

SOME CHEMICAL ASPECTS OF POWER SHS COMPACTING

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The influence of different treatments of the initial raw material, initial charge composition, and additives on the final product quality was investigated. Some physicochemical properties of the alloys were measured. The experiments allowed optimal compositions of synthetic refractory tool materials to be found.

The basic trends in the development of self-propagating high-temperature synthesis (SHS) are associated with the search for methods of producing refractory inorganic compounds, materials, and articles of different purposes. As is known, the methods are based on exothermal reactions between metals and nonmetals, metals, and metals as well as on reactions involving many compounds (oxides, azides, salt hydrates, organic compounds, etc.).

Power SHS compaction is now a most promising and intensively developing SHS variant [1]. It combines combustion and mechanical action upon the heated product, resulting in compact, low-porous and poreless materials and articles based on simple and complex carbides, silicides, borides, carbonitrides and others, most often with metal bindings and alloying additions.

The right choice of the reaction systems and investigation of the relation of the chemical and phase compositions of the final products with the parameters of the process and the conditions of the reaction mass cooling are of great importance for effective solution of particular problems in material or article production by SHS compaction.

The choice and preparation of the initial raw material and its properties affecting the final product quality are essential for producing synthetic hard-tool materials (SHTM). Among the main initial materials we can mention powdered titanium, chromium, molybdenum, nickel, cobalt, carbon, boron, etc. The main characteristics of the initial materials are dispersity, admixture compositions (especially admixtures tending to combustion gasification), particle shape, adsorbed, mechanical, and dissolved impurities. Various treatments of the initial materials were used in the experiments. Adsorbed moisture and water purposefully added to metal powders for transportation were removed by drying in vacuum chambers at 70-80°C for 12 h. Black and boron were dried in the air at the same temperatures for 24 h. Boron anhydride was separated from boron and removed by boiling in hydrochloric acid, followed by washing with hot water to a neutral reaction and subsequent drying. Insoluble finely dispersed impurities were decanted.

Mixing is an important stage in preparing the synthesis charge. Dry mixing was conducted in ball mills with a ball-to-charge ratio of 1:3. The mixing time was determined by continuous control of the charge homogeneity, performing chemical analysis of samples taken from different parts of the mixture. Heptane and benzene were used for moist drying; the liquid amount was 0.5 kg per 1 kg charge. The advantage of moist drying is production of highly homogeneous charge for a short time; its drawback is difficulty of removing the residual liquid. Keeping the mixture in vacuum at 700°C for 2 h removed the "solvent" residue completely. All of the studies comprise the chemical part of the power SHS compacting development started in 1975.

Creation of tungstenless hard alloys for tool manufacturing, in particular, the development of a basically new production method of nonresharpenable tips based on carbides, borides, etc. with bindings (Co, Ni, Cu, Mo, etc.) and alloying additions was one of the first trends derived from SHS compaction. The materials were called synthetic hard tool materials (SHTM).

Studies concerned with the chemical part of the process were aimed at finding the factors controlling the completeness of the combustion reaction and the chemical and phase compositions of the products, as well as determining the relation of the process conditions with porosity, strength, and other operating characteristics of materials.

The synthesized materials were investigated using chemical, x-ray, and metallographic analyses; density, bending strength, and other characteristics were studied.

TABLE 1. Characteristics of SHTM Alloys with Different Compositions

Alloy	Composition, mass %	Density, g/cm ³	Hardness, HRA	σ_{bend} kg/mm ²
SHTM-É	40TiC—60TiB ₂	4,66—4,67	92,5—93,0	35—60
SHTM-1	40TiC—60TiB ₂ —6Co	4,76—4,78	92,5—93,5	40—70
SHTM-1A	40TiC—60TiB ₂ —12Co	4,94—4,95	—	—
SHTM-1B/1	40TiC—60TiB ₂ —5Cu	4,74—4,76	92,5—93,0	40—75
SHTM-1B/2	40TiC—60TiB ₂ —10Cu	4,84—4,85	92,5—93,0	40—75
SHTM-1B/3	80TiC—20TiB ₂ —5Cu	4,93—4,94	92,5—93,5	70—80
SHTM-2	79TiC—16Ni—5Mo	5,4—5,43	90,0—91,0	100—110
SHTM-2A	TiC—50(Ni—Mo—Cu)	6,18—6,19	85,0—86,0	170—180
SHTM-3A	TiC—Cr ₃ C ₂ —10Co	—	—	—
SHTM-3B	TiC—Cr ₃ C ₂ —10Ni	5,37—5,38	92,5—93,0	90—100
SHTM-4	TiB ₂ —Ti	4,20—4,25	85,5—86,0	110—120

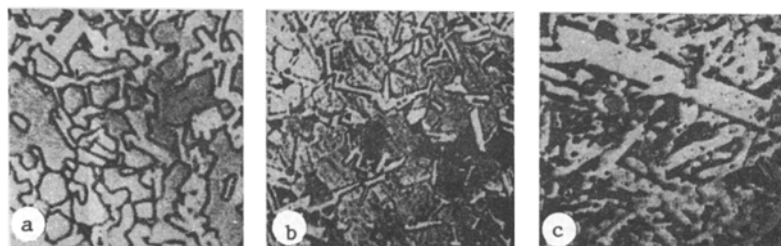


Fig. 1. Microstructure of SHTM-1B/3 alloy: eutectic composition (a), pre-eutectic composition (b), post-eutectic composition (c). $\times 2000$.

Table 1 gives the characteristics of the systems studied.

Depending on the wear-resistant component, SHTM alloys may be divided conventionally into carbide—boride, carbide, and boride groups.

The first group comprises alloys with a wear-resistant TiC—TiB₂ carbide-boride component (SHTM-É, SHTM-1, SHTM-1A, SHTM-1B/1, SHTM-1B/2, SHTM-1B/3); the second group contains alloys with a TiC carbide wear-resistant component or solid solution of Cr₃O₂ in TiC (SHTM-2, SHTM-2A, SHTM-3A, SHTM-3B); the third group consists of alloys with a wear-resistant boride component (SHTM-4 and others).

In the development of carbide—boride SHTM the following objectives were pursued: to produce an alloy with a homogeneous microstructure and good physical and mechanical properties by varying the proportions of Ti, C, and B in the initial charge; to select a binding which would decrease the blank cracking, simultaneously increasing the alloy hardness, and would be convenient for controlling the grain shape and size.

In order to attain the first objective, charges with component proportion such that the final alloys would be eutectic, pre-eutectic, and post-eutectic, i.e., would represent different regions of the constitution diagram, were prepared. The TiC—TiB₂ constitution diagram is eutectic. As reported by S. S. Ordan'yan, the eutectic composition is 43.6 mol.% TiC and 56.4 mol. % TiB₂ [2].

1. *Eutectic SHTM-É alloy* is a so-called diluted eutectic since there is no eutectic colony as such but a conglomeration of crystals of solid TiC and TiB₂ phases. The crystals grow independently of one another before their collision. By the collision moment no liquid which could be a source of eutectic colonies remains.

2. *In pre-eutectic alloys* rounded TiC grains hinder the growth of TiB₂ grains. The size of the TiB₂ grains is 5-7 μm ; they are shaped as very thin platelets or needles. They function as a kind of reinforcement for TiC grains because of which the alloy appears substantially stronger.

3. *In posteutectic alloys* TiB₂ grains are shaped as extended regular plates or needles, which may be as large as 40 μm in such alloys. This results in poorer physical and mechanical properties of the eutectic alloys (Fig. 1).

For the alloys with a wear-resistant carbide—boride component powdered Ti, B, C were used in different proportions, depending on the type of material. Before synthesis, the initial components were pretreated (in particular, boron was washed to remove boron anhydride and other impurities). This was favorable for the final material structure: variations of the densities were small within one type of material because of high homogeneity of the phase and chemical compositions and low porosity

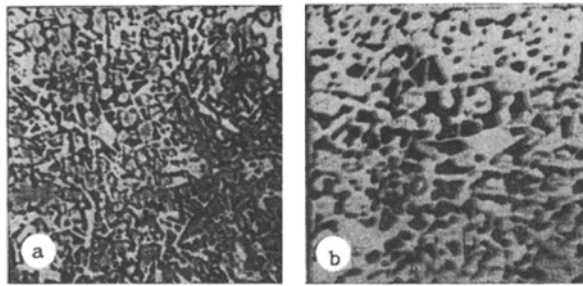


Fig. 2. Microstructure of SHTM-1B/3 alloy with 6 mass % Co (a), with 12 mass % Co (b). $\times 200$.

of the material. Apart from investigation of the microstructure and search for rejection indications in the structure, the strength characteristics of the alloys were studied. From an analysis of the results the exact composition of the initial charge can be found for production of an alloy with TiC–TiB₂ chosen as a wear-resistant component [3].

Higher brittleness exhibited by frequent cracking of the synthesized blanks is the main drawback of SHTM-É alloys. Bindings and additions were brought into the alloys to decrease cracking and to improve the strength characteristics. Co and Ni were tested as additions. The binding proportion varied from 3% to 15%. As the Co percentage rose from 3 to 12 mass %, the shape and size of carbide grain changed. The larger the Co percentage, the more separated and rounded were the Ti grains (Fig. 2). The cobalt binding was homogeneously distributed between the titanium carbide and boride grains with simultaneous formation of cobalt borides, which increased the alloy brittleness. Along with cobalt which, as was already mentioned, interacts rather actively with the main alloy components, chemical elements, the interaction of which with the main components was negligible, were selected. Copper and various bronzes may be mentioned first among them. With Cu (5-10 mass %) used as a binding, the amount of the binding did not affect the TiC and TiB₂ grain size and shape so markedly as Co did. The copper binding was located mainly in the places where TiB₂ grains accumulated, in the spaces between the grains, but moistened TiC grains poorly. In order to increase the wettability of TiC by copper, various alloying additions (Al, Ni, Mo, Y, Cr, Si) were introduced into it. Thus, an optimal alloy composition, called SHTM-1B/3, with 80 wt.% TiC – 20 wt.% TiB₂ and 5 wt.% Cu, density 4.93-4.94 g/cm³ and hardness of 92.5-93.5 HRA, $\sigma_{\text{bend}} = 70\text{-}80 \text{ kg/cm}^2$, was found.

Alloys SHTM-2, SHTM-2A, SHTM-3A belong to the group with a wear-resistant carbide component. SHTM-2 is similar in its structure to TH-20, widely used in industry which is manufactured by sintering powdered TiC with finely dispersed Ni and Mo. In the production of SHTM-2, powdered Ti, Ni, Mo, C, mixed in definite proportions in ball mills were used as initial components. Just as in the production of SHTM-1B/3, great care was taken of the initial component purity.

In connection with the development of alloy SHTM-2, Mo and Ni solvabilities in TiC and their effect on the TiC grain shape and size were investigated. The limiting solvability of Mo in TiC was found to reach 50 mass %; a slight amount of Mo added (up to 20 mass %) did not considerably influenced the size and shape of carbide grain.

No marked solvability of Ni in TiC and of TiC in Ni was found. However, Ni had a considerable effect on the TiC grain size. The grain diminished to 10-15 μm in the 5% Ni alloy and to 1-2 μm in the alloy with 50% Ni (Fig. 3a, b).

The joint effect of Mo and Ni on the carbide component and the properties of alloy SHTM-2 were investigated. The largest part of Mo was found in TiC, the amount of Mo in Ni was insignificant. Nickel is present largely in the binding, forming narrow interlayers between titanium carbide grains. The so-called "ring structure" frequently occurs in those alloys. It can arise due to incomplete homogenization or cooling-induced recrystallization when new solid solution layers fall out of the liquid phase onto the grains formed.

The results of JXA-733 microanalysis have shown that the middle of an SHTM-2 grain consists of pure TiC, whereas its edges are rich in Mo.

Thus, the optimal SHTM-2 composition is 79 mass % TiC, 16 mass % Ni, 5 mass % Mo. Its density is 5.4-5.45 g/cm³, hardness 90 HRA, and σ_{bend} up to 110 kg/mm². The size of TiMoC solid solution grain size in the alloy is 2-3 μm , the binding is uniformly distributed with a maximal interlayer thickness of 1 μm .

Various types of alloy were synthesized by varying the proportions of the wear-resistant component and the binder. One of them is SHTM-2A, a TH-50 analog, with a small Cu amount in the binding. The SHTM-2A density is 6.18-6.19 g/cm³, hardness 85-86 HRA, and bending strength 170-180 kg/mm².

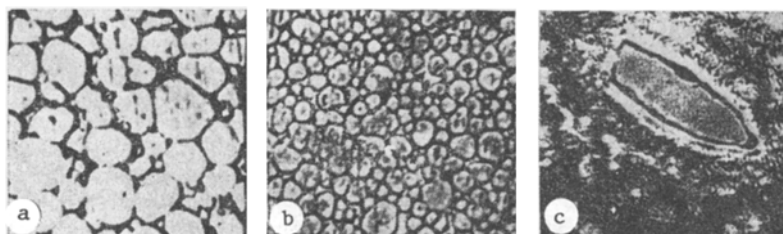


Fig. 3. Microstructure of SHTM-2 alloy with 50 mass % Ni (a) and 10 mass % Ni (b), diamond grains embedded in SHTM-2 alloy (c). $\times 2000$.

TABLE 2. Changes in SHTM-2 Density by Introducing Alloying Additives

Alloy	SHTM-2	SHTM-2+1,5%Lu	SHTM-2+1,5%Ho	SHTM-2+1,5%Yb
Density, g/cm ³	5,37—5,38	5,41—5,42	5,39—5,40	5,41—5,42

It is very interesting to investigate the effect of various additives brought into the charge as that facilitates homogenization of the alloy or reduces the grain size. As is known, addition of small amounts of rare earth metals (REM) improves the structure and properties of many metals and alloys. The addition of slight amounts of Lu, Ho, Yb increased the SHTM-2 density significantly. Table 2 contains the measured density of SHTM-2 with alloying additives. In order to diminish the SHTM-2 carbide grain size, plasma-chemical titanium nitride ($\text{TiN}_{\text{pl.ch.}}$), whose particles are highly refractory ($T_{\text{ml}}^0 = 2950^\circ\text{C}$) and therefore serve as crystallization sites, was added to the initial charge. This resulted in a material with a homogeneous carbide grain size, $10\ \mu\text{m}$ maximum.

Dilution of the charge with the prepared product is a means of decreasing the combustion temperature frequently used in SHS material production. In SHS compaction this technique appears very useful for controlling the alloy density, grain size, and other parameters. Simultaneous addition of 15% titanium carbide and 0.5% $\text{TiN}_{\text{pl.ch.}}$ gave a material with a bending strength of $100\text{--}110\ \text{kg/mm}^2$, hardness of 90-91 HRA. The wear resistance of SHTM-2 alloys was increased by the addition of diamond powders with a grain size of $50\text{--}100\ \mu\text{m}$ to the initial charge. On the one hand, the diamond powders supplied carbon to the alloy; on the other, they served as a wear-resistant component (Fig. 3c).

Also, SHTM-3A and SHTM-3B are alloys with a carbide wear-resistant component. The power compaction forming of the alloys, their operating properties and application areas are described in detail in [4-7]. In SHTM-3A and SHTM-3B solid Cr_3C_2 solution in TiC is a wear-resistant component, and Ni and Co are used as a binding. Alloys with a 10-30 mass % Cr_3C_2 content in TiC were produced by power SHS compaction. Solid Cr_3C_2 solution in TiC has a structure to be hardened; therefore, investigation of decaying of the solid solution subjected to heating is important when it is necessary to produce an alloy with the highest hardness. Specimens of alloys with 10-30% Cr_3C_2 in TiC were annealed at $T = 1300^\circ\text{C}$ for 4-6 h. The annealing resulted in decay of 30% solid solution and isolation of Cr_3C_2 as large plates, whereas 10% and 20% solid solutions remained a single phase under the same conditions. As was shown, Cr_3C_2 formed during annealing decreased the alloy hardness insignificantly. A study was conducted to investigate the binding effect on the grain size and shape as well as on physical and mechanical properties of SHTM-3A and SHTM-3B alloys. The binding proportion varied between 5 and 20 mass %. An increase of the binding percentage resulted in smaller grains of the carbide component. The alloy with 20% of binding had the best characteristics (Fig. 4a, b).

The best SHTM-3B alloy (70 mass % TiC + 30 mass % Cr_3C_2 + 20 mass % binding) has a density of $5.3\text{--}5.4\ \text{g/cm}^3$, hardness of 92.5-93 HRA, and bending strength of $90\text{--}110\ \text{g/cm}^2$.

Using the experience gained in producing the above alloys, namely, introduction of alloying REM additions into the initial charge, plasma-chemical titanium nitride, composite binding of Cr, Cu, Si, Al, etc. allowed the synthesis of very promising SHTM-3-based tool materials SHTM-4 and SHTM-5.

Power SHS compacting in the Ti-C system with different component proportions gave original alloys which were not described earlier [8]. Titanium carbide is known to have a wide homogeneity range. X-ray and metallographic studies have shown that SHS alloys with $\text{TiC}_{0.6}$ to $\text{TiC}_{0.99}$ synthesized by SHS compacting are nearly single phases.

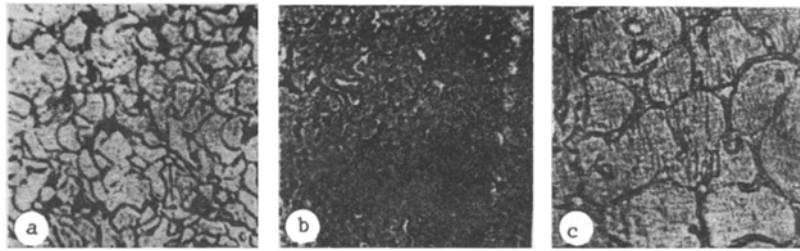


Fig. 4. Microstructure of SHTM-3B alloys with 5 mass % Co (a) and 20 mass % Co (b); the alloy microstructure with $TiC_{0.68}$ (c). $\times 2000$.

TABLE 3. Physical and Mechanical Properties of the Alloys with Different Design Compositions

Design composition	Density, g/cm ³	Hardness, HRA	σ_{bend} , kg/mm ²	Design composition	Density, g/cm ³	Hardness, HRA	σ_{bend} , kg/mm ²
$TiC_{0.54}$	4,18	80—83	—	$TiC_{0.43}$	4,53	86—87	59,2
$TiC_{0.5}$	4,30	85—86	—	$TiC_{0.42}$	4,54	86—87	65,2
$TiC_{0.48}$	4,35	85—86	—	$TiC_{0.41}$	4,51	85—86	62,4
$TiC_{0.46}$	4,40	86—87	—	$TiC_{0.40}$	4,49	85—86	—
$TiC_{0.44}$	4,47	87—88	—	$TiC_{0.29}$	4,49	84—85	—

TABLE 4. Annealing Effect on the Bending Strength for Nonstoichiometric Alloys

Composition	Annealing temperature, °C	$\sigma_{bend.av}$, kg/mm ²
$TiC_{0.43}$	0	47,6 \pm 1,2
	900	59,2 \pm 4,1
$TiC_{0.42}$	0	45,4 \pm 11,7
	900	65,2 \pm 3,3
$TiC_{0.41}$	0	37,8 \pm 11,9
	900	62,4 \pm 2,7

In carbides with $TiC_{0.6}$ to $TiC_{0.38}$, X-ray and metallographic analyses revealed two phases, namely, nonstoichiometric titanium carbide and titanium located along the carbide boundaries. In this case titanium served as a binding, and its percentage grew as the carbon proportion decreased (Fig. 4c).

The design composition $TiC_{0.38}$ proved to have the lowest carbon content at which chemical interaction occurs under SHS compacting.

Table 3 gives some physical and mechanical properties of the alloys consisting of nonstoichiometric TiC_x and Ti as a binding.

Table 4 presents the measured bending strength for $TiC_{0.43}$ – $TiC_{0.41}$ alloys with a maximal density. They were annealed to remove the SHS compacting-induced temperature stresses. The specimens annealed at $T = 900^\circ C$ have a substantially higher bending strength than the nonannealed ones do.

Subsequently, the nonstoichiometric carbides were successfully used for $TiC_{0.47}$ superplasticity synthesis [9].

The results of the relation of the chemical and phase compositions as well as of the structure and properties of the combustion products with the parameters of the SHS process were the basis for the original trend of power compaction. At present this trend is being actively developed at the Institute for Structural Macrokinetics, Russian Academy of Sciences, and at other institutions in this country and abroad. SHS compaction has been used to produce high-efficiency hard tool tips, gradient materials, large-size nonferrous rolls, dies, and targets for thermal gas coating.

The experiments for optimizing the SHTM-1B/3 alloys were carried out with participation of L. V. Kustova.

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