Modifications of SHS processes

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Abstract- Proceeding from the kind of the chemical bond, the majority of the processing versions of the self-propagating high-temperature synthesis (SHS) of the refractory inorganic compounds can be divided into two groups: element and oxide. By performing the chemical transformation in the combustion mode and employing the high exothermic nature of the initial systems, processing techniques and special equipment, it is possible to tackle the various practical problems and obtain the SHS spectrum of the products, namely: powders and compacts (TiC,SiC, CrC2,
TaC, B4C, TiB2, CrB2, MoSi2, TiSi2, VSi, TiN, BN,AlN, Si3N4, YBa2Cu3O7-x and others), high-dense items manufactured from the above-listed materials (rollers,pipes, milling cutters, cutters, electrodes, bushings, rings etc.) and the items with the preset porosity (filters), as well as to weld the refractory materials (graphite with graphite, steel with carbide alloys, molybdenum with molybdenum and so on) and to obtain the protective coatings of various thickness.

INTRODUCTION

In 1967, A.G.Merzhanov, I.P.Borovinskaya and V.M.Shkiro have discovered the phenomenon of self-propagating high-temperature synthesis of refractory inorganic materials: carbides, borides, silicides, hydrides, oxides, chalcogenides, carbide alloys, composite materials and so on (ref.1). Within more than 20 years, the school of professor A.G.Merzhanov fundamentally investigated the SHS process developed the various SHS processing techniques and special equipment obtained the wide range of materials, items and coatings , as well as studied the raw materials and commercial efficiency for some practical problems (ref.1-35).

The chronology of creating (editions) of the SHS versions in the USSR is as follows: 1967 - the long-propagating high-temperature synthesis of the elements in vacuum, inert gas or reacting gas (ref.1); 1975 - the long-propagating high-temperature synthesis with reducing medium, SHS metallurgy, centrifugal SHS casting, SHS surfacing (ref.22); 1976 - SHS welding of refractory materials (ref.23); 1978 - SHS process with sintering under high gas pressure (P>108 Pa) (ref.5); 1980 - SHS process with action of shock waves (ref.34); 1981 - SHS process with extrusion (ref.35); 1986 - SHS process with the use of gas-transport medium (ref.9). At the present time, many cities of the USSR have the scientific and engineering centers of the SHS processes (Moscow, Erevan, Tbilisi, Alma-Ata,Minsk, Samara, Dnepropetrovsk, Tomsk etc.). At the beginning of 80th, the scientists from the USA (ref.36,37,43 to 45,51 to 54) Japan (39 to 42,46,48 to 50,56 to 58) and other countries also started to investigate the SHS processes.

SPECIFIC FEATURES OF SHS PROCESSING TECHNIQUES AND COMBUSTION PROCESS

In the processing steps, three stages can be distinguished: preliminary operations, SHS process and the working process of the self-propagating high-temperature synthesis (ref.15). To obtain the compacts and items, the additional operation is performed: after combustion is over, the mixtures heated up to the high-temperature are subject to pressing, extrusion, explosion reduction, rolling etc.).
The most specific stage among the above-listed is the SHS process proper. It is effected in the following way. The initial mixture in the form of pellets or in bulk prepared for synthesis is placed in the reaction envelope (reactor) and becomes ignited in any point of the surface layer. After ignition (within the small time period), the combustion front is formed which spontaneously moves over the mixture. The linear average rate of combustion \( U_0 \) is in an interval of 0.1 to 10 cm/s depending on the chemical composition of the mixture, reagent dispersity and other parameters. In the front of combustion, the thickness of which amounts 0.1 to 1 mm, the initial mixture is chemically transformed into the synthesis products. The chemical transformation is accompanied by evolution of great amount of gases which heat the synthesis products up to 1000 to 4000°K (ref.15).

When developing the process techniques, the specific features of interaction of the condensed and gaseous phases of the self-propagating high-temperature synthesis process shall be taken into consideration. In the combustion wave, the gaseous substances can be evaluated \( \text{H, N and so on} \), be absorbed (filtration combustion - synthesis of nitrides and hydrides) or be practically absent (free-of-gas combustion (ref.6 to 8).

Volume \( V \) of the gaseous products reduced to the nominal conditions may amount from 10 to 100 per 1 kg of the initial mixture. The above-listed peculiarities must be taken into account when developing the processing techniques and equipment for combustion of large amounts of products and to provide for the high quality of SHS materials and items. At the present time, the SHS processing technique uses the following combustion modes (Fig.1): open flame (a), combustion in the tight volume (b), combustion with the dosed outlet of gases from the volume (c), combustion in the continuous-flow reactor (d).

Systems (a), (b), (c) provide for gas outlet from the reaction vessel in the process of combustion and all the gases formed in the process of combustion (see b) remain in it. Systems (b) and (d) make it possible to introduce active gas \( N_2, H_2 \) into the chemical reaction. Besides, system (b) makes it possible to initiate the SHS process in vacuum.

In all versions, the problem of reactor overheating by the synthesis high-temperature products exists when their mass is great. In versions (b) and (c), simultaneously with heating of the reactor walls the pressure in it rises.

This may lead to reactor damage in the process of the self-propagating high-temperature synthesis. If we assume that the contact of the heated SHS combustion products with the reactor wall is ideal, the temperature of reactor wall can be estimated according to formula (ref.28):

\[
T_k = T_o + \frac{(T_c - T_o)}{z/(l + z)}
\]

where \( T_o \) is the sintering mixture initial temperatures; \( T_c \) is the combustion temperature; \( z \) - is the ratio of the thermal activities of the sintering mixture versus the reactor.
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For the typical values of the parameters \( T_0 = 3000^\circ \text{K}, T_0 = 3000^\circ \text{K}, z = 1 \), we have the 
\( T_k \) value which is approximately equal to 1650\(^\circ\text{K}\). The temperature in the reactor wall can be considerably reduced by placing the graphite casing between the wall and sintering mixture or by cooling the reactor with running water. In the last case, according to the thermocouple measurements, temperature \( T_k \) can be reduced down to about 100\(^\circ\text{K}\). The dynamics of the reactor pressure in the process of combustion depend upon combustion shown in Fig. 2.

It is evident that the maximum pressure in the reactor \( (P^*) \) should not exceed some critical pressure value \( (P^+_{\ast}) \) determined by the reactor strength:

\[
P^* \leq P^+_{\ast}
\]  \hspace{1cm} (2)

Assuming that the destruction of the reactor is connected with the yield point \( \sigma_y \) for calculation \( P^+_{\ast} \), proceeding from force balance, we have:

\[
P^+_{\ast} \leq 4\sigma_y \Delta/d_p
\]  \hspace{1cm} (3)

where \( d_p \) is the internal diameter; \( \Delta \) is the reactor wall thickness. As it follows from formula (3), in order to increase the maximum permissible pressure in the reactor, it is necessary to increase the thickness of its walls and to reduce the diameter. It should be noted that value \( \sigma_y \) in expression (3) quickly decreases when the temperature rises.

The maximum pressure in the tight reactor \( (P^*) \) in the adiabatic approximation can be estimated by the formula:

\[
P^* = P_1(T) + P_2(M/V_g)
\]  \hspace{1cm} (4)

where \( P_1 \) is the part of the pressure which is built up at the expense of gas heating in the reactor; \( P_2 \) is the part of the pressure which is created due to gas evolution from the combustion products; \( T \) is temperature; \( M \) is the sintering mixture mass in the reactor; \( V_g \) is the sintering mixture specific gas-evolution value.

If we assume that the equilibrium temperature in the reactor \( (T = T_0) \) is equal to each other, it follows (for calculations \( P_1 \) and \( P_2 \)) that:

\[
P_1 = P_o (T_g/T_0)
\]  \hspace{1cm} (5)

\[
P_2 = P_o (V M/V_g) (T_g/T_0)
\]  \hspace{1cm} (6)

where \( P_o \) is the initial pressure in the reactor; \( P_a \) is the atmospheric pressure; \( V \) is the reactor volume; \( \varepsilon \) is the fraction of the vacant volume of the reactor.
Proceeding from formulas (4) to (6), it follows that the maximum pressure in the reactor is simply regulated by fully loading the reactor ($M_0$ $V_p$, c) and by its initial pressure ($P_0$). For the typical values of parameters $P_0 = 10^6$ Pa, $P_p = 10^5$ Pa, $T = 30000\text{K}$, $T = 300\text{K}$, $M = 10$ kg, $V = 10^{-2}$ m$^3$/kg, $V_p = 2 \times 10^{-2}$ m$^3$, $c = 0.5$ we obtain the following estimation value: $P_1 = 10^7$ Pa, $P_2 = 10^7$ Pa and $P' = 2 \times 10^7$ Pa. For the multipurpose reactors developed in the Institute of Structural Macrokinetics of the USSR Academy of Sciences, value $P'$ amounts to $(2$ to $3) \times 10^7$ Pa (taking into account the safety margin) and therefore estimation value $P'$ satisfies equation (4). It should be noted that for the filtration synthesis of nitrides and hydrides, the addent in formula 4 has the negative sign since in this case the gas is absorbed but not evaluated.

For the SHS reactor provided with the dosed outlet (Fig.1c), the maximum pressure is calculated proceeding from the balance of the gas feed from the combustion front and reactor gas-escape pipe (ref.28).

Assuming that the filtration of gases from the synthesis products does not limit the gas vent (discharge) process and the pressure drop in the gas-escape channel can be averaged out, we have that (ref.28):

$$P' = P_a + \left(\frac{U M}{L K}\right) \left(\frac{d_p}{d_k}\right)^2$$

where $U_M$ - the mass rate of combustion; $L$ and $d_k$ - length and diameter of the gas-escape channel; $K$ - the proportionality factor.

It pressure in the given formula (9) that the simplest method of adjusting the pressure in the given type of the reactor is to change the diameter of the gas-escape channel.

**TYPES OF SHS PROCESSING TECHNIQUES**

According to the classification suggested by professor Merzhanov A.G. (ref.15), all known SHS processing techniques can be divided into six types: SHS process of manufacturing the blanks and powders, SHS sintering, SHS power compacting, SHS metallurgy, SHS welding and the production process of the SHS coatings. Within the framework of the said SHS versions, it is possible to obtain the wide spectrum of powders and compacts, items and coatings. The quality and process of manufacturing the SHS materials, items and coating application are controlled both with the help of the internal (composition and density of the sintering mixture, relation and dispersivity of reagents etc.) and external parameters (gas pressure, compacting pressure, centrifugal action, action of the electromagnetic field and ultra sound, initial heating by various heat sources and so on).

It should be noted that in the USSR, the intensive works are performed since 1975 pertaining to manufacture of the compact refractory materials and items, thin and thick coatings by the SHS method. Anyhow, the publication of the papers on these tendencies was limited. At the present time, we wait for the publication of the great amount of papers and reviews dealing with the above-mentioned tendencies of the SHS processes.

**SHS PROCESS OF MANUFACTURING BLANKS AND POWDERS**

The SHS processing technique for manufacturing powders and blanks is the simplest one. For performing the main technological SHS operation, the various types of the reactors are developed in the USSR which are differ from each other by the method of combustion, dimensions and different design versions. Since 1972, the universal SHS apparatus is used for mass production (ref.21) which is essentially a high-strength steel cylinder provided with two tight locks and quipped with the reactor gas inlet/outlet systems, water cooling and ignition, check and remote control of the SHS process. The reactor design makes it possible to conduct synthesis in vacuum, in the medium of inert gases (Ar, He) and reacting gas ($N_2$, $H_2$) under the pressure of up to $2.5 \times 10^7$ Pa, in the mode of the tight combustion and dosed gas discharge (see Fig.1b,c). Depending on the volume of the working chamber, the output of the universal SHS apparatus amounts to 10-20 t per one year.

The main role of the inert gas at the SHS process used to manufacture the refractory inorganic compounds from the solid elements (Ti+C, Si+C, Zr+B, Mo+Si and others) is to create the protective atmosphere which hinders the penetration of air oxygen and nitrogen into the SHS products. As a rule, the SHS product (after removing from the reactor) is essentially the sinter with low strength and can be mechanically powderized (ref.21).
For synthesizing the oxide mixture with Mg and nonmetals (see schematic 2), the increased pressure of argon both ensures the protection against the product contamination and suppresses the evaluation of volatile component and also helps to increase the completeness of chemical transformation (ref.7). After grinding the sinter, the final product (TiC, TiB$_2$, B$_4$C and others) is purified of MgO by dissolving it in the hydrochloric acid. After dissolving (without the additional grinding, small-dispersed SHS powders are obtained). This SHS version is referred to the SHS reduction stage.

To obtain the nitrides, carbonitrides and hydrides (TiN, Ti-C-N, BN, Si$_3$N$_4$, AlN, TiH$_2$, ZrH$_2$ and others), the active gas pressure is built up in the reactor volume (N$_2$, H$_2$). In this version, the SHS nitrogen pressure is the important parameter which defines the completeness of absorption of its elements (ref.12). Besides, the complete chemical transformation is greatly influenced by the filtration characteristics of the mixture and the combustion forms (ref.18).

Except for the universal SHS apparatus and various versions of its design, the SHS process of producing powders and materials uses the continuous-flow reactors. The processing schematic (Fig.1d) and the design of the continuous-flow reactor were developed by the author together with Merzhanov A.G. and Borovinskaya I.P. in 1974-1975. The investigation of the regularity and mechanism of the SHS process with forced filtration in the continuous-flow reactor makes it possible to work out the methods which permit to obtain nitrides (TiN, TaN, NbN) carbides and carbonitrides (TiC, Ti-C-N), as well as the nitride coating on titanium (ref.32). Later on, this procedure was used to obtain the superconductive ceramics and other materials.

At the present time, the SHS process makes it possible to obtain more than 500 materials: carbides, silicides, nitrides, hydrides, carbonitrides, chalcogenides, oxides (ref.7,12,14,36,37,42) and so on. On an industrial scale, the SHS process of manufacturing the powders was introduced at the end of 70 at the Kirovokan plant of high-temperature heaters where molybdenum disilicide was produced (ref.15). As a result, the SHS process revealed its evident advantages in comparison with the furnace process, namely: the increase of the production rate and quality of the heaters, decrease of the energy and labour consumption, as well as the increase of the heater service life etc. Besides, the said SHS process for producing the silicon carbide powder was introduced in Japan (ref.70). This process is employed for manufacturing the items, refractory bricks and abrasives.

**SHS SINTERING**

In the process of self-propagating high-temperature synthesis, the synthesis products heated to a high-temperature become sintered, but their strength is not high. Usually, the compression strength for the sinters obtained in the reactor at a pressure of $P=10^5$ to $10^7$ Pa does not exceed $10^6$ Pa. The density and strength of the sintered materials can be considerably increased by conducting the self-propagating high-temperature synthesis in the tight reactors at a pressure of $10^7$ to $10^9$ Pa (ref.5). For carrying out this kind of synthesis which is called gas-static version, some special apparatuses were made in the USSR, in 1975 through 1979, (fig.3) which incorporate a high-strength reactor and a device for creating the gas pressure in the reactor (ref.26).
The device includes a booster and an oil station which helps to transfer the gas found in the cylinder or gas line into the reactor under a pressure of $5 \times 10^6$ to $1.6 \times 10^8$ Pa and to build up a pressure in it of up to $10^8$ Pa. This gas-static SHS process makes it possible to obtain the samples of titanium nitride with a porosity of 8 to 40 per cent, silicon nitride with a porosity of 40 per cent and a bending strength of $(1.2$ to $1.5) \times 10^8$ Pa, the composite materials based on SiC-Si$_3$N$_4$ having a porosity of about 5 per cent and a bending strength of $(3$ to $6.5) \times 10^8$ Pa at $T=1800^\circ K$. The gas-static SHS process makes it possible to obtain both the compact materials and the items with the preset shape and dimensions: electrodes and the items for electrolysis, crucibles for melting refractory and active metals, insulating tubes, rings and bushings for the oriented crystallization furnaces, corrosion- and erosion-resistant linings etc. The designs of the apparatuses existing in the USSR make it possible to obtain the items with a length of up to 25-30 cm and a diameter of up 8 cm. Some of the above-mentioned designs are used in the industry.

Great success in the technology of SHS-sintering under the high pressure of gas have been done in Japan in the works Y.Miyamoto, M.Koizumi et.al. beginning in 1986 (ref.39). Unlike the studies carried out by the soviet scientists, these works have not been dealing with the synthesis of the high-compact nitrides and their composites with other materials. The main task of their studies is to obtain the compact compounds of carbide and titanium boride with metallic bonds or oxides, as well as to manufacture the high-compact items of the complicated shape (ref.40 to 42). In these studies, the self-propagating high-temperature synthesis was carried out in the gas-static apparatuses HIP at an argon pressure of $(4$ to $10) \times 10^8$ Pa. The initial mixtures were consumed in the tight envelopes made of glass or metal. The form of the item is preset by the shape of the envelope. The SHS mixture is ignited by electrically heating the envelope or by the ignition mixture into which the envelope containing the mixture is placed. The SHS product is compacted after melting of the tight envelope. The combination of the SHS process with the gas-static compression makes it possible to obtain the compact value of 95 to 99 per cent.

In 1988, the samples of the compact material made of A1N-A1 were obtained in the USA having a diameter of 7.5 cm and a thickness of 1.3 cm. The compactness was 92 to 97 per cent of the theoretical value (ref.43,44).

**SHS POWDER COMPACTING**

The methods of the SHS sintering make it possible to obtain the compact materials but fail to achieve the free-of-pores state. This problem can be solved by subjecting the red-hot blank (after passing the synthesis wave) to the forced mechanical compacting. At the present time, we have several versions which combine the SHS process with mechanical compacting: SHS compaction (ref.20, 27, 30, 46 to 53), SHS extrusion (ref.35, 12, 15), SHS with explosion treatment (ref.34, 10, 54, 55) and SHS rolling (ref.53).

1. SHS compaction. The SHS compaction system which is most frequently used in the Soviet Union is presented in Fig.4 (ref.27,30).

![Fig.4. SHS Compaction Process](image-url)

**Fig.4. SHS Compaction Process**

- 1 - mould punch;
- 2 - heat insulator;
- 3 - SHS sintering mixture;
- 4 - mould;
- 5 - initiating device;
- $F_p$ - pressing force.

- **a** - pressing in heat insulator powder;
- **b** - pressing in hard mould;
For conducting the synthesis, the initial sample made of SHS sintering mixture is placed in a special mould and then the latter is positioned under the press punch. Then, the sample is subsequently ignited, kept under pressure and compacted. Further on, the pressure is relieved and the sample is unloaded from the mould. For compaction, used is made of the hydraulic presses having a force of 100 up to 2000 t. The compacting pressure amounts to more than 10^7 Pa. As a rule, the compacting in the medium of the heat insulator (Fig. 4a) is employed for obtaining the small-size plates and that in the "rigid" moulds (Fig. 4b), for obtaining the bulky items having a weight of up to several tens of kilograms with a complicated shape.

Most frequently, this SHS version uses powder mixtures Ti, Cr, Ni, Mo, Cu with C and B, as well as the oxide systems. The products of the synthesis are the high-compact materials and items made of synthetic solid tool materials, oxide-carbide and oxide-boride composite materials, as well as the high-temperature materials (ref. 15). As a rule, the porosity of the synthetic solid tool materials obtained under optimal conditions does not exceed 0.5 per cent. Depending on the composition of the synthetic solid tool materials, their hardness amounts to 86-93.5 HRA and the bending strength, 7 to 20·10^7 Pa. The SHS compacting process was used for obtaining the rollers for rolling metals, dies, press-tool equipment, cutting plates and so on. At the present time, the SHS processing technique for the cutting plates is in the stage of using on an industrial scale.

The like researches have been started in Japan in 1984 (ref. 46) and in the USA in 1985 (ref. 52) (combination of the SHS compaction process). In Japan, for building up the pressure, use was made of the hydraulic press and spring system (ref. 48). The said apparatuses helped to obtained the following compact materials TiB_2 (ref. 46), SiC (ref. 49), TiC (ref. 50) and TiB_2-TiC (ref. 48) having the compactness degree of 95 per cent relative to the calculated value. In the USA, the SHS compacting method helped to obtain TiC having a porosity of 5 per cent and TiB_2 with a porosity of 8 per cent (ref. 38, 51).

In 1985, the Australian scientists obtained compact materials MoSi_2-Al_2O_3 with a porosity of 0.5 per cent (ref. 46) using the SHS method with pressing and pneumatic press.

In 1987-1988 the works of N. Sata, H. Miyamoto, and M. Koizumi on functionally gradient materials TiB_2-Cu (ref. 40-42, 48) were published for the first time in Japan. Their utilization for cosmic technic and atomic reactors is supposed. Almost at the same time in the USSR, Merzhanov A. G. with collaborators started the investigations on creating the gradient materials having the height-variable composition. These investigations brought to creation of some gradient materials based on TiC with different distribution of solid and plastic (moldable) phases which were called the synthetic gradient materials. The main distinction of these materials with respect to the synthetic solid tool materials is their high impact strength 6 to 13·10^6 J/m^2.

The main difference of SHS-Extrusion from the SHS compacting method is that when the pressure is applied to the hot-red SHS products, they get forced out through the shaped holes made in the mould (ref. 15, 35).

During extrusion, the SHS materials become compacted and the shape of the item is formed. The apparatus employs the principle of the backward extrusion the punch is fixed and the body under the action of the plunger moves over the punch. The SHS extrusion makes it possible to manufacture the long items in the form of the shaped bars made of the synthetic solid tool material alloys, molybdenum disilicide and other materials (ref. 58, 27). The bars made of hard alloys can be used for electric spark alloying and those manufactured from molybdenum disilicide for production of the high-temperature heaters.

2. SHS with Explosion Treatment. For the first time, the SHS technique with explosion treatment was introduced in the Soviet Union in 1980 (ref. 34). Within some years, the compact specimens were obtained in the form of bars, pipes, disks made of TiC, TiB_2 and other compounds of transition metals, as well as of hard alloys TNM-20 and TNM-50 and ceramics TiC-Al_2O_3. The porosity the compact materials was about 3 per cent and the size of the carbide and boride grains, 1 to 3 μm.

Since 1987, the Institute of Structural Macrokinetics carries out the fundamental researches dealing with action of explosion on the SHS process and its products in the hot and cold states (ref. 10, 11). At the present time, two SHS processing techniques are developed using the explosive pressing (Fig. 5) ensuring the pressure of 10^7 Pa (ref. 55).
Fig. 5. SHS Process with Explosion Treatment

a - pressing with reduction of by explosion products;
b - pressing with throwing the bulky piston.

In one case (Fig. 5a), the products of explosion behind the front of the sliding detonating wave reduce the thin-wall cylindrical container with the SHS products. In the other case (Fig. 5b), use is made of the normally falling detonating wave which reduces the SHS products in the bulk metallic container. In both cases, explosion was initiated after the combustion process. In both systems, the problem of discharge of the gaseous products from the assembly and heat insulation of the explosive against the hot SHS products is solved.

The similar researches dealing with the SHS compacting process were started in the USA in 1988 (ref. 54) where the compact materials (Fig. 5b) were obtained from Ti-C and Ti-B with additions Cu, Fe, Al, Mo, Al₂O₃ and ZrO₂, as well as Ti-Al₂O₃. It should be noted that the SHS method with explosion helped to obtain the compact products of filtration combustion (ref. 55).

SHS METALLURGY

One of the SHS versions which permits to obtain the free-of-pores cast refractory materials, items and coatings is the SHS metallurgy (ref. 13, 16, 19, 24, 27 to 31). In this case, the high exothermal mixtures of metal and nonmetal oxides with reducing agents (Al, Mg and so on) and nonmetals (C, B, Si) are used as the initial mixture (2). The wide circle of such mixtures is capable of combustion and the temperature of combustion exceeds the melting temperature of the final products that is why they are manufactured in the cast form.

At the atmospheric pressure, the considerable part of the combustion products (up to 10 per cent of the mass) can be in the gaseous state in the form of vapours, suboxides and CO that is why when the mixture is consumed open, the combustion process is accompanied by strong spread and the loss of the mass in some cases can be full. The high gas pressure and centrifugal action suppress the spread that is why the synthesis is conducted in the reactors at high gas pressure and centrifugal machines. Taking into account the above-listed specific features, the SHS metallurgy versions are developed which make it possible to solve some practical problems using the high-temperature liquid-phase state of the SHS metallurgy products after the combustion process is over.

1. SHS Casting under Gas Pressure (ref. 6, 19, 22, 27, 28). This version of the synthesis is affected in the reactors of different designs under the gas pressure (argon, nitrogen, air) of 10⁴-5·10⁶ Pa (excessive) in the tight combustion mode or dosed gas discharge (Fig. 1b, c). The mass of the sintering mixture loading into the reactor is determined by its working volume and strength. To obtain the cast items, the SHS sintering mixture is subject to combustion in the refractory envelopes which repeat the shape of the item. Most frequently for the SHS casting, use is made of universal reactor SHS-20 which makes it possible to obtain the ingot or item having a mass of up to 20 kg within the first synthesis. Now, the cast materials and carbide items (Cr₇C₃, WC-W₆C, VC, MoC, Cr-Ti-C, Mo-Ti-C and so on), the items made of hard alloys with the metals of the iron group and borides (CrB₂, VB₂, MoB₂, WB₂, CoB, NiB, FeB, Cr-Ti-B and others), silicides (MoSi₂, V₃Si, NbSi₂, Ti-Mo-Si and so on), oxides (Cr₂O₃, Al₂O₃, LaCrO₃, Cr₂O₃-Al₂O₃, Cr₂O₃-MgO and so on), intermetallic compounds (NiAl, CoAl, Ni₃Ti and so on) gradient and oxide-cermetic
materials $\text{Al}_2\text{O}_3$-WC, $\text{Al}_2\text{O}_3$-TiC-Fe, $\text{Al}_2\text{O}_3$-Cr$_3$C$_2$-TiC and others (ref.6, 19, 22) are obtained using the SHS casting procedure. The methods of the SHS casting helped to make the press tools for the high-temperature stamping and the electrodes for electric-arc surfacing manufactured from hard alloys.

The tests of the crushed and classified cast materials conducted in the industry and scientific-research centers of materials technology show the horizons for obtaining the protective coatings, abrasive materials, catalysts etc. At the present time, the experimental-industrial foundry bay for the SHS casting is made in the scientific-industrial association "Chernetmekhanizatsiya" (Dnepropetrovsk city, USSR) having the output of 10 t of cast products per a year.

2. SHS Centrifugal Casting (ref. 6, 24, 25, 28). The centrifugal force is a powerful instrument in the SHS metallurgy which influences all the stages of the synthesis: combustion and formation of the chemical composition of the melt, phase separation and formation of the microstructure. Besides, it helps to suppress the melt scattering during combustion and ensures formation of the item with a complicated shape under the conditions of quick cooling (ref.24). This version of the SHS metallurgy is affected in the centrifugal machines of various designs developed in the Institute of Structural Macrokinetics of the USSR Academy of Sciences (Fig.6), radial and axial (ref.28), in the open and tight combustion modes, as well as in the mode of the dosed gas discharge from the chamber.

The last combustion mode is the most expedient since it permits to combine the g-load action with the gas pressure and does not need the remote control of gas discharge.

The existing radial designs of the centrifugal machines make it possible to create the g-load of up to 2000 g ($g$ is the free fall acceleration) and to obtain the cast items of up to 1 kg. Manufactured with the aid of these machines are the blocks and cutting picks of drill bits, rings and bushing made of hard alloys on the base of titanium-chromic carbide, gas torch nozzles and protective wear-resistant elements from the gradient and oxide-cermet materials. The hard alloys based on the titanium-chromic carbide have the hardness of up to 90 HRA and the bending strength of up to $10^9$ Pa.

The axial centrifugal machines are used in the Soviet Union since 1977 (ref.24) mainly for pipe manufacture. The existing designs of the axial machines make it possible to create the g-load of up to 1000 g and to make the pipes of length up to 1 m and of diameter up to 120 mm. These machines help to manufacture the two-layer pipes. The external layer is made of steel, hard alloys, refractory metals (Mo, Cr, W) and the internal layer, of $\text{Al}_2\text{O}_3$. Besides, the single-layer oxide-cermet pipes and the pipes with the gradient structure (ref.24, 15) can be manufactured with the help of the said machines. The commercial tests of the pipes having the oxide-cermet structure showed that they have high resistance to nonferrous metal melts and can be used as metal wires (conductors).

Great results in centrifugal SHS-technology have been done in Japan in the works of O. Odawara (ref.56, 57). At the present time, they developed the industrial centrifugal apparatuses which make it possible to obtain the iron-aluminum-thermit pipes having a length of up to 5.5 m.
3. SHS Surfacing. This version of the SHS metallurgy is affected by combustion of the high exothermic sintering mixture layer on the surfaces of metallic (ref.6, 15, 13, 24, 29) and oxide items (ref.31). In the process of the SHS surfacing, the synthesis of the coating material takes place and it becomes reliably fused to the base. Depending upon the practical tack, the SHS surfacing is affected under the gas pressure in the reactor, in the centrifugal machine under the action of the overload or under field conditions at the atmospheric pressure. As a rule, the centrifugal version is used during surfacing to the internal surface of the pipe.

It should be noted that in 1986, the method of applying the reaction melt on the complicated tubular pipes (ref.46) which is similar to the SHS surfacing of the oxide-carbide coatings (ref.31) was developed in Japan.

**SHS WELDING**

This version of the SHS methods is intended for reliable connection of the parts made of refractory materials with the aid of the SHS process and products. To perform the SHS welding, the layer of the SHS sintering mixture is placed between the parts to be joined. After that, the electric current is passed through this layer (ref.23, 15).

The volumetric heating of the sintering mixture leads to its self-ignition. The total heat release from the current source and chemical reaction ensure melting of the sintering mixture and formation of the high-temperature melt. Owing to this fact, the parts are joined. Depending on the fact that the part surfaces to be joined get melted or not, the SHS process distinguishes the SHS welding and SHS soldering.

The method of the SHS welding helps to join the following pairs: tungsten-molybdenum, graphite-molybdenum, graphite-tungsten, zirconium-steel, niobium-steel, graphite-steel, hard alloy-steel (ref.15, 23). Depending on the pair to be welded, the respective composition is selected which ensures the maximum reliable joints. For example, for joining, the following mixtures were used: Ti+C, Nb+C and others. The rupture strength of the welds reaches \((6 \text{ to } 7) \times 10^8\) Pa.

In 1986, the molybdenum-to-carbide and molybdenum-to-titanium boride joints were made in Japan with the help of the SHS welding (ref.58). In the first case, the weld strength was \(10^9\) Pa and in the second one, \((2 \text{ to } 4) \times 10^7\) Pa. In spite of the low level of the strength value, the recommendation is given for using this result in the structure of the first wall of the thermonuclear synthesis reactor.

**TECHNOLOGY OF GAS-TRANSPORT SHS COATINGS**

This version of the SHS process is intended for obtaining the thin protective coatings by combining the SHS process with the gas-transport reactions. For the purpose, the gas-transport agent (halogen) is introduced into the element or oxide SHS sintering mixture. During SHS process, halogen carries the sintering mixture elements to the part surface where they interact and form the coatings (ref.9). The process takes place in the open or continuous-flow reactor into which the sintering mixture and part are positioned. After ignition and combustion of the sintering mixture, a coat having a thickness of up to 150 µm is formed on the item surface. The mixtures of metals and nonmetals: Ni+Al, Ti+B, Zr+Si, oxide systems: \(\text{Cr}_2\text{O}_3+\text{Al}, \text{B}_2\text{O}_3+\text{AL}\) and others are used as the initial compounds and iodine is used as halogen.

For the commercial tests, the coatings on cutting plates (VK-6, VOK-60) and conbushings were made. The tests of the parts provided with the SHS gas-transport co showed the increase of the service life by 5.3 and 6 times respectively.

**CONCLUSION**

For the problem of the self-propagating high-temperature synthesis, the development process versions and experimental apparatuses plays a leading role for comm employment. In its turn, the reliability of the production processes, high quality a regeneration of the SHS product properties are stipulated by the depth of the funda researches. The intimate connection of these two directions in the USSR, USA and determined the success of the self-propagating high-temperature synthesis which ha achieved during last ten years. The mutual cooperation of the SHS process researcher exchange of the conceptions and the industrial potential of the West will probably the development of the SHS processes in the next ten years.
Modifications of SHS processes

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