

Lecture 12. SHS-technologies for obtaining materials

The purpose of the lecture: consideration of various types of SHS technologies for obtaining materials.

Expected results: students receiving information on various types of SHS technologies, their features and application possibilities.

The technology is based on burning the mixture in special reactors with a capacity of up to 30 liters. The SHS product obtained under such conditions is a shapeless mass — a cake or an ingot of practical importance. This technology allows you to get a wide range of simple and complex porous products, including filters, pistons, friction pairs of electrical contacts, catalysts from intermetallic compounds.

The most widely used SHS-technology of powders. The general technological scheme for the preparation of SHS-product powders includes the following operations: preparation of the charge (sieving, grinding, drying of the components, mixing); filling the reactor with a charge and gases; directly synthesis after short-term thermal initiation; subsequent redistribution of the synthesis products (grinding, acid enrichment, sieving, drying).

According to this technology, the Institute of Structural Macrokinetics and Problems of Materials Science of the Russian Academy of Sciences launched the production of various powders: β - Si_3N_4 , α - Si_3N_4 , TiC, TiB_2 , TiN, TiC_xN_y , SiC, B_4C , AlN, SiAlO_xN_y and others.

SHS sintering. One of the promising tasks is the organization of sintering of a solid product formed during SHS in order to obtain products of a given shape and size.

Traditional methods of sintering ceramic products (hot pressing, gas-static hot pressing) are characterized by high material and energy costs.

Of great interest is the preparation of ceramic materials and products by direct synthesis of metal or non-metal with gas in a combustion mode, bypassing the stage of preliminary preparation of ceramic powders and subsequent compaction to a given shape and size. This option is implemented in special SHS gas thermostats, which allow the synthesis of end products and the simultaneous formation of products at pressures of the active gas up to 8000 atm and temperatures of 1000-3000 °C, developing due to the heat of the exothermic reaction.

The main technological parameters are: reagent gas pressure; the degree of dilution of the mixture of the final products. These parameters make it possible to provide a layer by layer filtration combustion and the required porosity of the material. Porosity can vary within wide limits: 10-50 %.

Examples of gas-static SHS technology are the production of materials from oxygen-free ceramics based on silicon nitride - β - Si_3N_4 , high-temperature-resistant ceramics Si_3N_4 -SiC, the production of insulating sleeves from BN for directional crystallization furnaces, turbine blades from Si_3N_4 -TiN-TiC, ceramic metal wires based on TiB_2 -AlN for casting steel and slag.

The direction of SHS-sintering includes the production technology of refractory SHS-materials and oxides.

The composition of the initial mixture is selected based on the requirements for refractories (refractoriness, heat resistance) and the requirements of sufficient exothermicity of the mixture, small shrinkage and low weight loss during combustion. Refractory products are prepared from a mixture of alkaline earth metal chromate (MgCrO_4 , CaCrO_4 , BaCrO_4), a metal reducing agent (Al, Mg) and refractory oxide (Al_2O_3 , MgO, CaO). The mixture is formed, placed in special forms and initiate a combustion reaction in air.

So get refractory bricks with a porosity of 30-40 % and refractoriness up to 1900 °C. The achievement of this direction was the possibility of applying refractory coatings on the surface of a complex profile, as well as the development of technologies for producing porous plates from composite materials (by reaction of the type $\text{TiO}_2 + \text{B}_2\text{O}_3 + \text{ZnO}_2 + \text{Al}$) and complex oxides for electronic equipment - titanates, zirconates, niobates, ferrites, etc.

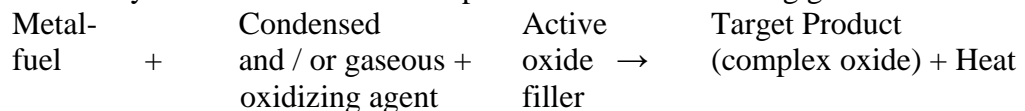
The essence of the technology for the production of refractory protective coatings consists in preparing the mixture, moistening it with a binder solution (usually aqueous solutions of mineral salts are used), applying a moistened mass to the surface to be protected, drying and initiating the combustion process in the mixture. The choice of binder determines the drying regimes, molding characteristics and properties (strength, porosity) of the final products.

An analysis of existing methods for producing compounds for electronics by SHS showed that basically two types of reactions were carried out.

The reactions of the first type are reactions with the participation of peroxides, which are a source of active oxygen necessary for the combustion of the initial mixture.

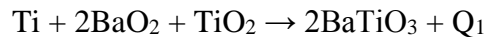
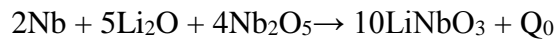
Reactions of the second type are reactions whose course is possible only when external oxygen is supplied. Such reactions include: obtaining garnets, aluminates, vanadates, etc. by burning the initial mixtures in gaseous oxygen.

The chemical synthesis scheme can be represented as the following generalized reaction:

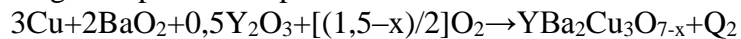


For example:

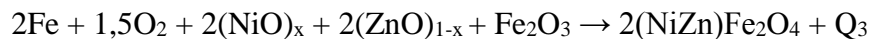
1) Synthesis of lithium niobate and barium titanate:



2) Synthesis of high temperature superconductors:



3) Synthesis of nickel-zinc ferrite:



The first two reactions proceed in the combustion mode due to the low dissociation temperature of lithium and barium peroxides.

The synthesis technology of niobates, tantalates, titanates has a high performance and simple hardware design, since the synthesis is carried out in open containers in air. The indicated complex oxides are used in electronic engineering mainly as single crystals.

The main advantages of HTS SHS technology are: high productivity (up to 20 kg of material per synthesis); lack of energy consumption and sophisticated equipment; satisfactory quality of powders.

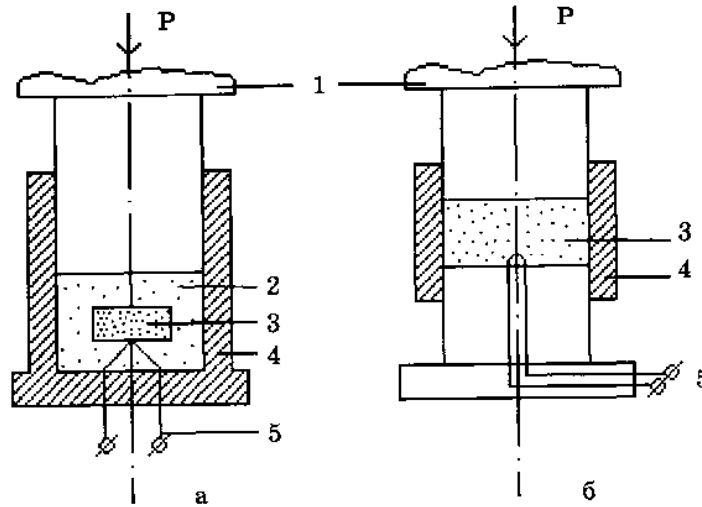
The synthesis is carried out at temperatures of 800-950 °C for several minutes. The main parameters affecting the speed, combustion temperature, and properties of the final products are oxygen pressure, charge density, mixing uniformity, dispersion of reagents, especially copper, briquette diameter.

Power SHS compaction. To obtain non-porous products, a set of techniques was developed in which the SHS product heated by a combustion wave is subjected to compaction by pressure treatment.

The method of power SHS compaction is of great interest for the problem of creating unique materials, especially tungsten-free hard alloys with a metastable structure. A number of new compositions have been developed in a wide range of physical and mechanical properties. SHS alloys have high impurity purity and perfect single crystallinity of grains. These alloys are called SHTM - synthetic hard tool materials.

The advantage of this method is the simplicity of the process. Schematic diagrams of the SHS-pressing process are shown in Fig. 12.1. After the extrusion pressure is applied to the combustion products, compaction (shrinkage) occurs. The mechanism of compaction of synthesis products is fundamentally determined by the composition of the final products. Obviously, the greatest compaction occurs in the case of pressing products containing a liquid melt of one of the components (bundles). The presence of ligaments significantly accelerates the sliding of carbide grains, and the liquid ligament acts as a lubricant. If the synthesis product is in a solid state of

aggregation (as in the case of $Ta + C \rightarrow TaC$), then compaction is possible only due to the sliding of carbide grains and diffusion healing of pores. Finally, when compacting the product of the interaction of titanium and carbon ($Ti + C \rightarrow TiC$), compaction is carried out in several stages: 1 - grain sliding; 2 - plastic deformation of grains; 3 - diffusion healing of pores.



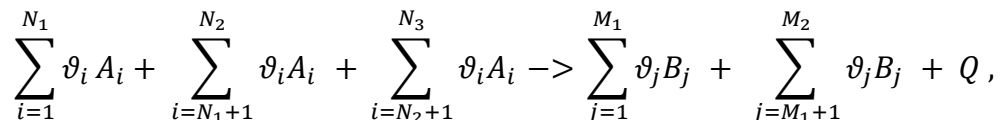
a - for thin workpieces; b - for bulky workpieces. 1 - punch; 2 - heat insulator; 3 - SHS charge; 4 - mold; 5 - initiating device.

Fig. 12.1. Schematic diagrams of the SHS-pressing process

The SHS-pressing technology is used to obtain carbide products - rolls, dies, tool accessories, cutting plates, targets for magnetron and cathode sputtering, electrodes for electrospark alloying, etc.

SHS metallurgy. A wide range of mixtures of metal oxides with a reducing agent and non-metal can burn. The products of their combustion are carbides, borides, silicides, nitrides, simple and composite oxides, hard alloys, cermets. For mixtures with a thermal effect >1000 cal/g, the combustion temperature exceeds the melting point of the combustion products, and therefore, after crystallization, they are obtained in cast form.

The chemical scheme for producing cast refractory compounds and hard alloys can be represented as:



where $(i + 1) \div N_1$ — starting oxides (CrO_3 , TiO_2 , Ni_2O_3 , MoO_3 , FeO),

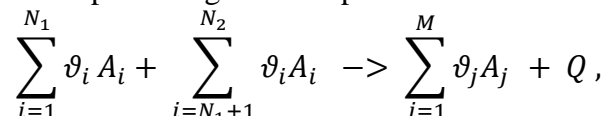
$i = (N_1 + 1) \div N_2$ — reducing metals (Al , Mg , ...),

$i = (N_2 + 1) \div N_3$ — non-metals (C , B , Si , N_2 , SiO_2 , B_2O_3 , ...),

$j = 1 \div M_1$ — carbides, borides, silicides, nitrides of Cr , Ti , Ni , Mo ..., hard alloys, etc.

$j = (M_1 + 1) \div M_2$ — reducing metal oxides (Al_2O_3 , MgO ...) and other condensed and gaseous combustion products.

The chemical scheme for producing cast composite oxides has the form:



where $i = 1 \div N_1$ — starting oxides; $i = (N_1 + 1) \div N_2$ — reducing metals (Al , Mg , Ti , ...); $j = 1 \div M_1$ — lower oxides and oxides of reducing metals. For example: $CrO_3 + Cr \rightarrow Cr_2O_3$, $2CrO_3 + 2Al \rightarrow Cr_2O_3 + Al_2O_3$.

The technological scheme for preparing, conducting experiments at pilot plants and operating time for testing for all synthesis options is the same and includes drying the components, dosing, mixing, filling in the mold, synthesis in the reactor (stationary or centrifugal),

disassembling the mold and removing the cast material or products. If necessary, mechanical treatment of ingots and products is carried out.

SHS welding. The main objective is a solid one-piece connection of refractory parts from dissimilar or homogeneous materials using SHS processes and products. SHS is a source of high temperature, and SHS is a welding material.

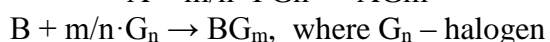
Typically, for welding, the SHS process is carried out in the gap between the parts to be welded so that a high-temperature melt is formed. To increase the heat dissipation power, an electric current is usually passed through the charge and an electric thermal explosion is carried out.

Good contact of the combustion products with the parts is ensured by preloading the parts with little effort.

The main advantage of SHS welding is the ability to make a non-detachable connection of difficult to weld materials, such as graphite, titanium, steel, tungsten, molybdenum, etc. The strength of the weld is at the level of the strength of the welded materials.

Technology of gas transportation SHS coatings. To implement the technology, gas transport additives (for example, iodine) and coated parts are introduced into the SHS mixture. In the process of combustion, gas transport of the reagents to the surface on which the chemical reaction occurs (the same as in the bulk of the substance) with the formation of the target SHS product in the form of a coating.

Due to the main solid-phase SHS reaction between the elements A and B, the combustion front propagates with a velocity U_g along the powder mixture. In this case, reactions of the type:



At low temperatures gaseous compounds are formed, and at high temperatures these compounds decompose. Gaseous compounds are first deposited on the surface of the product, and the formation of the initial coating of $A_x B_y$ occurs at high temperatures. The length of the diffusion path of the volatile halide of the same order with the width of the heating zone is ~ 0.1 mm.

Combining various carriers, adjusting the composition of the charge and the stage of its reaction, it is possible in one process to obtain complex multicomponent coatings (borides, silicides, intermetallics, and others) 5-150 microns thick.

Currently, two methods of coating in the combustion mode are implemented: reactor and open. Each of them has its own merits. The reactor is used to supply an inert gas to the mixture, which prevents oxidation of the coating. In the open method, systems are used that do not require an inert environment and can be implemented in air. These include, first of all, aluminum-magnesium thermal systems.

In the implementation of gas transportation SHS coatings, various raw materials are used. Conventionally, it can be divided into three classes:

1. Elements in the form of a mixture of metals and metal with non-metal (Ni+Al, Ti+Al, Ti+B, Zr+Si).
2. Oxide systems (Cr_2O_3+Al , B_2O_3+Al).
3. Ores and production wastes.

Literature

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