SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS)

Ladies and Gentlemen!

You are welcome to the pages of our Information brochure describing the processes of Self-propagating High-temperature Synthesis (SHS), i.e., combustion processes forming practically valuable substances, materials, and items. It is a key subject in the work of the Institute of Structural Macrokinetics and Materials Science of the Russian Academy of Sciences. Almost all the directions of this problem are being developed in our Institute:

- investigation of SHS processes and products (kinetics, thermodynamics, experimental diagnostics, mathematical modeling, combustion structure formation, chemical and physical effects on the processes, physical materials science of SHS products, etc.);
- development of basic SHS technologies and fabrication of specialized equipment;
- synthesis of novel materials and items;
- SHS industrialization and commercialization (participation).

ISMAN is the only organization in the world which carries out a wide range of the works. No wonder. It was our team that in 1967 discovered the phenomenon of solid flame and elaborated the SHS method. Our researchers took the most active part in the development of this R&D area. The stages of our work are the following:

1967 - 1972 Initial investigation. Study of the process mechanism by a small research group within the Department of Macroscopic Kinetics of the Branch of the Institute of Chemical Physics, USSR Academy of Sciences.

1972 - 1980 Initiative branching of investigation. Activity of research teams in Tomsk, Erevan, Kiev, and other cities of the USSR. First technological work in obtaining powders, compact materials, and items, applying coatings, joining items. First industrial realization of the SHS technology (Kirovakan plant of high-temperature heating elements).

1980 - 1992 Encouragement from the State. Resolution of the USSR Council of Ministers on introduction of the SHS technologies into the national economy and on establishment of the Interbranch Scientific-and-Technological Complex "Termosintez" with the Institute of Structural Macrokinetics of the Russian Academy of Sciences at the head.
Work of the Scientific Council of SHS Theory and Practice within the State Committee of Science and Technology of the USSR.
Creation of pilot-scale production sites (workshops) in fifteen enterprises of the USSR.
Study of engineering and economic efficiency.

Since 1980 Outset of SHS works abroad. Growing interest for the problem in the USA, Japan, Poland, China, and other countries. First publications in international journals. ISMAN's activity in creation of the International SHS Journal, organization of International Symposia.

Since 1992 Disorganization of the Interbranch Scientific-and-Technological Complex. Struggle for existence (ISMAN survived thanks to the SHS). Work under the terms of market economy by self-supporting agreements, contracts, grants. Strengthen of international links.

On overcoming all the difficulties and occupying their own place in science and technology, the collaborators of ISMAN are ready for subsequent large-scale work and co-operation.

Welcome to ISMAN, World of SHS!

Director of ISMAN
Academician A.G. Merzhanov

INSTITUTE OF STRUCTURAL MACROKINETICS AND MATERIALS SCIENCE

Discovery No. 287 “Phenomenon of Wave Localization of Autobraking Solid-Phase Reactions”, so called “Solid Flame”, made by the Russian scientists A.G.Merzhanov, I.P. Borovinskaya, V.M. Shkiro marked the birth of a novel scientific and technological direction – Self–propagating High–temperature Synthesis (SHS) of inorganic compounds, materials, and items.

- metal and non-metal phosphides;
- monophase solid solutions and heterogeneous multi-component systems.

SHS products are widely used for obtaining:
- hard alloys and abrasives;
- high-temperature structural and heat-resistant ceramics;

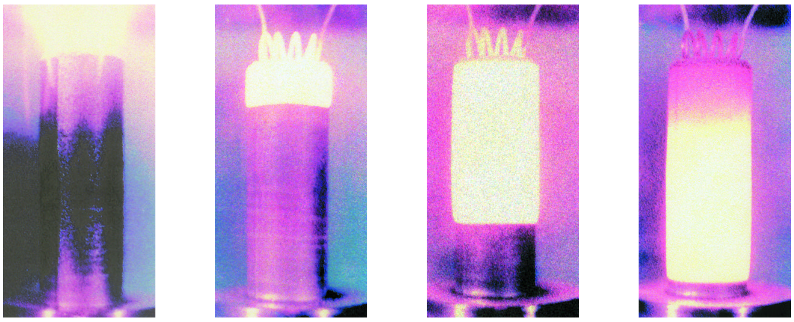
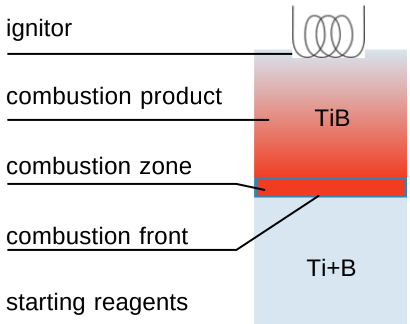


Photo of SHS process



Schematic of SHS process

The SHS is based on the principle of maximum utilization of chemical energy of reacting substances for obtaining inorganic compounds, materials, and items of various application purposes and also for organizing highly efficient technological processes.

The following mixtures of elements can be used as reacting systems:
- metals with non–metals;
- metals with metals;
- non–metals with non–metals or their compounds.

A remarkable feature of the mixtures is their ability to evolve a large amount of heat during the interaction.

SHS products are practically valuable inorganic compounds, such as:
- refractory compounds – carbides, borides, nitrides, silicides, metal oxides;
- metal hydrides;
- chalcogenides – sulfides, selenides, tellurides;
- intermetallics – aluminides, nickelides, germanides, etc.;
- materials for electronics, electrical engineering and up-to-date superconducting materials;
- corrosion-resistant protective and wear-resistant coatings;
- catalysts for chemical industry;
- shape memory materials for medicine.

Structural Macrokinetics is the basis of fundamental investigations in the SHS field. It studies the mechanism and kinetics of product structure formation during chemical transformations and develops methods for controlling an SHS product composition, structure, and properties.

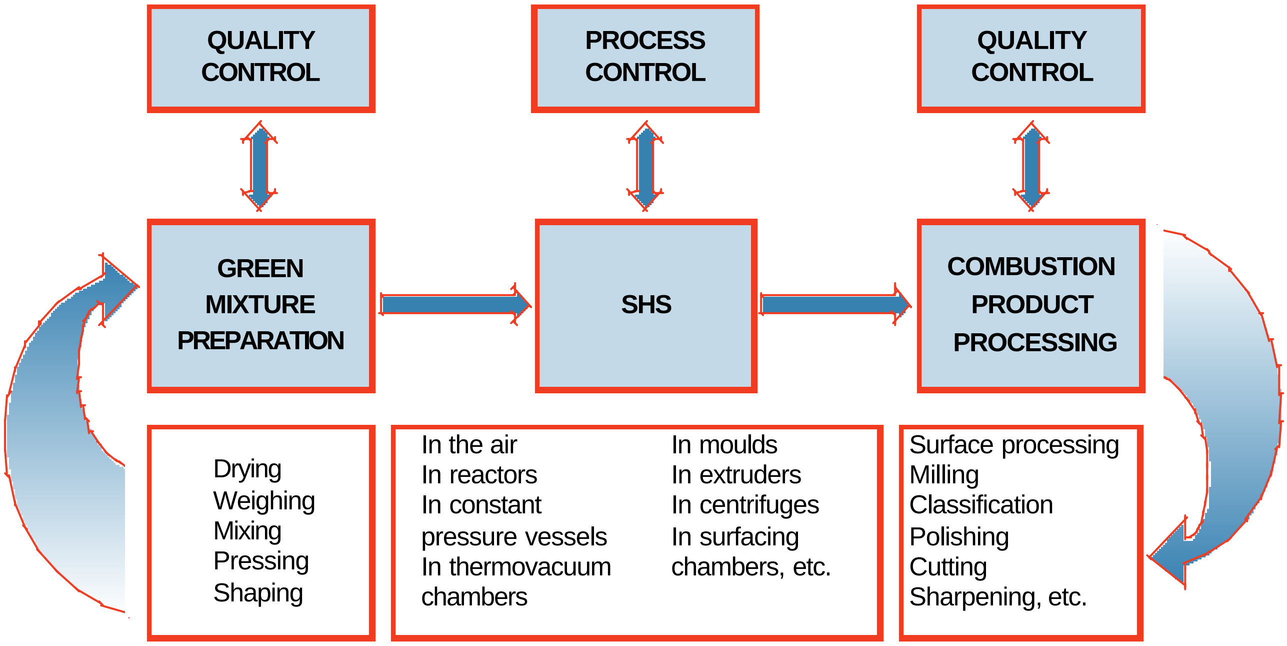
Combination of remarkable peculiarities of SHS processes with a wide complex of scientific and technological investigations carried out by the researchers of the Institute of Chemical Physics and Institute of Structural Macrokinetics and Materials Science of the Russian Academy of Sciences in collaboration with materials technologists, metallurgists, physicists, and chemists of other research institutions and enterprises of the former USSR allowed converting the discovery into radically new production methods and technologies.

The SHS processes are characterized by a wide range of features distinguishing them from conventional methods of inorganic material production:

- high self-heating of a reactive mass as a result of chemical reactions. It allows synthesizing and forming materials at temperatures of 800–4500°C due to the system internal sources only, without external heating;
- high process rates (up to 0.15 m/s);
- high conversion degree of reacting substances into final products and evaporation of volatile impurities due to high temperatures of the process.

Nowadays, more than 30 technological varieties of SHS have been developed and are in use.

Scheme of SHS Technology



Self–propagating High–temperature SynthesisTechnological Types (TT)

SHS Technological Types

TT-1. SHS Powder Technology
TT-2. SHS Sintering
TT-3. SHS Force Compaction
TT-4. SHS Metallurgy
SHS Technology of High-temperature Melts
TT-5. SHS Welding
TT-6. SHS Technology of Gas-transport Coatings

They are united into six technological types.

These technological types are characterized by the following features:

- low energy consumption (in most cases it is only necessary for initiating an SHS process);
- simple technological equipment, its high productive capacity and ecological parameters;
- decreased number of technological stages in comparison with conventional technologies;
- feasibility of production lines adaptable to production of different materials and items and amenable to mechanization and automation;
- possible substitution of raw materials with cheaper ones for producing one and the same product;
- high technical and economical parameters of a great number of valuable materials and items for up-to-date engineering.To-day more than 700 various inorganic compounds and materials have been obtained by the SHS methods. Our experience in the SHS has shown that a variety of techniques and a wide range of parameters make it possible to produce practically any known valuable high–melting, heat–resistant, hard, wear–resistant powders, materials, and items as well as a great number of composites distinguished by their new operation properties.

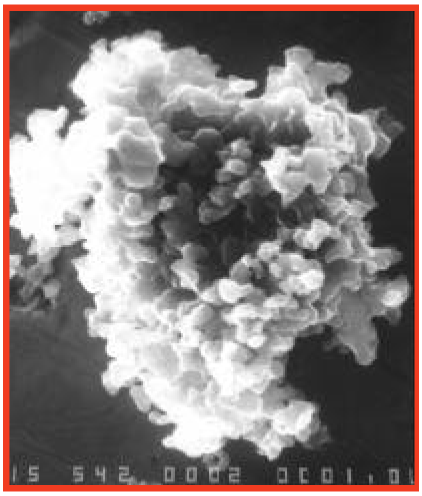
SHS as an Alternative Technology

Conventional technology	Alternative SHS technology	
Synthesis in furnaces, Plasmochemical synthesis	SHS Powder Technology	(TT–1)
Sintering, Hot Pressing,	SHS sintering	(TT–2)
Isostatic Pressing	SHS Force Compaction	(TT–3)
Casting, Centrifugal Casting	SHS casting	(TT–4)
Plasma and Detonation Spraying	SHS technology of gas–transport coating	(TT–6)
	Induction SHS surfacing	(TT–4)
Gas–phase Precipitation, CVD–processes	SHS technology of gas–transport coating	(TT–6)
Electric Arc and Induction Surfacing	SHS surfacing	(TT–4)
	Induction SHS surfacing	(TT–4)
Electric Welding	SHS welding	(TT–5)

TT–1 SHS Powders

The technology is based on burning initial mixtures of components in special reactors in the medium of inert or reactive gases as well as in vacuum or in the open air. The reactor capacity ranges from one to several tens liters. The products are obtained as powders, cakes or ingots with subsequent mechanical or thermochemical processing, sieving, etc.

Single crystal powder



Agglomerate powder

Powder SHS Technology

The technological scheme of powder production includes the following operations:

- preparation of a green mixture - sieving, milling, drying of components, mixing;

SHS powder reactor

- filling of a reactor with a green mixture and gases;
- synthesis after a short–time thermal initiation;
- subsequent processing of synthesized products – milling, acid enrichment, sieving, drying.

Due to the specific features of the technology, the SHS powders differ from the analogs obtained in furnaces by their structure and purity. Three types of the SHS powder are spread wider: single–crystal, agglomerate, and composite ones.

A single–crystal SHS powder consists of individual perfect single crystals. The particle size ranges from 0.5 to 3.0 μm. The powders appear to be an excellent raw material for sintering. (3.0 μm)

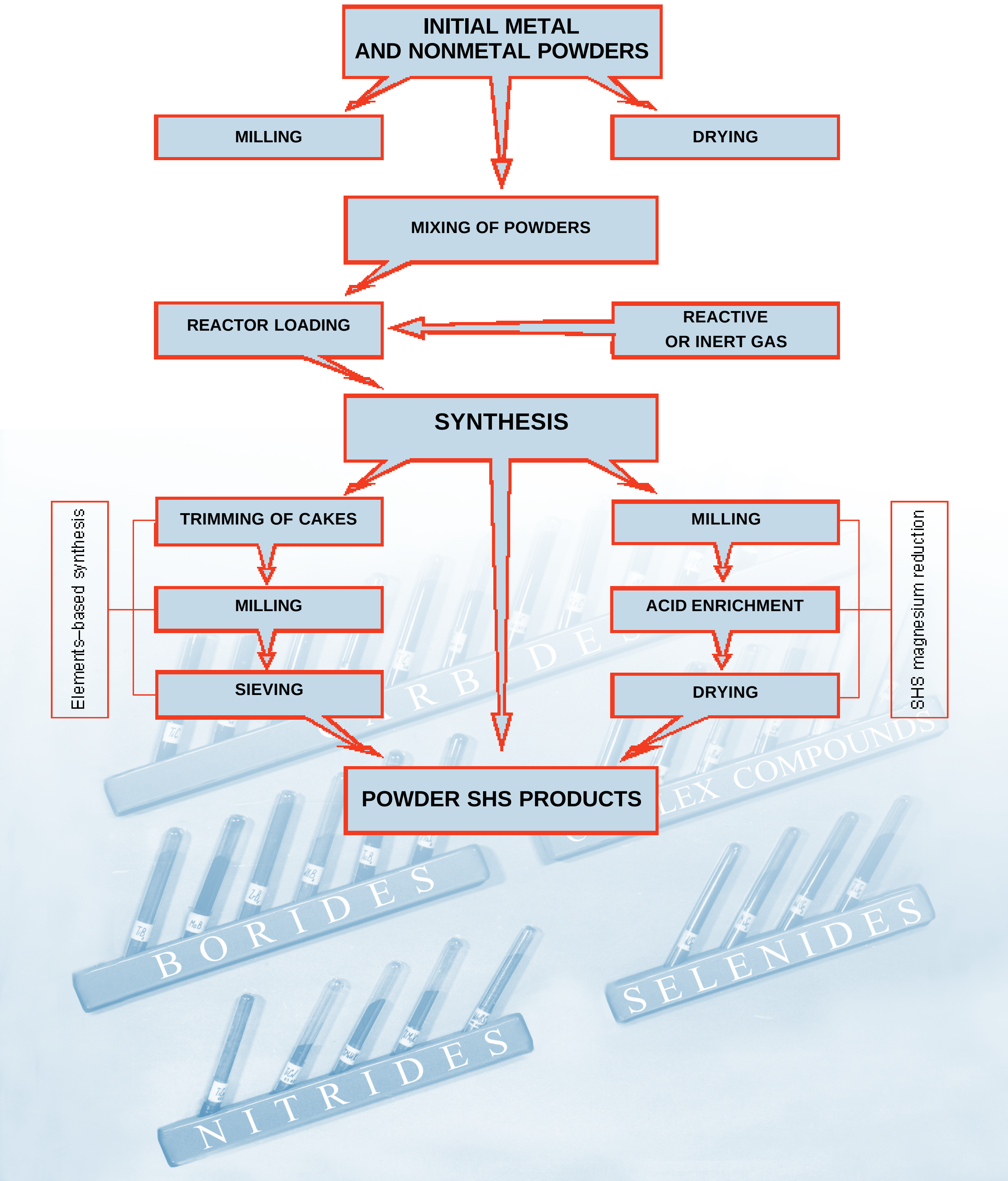
Agglomerate SHS powders have no analogs in powder metallurgy. The powder consists of particles, comprising individual well coupled crystals, and can include pores. The particle size ranges from 10 to 200 μm.

An example is an SHS–titanium carbide powder. It is used for manufacturing highly efficient abrasive pastes. Due to the processes of agglomerate grain destruction occurring during the item grinding, it is possible to carry out two different operations, i.e., grinding and polishing, within one technological stage. Use of these pastes for finishing any items of ferrous and nonferrous metals results in improving the surface roughness by 1–2 class, increasing in labor productivity 1.5–2 times, prolonging the item service life in comparison with the items finished with conventional pastes.

Agglomerate non–porous SHS powders can be characterized by high strength and used in grinding wheels for rough machining of surfaces.

Particles of an SHS composite powder consist of phases of different compounds. Powder ceramic materials containing non–oxygen refractory compounds (carbides, borides)

SHS powder production technology



Characteristics of Ceramics Based on Composite SHS Powders

Composition	Density g/cm^3	Bending strength, H/mm^2	Young's modulus, KH/mm^2	Rockwell hardness	IWear, g/cm^3
$TiB_2 \cdot Al_2O_3$	4.07	1074	780	95.5	0.01316
$B_4C \cdot Al_2O_3$	3.42	490	413	95.7	0.00815
$B_{1\ 3}C_2 \cdot Al_2O_3$	3.42	718	628	95.5	0.00560

Chemical Composition and Specific Surface Area of BN Powders

Content, wt.%	SHS product		Furnace product	
BN	Super pure	Technically pure	ORPAC, GRADE 99	Denka, JAPAN
Nitrogen, N	>55.7	54.9	54 – 55	54.5
Basic constituent, B+N	99.5	97.3	98 – 99	^{33}98
Oxygen, O	<0.5	1.5	1.5	1.5
Carbon, C	<0.01	0.3	—	—
Metal impurities (Mg, Fe)	<0.2	0.3	—	—
Specific surface area, m^2/g	11.0	8 – 14	10.0	—

Chemical Composition and Specific Surface Area of AlN Powders

Content, wt.%	SHS product		Furnace product	
AlN	Super pure	Technically pure	ART USA A–100	STARCK Germany (Grade B)
Nitrogen, N	33.9	32.7	33.0	33.3
Basic constituent, Al+N	99.7	98.8	99.0	98.1
Oxygen, O	0.3	0.6	1.0	2.3
Iron, Fe	0.07	0.12	0.005	100 ppm
Specific surface area, m^2/g	2.0 – 20	1.5	2.5–4.0	1.0–8.0

and alumina or magnesia are widely spread.

The specific feature of these powders is their excellent sinterability.

Composite SHS powders are characterized by high service parameters in comparison with those obtained from mechanical mixtures of the same composition.

SHS cermet powders are also of great interest.

A powder of ($TiC–Cr_3C_2$)+Ni is successfully used for gas–thermal application of protective coatings on items operating under high temperatures (up to 900°C).

These powders can compete with cladding powders of the same composition.

One of the main peculiarities of SHS powders is their purity which is achieved due to high conversion degree under synthesis optimum terms, a product self–purification from impurities, and impossibility of combustion product contamination by container materials. Usually the main product content in SHS powders is from 99.0 up to 99.5 weight %. It is significantly higher than that of existing analogs.

TT–2 SHS sintering

SHS sintering is carried out in thermal vacuum chambers, in the open air or special constant pressure vessels (SHS gasostats).

An initial mixture is shaped as an item to be sintered. Combustion is organized in such a way to preserve the billet shape and size. The combustion product is a required item with a porosity of 5–50 %.

SHS constant pressure vessel (gasostat)

The SHS gas–statting technology is efficiently used for synthesizing nitride ceramics. It combines the synthesis process with high gas pressures (up to 500 MPa). Nitrogen is often used as a gaseous reagent and a gas–statting medium. The SHS gas–statting carried out in one stage results in synthesizing a simple compound or a composite and forming its geometry and structure.

It is possible to synthesize materials and items with a porosity ranging from 1 to 80 %:

-high–temperature, corrosion–resistant ceramics based on sialons, aluminum nitride and its compositions with transition metal borides;

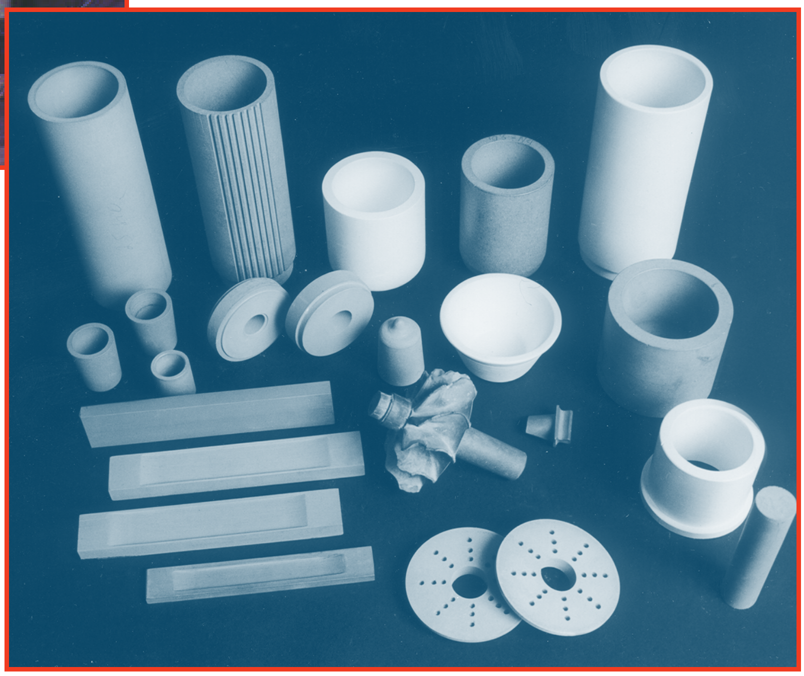
- structural non–metal nitride, nitride–carbide, nitride–boride ceramics without sintering activators;
- boron nitride and its mixtures with oxides;
- functional ceramics based on non–metal silicon and aluminum nitrides;
- tribo–technical ceramics based on silicon nitrides and carbides, boron nitride, and characterized by excellent operation properties;
- novel original multicomponent compositions of non–metal silicon, aluminum, boron nitrides, carbides with metal–like heat–resistant compounds.

SHS gas–statting imparts unexpected properties to the materials and items:

- abnormal high corrosion resistance of porous SHS–ceramic items in metal melts;
- excellent thermal shock resistance of many items;
- high hardness.

Of particular importance for up–to–date engineering are the following items made of nonmetal SHS ceramics:

- crucibles, evaporation boats, pipes for ferrous and non–ferrous metals melting and transportation;
- ceramic engine parts;
- filters, honeycomb structures, catalyst carriers;
- high–temperature refractory plates, bricks, parts, and devices for their fastening;
– microcircuit substrates.



Items obtained by SHS sintering in constant pressure vessels (gasostats)

TT–3 Forced SHS Compaction

In the case of this technology, the synthesis process is combined with compaction of still hot products (pressing, extrusion, rolling, explosion working). This SHS variation offers great possibilities of filling the market with items made of novel tungsten–free hard alloys:

- cutting plates;
- press devices;
- dies;
- large–scaled rolls;
- drawing dies for metal rolling;
- wear–resistant machine parts;
- long–sized electrodes for surfacing and electric–spark alloying;
- targets for magnetron and cathode spraying, etc.

Tungsten–free hard alloys named STIM, i.e., synthetic hard tool materials, are based on carbides, borides, nitrides, carbonitrides, and other compounds of refractory metals (Ti, Zr, Nb, Ta, etc.).

STIM alloys are various in their composition and can be identified as superhard (hardness – 90–110 HRA) as well as superstrong materials (bending strength – 800–1300 MPa). Some of them possess rather unique properties. For example, STIM–5 is distinguished by high cutting ability. STIM–1B/3 is also characterized by excellent cutting parameters. When operating at high cutting rates, unreground cutting tools made of this alloy can be compared with the best ceramic unreground plates.

STIM–4 is remarkable for its high corrosion and thermal–cycle stability and excellent technological parameters. Large–scaled hard–alloy items such as rolls for nonferrous metal rolling are manufactured on the base of STIM–4 by the SHS method.

Practically, large–scaled hard–alloy SHS items have no analogs in powder metallurgy. Economic analysis of the situation in production of such items has proved doubtless advantages of the SHS technology.

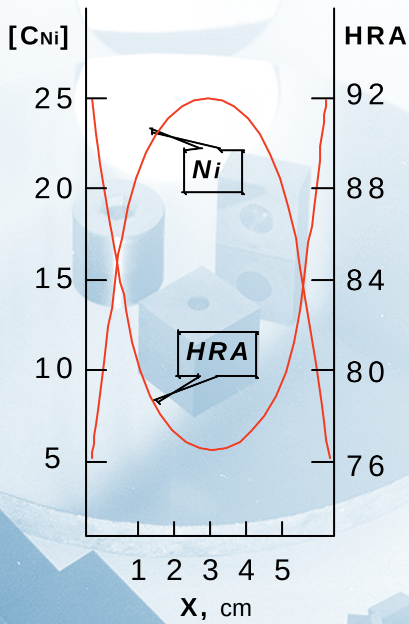
One of the directions of the forced SHS compaction (TT–3) is manufacturing functionally graded materials (FGM), i.e., those with the composition changing over the volume. At present, two types of hard–alloy graded plates can be obtained: those with symmetric and asymmetric distribution of a binding component (SIGMA–1 and SIGMA–2).

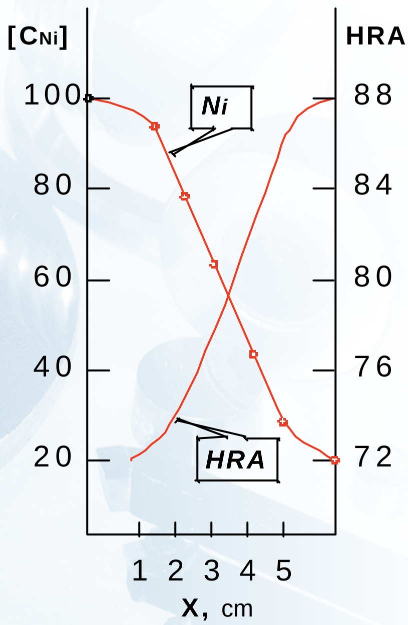
The mechanical characteristics given in the Table below prove the evident advantages of the SHS hard alloys in comparison with both homogeneous materials of the same composition and some Russian hard alloys. Graded hard–alloy SHS products can be used as shock– and wear–resistant materials.

Also, the TT–3 version is successfully used for one–stage manufacturing of targets (spraying of coatings), creation and application of heat–resistant structural TaC and HfC–based materials, $MoSi_2$ high–temperature heating elements, etc.

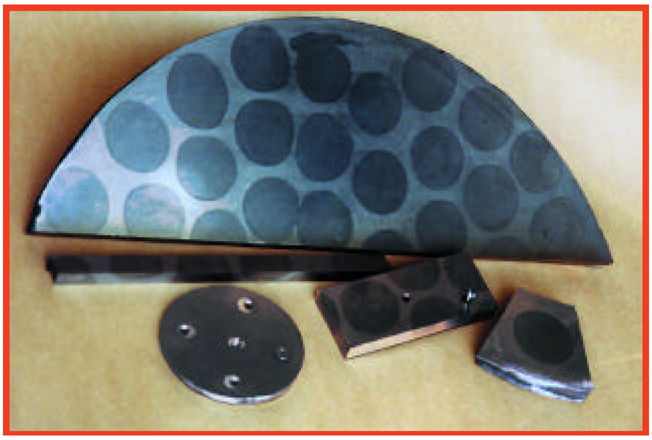
Press installation for obtaining large sized items by SHS compaction

Ni content and strength of graded hard alloys





Targets for magnetron spraying



STIM–based macrocomposite

Characteristics of STIM Materials

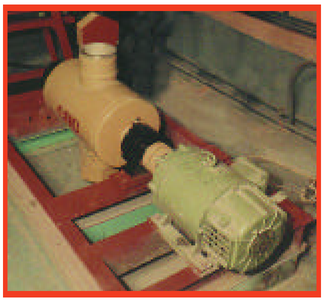
STIM alloy	Main composition	Density, g/cm^3	Average particle size, µm	Hardness, HRA	Bending strength, MPa	Application
STIM–B/3	$(TiC–TiB_2)$ +Cu	4.94	5–7	93.5	700–800	Cutting plates
STIM–2	TiC+Ni	5.50	5–7	90	1000–1100	Armor plates
STIM–2A	TiC + (Ni–Mo)	6.40	1–2	87	1600–1800	Press devices
STIM–3B	$(TiC–Cr_3C_2)$+Ni	5.37	3–4	92.5	800–1000	Cutting plates
STIM–3V	$(TiC–Cr_3C_2)$ + steel	5.40	2–4	92.5	700–800	Scale–resistant items
STIM–4	TiB+Ti	4.20	1–2	86	1200	Thermal shock–resistant items
STIM–5	(TiC–TiN) +(Ni–Mo)	5.80	1–2	91.5	1200–1400	Cutting plates

Impact Strength of Hard Alloys

SHS alloys	Alloy type	Impact strength, kgm/cm^2	Hardness HV, kg/mm^2
	SIGMA–2	1.3	1160 (on one side) 115 (on the other)
	Homogeneous analog of SIGMA–2	0.09	1350
Russian commercially available alloys	VK–20	0.48	930
	VK– 8	0.35	1210
	T15K6	0.08	1570
	T30K4	0.07	2350

TT–4 SHS Metallurgy

This variation of SHS is based on burning highly caloric mixtures of metal oxides with reducing agents (Al, Mg, Ti, etc.) and nonmetals (C, B, Si, B_2O_3, SiO_2, etc.). The burning temperatures of these mixtures are higher than the melting points of initial, intermediate and final components and reach 3000–4500°C. It is the only way for obtaining melts of very high–temperature composites in order to form items of a required shape without the external energy supply, only due to the heat released in chemical reaction.



Radial centrifugal SHS installation

SHS casting equipment includes:

- original SHS reactors;
- chambers for surfacing;
- SHS centrifugal machines;
- continuous automated lines for applying wear–resistant coatings.

The liquid state of the products synthesized allows us:

- to obtain ingots of refractory inorganic materials;
- to make items of various structure and shape;
- to apply protective coatings onto item surfaces.

Cast carbides, borides, silicides, intermetallics, hard alloys, cermet materials and items, graded plates, pipelines and other products are actively used as:

- wear–resistant coatings on some parts of agricultural, earth–moving, boring machines;
- parts of metallurgical equipment for steel and alloy pouring;
- pipelines for aggressive media;
- abrasive tools, etc.

The wear resistance of the SHS surfacing based on titanium–chromium carbide is 4–5 times higher than that of the coatings made of the well known TiC–based alloys of “Sormait” and “Relit”s.

Examples of successful practical application of the SHS casting have proved great possibilities of this unique field of the SHS metallurgy.

Characteristics of Gas–thermal Coatings Obtained from SHS Powders

Coating material	Adhesion strength Ï ·10^{-7}, H/m2	Porosity, %	Microhardness H·10^{-7}, H/m2	Coating thickness, mm
Cr_3C_2–Ni	1.5	8–10	1500	350
Cr_3C_2–Ni–Al	5.6	5–10	2500	–

The technology of SHS surfacing allows obtaining wear-resistant cast coatings of more than 2 mm in thickness.

Industrial Test Results of Items With SHS Surfacing

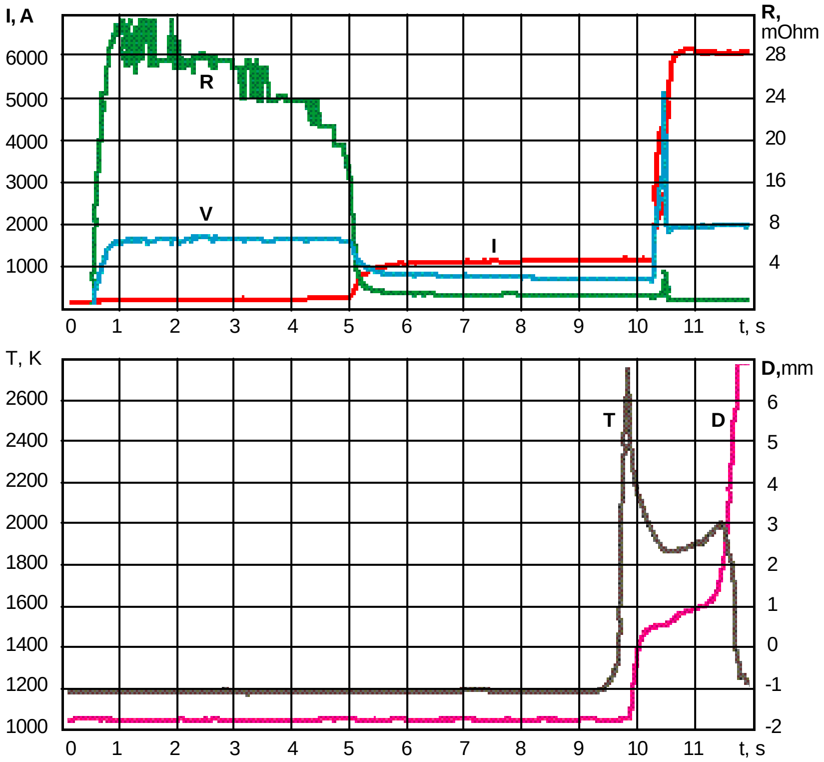
Item	SHS cast coating composition	Commercial analog	Increase in service life, %
Mixer blade	Ti–Cr–Ni-Mo	Steel Ã35Ë (Russia)	2000
Chisel	Ti-Cr-C-Fe	Sormait	200-500
Skim share	Ti-Cr-C-Fe	Sormait	270
Landside	Ti-Cr-C-Fe	Sormait	240-280
Stop valve of cryogenic installation	Ti-Cr-C-Ni	Steel 40X (Russia)	300

TT–5 SHS Welding

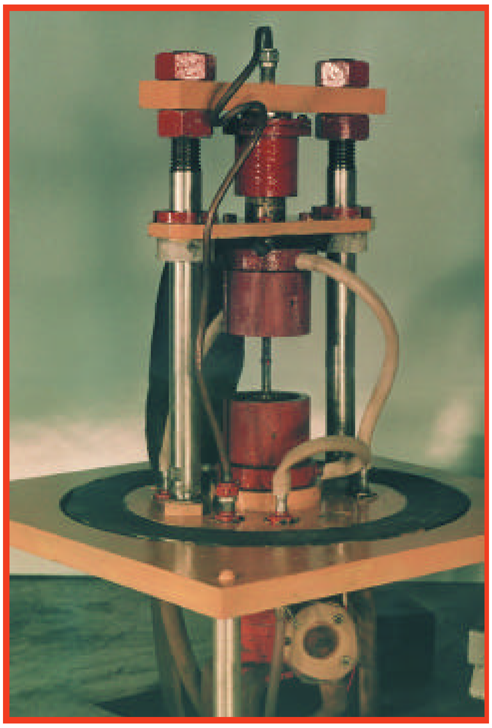
The process of SHS welding is carried out in the clearance between items to be welded; the combustion products being a weld material, and the process being a high temperature source.

SHS welding allows obtaining a strong non–detachable joint of high–temperature materials and parts.

The SHS welding is necessary for creating constructions where a combination of contradicting properties is required, e.g., heat resistance–strength, wear resistance– strength, etc. This process is used for manufacturing hard–alloy tools, high–speed and structural steel, combined cathods of high–power lamps (tungsten–molybdenum), items of rocket and space engineering.



Modes of SHS Welding



SHS welding installation

Metal Joint Strength		
Materials to be welded	**Test temperature, °C**	**Tensile strength, kg/mm^2**
Mo–Steel 961 (Russia)	**20**	**28–32**
Mo–Steel 961 (Russia)	**500**	**22–25**
Mo–Steel 961 (Russia)	**800**	**14–18**
W–Mo	**20**	**20–25**
Steel 12X18H10T (Russia)–Zr	**20**	**11–14**
Steel 12X18H10T (Russia)–Nb	**20**	**15–20**
Steel 45 (Russia)–Steel P6M5 (Russia)	**20**	**60–70**
Graphite–Mo	**1500**	**60–70**
Graphite–Graphite	**1500**	**60–70**
Graphite–W	**1500**	**60–70**
Graphite–Steel 12X18H10T (Russia)	**20**	**90**

TT–6 Gas–transport SHS technology

The up–to–date engineering pays great attention to thin (μm, mm), wear–and corrosion–resistant coatings. These tasks can be solved by the technology of gas–transport SHS coatings, when during the burning process of specially selected powder mixtures the product obtained is transferred through the gas phase to a surface to be coated, and a thin coating (5–150 μm) is applied. Characteristics of some SHS coatings are given in the Table below.The process can be carried out in the open air. A shape of an item to be coated is of no importance, i.e., it is possible to protect hard–alloy cutting plates, graphite items, steel jig bushings, etc. The most promising coatings are those made of chromium boride. They increase wear resistance of steel substrates 4–6 times. Thickness of such coatings ranges from 30 to 60 μm. Their microhardness is from 21,000 to 25,000 MPa.

SHS coatings

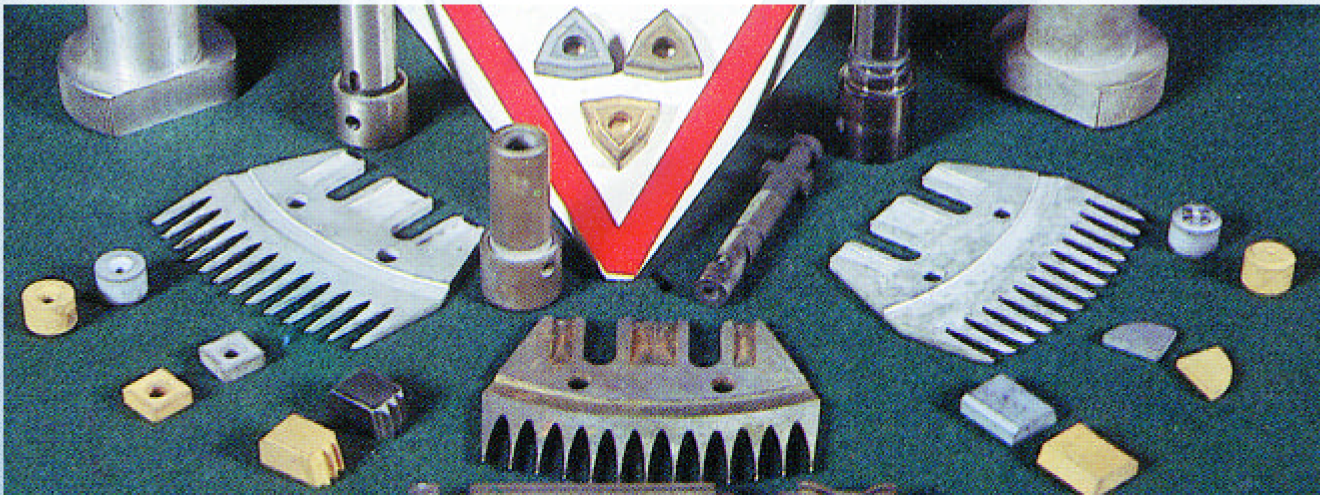
Item to be coated	Item material	Aim of coating application	Coating composition	Coating thickness, μm	Gain in service parameters, times
Jig bushing	Steel 45 (Russia)	increase in wear resistance	Fe–Cr–B	60	6 – 8
Press mold	Steel XBÃ (Russian abbrev.)	«–»	Fe–Cr–B–Al	40	3–4
Hard alloy	VK–6, VK–8	«–»	TiC, TiCN, TiN	12	3–3.5
Hot pressing die	Graphite	«–»	Cr–Ni–Al–Y	70	2–3

Promising SHS Directions

In the past years, SHS has intruded into allied fields of R&D, such as superplasticity, mechanochemistry, materials science of nanostructures, microgravity, organic synthesis, polymer chemistry.

To date, about ten SHS reactions in organic powders have been reported. The organic SHS is characterized by low temperatures and burning velocities. It simplifies the requirements to experimental facilities.

SHS studies under microgravity are oriented toward research in space. The first microgravity experiments aimed at obtaining porous materials, so called foam materials, i.e., highly porous substances with closed porosity. Experiments under «zero» gravity have proved that highly porous structures are formed by gases, evolved during combustion, and preserved upon cooling. The products obtained under microgravity are characterized by a porosity of 96 %, i.e., under such conditions, it is possible to increase the volume of SHS products twice as compared with that of the products obtained under normal conditions.



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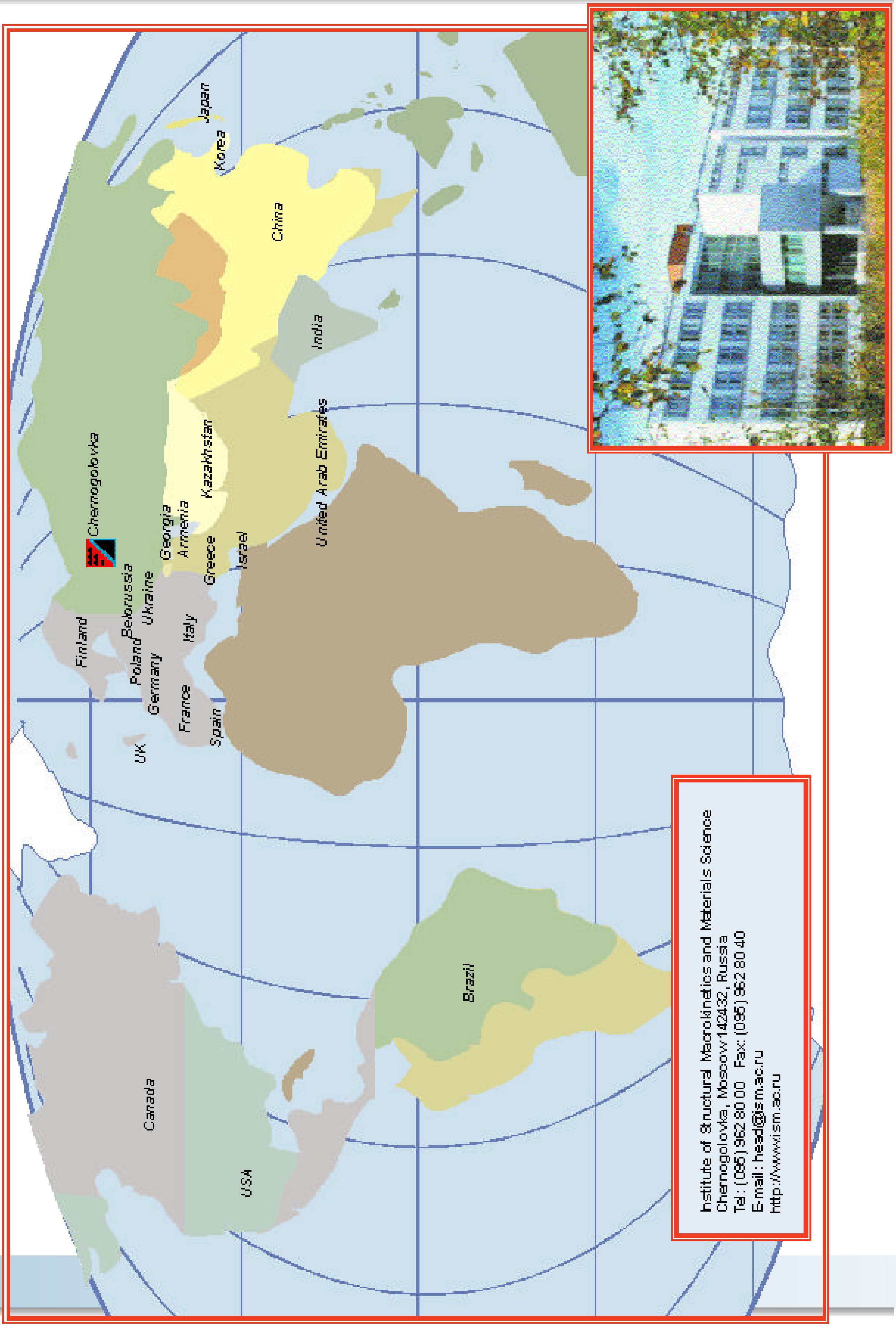

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