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Structural macrokinetics of SHS processes

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Abstract - Development of structural macrokinetics as a new field of science in the 80s and in the beginning of 90s is analyzed. Results having principal importance for working out procedures of controlling structure of products and materials prepared by self-propagating high-temperature synthesis is reviewed. Major attention has been paid to refractory products (carbides, borides, nitrides, silicides, etc.) and refractory base materials, viz. oxygenless ceramics, cermets, and hard alloys, as well as to high-temperature superconductors. It is shown that the structure of these materials produced in the combustion mode, in general, can be effectively controlled by changing relevant parameters of the synthesis. In connection with this, detailed studies on the mechanism of product structurization and the structure of combustion wave itself are necessary.

INTRODUCTION

The technique of self-propagating high-temperature synthesis (SHS) is applied in production of many ceramic and metalloceramic materials, cemented carbides, super alloys, high-temperature superconductors, and various powders designed for industrial use. Strict requirements demanded to modern materials influenced studies on structure and structurization of SHS products undertaken in recent years. This is not accidental since the structure of a product determines its properties to a great extent, especially, if structural and tool materials are concerned. It would not be overestimation to state that problem of controlling product structure is one of the most important tasks in further development of SHS. Here the structure is meant as a wide range of characteristics including

macrostructure (composition distribution, macroscopic defects),

microstructure (arrangement of phases and crystals with respect to each other, grain structure of products, porosity and pore structure, localization of impurities), and

crystal structure (crystal lattice type and lattice parameters, presence of defects, ordering with formation of superlattices, amount and distribution of dislocations).

The structure of combustion wave itself needs to be added to the above classification since distribution of temperature and concentration in the combustion and after-burning zones markedly affects all of the processes of high-temperature synthesis and the composition and structure of products.

For product structure to be controlled profound knowledge of the regularities and mechanisms of structure evolution in the combustion wave at each structural level is necessary. Recognition of this necessity led to emergence of a new field of science in the early 80s called "structural macrokinetics" (SMK). This work deals with the general ideas of SMK and the progress made in this field for the last decade.

Structural macrokinetics studies evolution of structure in the course of chemical transformation taking into account heat and mass transfer processes. A place of SMK in the number of other fields of science can be schematically presented with the use of following equations (Ref.1)

$$\text{classical macrokinetics} = \text{chemical kinetics} + \text{heat and mass transfer theory}$$

$$\text{structural macrokinetics} = \text{classical macrokinetics} + \text{kinetics of structural transformations}$$

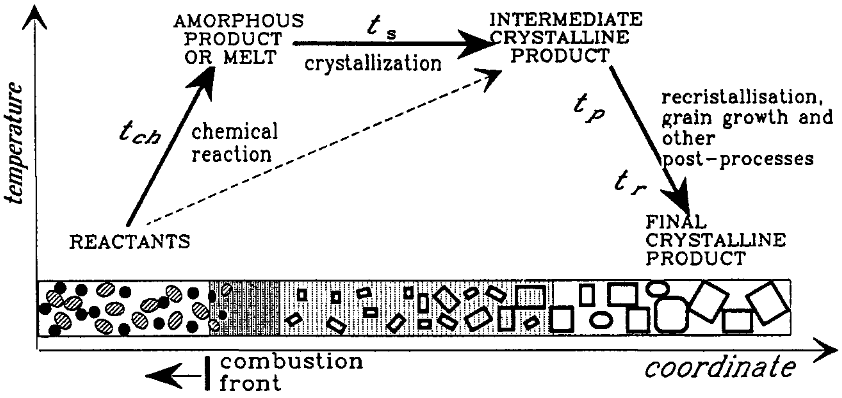


Fig.1. The principal concept of structural macrokinetics.

A principal concept of structural macrokinetics is illustrated in Fig. 1. It is based on the assumption first made by Borovinskaya (Ref.2) and later substantiated experimentally that transient products and structures in the reaction zone of SHS wave have an non-equilibrium nature. Under the extreme conditions in combustion wave, chemical interaction accompanied by destruction of initial structure can occur so rapidly that the structure of equilibrium products have no time to be formed simultaneously with the process. In this case the structurization proceeds behind the combustion front and does not affect the features of front propagation. This can be expressed more exactly if comparing characteristic times of chemical reaction t_c, of crystallization of solid phase t_s, of crystallization of final product t_p, and of thermal relaxation (cooling) of a burnt sample t_r. A necessary condition for propagation of SHS wave with a constant velocity is the fulfillment of requirement $t_c \ll t_r$. If the latter is fulfilled, the following modes are possible

$t_c < t_s \le t_p$: a reaction results in amorphous products or a melt (while crystalline products are formed posteriori when the reaction almost have been completed;

and $t_s \le t_p < t_c$: crystalline products are formed directly in the course of chemical reaction, formation of intermediate nonequilibrium phases being possible if $t_s < t_p$; but the phase composition of product in the reaction zone corresponding to the equilibrium one when $t_s = t_p$.

Variation of cooling time t_r makes it possible to obtain a product with either equilibrium or nonequilibrium structure.

The analysis of SMK data allows two typical approaches to be distinguished in these studies. At present, the most detailed information is available for the relation between structure of SHS products, properties of the stock charge, and conditions of the combustion. A lot of

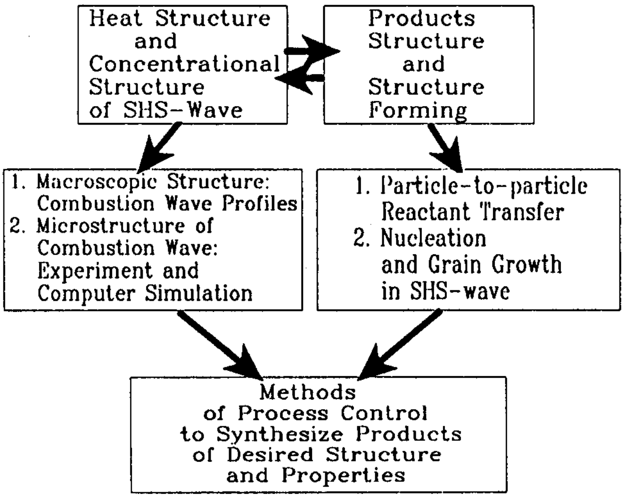


Fig.2. Objects of structural macrokinetics.

empirical data was collected without intention of disclosing mechanism and dynamics of structurization. This approach, sometimes called "structural statistics" is, in essence, the applied materials science of SHS products. The second approach known as "structural dynamics" is concerned with the study of evolution of structure of matter in a SHS wave. Both quenching of combustion processes or intermediate products and direct measurements in the course of combustion are used for this case.

Structural macrokinetics of synthesis in combustion wave is composed of a series of topics and problems connected not only by a mutual subject of study but by the above described general idea of SMK and by common objective, i.e. manufacture of products with a prescribed structure. These problems are schematically represented in Fig.2. All of the further considerations will follow this scheme.

THERMAL AND CONCENTRATIONAL STRUCTURE OF SHS-WAVE

Experimental techniques and results

Quasi-one dimensional structure. Studies on the quasi-onedimensional structure of combustion wave are carried out for at least few decades (Refs.3 and 4). They are based on the simplifying assumption that isotherms of combustion wave have a planar form. In this case the structure of combustion wave can be described by one-dimensional distributions of temperature and degree of chemical conversion along the axis coinciding with the direction of wave propagation. The width of SHS wave zones, viz. preheating up zone, chemical reaction zone, structurization zone, etc., is measured along the same axis. To determine experimental methods using thermocouple probe technique (Refs.6,7 and 8) and optical pyrometry methods based on local measurements of color temperature of a burning sample (Refs.9 and 10) were developed.

Table 1. Some characteristics of SHS-waves. T_c-combustion temperature; l_m-preheating zone width; L-total wave width; τ-time of chemical reaction; $dT/d\tau$-heating rate in combustion front.

System	T_c	L_M, mm	L, mm	τ, s	$dT/d\tau$, K/s
Nb + 2B	2270	0.170	1.0	0.13	36000
Zr + B	1970	0.080	0.6	0.13	49000
Mo + B	1870	0.200	1.2	0.4	12000
Ti + B	2570	0.050	2.0	0.5	752000
Ti + H_2	1170	0.140	0.29	-	-
Ti + Si	1900	0.080	2.3	0.15	147000
Zr + 2Si	1790	0.250	1.55	0.42	10000

The inflexions, isothermic "shelves", and other features of thermograms related to complex multi-stage type of interactions in the combustion of heterogeneous system are considered in more detail elsewhere (Ref.11). The analysis of temperature profiles made it possible to determine such SHS characteristics as heating-up rate in the wave, heating-up time, duration of chemical reaction, and SHS wave width. These characteristics for some systems are listed in Table 1 (Refs.12). They clearly show how extreme the conditions of synthesis in combustion wave are, viz., a heating rate can exceed tens of thousand degrees per second, the temperature may reach several thousand degrees, the synthesis reaction takes fractions of second, etc.

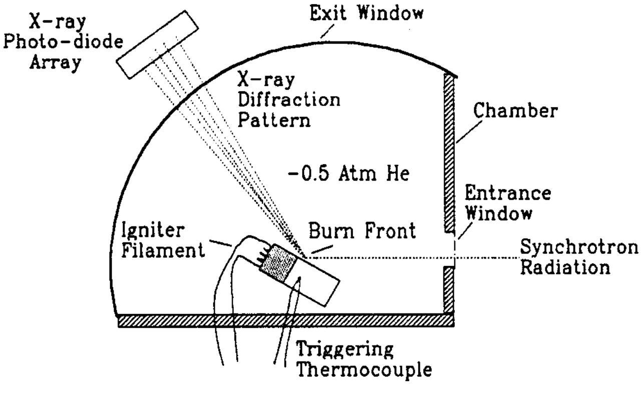


Fig.3. Schematic drawing of diffraction chamber that is used for TRXRD (Brookhaven National Laboratory, USA)

Mathematical treatment of temperature profiles can provide profiles of degree of conversion in combustion wave. To get these, however, it is necessary to know thermophysical properties of a medium (heat conductivity, and heat capacities for reactants and products) not only for initial and final states but directly in the course of combustion also. Since data of this sort have been determined quite approximately, essential errors in concentrational structure of combustion wave determined on the basis of temperature profiles are inevitable. A technique of direct observation of change in concentration of reactants and products in the course of combustion thus appears to be rather attractive. This technique has been invented and first applied by Alexandrov and co-workers (Refs.13 and 14) and now it is successfully elaborated by Holt et al. (Refs.15 and 16). The method is based on utilization of synchrotron radiation for time-resolved X-ray diffraction analysis (TRXRD) of the surface of burning sample. The idea of the method is obvious from Fig.3 (Ref.15). Due to high intensity of synchrotron radiation, the time consumed for determining of phase composition (the time of single measurement) can be reduced to 0.1 s. The locality of measurements is not large because the irradiated spot on the sample surface is few millimeters in size. Therefore, this method is more appropriate for observation of processes of phase formation and structurization occurring after combustion front passage. In this sense, the microthermocouple probe technique as the most suitable for studying the combustion front itself and the dynamic X-ray phase analysis method supplement each other.

Some of the most interesting results obtained with the use of TRXRD are produced with Ni-Al system. Alexandrov and co-workers found that the final product NiAl was formed far behind the combustion front, in 60-70 seconds after its passing. The time of one measurement was 0.5-1.0 s and two unknown intermediate products were detected as shown in Fig.5.

Holt and other detected four intermediate phases with the recording time of 0.1 s, the compound NiAl appearing 30 seconds after combustion front passage. Besides the above considered methods, some other physical techniques are applied in dynamic determination of composition (Ref.17) such as synchrotron radiation X-ray absorption and fluorescence spectroscopies which also provide a possibility of direct measuring concentration profiles of combustion wave.

Real structure of combustion wave in a heterogeneous medium. Whereas the one-dimensional function describes well a rough-scale structure of the wave characteristics of combustion (the average rate, the mean degree of conversion, etc.), transition to microscopic scale turns out need a real heterogeneous structure of medium to be taken into consideration. Fig.7 shows a typical microstructure of Ti + C(graphite) mixture.

Stereological treatment of this image showed that metal particles form a spatial framework, each particle being in contact, in average, with three particles, Nonmetal (carbon) particles do not form a continuous framework. The quality of contact between particles is not less important than the number of contacts. As known, heat conductivity of powder mixture may be many time less than that of the bulk conductivity of each separate powder particles because of low heat conductivity of the contacts. Omitting mechanism of this effect it is to say that all of the above is typical for SHS charges. Measurements of thermophysical parameters of SHS mixtures (Ref.18) showed their heat conductivity to range 0.63 to $0.83 W \cdot m^{-1} K^{-1}$ (a thermal diffusivity of $4.7x10^{-1}$ to $6.2x10^{-7}$ $m^2 S^{-1}$ at room temperature) while the heat conductivity of aluminum and titanium is 238 and 21.6 $W\ m^{-1} K^{-1}$, respectively (Ref.19). Transport factors for a heterogeneous mixture strongly depend on porosity (Ref.20).

These are the specific features of structure of heterogeneous medium considered above which cause a complex twisting form of the combustion front which is observable even at a 10-20 fold magnification. such results were obtained by Levashov et al. (Ref.21) with the use of high speed cine camera. Experiments carried out by Eshina with co-workers (private communication) included quantitative treatment of macroimages of combustion front. The form of front and dynamics of its change with time are shown in Fig,9. A sequence of stills makes it possible to measure the velocity of a separate point of front at every moment of time (or, properly speaking, the projection of this velocity vector to the axis of SHS wave propagation). The results of these measurements presented in Fig.10 show that instantaneous front velocity oscillates randomly around its mean value, the amplitude of oscillation hardly being able to be accounted for within the limits of current combustion theory. Let us consider basic ideas suggested for theoretical explanation of the observed phenomena.

Theoretical considerations

Typical for the one-dimensional model of SHS wave is aplitting of the whole of a wave complex into zones of chemical and structure transformations. A "traditional" approach worked out by Khaikin, Merzhanov, and Aldushin (Refs.22-24, 1, and 11) is concerned with only chemical reaction and heat evolution zones while a particular structure of products (phase composition and microstructure) is not considered yet. It is assumed, however, that a layer of stable products grows between reacting components as the reaction proceeds, i.e. the reaction occurs

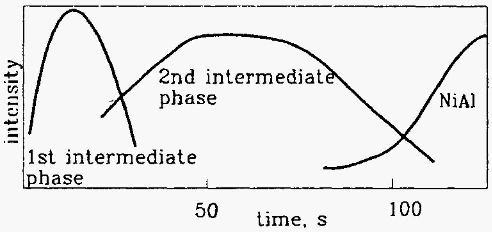


Fig.4. TRXRD analysis of the Ni-Al system combustion.

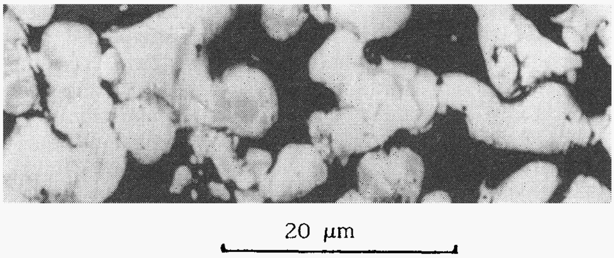


Fig.5. Microstructure of Ti + C mixture

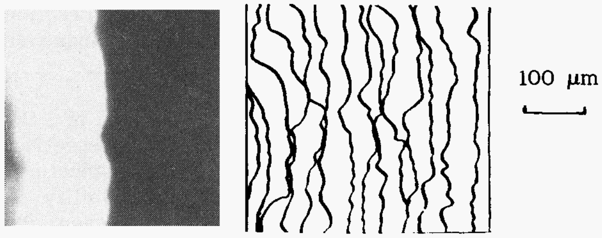


Fig.6. Form of SHS-front (a) and dynamics of its change with time (b) for Ti + 0.6C system.

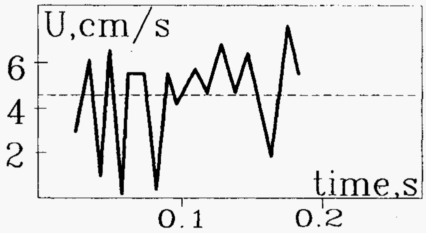


Fig.7. Local velocity of combustion front shown in Fig. 6.

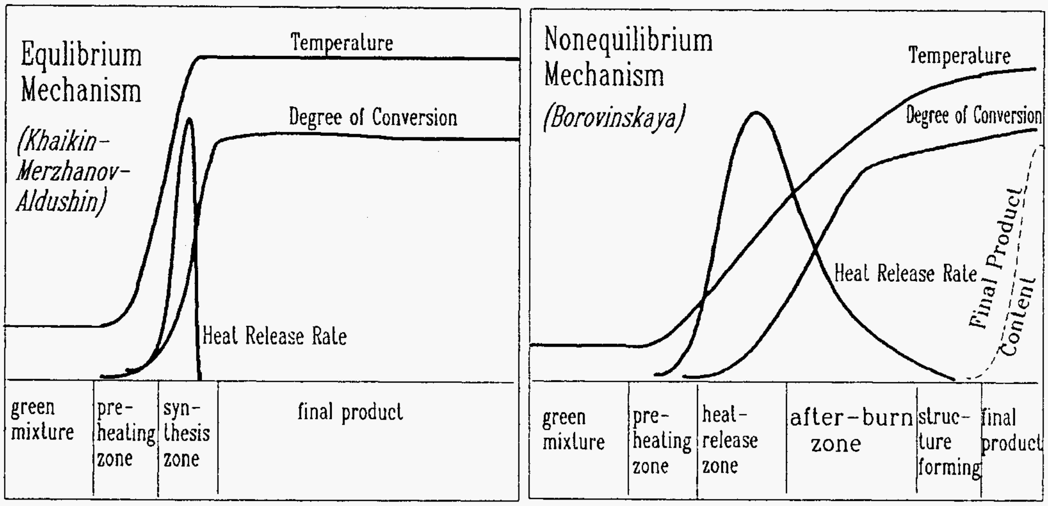


Fig.8. One-dimensional structures of an SHS-wave.

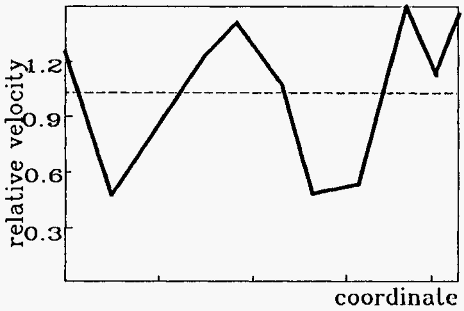


Fig.9. Calculated local velocity for a two-dimensional lattice with randomly arranged pores.

Table 2. SHS-quenching

Quenching method	max cooling rate, k/s
In liquid Ar	≃ 10^2
In the werge or by cold wall	up to $3\cdot10^3$
By water jet (jet velocity 150 m/s)	up to $1.6\cdot10^4$

at equilibrium. In a nonequilibrium mechanism suggested by Borovinskaya (Ref.2) the structurization region is already distinguished as a separate zone of SHS wave which may not coincide with the chemical reaction zone. One-dimensional combustion structures corresponding to equilibrium and nonequilibrium SHS mechanisms are shown in Fig.11 (Ref.1). As data describing a complex structure of combustion wave were accumulated, theoretical works taking into account the multi-dimensional nature of the process appeared. Yhe basis of this approach was founded already in early studies by Khaikin and Aldushin (Ref.25) and in the work by Hardt and Fang (Ref.26).

Considering a layer model of heterogeneous medium Khaikin and Aldushin came to the conclusion that there in a system of equations describing the combustion wave in a given medium exists a small parameter $\varepsilon = D/a\gamma$, where D and a are the maximum values for reaction diffusion and temperature conductance coefficients, respectively, in the given combustion model, and a parameter $\gamma = RT_c^2/E\ (T_c - T_o)$, where T_o is the initial temperature, T_c the combustion temperature, and E the apparent activation energy. After some analysis Khaikin and Aldushin showed the temperature drops at distances of about the layer width in the direction perpendicular to the layer $\Delta T_\perp$ to be approximately equal to $\varepsilon RT_c^2/E$. Evaluations of parameter ε have given $D/a < 10^{-3}, \gamma \simeq 0.1$, and $\varepsilon < 10^{-2}$ for condensed systems, hence, $\Delta T_\perp \ll (T_c - T_o)$. This inequlity means that a temperature distribution in combustion is almost of the onedimensional type along the front propagation, i.e. it comes to be a theoretical substantiation of the above considered onedimensional models of combustion wave structure. But consideration of the parameter ε makes it possible to see the limits of applicability of such approach. The smallness of ε reflects the fact that the transport of component by diffusion through a layer of solid products takes place much slower than heat transfer to a colder part of the system. If going out of the limits of this model and assuming the reactant transfer to be realized via other mechanisms (capillary volume and film flow of melts , gas phase transport, etc.), the rates of substance and heat transfer turn out to be comparable. The above considered experimental data on high thermal resistance of interparticle contacts decreasing the apparent value of heat conductance should be taken into consideration. Thus, the conditions of existing of small parameter ε are not fulfilled. E.g., a time of capillary impregnation of a layer with a thickness l can be approximately expressed as τ_{cap}, where σ and η are the surface tension and the viscosity of melt, respectively, and r the radius of capillaries. Comparing this value with the characteristic heating up time $\tau_{th} \sim l^2/a$ we get $\tau_{\tau\eta}/\tau_{cap} \sim \sigma r/ 2\eta a \simeq 300$ (in conditions of $\delta = 1650$ mN s^{-1}, $\eta = 5.2$ mN s m^{-2} for titanium at the melting point, $r = 10^{-6}$m, and $a = 5 \times 10^{-7}$ $m^2 s^{-1}$ as given by the above considered literature data), i.e. the substance transfer occurs more rapidly than equalization of temperature along the front does. Experimental evidences for existing of different mechanisms of mass transfer will be considered later. Here it is important to emphasize that the existence of these mechanisms results in thermal heterogeneity and none-one dimensionally of models of SHS wave were developed in theoretical studies concerned with spinning combustion (Ref. 27). However, the first models taking into account thermal heterogeneity of medium and random nature of interaction of powder particles appeared only recently (Refs. 28 and 29). Calculated combustion wave temperature maps sow a structure similar to the one observed experimentally (Ref. 21). As we know, models for combustion wave in heterogeneous mixtures with random contacts between particles are being worked out at present in many research centers. Any results have not been yet published but rapid development of this area in coming years can be anticipated. Figure 9 shows a local velocity oscillations calculated for a two-dimensional lattice with randomly arranged pores (Ref.30). Clearly seen there is the nonuniformity of the wave which determines conditions of synthesis and structurization of combustion products to a great extent.

FORMATION OF MICROSTRUCTURE OF PRODUCTS IN SHS-WAVE

Experimental techniques and results

Combustion wave quenching. Quantitative information on phase composition and microstructure of products in different zones of SHS wave can be obtained by fast cooling of burning sample so that to extinguish the combustion and to chill all transient states of reactants and products. This procedure was called SHS quenching. The rate of cooling must be sufficiently high for the "frozen" combustion wave to reflect adequately the processes occurring for the time of combustion propagation. There are fem variations of the procedure of SHS quenching worked out to the present. Their characteristics are given in Table 2. Quenching in liquid argon was practiced first (Ref.31) but the formation of gaseous interlayer around a burninghot sample retarded heat withdrawal so the chilling rates were comparatively small. A higher rate is provided with methods based on heat removal to a cold metal wall; these are combustion of a mixture pressed in a wedge-shaped cut out of a bulky cooper body (Refs.32 and

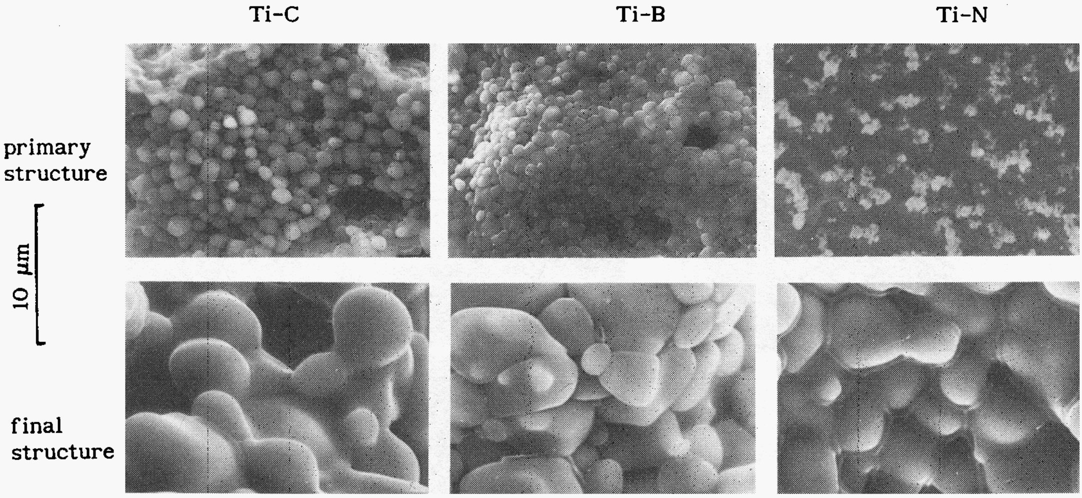


Fig.10. Microstructures of quenched SHS-waves.

33) and quenching of a thin burning layer by metal plates which are slapped together after the combustion has begun (Ref.33). But finally, Kulebyakin and Khusid with their coworkers from the Institute of Heat and Mass Transfer (Minsk) quite recently decided to come back to quenching by means of a liquid. In order to prevent the formation of gaseous interlayer, they played a powerful jet of water on a sample so that its velocity approached 150 $m\ s^{-1}$ (Ref.34). From preliminary data kindly presented by the authors it is seen that a maximum rate of cooling is attained with the use of this method but a quenching time is nearly the same as for heat removal with a cold wall.

Investigation of samples prepared with the use of the latter three procedures of quenching (2 and 3 in Table 2) shows practically identical picture of structurization. Besides, quite a similar sequence of microstructure transformations is observed in metal-carbon (Refs.32 and 33), metal-boron (Ref.32), and metal-nitrogen (Ref.35) type systems with the melting metal component, as can be seen from Fig.14. Consequently, there some general regularities of formation of microstructure of SHS products common for the above systems. The most important common feature is occurrence of the process in two stages which are called primary and secondary structurization. The former takes place in the leading zone of combustion wave simultaneously with the chemical reaction. The structure of initial reactant mixture undergoes, the reaction product is formed, and large amount of heat is evolved in this zone. To the moment when the chemical reaction is actually completed and the reactants have been consumed, the product with a primary microstructure is formed. As one can see from Fig.14, very fine grain structure with a grain (crystallite) size of 0.1 to 1.0 μm, or by 2-3 orders of magnitude less than that of initial metal particles, is typical for this product. Note that the primary product can have no structure at all being in its liquid or amorphous state. The primary structure of product is a starting point in the formation of structure of a SHS material. A high temperature (up to 3000-4000 K) in this zone enhances the processes of sintering, coalescence and grain growth, and recrystallization, i.e. of the secondary structure formation. Therefore, the primary structure turns out to be transient, i.e. it exits for a very short time and quickly transforms to the structure of final product as shown in Fig.10. A quantitative characteristics for structure evolution can be a grain size of high-melting compound. Functions describing the grain growth in the region of secondary structurization are show in Fig.11. The observed rate of growth of the mean grain size ranges within 1-30 μm/s, i.e. the primary small grains grow to several micrometers or even tens micrometers right in few seconds after combustion front passage.

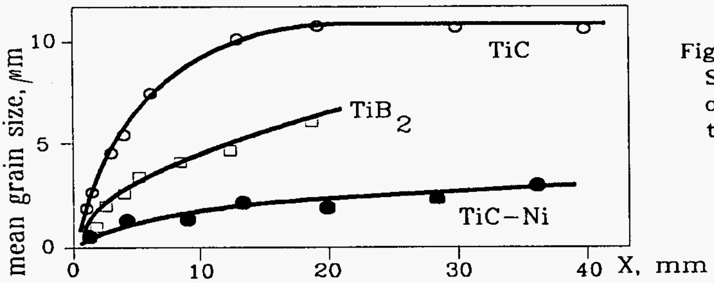


Fig.11. Kinetics of grain growth in some SHS-systems (according to the results on quenching). x=0 corresponds to the combustion front position.

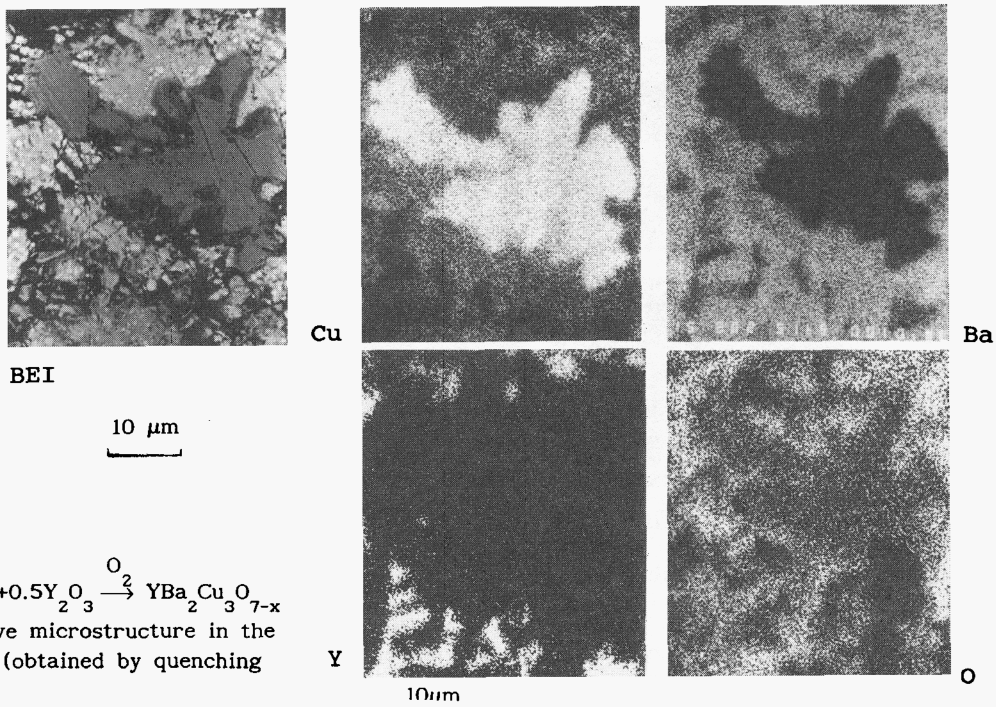


Fig. 12.
The $3Cu+2BaO_2+0.5Y_2O_3 \xrightarrow{O_2} YBa_2Cu_3O_{7-x}$ combustion wave microstructure in the reaction zone. (obtained by quenching technique).

The most complicated and diverse picture of structurization is observed upon quenching of so-called hybrid systems in which some reactants are in condensed state and the other ones in the gas state. The SHS process in these systems occurs with filtration of gaseous reactant through sample pores, which leads to very wide secondary structurization zones, their shape and size depending on sample geometry, gas pressure, porosity, and some other parameters. A significant contribution to understanding of structurization in such systems was made in works by Pityulin et al. (Ref.36). They showed, for instance, that the self-propagating high-temperature synthesis of tantalum nitride produces only seminitride Ta_2N immediately in the combustion front which can be isolated in a pure form with the use of quenching. In the after-burning zone this intermediate product transforms to the cubic or hexagonal modification of TaN depending on conditions of the synthesis. Some interesting results were obtained by Munir et al. (Ref.37) for the $Ti\text{-}N_2$ system. It turned out that under certain conditions of combustion of titanium in nitrogen a thin layer of nitride was formed on the surface of metal particles at the beginning of interaction and then the layer was dissolved in the metal but at the end of the synthesis the nitride was formed again throughout the whole volume of reacting mixture. These results are in good agreement with data obtained by Mukasiyan at al. (Ref.35). In recent years, in relation to the outlined break-through in the area of superconductors, the self-propagating high-temperature synthesis of many superconducting ceramics including $YBa_2Cu_3O_{7-x}$ was mastered (Ref.38.,39). The latter ceramics is obtained in the combustion of $3Cu + 2BaO_2 + 0.5Y_2O_3$ mixture in oxygen. The mechanism of phase formation in this system was also disclosed with the use of quenching techniques (Ref.40). The macrostructure of the leading zone of reaction is shown in Fig.16. A high warm up rate in the combustion wave results in the fact that the cooper metal directly enter the reaction with the melt containing barium and oxygen. Particles of Y_2O_3 appear, as seen from Fig.16, in peripheral regions of the reaction; they enter interaction in the after-burning zone.

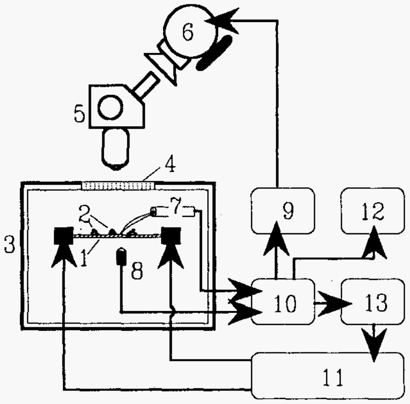
The Y_{123} phase is formed in fine crystals by crystallization from solution in the melt. A mechanism of the interaction can be approximately described with the following scheme:

$$\begin{array}{ll} & \overset{O_2}{\nearrow}\ Ba_2Cu_3O_5 + 0.5Y_2O_3 \xrightarrow{O_2} YBa_2Cu_3O_{7-x} \\ 3Cu + 2BaO_2 + 0.5Y_2O_3 & \\ & \searrow\ 2CuBaO_2 + Cu + 0.5Y_2O_3 \longrightarrow 0.5Y_2CuBaO_5 + 1.5CuBaO_2 + Cu \end{array}$$

which shows that the combustion can occur in the gasless mode but the Y_{123} phase is formed only with a sufficient oxygen gas supply.

Reaction cell model experiments. In a real combustion wave, a variety of phisico-chemical processes takes place simultaneously so that it is not the easy matter to distinguish and study any one of them. This can be done much easier if considering the interaction of one particle of reactant with another reactant, i.e. an elementary reaction cell (cage). This microscopic system (cage) can be heated at a rate comparable with the combustion wave, and cooled fastly if quenching of the transient states of products is needed. An approach like this was developed for metal-gas systems in electrothermographic studies (Ref.48). The idea of electrothermographic technique consists in heating a thin filament by electric current in the medium of gaseous reactant up to a temperature when the reaction products are formed on the filament surface. Under these conditions the reaction kinetics is monitored directly in the course of experiment by change in resistance of the filament and the structure of product is studied after cooling the filament.

Condensed systems are studied by means of fast controlled heating of particles of one reactant on the surface of thin foil made in another reactant (Ref.42). A schematic diagram of a reactor and a thermorgam of heating in comparison with the thermorgam of combustion wave are shown in Fig.13. Switching off electric heating results in fast quenching which makes it possible to study the initial stages of structurization. Spreading out of a low-melting reactant and nucleation of primary product crystals in the spreading front are illustrated in Fig.14 for Nb-B and Ti-C systems.



1-foil,
2-particles,
3-vacuum chamber,
4-quartz window,
5-microscope,
6-camera,
7-thermocouple,
8-photodiode,
9-camera launching unit,
10-temperature control,
11-heating element,
12-the temperature registration unit,
13-heating element switch

Fig.13. Schematic drawing of the device for model experiments (Institute of Structural Macrokinetics)

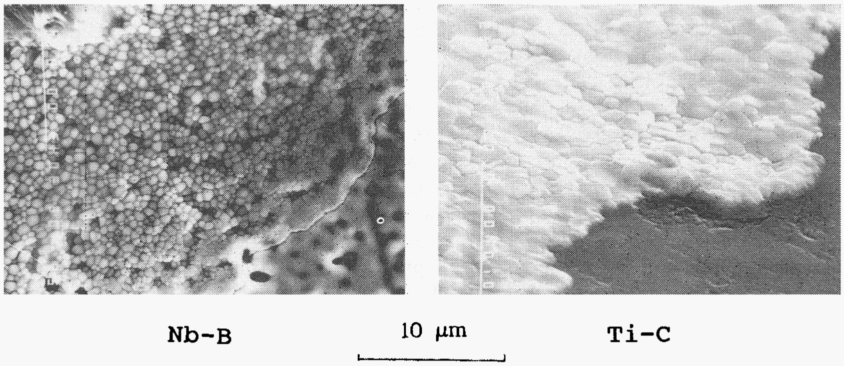


Fig.14. Microstructures of model "reaction cells" for Nb-B and Ti-C systems

Theoretical representations of product structurization

Theory of structurization in a SHS process has not been yet developed as a whole. To account for processes of secondary structurization the mechanisms of Ostwald ripening (Ref.32, 33, 43 and 44) and the Lifshits-Slezov-Wagner theory (Ref.45) are employed. Nekrasov et al. in a series of works (Ref.46 and 47) theoretically analyzed an interaction model implying that the layers of all intermediate phases are formed at the boundary between reactants, boundary conditions for each layer being determined from the phase diagram. Thus, the formation of product occurs as the growth of the corresponding layer. The layers of intermediate products first increase but then they decrease and disappear. Such a model is useful in the analysis of kinetics of interaction though it does not permit conclusions on a real microstructure of products to be drawn and does not take into account new experimental data in this field. Formation of porous structure in combustion was theoretically considered by Munir and Wang (Ref.48). They showed thermal migration to be an important cause of formation of pores in SHS process.

A very important problem which has not been yet solved is that of interrelation of microstructure of product with the initial reactant structure and conditions of self-propagating high-temperature synthesis. Having analyzed experimental data concerned with this issue, let us make some assumptions. A determining effect exerted on structurization is created, to our opinion, by the parameters of SHS wave such as temperature profile, presence and composition of melts, volatile impurities or dopes, mechanical or other action on a burning sample, etc. As far as dimensions and morphology of rectants are concerned, they are not related to the structure of product directly though determine the combustion features in some way and, hence, exert indirect effect on the product structure. For example, the use of coarse particles of reactants can lead to underburning and decrease in combustion temperature which will result in decrease in product grain size.

It is possible to obtain material with a prescribed structure by changing the initial structure through action on the reaction zone of combustion wave and/or affecting the process of secondary structurization. In general, the known cases of successful controlling the structure confirm fruitfulness of this way in spite of the fact that many of these technological solutions have been found empirically.

SOME EXAMPLES OF PRODUCT STRUCTURE CONTROLLING

Figure 15 shows changes in microstructure of carbide grain sizes caused by various actions on the Ti + C + Ni combustion wave. As seen from the figure, finely dispersed grains can be obtained with different methods, viz. by decreasing combustion temperature, introducing modifiers, acting on the process or its products by shock wave or ultrasonic wave, by fast cooling of a sample after the synthesis. The next example given in Fig.16 shows a possible way of affecting both microstructure and crystal structure of a product. Using the same reactants silicon powder and gaseous nitrogen but interfering the processes of synthesis and structurization it is possible to prepare either α- or β-forms of silicon nitride. A strong difference between particles of these forms and silicon particles is seen from Fig.16 which indicates one more dominating effect of structurization processes on the microstructure of products compared with the influence of structure of the initial medium. Controlling materials microstructure as well as distribution of chemical elements and phases is vital for production of functionally gradient materials. At present, there are two ways of solving the problem as we see it (Fig.17). The first one (Fig.17c) consists in creation of a concentration profile in a starting charge to correspond to the profile which has to appear in the material (playing regard for profile diffusion in the synthesis). This sort of approach is worked out by Sato et al.(Refs.49 and 50). they obtained impressive results inventing an automated procedure of preparation of charge specimens with required reactant concentration profiles. The second way (Fig.17a and b) worked out by Pityulin et al. (Ref.51) is based on the use of impregnation and migration processes occurring simultaneously with SHS and with forced compaction of porous hot product. In this case the final concentration gradients may differ considerably from these on the stock charge. The formation of very steep profiles is possible as well as paradoxic distributions of a type shown in Fig.17b may happen when the maximum concentration of element (nickel) in the finished article is found in essentially another place than it has been in the billet. A prospective procedure for affecting microstructure consists in the use of medium-frequency elecromagnetic (MFE) waves. This procedure was developed by Trofimov and co-workers (Ref.52). The spirit of this technique is that, even consisting of metal particles, an initial charge possesses, as has been already mentioned; low conductivity and is thus transparent for microwave radiation. When a melt appears in the reaction zone, the conductivity dramatically increases and this zone absorbs the energy of MFE field. Thus it is possible to affect selectively separate zones of combustion wave by changing, e.g. thermal conditions of the synthesis. It is seen from Fig.18 that the action of MFE field on the combustion and structurization zones of Ti + C + Ni mixture results in MFE increasing carbide grains in the product. Not that since it is quite easy to control the intensity of MFE field and to switch it on or off, this procedure appears to be very promising as far as controlling SHS product structure is concerned.

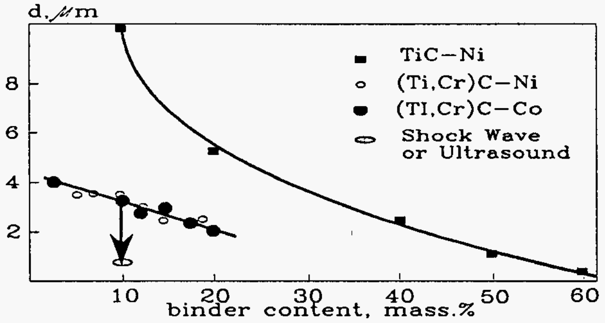


Fig.15.
Sizes of carbide grains in TiC-Ni based cermets.

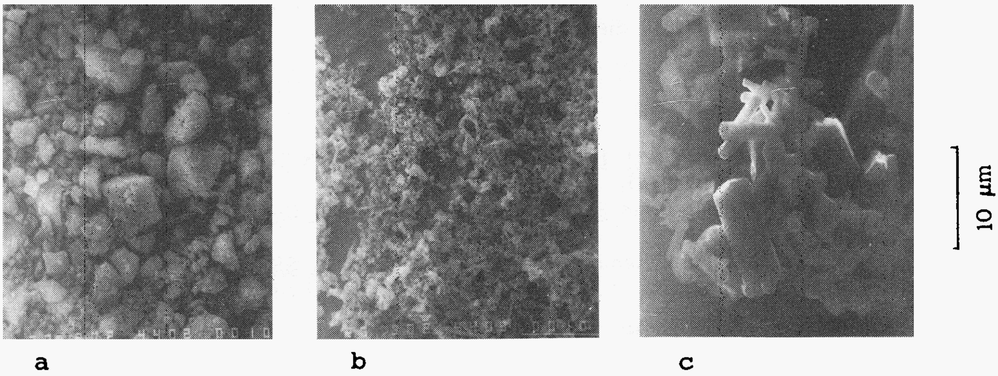


Fig.16. Parent silicon powder (a), α-(b) and β-phase of Si_3N_4 produced by SHS.

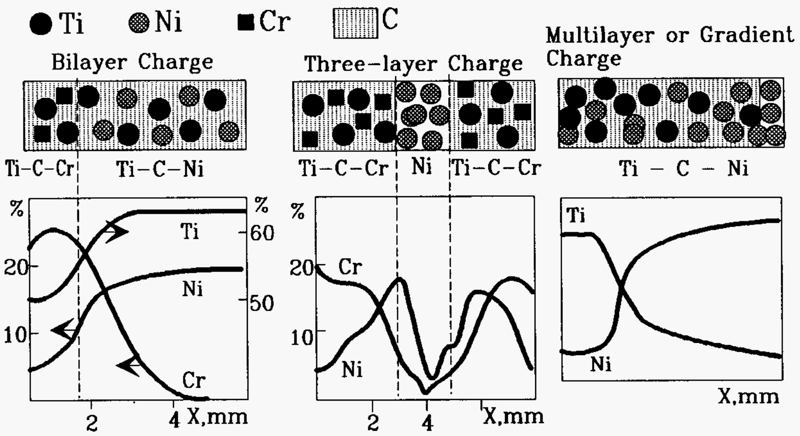


Fig.17.
Functionally gradient materials.
Kinds of production methods.

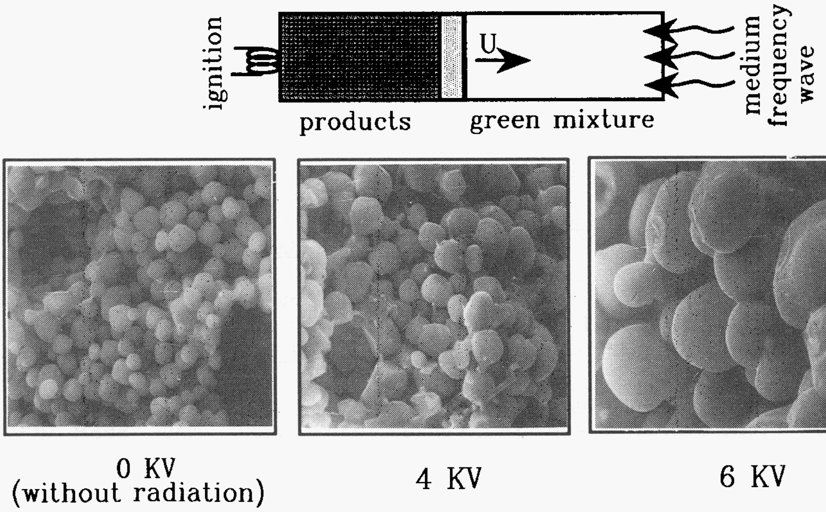


Fig.18. Medium frequency electromagnetic wave influence on 65TiC - 35Ni cermet microstructure.

CONCLUSION

A limited volume of this paper does not permit us to consider all of works performed in the field of structural macrokinetics in recent decade so only the most representative, from our point of view, results have been analyzed. As we see it, the consideration of these results convincingly shows that a way to structure control of SHS products and materials lies through thorough investigations of mechanism of structurization of products and structure of the combustion wave itself.

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