemical reaction. This is an example of detonation-driven SHS (see above).

A comparison of various characteristics of products prepared by different methods allows correct choice of a synthetic procedure depending on the practical task.

VII. Material-synthesising and material-affecting combustion and explosion processes in technology and industry

Combustion and explosion processes present substantial practical interest.

Numerous unique technologies based on combustion and explosion processes have been developed; the number of SHS processes alone, which include six technological types, exceeds 30.[27]

The advantages of combustion and explosion technologies are well known. They include considerable saving of electric energy, simplicity, high productivity, structural and functional diversity of final products, possibility of attaining high quality and optimum parameters, *etc*. Their main disadvantage (especially with regard to material-synthesising processes) is non-versatility. Combustion and explosion can be implemented exclusively in high-energy self-transforming systems. To other drawbacks of these technologies one can add high inflammability and explosibility of high-energy systems used therein. However, in spite of these 'drawbacks' these processes have occupied a prominent place in up-to-date technology.

By virtue of their specific features, combustion and detonation processes are related to the category of alternative (as opposed to conventional) techniques for synthesising inorganic materials. Combustion and explosion can be used in virtually all currently known technological processes. Some examples of conventional technologies and alternative combustion and explosion processes used for synthesising inorganic materials are given in the table below.

Conventional technologies	Combustion and detonation analogues of conventional processes
Furnace and plasma-chemical synthesis of powders	SHS
Synthesis of superhard materials under static conditions	shock wave and detonation synthesis
Sintering, hot-pressing	SHS sintering, STIM technology (STIM stands for synthetic hard instrumental materials)
Plastic metal working	explosive compaction, STIM technology
Flame spraying	powder spraying
CVD processes, diffusional saturation	gas-transport SHS technology
Metallothermic melting of materials, alloys, compounds	SHS metallothermy
Electric arc welding	SHS welding
Electric welding	explosion-induced welding, SHS welding

In choosing a particular technological process, special attention should be given to its efficiency and expected characteristics of final materials. Unfortunately, it does not always work.

There is a large body of evidence on practical applications of materials prepared or processed with the use of combustion and explosion technologies. Without going into details, we shall confine ourselves to providing a cumulative list of materials (which is far from being complete) and branches of industry where they are employed.

Branch of industry	Materials
Mechanical engineering	abrasives, hard alloys and articles thereof, welded parts including bimetallic rolled stock, superhard materials (diamonds, wurtzite-like BN)
Metallurgy	cast iron; ferro- and foundry alloys including nitrogenated alloys; refractory materials including oxygen-free (nitride) materials; particulate materials for powder metallurgy; moulded high-melting articles including pipes with internal wear-resistant coatings; heat-resistant alloys
Chemical industry	technical-grade carbon; boron and its compounds; pigments; luminophores; fumigants; catalysts; filters for gases and liquids
Electrical and electronic engineering	ceramic (including ferrite) powders; thermal insulators; microcircuit boards; high-temperature heaters; solid conductive lubricants; green mixtures for growing oxide single crystals; powders of high-temperature superconductors
Medicine	storage media and implants

Combustion and explosion products are used successfully in building materials, aircraft industry, *etc*.

Of special importance are industrial applications of combustion and explosion technologies. This includes large-scale production of cast iron and ferroalloys, which have long been known to metallurgy and chemical industry, and some novel SHS technologies carried out in proving grounds and blasting chambers.

Numerous works aimed at assimilation of SHS technologies and organisation of production lines at pilot plants and experimental-industrial enterprises have been carried out at ISMAN together with the Interbranch Research-and-Production Complex (IRPC) 'Termosintez'. Other developments included large-scale production of technical-grade boron (Dal'negorsk), $MoSi_2$ (Kirovakan), TiC, BN and AlN (Baku), β-Si_3N_4 (Makeevka), ferrites (Razdan), $LiNbO_3$ (Dzerzhinsk), refractory materials ('Furnone') (Alma-Ata), cutting blades (Nizhny Novgorod), high-temperature ceramic insulators (Samara), nitrogenated ferroalloys (Chusovaya, Izhevsk), titanium alloys (TiC, TiC – Cr_3C_2, TiH_2) (Transcarpathia) and other SHS products (Chernogolovka). Altogether, over 2 000 tons of miscellaneous products were manufactured in the last year of existence of the USSR (and, actually, of the IRPC 'Termosintez'). The most recent SHS developments were realised at the fully automated plant 'SHS Ceramicas' (Spain) utilising the ISMAN technology. The production of pipes with internal antiwear coating for transportation of abrasive media (*e.g*., cement, carbon, minerals, *etc*.) has been set up in China. This production successfully combines the fundamental concepts of the effect of an artificial gravity field on combustion developed by researchers at ISMAN [112] with the rich experience of Japanese specialists in the production of large-diameter pipes.[113, 114] This technology has been introduced at ten Chinese plants with the annual output of 10 000 tons.

Pioneering works aimed at industrial implementation of explosion technologies were undertaken by researchers at the Lavrentyev Institute of Hydrodynamics. Their longstanding efforts have culminated in the establishment of an Engineering-and-Design Institute for Hydraulic Pulse Technology. Its main products include bimetallic (steel – copper, steel – titanium, steel – AO20) preforms. Production of diamond nanopowders in a blasting chamber has been started at the Federal Research-and-

Production Centre 'Altai'. This blasting chamber allows explosion of charges weighing up to 6 kg with frequency of 30 blasts per hour; its productivity is 2.5 tons of refined diamonds per year, which is more than satisfactory for detonation synthesis.

The detonation line installed at the Penza State University and designed for batch production of segnetoelectric materials and articles by explosion-induced compaction of metal powders followed by sintering is also operating with high efficiency. The operational characteristics of these materials have been improved through the formation of fine-grain high-strength structures with well-developed contact surfaces.

The construction of stable explosion chambers has made it possible to enlarge industrial implementation of explosion technologies.

Despite the 'uncommonness' of combustion and explosion technologies, they hold great promise.

VIII. Conclusion

Studies of material-synthesising and material-affecting combustion and explosion are under way. Theorists are working out structural and macrokinetic combustion models which would provide a description not only of characteristics of the combustion wave but also of the structures of final products. Similar problems are being explored in explosion studies aimed at the construction of structural and gas-dynamic detonation models. The first theoretical works in this area were devoted to the solution of three-dimensional combustion problems. Three-dimensional simulation presents interest in principle, since it permits one to follow transformations of substances in the bulk of a burning or detonating body, which cannot be attained by conventional methods.

Many important problems remain to be solved by methodologists. These include studies of structural dynamics of combustion and explosion processes by methods similar to dynamic X-ray diffractometry. Another important task is adequate monitoring of changes in porous structures and microstructures (*e.g.*, grain size) of substances in combustion and detonation waves.

Experimentalists are actively engaged in the study of processes occurring in chemically and physicochemically complex systems. The problem of separation of the primary from the secondary in the totality of processes has been a challenge to investigators at all times.

Some new trends, *viz.*, gas-phase and gas-disperse SHS,[115,116] mechanochemical SHS,[117–121] thermal explosion SHS and high-field-assisted SHS, have emerged relatively recently.[122–124] Practical implementation of gasless detonation processes is an important task.[125]

Production engineers are concerned with the development of continuous combustion and explosion processes. Some progress has been made in the field of high-energy technologies. However, continuous material-synthesising processes based on combustion and explosion, *e.g.*, production of powders, melts, compacted long-sized items, *etc.*, are still very rare.

This problem is closely connected with utilisation of combustion energy and its transformation into electric energy by conventional methods. Thus, development of energotechnological processes is of interest.[126] This is topical for continuous processes. Implementation of thermoconjugated modes where one (strongly exothermic) reaction initiates another (weakly exothermic) reaction is especially important for periodic processes.

The use of 'chemical furnaces' is becoming a popular trend in modern research practice.

The major challenge facing designers is in the construction of quasi-adiabatic SHS reactors with large cooling times (of the order of weeks) allowing the synthesis of SHS products in the form of small (of the order of millimetres) crystals. Works on the construction of an SHS attritor for mixing reactants, SHS conducting and grinding the product in one technological step are currently under way. Many practical tasks are related to the design of special moulds for SHS compaction and tubes for loading and conservation of substances under shock waves, *etc.*

Yet another important trend is a search for novel applications of material-synthesising and material-affecting combustion and explosion technologies.

Recently, the Scientific Council for Combustion and Explosion at the Presidium of the Russian Academy of Sciences has worked out the concept on the development of combustion and explosion processes as a branch of scientific and technological progress. All those who are interested in this problem are referred to the recently published book [127] which contains sections devoted to materials and technology.

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