

**Institute of Chemical Physics NAS RA  
Technion – Israel Institute of Technology  
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**ՀՀ ԳԱԱ Քիմիական Ֆիզիկայի Ինստիտուտ  
Տեխնիոն – Իսրայելի Տեխնոլոգիական Ինստիտուտ  
Երևանի Պետական Համալսարան**

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**First Armenian-Israeli Workshop  
on Self-Propagating High-Temperature Synthesis  
(AIW SHS-2005)**

**Առաջին հայ-իսրայելական սեմինար  
“Բարձրջերմաստիճանային Ինքնատարածվող Սինթեզ”**



**Book of Abstracts  
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*26-29 September, 2005  
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# Synthesis of Dense *in situ* Composites via Pressure Assisted Thermal Explosion Mode of SHS: From Science to Application

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Over the last decade a gradual shift from the basic to applied research has led to the development of a number of unconventional SHS processes that allow simultaneous synthesis and consolidation of the inherently porous combustion products. Pressure assisted thermal explosion (TE) mode of SHS results in dense products in cases when the heat evolved during TE and pressure applied are sufficient for consolidation. Reactive Forging (RF) SHS/TE-based method has been developed: in RF, a self-sustained reaction is ignited in a reagent blend by rapid heat transfer from preheated press rams, and a moderate uni-axial pressure is applied while a sufficient amount of a liquid or very soft phase is present in the combustion product. Combined with the developed Short Distance Infiltration (SDI) approach, RF provides conditions for fabrication of discontinuously reinforced and interpenetrating phase *in situ* composites with binary ( $\text{Al}_2\text{O}_3$ ,  $\text{TiB}_2$ ,  $\text{TiC}$ ) or ternary ( $\text{MgAl}_2\text{O}_4$ ,  $\text{Ti}_3\text{SiC}_2$ ,  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_2\text{AlC}$ ) ceramic matrices, as well as intermetallic-ceramic and metal-ceramic composites ( $\text{MgB}_2$ -Mg,  $\text{Mg}_2\text{Si}$ -Mg,  $\text{Ti/Nb-Al}_2\text{O}_3$ ,  $\text{TiNi-Al}_2\text{O}_3$ ). Compared to traditional melt infiltration, SDI has the advantage of the considerably shorter infiltration distances (microns vs. millimeters/centimeters). SDI is based on the presence of low melting phases (e.g. Al, Mg, Ti-Ni eutectic) in the powder blend. Rapid heating of compacts above  $T_m$  (required to avoid reactions in solid state) followed by application of pressure results in squeezing the liquid phase into the pores which promotes SHS reactions and consolidation and results in dense products with fine homogeneous microstructures. Close temperature monitoring during processing provides a deeper insight into the SHS reaction mechanisms. The exothermicity of the SHS reactions involved, as well as the rate of heat release can be varied by diluting reagent blends with the combustion products, by mechanical activation, or by changing the reagent powder size and dispersity. The formation of a liquid phase during RF-SDI processing speeds up exothermic reactions whereas the presence of a liquid phase in the combustion product promotes full density consolidation. The approach has been successfully applied to the processing of homogeneous and functionally graded composites with a highly exothermic matrix and large volume fractions of diluents. Thermo-physical modeling allows one to gain a

better control over the RF-SDI processing and over the microstructure of the *in situ* synthesized composites.

The RF-SDI approach has also been successful in fabrication of dense superconducting MgB<sub>2</sub>/Mg composites, ceramic matrix-diamond (or -CBN) grinding wheels and light armor tiles (up to 100 mm diameter). Simultaneous RF processing of several thin tiles stacked one on top of the other allowed more effective utilization of the exothermic heat of SHS reaction.

## On Thermal Regimes and Kinetic Features of SHS Processes

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SHS is a specific form of proceeding of a high exothermal reaction, where both the maximum reaching temperature and temperature-time history are conditioned by the reaction. The characteristic feature of SHS is, that after initiation locally, the self-sustained reaction wave propagates through a heterogeneous mixture of reactants and converts the initial reagents into products. As usual, the process is characterized by high temperatures (1500-4000K), high heating rates ( $10^3$ - $10^6$  K/s) of initial components, and short times of reactions (0.1-10 s). However, coming from the results obtained in our group especially in the last decade, the range of main parameters is significantly widened. So, the self-sustained reaction front propagation is possible for both the low combustion temperatures (up to 700-1000K), and low preheating rates of substances ( $dT/dt$  amounts for some K/s). As a result the velocity of combustion wave propagation may be as low as 10-100  $\mu\text{m/s}$ .

Existence of such wide intervals for characteristic parameters, especially for heating rates, provokes a natural question about the specific features of chemical reactions proceeding, as well as the role of non-isothermicity in the SHS processes.

However, the same extreme conditions that make SHS an attractive technology also make it difficult to study the mechanism of reaction wave propagation, which is essential in order to control the process and to form materials with tailored microstructures and properties.

All these statements stimulate detailed kinetic studies of solid-phase chemical reactions under unique conditions of rapid isothermal and strongly non-isothermal transformations, that is in a totally new and wide temperature-temporal interval.

One of few methods, known to date, which provide the possibility to study the solid-phase high temperature fast reactions at both the isothermal and non-isothermal regimes, as well as allows to measure directly the reaction rate, is the Electrothermography.

In the lecture the following questions are discussed:

- a number of new SHS reactions with variety of temperature regimes;

- current state of the Electrothermography and some experimental results on kinetics of SHS reactions obtained in the last years at isothermal and strongly non-isothermal conditions;
- the basic characteristics of the novel *Computer Assisted Electrotherographical* (CAE) set-up designed and built in the Institute of Chemical Physics NAS of Armenia.

### **Summary**

- The thermal regime of SHS, depending on the system, can be accepted as isothermal or non-isothermal;
- Heating rate of initial substances has an important role in both the reaction mechanism and kinetics. It has also dominant role in providing favorable conditions for self-sustaining propagation for a number of reactions with participation of solids;
- Electrothermography with new functional resources is a powerful tool for study fast processes both at isothermal and non-isothermal conditions, as well as simulation of SHS reactions.

## **Two-Dimensional Combustion Modes at Natural Counterflow Filtration of Oxidant**

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We consider a two-dimensional model with all boundaries closed to the gas penetration except one, which is open to exchange with a large bath of gas so that the pressure is that of the bath at that end. The initial blend composed of a solid reagent and diluent powders is ignited at the opposite end of the sample by a short-term thermal pulse, which initiates the combustion wave propagation due to the heat released during the exothermic gas - solid reaction, yielding a solid product. The gas consumption in the reaction front causes a pressure gradient which drives natural filtration of oxidant through a porous substance towards the reaction front. For describing the processes of heat-mass transfer, proceeding in the sample during the filtration combustion, the time-dependent two-dimensional system of equations is used, which reflects the laws of the conservation of masses for solid and gaseous reagents, energy, the equation of state of perfect gas and Darcy's law. Boundary conditions reflect the absence of gas exchange through lateral sample surface and take into account the heat losses. It is shown that due to heat losses the field of gas flow in the sample is essentially two-dimensional. It results in obtaining the maximum conversion degree in the cross-section near the lateral face. Theoretical profiles coincide with experimental ones.

# Combustion Peculiarities in the B-TiN System and Synthesis of BN-TiN(TiB<sub>2</sub>) Composite Powders

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The work is devoted to studying macrokinetic laws of combustion in the B-TiN system with the aim at synthesizing some boron nitride-based composites (BN-TiN(TiB<sub>2</sub>)). Investigations have testified that B+TiN mixtures do not burn in the argon atmosphere, so further experiments were carried out in the nitrogen atmosphere. It has been shown that the combustion limit on boron amount (**k**) for **k**B-TiN initial mixtures is reached at **k**=1 (P(N<sub>2</sub>)=3 MPa). It was shown (Fig.1) that growth in boron amount primarily resulted in increase in combustion velocity and temperature, caused by significant role of boron nitriding. However, then this led to certain diminishing in the combustion velocity, which may be related to infiltration difficulties. X-ray analyses of burned down samples have indicated that

for the 1<**k**≤3 interval the products represent a mixture of BN and TiN. For greater **k** values the amount of TiN in the product decreases, and the opposite is observed for the TiB<sub>2</sub>. Also dependences of combustion parameters, phase composition and microstructure on the pressure and composition of gas atmosphere (argon and nitrogen mixture), density of the initial sample and other factors were studied.

It has been shown that at **k**≤3 only nitriding of boron takes place resulting in formation of the BN-TiN composite. At **k**>3 the nitriding of boron is prevailing at the beginning stage. The results of microstructure analyses have indicated that the size of product particles obtained at optimal conditions does not exceed 2-3 μm. Optimum conditions for obtaining composite powders BN-TiN and BN-TiB<sub>2</sub> containing 35-60 wt.% boron nitride were determined.

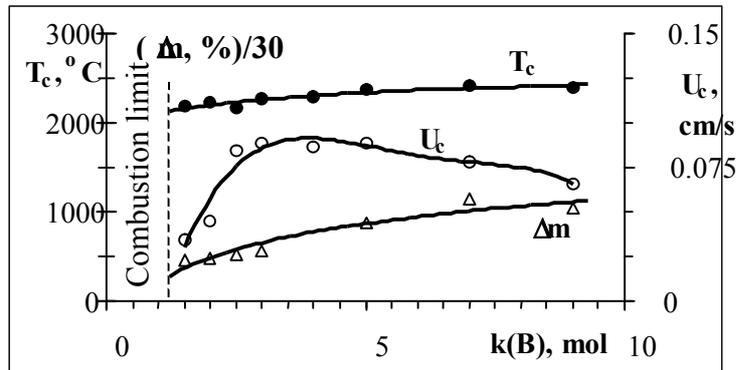


Fig.1. Combustion temperature ( $T_c$ ), velocity ( $U_c$ ) and relative mass change ( $\Delta m$ ) of burned down samples vs. **k** value for the **k**B-TiN-N<sub>2</sub> system, at P(N<sub>2</sub>) = 3 MPa.

## **Effect of High Nitrogen Pressure on Combustion Synthesis of Niobium Nitride**

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Among the nitrides of transitional metals NbN possess the highest superconducting transition temperature. The value of the superconducting transition temperature depends significantly on the stoichiometry. High pressures are required to attain the stoichiometric composition. The aim of the present work is to study the effect of high pressures on stoichiometry (magnitude of the N/Nb ratio) and lattice parameter of NbN.

The synthesis of niobium nitride by combustion of packed niobium powder under high pressures (10-230 MPa) of gaseous nitrogen was investigated. It was shown that the nitrogen content in the combustion product increased as the initial gas pressure increased. X-ray diffraction analysis of the combustion product showed the presence of a NbN<sub>x</sub> cubic phase. The value of the index (x) varied in the range from 0.79 to 1.0. It was calculated on the assumption that weight gain of the sample after synthesis is a consequence of the nitrogen absorption. A lattice parameter of analyzed samples varied non-monotonously in the range 0.4384 – 0.4399 nm and had the highest value at the pressure 90 MPa. X-ray spectral microanalysis of the sample obtained at the pressure 230 MPa showed that the nitrogen content in the probes was higher than stoichiometric one and corresponded to NbN<sub>1.08</sub>.

## Effect of Blowing Agents on SHS of Porous Ti-Based Materials

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In the present work, the SHS processing of macroporous Ti-based materials has been studied. Specifically, we concentrated on the Ti-Co and Ti-Ni systems that can yield corrosion resistant and biocompatible CoTi and NiTi alloys. Porous CoTi and NiTi are attractive potential materials for biomedical implants, e.g. strong scaffolds for filling bone voids and large defects.

It is now well-established that in order to obtain a porous material by SHS, the evolution of gases during synthesis should coincide with melting [1,2]. To achieve this condition, various blowing agents (TiH<sub>2</sub>, NH<sub>4</sub>Cl, C<sub>2</sub>F<sub>4</sub>) were added to the starting blend. The effect of the added blowing agent, as well as of other synthesis conditions (temperature, green composition, green density) on the porosity, phase composition and mechanical properties of materials synthesized has been studied.

The mechanical properties of CoTi and NiTi-based materials produced under certain SHS conditions, as well as their porosity size and distribution were found to meet the requirements of porous scaffolds for bone ingrowth. These materials have been recommended for preclinical testing.

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# Combustion Synthesis of Tungsten and Molybdenum Nanopowders, SPS-Consolidation and Mechanical Testing

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The purpose of this research is SH-synthesis of nanostructured tungsten and molybdenum powders, consolidation by Spark Plasma Sintering (SPS) method and mechanical testing of compact specimens obtained.

Nanostructured tungsten and molybdenum were synthesized via combustion reaction by solid-state reacting metals oxide ( $\text{WO}_3$ ,  $\text{MoO}_3$ ) and sodium borohydride. Sodium chloride as an inert diluent has been used to control reaction temperature and the size of metals particle. The effect of sodium chloride on the combustion temperature, product composition and morphology were evaluated using transmission electron microscopy, X-ray diffraction and BET analysis. It was shown that in 700-800°C temperature interval tungsten and molybdenum nanopowders with average size less than 100 nm and specific surface area 5~15  $\text{m}^2/\text{g}$  can be obtained.

The SPS method has been used to produce small grain size and high dense molybdenum and tungsten compacts at comparatively low temperatures and short holding times. Different process parameters such as sintering temperature, holding time, sample diameter and applied pressure have been tested. The sintering temperatures were set to 1100-1600°C and the sample were heated at a rate of 50, 100 and 300°C/min and kept at the sintering temperature for times ranging from 0-20 min. The consolidation was carried out in vacuum and the applied pressure was about 50 MPa. High sintering activity of these powders was recorded during SPS experiments. It was shown that axial shrinkage of cold pressed samples starts at unusual low temperature (400-600°C), that had allowed to get specimens having relative density as high as 93-94 % for tungsten and 96-97 % for molybdenum at 1200-1400°C.

As-consolidated samples were prepared for examination in the scanning electron microscope to identify grain size, morphology and porosity. The average size of tungsten grains according to SEM analysis was about 3-5  $\mu\text{m}$  and the size of molybdenum grains  $\sim 1 \mu\text{m}$ . These grains surface was found to be smooth and the pores meanly were located at the triple grain junction. Rectangular type samples of 2×2×3 dimension were prepared and hardness test and compression strength test were performed. Metal specimens were found to possess high hardness (3.5-3.7 GPa for tungsten and 4.3-4.5 GPa for molybdenum) and compression strengths (1100 MPa for W and 1490 MPa for Mo). At that, elongations at the maximum strength were found to be 7-8 %.

## **Formation of Nanocrystalline Al due to Ball Milling of Microcrystalline Al in the Medium of Organic Solvents**

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The process of ball milling of microcrystalline Al powder in the presence of several organic solvents such as acetone, alcohol and toluene has been carried out. It has been shown that ball milling leads to considerable physical and chemical activation of the microcrystalline Al by changing its microstructure and particle size. XRD and DTA investigations have been applied to analyze the behavior of the activated powders in comparison with the initial ones. In spite of all the used organic solvents lead to some degree of activation of the initial Al powder, however, the activation process in the presence of different solvents leads to significantly different results. Considerable growth of the strain in Al particles and the formation of nanocrystalline Al with mean grain size of 40-60 nm have been established. The possible mechanisms of the current processes will be discussed.

# Thermal Explosion in Inhomogeneous Systems

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A new interactive software has been developed in order to analyze the thermal explosion process in inhomogeneous systems. In many cases, the inhomogeneity of a reactant blend leads to unnecessary superheating of the sample, grain growth and, thereby, to deterioration of the final product properties. In the proposed software, different types of inhomogeneity are considered: non-uniform grain size in initial powder mixture, non-uniform distribution of the reactants and diluents (non-reactive elements), etc. The developed software allows simulating the temperature and composition distribution along the sample for all stages of thermal explosion. This gives the possibility to modify the external conditions of the process and the parameters of initial powder mixture so as to optimize the combustion product properties.

The software is based on the proposed mathematical model of thermal explosion. The model incorporates the equations for heat exchange between different parts of the sample, equations for heat exchange with external medium and equations for chemical reactions including multistage processes.

The software has been used to analyze thermal explosion in Ti-C/TiC and Ti-B<sub>4</sub>C systems and good agreement between mathematical simulations and experimental results has been obtained.

# Oxidation of Copper Sulfides Under the Non-isothermal Conditions

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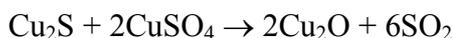
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In the present work oxidation of copper sulfides (Cu<sub>2</sub>S and CuS) in the air was studied under the linear heating conditions. Researches were carried out using Derivatograph Q-1500 D (MOM, Hungary) linked to the PC, which allows recording and processing the data obtained. The setup allows observing the behavior of the system in a linear heating mode with the possibility of changing the heating rate from 2.5 to 20°C/min.

It is shown that oxidation of these sulfides by heating them in air commonly leads to formation of the copper sulfate followed by its further decomposition into copper (II) oxide and sulfur dioxide.

As experiments have shown, in the case of CuS the oxidation proceeds just according to above-mentioned scheme independent on heating rate, while oxidation of the Cu<sub>2</sub>S displays various trends depending on the heating rate. At the heating rate 2.5°/min starting from 330°C Cu<sub>2</sub>S is completely transformed into copper sulfate, and starting from 720°C it decomposes by the scheme mentioned above. For the heating rate 20°/min in parallel with the mechanism described two additional stage were detected (on the TG and DTA curves). The former stage is characterized as an exothermal transformation accompanied by mass lose at temperature interval 500-580°C. To explain this phenomenon the well-known in the literature interaction scheme is suggested:



Next additional stage at Cu<sub>2</sub>S oxidation was detected to be accompanied with small mass gain. It is supposed that this stage is caused by conversion of Cu<sub>2</sub>O into CuO.

So the increase of heating rate more than 20°/min leads to lessening the part of copper sulfate formation in a whole reaction mechanism. Coming from this result it may be assumed that at higher heating rates the stage of copper sulfate formation will be absent at all.

Thus, the oxidation of Cu<sub>2</sub>S proceeds by different ways depending on the value of heating rate, unlike CuS oxidation for which the heating rate doesn't change the reaction direction.

# Kinetics of Niobium Carbiding under Nonisothermal Conditions

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The kinetics of carbide layers growth in diffusion multiphase zone was investigated by the example of high temperature carbiding of niobium. The investigations were carried out in the temperature range 1000-2200°C by linear heating of samples ( $V_{\text{heating}}=25-50000^\circ\text{C/s}$ ). The desired heating law was controlled by a CAE (computer assisted electrothermography) setup, allowing to carry out investigations within wide temperature intervals and at arbitrary heating laws. Carbiding of niobium was realized by heating up the initial niobium wires (100  $\mu\text{m}$  in diameter and 8.5 cm length) in the methane atmosphere by direct passing of the electrical current. Methane served as a source of carbon and its working pressure was 10 torr.

It is established that within the whole temperature range two carbide layers ( $\text{Nb}_2\text{C}$  and  $\text{NbC}$ ) are formed and they grow simultaneously. The dynamics of the diffusion zone evolution was tracked combining three independent approaches: gravimetric, metallographic and calorimetric analysis. By gravimetric and metallographic measurements S-shaped kinetic curves for the mass gain ( $\Delta m(t)$ ) and carbide layer thicknesses ( $\delta_i(t)$ ) were obtained, which were then used for determining kinetic constants. It was shown that at high heating rates characteristic parameters of the process tend to values typical for isothermal interaction at the same temperature. Correlating these results with the data of isothermal investigations [1] results leads to interesting conclusions. Starting from certain values of the heating rate the process may be described in accordance with isothermal kinetic laws. Besides, significant self-acceleration of the carbiding was observed for heating rates within certain interval, caused by appearance of a liquid phase at the temperature interval 2200-2300°C. This phenomenon could not be expected from the Nb-C equilibrium phase diagram [2], according to which the lowest point of liquidus (eutectic point) is registered at 2345°C.

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## SHS Processing of Functionally Graded Carbide Based Composites

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SHS using exothermicity of reactions is a powerful processing method of ceramic matrix composites. Pressure assisted thermal explosion (TE) mode of SHS results in dense products in cases when the heat evolved during TE and pressure applied are high enough for consolidation. In many cases graded structures are required with the outer layer containing large volume fraction of very hard particles not participating in TE and thus acting as diluents. In these cases matrices with highly exothermic reactions are needed to provide high rate of heat evolution compared to the rate of heat dissipation. Near fully dense functionally graded carbide based composites (or FGM's) were fabricated with  $B_4C$  and TiC particles as diluents employing Reactive Forging (RF) when pressure assisted TE takes place between heated rams. Ti-C, and Ti-3Al blends were used as highly exothermic reacting systems with formation of TiC, TiC-Ti and  $TiAl_3$ . Systems with higher exothermicity were used in layers containing larger fractions of diluents. Rapid heating with formation of low melting phase results in squeezing of the liquid phase into the pores between solid ceramic or/and metal particles at relatively low pressures. FGMs were prepared by stacking layers of highly exothermic Ti-C powder blends diluted with varying fractions of non-reacting  $B_4C$  particles. Only a limited amount of  $B_4C$  could be added as its diluting action reduces the overall exothermicity of the blend. Varying amounts of Ni were added to the starting blends in order to promote TE ignition and to improve the matrix toughness. In some cases,  $B_4C$  particles were precoated in order to prevent their interaction with Ti during combustion. Temperature evolution in (Ti-Ni-C)- $B_4C$  powder compacts corresponding to different FGM layers was measured separately and in the stacked form. TE in highly diluted blends (high  $B_4C$  fraction) was difficult to ignite, however stacking with the less-diluted compositions promoted ignition and increased the combustion temperature. The diluting action of  $B_4C$  particles of different size was studied experimentally and modeled based on thermophysical properties of  $B_4C$ . Good bonding integrity was obtained between layers. During RF processing of FGM's large residual tensile stresses may arise in retained liquid solidifying inside of hard particles skeleton if melting temperature of the liquid phase is lower than the temperature of heated rams. The better understanding of combustion process in  $B_4C$ -diluted blends coupled with well-devised geometrical design allows fabrication of FGMs with high volume fractions of  $B_4C$  in the outer layer.

## Syntheses of Magnesioferrites in Continuous Combustion Regime

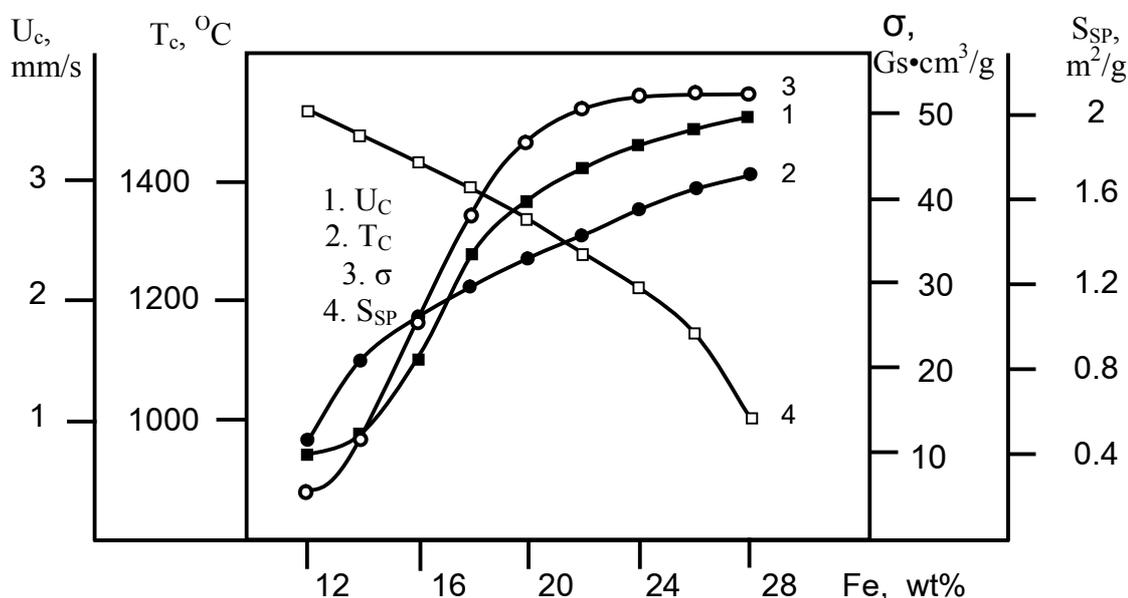
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At present the magnesioferrites ( $Mg_{0.49}Mn_{0.06}Zn_{0.45}Fe_2O_4$ ) are finding wide application in engineering due to the unique properties: magnetic permeability, thermal stability, low loss on vertical current, and specific magnetization. These ferrites easily can displace the Ni-Zn ferrites, which have high price.

Currently the production of ferrite materials reaches more than 100000 tons/year. However up to now the ferrites are being produced by the prolonged and power-intensive conventional furnace technology that adversely influences on their cost and competitiveness. Therefore, in this work possibilities to obtain ferrite materials in the combustion regime are studied, developing the technique and technology of producing oxide materials by the self-propagating high-temperature synthesis (SHS) method.

In this work the sintering kinetics and influence of the operating practices on the properties of the Mg-Zn ferrites were investigated. Optimum conditions for high degree of conversion of green mixture into the final product were determined.



*Fig.1. Combustion temperature ( $T_c$ ), velocity of combustion front propagation ( $U_c$ ), specific magnetization saturation ( $\sigma$ ) and specific surface ( $S_{SP}$ ) vs. amount of iron powder in the initial mixture for the  $Mg_{0.49}Mn_{0.06}Zn_{0.45}Fe_2O_4$  magnesioferrite.*

The combustion temperature and the velocity of combustion front propagation depend on amount of the fuel (Fe) in the mixture, average particle size and oxygen pressure.

Experiments have shown that in the MgO-MnO-ZnO-Fe<sub>2</sub>O<sub>3</sub>-Fe-O<sub>2</sub> system SHS may be realized when the content of Fe powder in the green mixture is more than 12%. The increase in the amount of the Fe powder results in growth of the relative intensity of phases, specific magnetization and diminishing of the specific surface. The highest ferritizing is achieved at the Fe powder content from 16 to 28 wt.%. However, when the content of Fe powder in the green mixture is more than 28 wt.% the conversion degree decreases.

The studies on microstructure of obtained ceramic articles and their electro-physical properties have shown that Mg-Zn ferrites made from powders synthesized by SHS are highly competitive with analogous ferrites produced by other methods.

# Kinetic Laws of Tantalum Carbiding under Non-isothermal Conditions

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Kinetic laws of tantalum carbiding are studied in the methane atmosphere within a wide temperature range (1000-2800°C) and linear heating conditions (heating rate of the sample was changed from 15 to 30000°/s).

The experiments were carried out by the Computer Assisted Electrothermography method under the strong conditions of temperature controlling. Tantalum wires (with the purity about 99.9%) 100 µm in diameter and 8.5 cm length were used, which were heated up by direct passing of the electrical current at 10 torr methane pressure. The use of methane as a source of carbon provides exactly controllable carbon flow to the surface of tantalum wire [1]. During the experiments three independent and mutually complementing main parameters (weight gain, carbide layer growth and chemical heat release) were measured.

It was established that similar to isothermal interaction [1, 2], two carbide phases are formed from the very beginning stages of the process, and they grow together. Kinetic curves for weight gain, carbide layers growth and chemical heat release are obtained. For the first two parameters S-shaped kinetic curves were obtained, caused by two competing factors: thermal acceleration and diffusion self-retarding. Depending on heating rate, the relative contributions of isothermal and non-isothermal interactions in the total process are different.

The reference value for the heating rate is determined, for which kinetic laws of non-isothermal interaction may be completely described by the well known parabolic law, obtained at isothermal conditions.

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## **The Influence of Accelerated Electrons Beam on Formation of Hydrides with Extremal Properties**

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The systematic investigation of thermal-radiation processes in systems Me-H; Me-N-H; Me-C-H; Me-Me"-H at irradiation in linear accelerator of electrons LAE-5 were conducted. A special camera providing electron beam processing of materials in vacuum and in hydrogen was prepared. The working parameters are: 4 MeV, mean current – 150  $\mu$ A. At irradiation of metals in H<sub>2</sub> with accelerated electron beam at a dose power of 0.05-1 Mrad/s, a thermal-radiation synthesis (TRS) of metal hydrides takes place. The TRS - a new direction of synthesis of hydrides transition metals, hydridonitrides and carbonitrides on the basis of fourth group metals and their alloys was elaborated. Scientific bases of metals and alloys interaction with hydrogen in the beam of accelerated electrons were studied. It was indicated, that the TRS takes place in the thermal explosion mode. A new phenomenon of "cold synthesis" (CS) was revealed. To observe it, after irradiation in vacuum at different dose rates (0.05-1 Mrad/s), a sample was cooled down to the ambient temperature, and hydrogen was filled into the camera. After 20-30 s the thermocouple registered a sharp temperature jump up to 420-700°C. In the CS regime, a hafnium hydride of superstoichiometric composition was obtained for the first time. More than 40 binary and composite hydrides were obtained in TRS and CS modes.

## Partially Sintered $B_4C$ - $TiB_2$ Preforms for the Reaction Bonding Process

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Hard ceramic materials are playing an ever increasing role in a variety of applications, among others lately, for personal armor. Boron carbide, the hardness of which is particularly high and which has low density is a choice armor material candidate. Monolithic boron carbide of full density can be fabricated only by hot pressing at elevated temperature. The "reaction bonding" process developed in the late nineties provided an alternative for the fabrication of  $B_4C$  (RBBC)-based armor material. According to this process a compacted mixture of carbon and boron carbide is infiltrated with molten silicon to yield a cohesive and hard ceramic consisting of boron carbide and silicon carbide. A further improvement can be attained by adding to the initial mixture titanium containing compounds that react with boron carbide resulting in the formation of  $TiB_2$  and in the *in-situ* release of free carbon. The latter reaction is strongly exothermic, the released free carbon is meant to act as a sintering enhancing additive and reduce the temperature necessary for pressureless densification of a two-phase,  $B_4C$ - $TiB_2$  ceramic. A partially densified two-phase ceramic preform can be subsequently infiltrated with molten silicon according to the RBBC process.

One approach for the first step of the above suggested procedure consists of mixing boron carbide and titanium hydride powders. At about 300°C, titanium hydride decomposes and releases hydrogen and at some higher temperature the reaction between boron carbide and titanium is initiated. It seems of interest to study the applicability of an SHS approach for the generation of a partially sintered  $B_4C$ - $TiB_2$ -C preform, appropriate for subsequent infiltration by molten silicon.

In the course of our talk, we shall describe the preliminary results of the reaction between boron carbide and *in situ* formed titanium and the structure of the Si-infiltrated preform. Various questions regarding the initiation of a SHS reaction to generate a partially sintered two-phase ceramic with controllable porosity will be examined.

# Effect of Silicon Particles Size on Self-propagating High-temperature Synthesis of Silicon Nitride

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In the existing industrial method of silicon nitride production by self-propagating high-temperature synthesis, the granulometric composition of the initial silicon powder is distinguished by high polydispersity: from 1 up to 100  $\mu\text{m}$ . The aim of the work is to study the effect of silicon particles size on the main synthesis parameters and final product characteristics.

Silicon powder was made by grinding technical silicon, classifying it into fractions sedimentation in liquid. The silicon powders of the dispersion degree from 0.1 to 25  $\mu\text{m}$  were obtained and then used for preparing the green mixture with 50 wt.% of silicon nitride added as the diluent. The experiments were carried out in the laboratory reactor of 2 litres capacity. The initial nitrogen pressure was 6 MPa.

The experiments have proved:

1. With an increase in silicon powder dispersion degree the combustion rate drops from 1.4 mm/s ( $D_{\text{av}}=0.97 \mu\text{m}$ ) to 0.3 mm/s ( $D_{\text{av}}=25 \mu\text{m}$  – combustion threshold).
2. The combustion temperature is maximum for the dispersion degree of 10–15  $\mu\text{m}$ , it becomes lower at  $D_{\text{av}}=1–5 \mu\text{m}$  and drops significantly at  $D_{\text{av}}>20 \mu\text{m}$ .
3. The completeness degree of the chemical transformation becomes remarkably lower (to 30%) with an increase in the average size of silicon powder particles.
4.  $\alpha$ -phase  $\text{Si}_3\text{N}_4$  content is increased (2.5 times) in proportion to an increase in the diameter of silicon particles.

## Synthesis of BN/B<sub>4</sub>C Composite Powders under the Activated Combustion Mode

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The opportunities on synthesizing boron nitride-boron carbide composite under the activated combustion mode were investigated. Much attention is given to *in situ* controlling the microstructure, particle size, as well as the ratio of compounds in the final products. As active compounds (activators) inorganic oxygen containing salts, particularly ammonium and potassium nitrates were used.

The influence of the type and amount of activators, density and diameter of initial sample, inert gas pressure, and other parameters on combustion laws and phase formation features was investigated. Products were examined by applying XRD, SEM, BET and chemical analyses.

It is established that at small amounts of the activator (less than 0.4 mol) combustion process can not be initiated. At the same time large amounts of additives are undesirable, as they lead to the very intensive combustion followed by sharp increase in pressure. At increasing the density of the initial samples combustion parameters tend to decrease independent of the type of additive.

Experiments carried out in the MgB<sub>12</sub>-nC<sub>3</sub>H<sub>6</sub>N<sub>6</sub>-KNO<sub>3</sub> system have shown that high contents of melamine in the initial mixture resulted in increase in the quantity of bonded nitrogen in the products. In the case of ammonium nitrate this effect was not observed. It is established that the use of potassium nitrate as an activator allows to obtain boron carbides with various amounts of carbon (e.g. B<sub>4</sub>C, B<sub>13</sub>C<sub>2</sub>).

Thus, using different additives it is possible to synthesize under the combustion mode composites containing 50%BN-50%B<sub>4</sub>C, BN-*n*%(B<sub>13</sub>C<sub>2</sub>/B<sub>4</sub>C), where the ratio of boron carbides can vary in the interval 0-0.6, while *n* changes from 40 to 60%.

## SHS-Silicothermy: Cast Copper Obtaining from Oxide Raw Materials

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It is common knowledge that the copper melting processes is multistage, power-consuming and usually break allowable ecological norms because of imperfective apparatus or technological schemes used. On the other hand, solid-state reactions of powder mixtures in high-temperature furnaces often do not go to completion, allowing unreacted substances to act as impurities and leading to poor-quality products. From this point of view the application of self-propagating high-temperature synthesis (SHS) technique as a non-traditional method for producing different materials, compounds and alloys allows to avoid above-mentioned shortcomings.

The work is devoted to studying a model system, that is: copper oxide silicothermal reduction under the combustion mode, revealing main combustion parameters (temperature and velocity), phase and microstructural characteristics of reduction products depending on different factors.

Preliminary thermodynamic calculations (performed by application of the THERMO software) have shown that adiabatic combustion temperature for the CuO-Si system is about 2500°C. It is evident that under such conditions reduction cannot be controllable, i.e. to obtain alloyed copper and separate metallic phase from the slag. For decreasing the combustion temperature, controlling the acidity, viscosity and lowering the melting point of the slag the initial CuO-Si mixture was diluted with some oxides (CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, etc.). Experiments were carried out for revealing the influence of diluent amounts, initial sample size, form and density on combustion parameters and yields of the target material. Optimum ranges on amounts of added oxides were established. Within these ranges the maximum combustion temperature did not exceed 1350°C. Optimum conditions on the density of the initial mixtures were determined for the maximum yields (~95 %) of the final product. Microstructural and phase formation mechanisms for the reduction processes are suggested.

# Self-propagation High-temperature Synthesis of ZnS Using Bi-Disperse Zinc

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Due to its unique qualities Zinc Sulphide finds the broad use in the different areas of optics and optic-electronics and especially it is not substitute in strong electromagnetic radiation.

The traditional ways of manufacturing of ZnS require significant amounts of energy, they are dangerously explosive and ecologically toxic. The authors used the method of self-propagation high temperature synthesis (SHS). The synthesis was done from Zn and S elements in closed reactor under the pressure of the inert gas. Earlier this method was used for the zinc powder with particle size no more than 20  $\mu\text{m}$  resulting in formation of ZnS with high completeness of synthesis. However, while using Zn with particle size up to 150  $\mu\text{m}$  the SHS process goes nonequilibrium and with low quality of ZnS. In order to improve the quality of ZnS while using the zinc of broad dispersion, one can use the widening of the zone of combustion (ZC).

The following criteria can be used to analyze the conditions of transition from narrow to broad ZC during the SHS of ZnS:

$$\pi = \frac{c \rho u d}{25 \lambda}$$

where  $c$ ,  $\rho$ ,  $\lambda$ ,  $u$  – represent thermal heat capacity, density, heat conductivity, and the speed of combustion front propagation in the mixture, accordingly;  $d$  is a parameter, determined from the concentration and the size of large fraction.

The experiment demonstrated that if  $\pi \geq 1$  the combustion of small fraction of particles determines the process, ZC is narrow and the completeness of the combustion is low, because the particles of zinc of large diameter do not have time to complete the combustion. If  $\pi < 1$ , the broad ZC is employed and the particles of large fraction combust with high completeness.

The manipulation of  $u$  and  $d$  parameters during the experiment allowed the researchers to achieve  $\pi < 1$  and to obtain high level of the end-product ZnS. The fixed purity of the product was 99.5-99.8%.

## Interaction Laws of Niobium with Silane in the Diffusive Mode

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The silicides of transition metals exhibit a number of extraordinary properties and are widely applied in different areas of modern engineering. They are successfully used in metallurgy, chemistry, microelectronics, in the technology of the integrated circuits, as components of multiphase composite materials, etc. High-temperature and corrosion resistance of disilicide phases make it possible to apply them as protective coatings working in aggressive environments.

One of perspective methods for applying a coating is the diffusive saturation of surface layer of the transition metals by silicon. However high-temperature heating of the refractory metal - disilicide coating system results in transformation of higher silicides into the lowest ones, thus changing phase composition of the surface layer. These processes have diffusive character and for their quantitative description diffusion coefficients of silicon in silicide phases at high temperatures are necessary. However the data on diffusion coefficients of silicon in the niobium disilicide mainly deal with narrow temperature intervals ( $T=1200-1350^{\circ}\text{C}$ ), with upper limit usually not exceeding the melting point of silicon.

This work presents experimental results on the kinetics of diffusive silicide layer growth at siliconizing the Nb in the medium of rarefied silane ( $P_{\text{SiH}_4}=0.08-4$  torr), as well as on the diffusion of silicon in the  $\text{NbSi}_2$  silicide at  $T=980-1550^{\circ}\text{C}$ . The temperature range studied covers the conditions of niobium disilicide synthesis under the combustion mode [1]. The experiments were carried out using the electrothermography method [2]. As initial materials niobium wires (ESPI Metals, 3N, 99.9 % purity) 100  $\mu\text{m}$  in diameter and working length of 8.5 cm, and gaseous silane diluted by argon were used. The silane partial pressure was changed in the interval of 0.1-4 torr.

Metallographical analyses have shown that two silicide layers of niobium ( $\text{NbSi}_2$  and  $\text{Nb}_5\text{Si}_3$ ) were formed and the thickness of the latter silicide is approximately 10 times smaller as compared with that of for the  $\text{NbSi}_2$  layer. The growth of the  $\text{NbSi}_2$  layer thickness obeys a parabolic rate law under the conditions studied with a parabolic rate constant:

$$K=3.01 \cdot 10^{-3} \cdot \exp(-38000/RT), \text{ cm}^2/\text{s}$$

where the activation energy is expressed in cal/mol.

Determining experimentally the values of parabolic constants at different temperatures have allowed to calculate diffusion coefficients (D) of silicon in the NbSi<sub>2</sub> silicide starting from the own-derived formula:

$$D=C_{11}K^2/2(C_{12}-C_{11})$$

where C is the concentration of silicon on the appropriate boundaries of silicide phases formed. Using more exact data [3] for these concentrations: C<sub>11</sub>=1.091 g/cm<sup>3</sup>, C<sub>12</sub>=1.101 g/cm<sup>3</sup>, C<sub>21</sub>=2.038 g/cm<sup>3</sup>, C<sub>22</sub>=2.27 g/cm<sup>3</sup> an expression for temperature dependence of the diffusion coefficient is obtained:

$$D=1.32 \cdot 10^{-2} \cdot \exp (-38000/RT), \text{ cm}^2/\text{s}.$$

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## **Production of Ti/TiB Master Alloy by the SHS Process for Obtaining Ti/TiB Composites for Automotive Industry**

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High technology transport sectors are looking for higher performance materials, competitive in terms of cost, lighter than conventional titanium alloys and recyclable, which could improve efficiency of several components and reduce fuel consumption through weight reduction.

This work has been carried out in the framework of Growth NEWTIRAL project (Contract No G5RD-CT01-00529) financially supported by the European Commission, which investigates the production of *in situ* Ti/TiB master alloy (with a high volume fraction of reinforcing phase) that is further melted together with titanium ingots. This way a composite with controlled TiB reinforcement volume fraction can be obtained via conventional casting route.

This study focuses in the investigation of the production technique of the Ti/TiB master alloy, which is produce by SHS (Self Propagating High temperature Synthesis). This technique is a self-sustaining combustion process of any chemical compound that results in the formation of valuable condensed products. The SHS is based on the principle of maximum utilization of chemical energy of reacting substances (exothermicity) for obtaining inorganic compounds, materials, and items of various application purposes and also for organizing highly efficient technological processes.

The obtained product is characterised using different techniques: XRD, SEM, and optical microscope.

## Combustion Laws in the $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-Al(Si)}$ , $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-Al-Si}$ Model Systems and SHS of Cast Ferrochromes

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Among currently intensively investigating multicomponent systems of the *metal oxide-nonmetal oxide (or oxide of another metal)-reducer* type the thermit ones, in which SHS-metallothermy (or SHS-metallurgy) is realized, are viewed as promising.

In this investigation we study the possibilities to apply SHS-metallurgy for obtaining cast ferrochromes from appropriate oxides using aluminum, silicon or their mixture as reducers.

For this purpose combustion laws in the  $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-Al(Si)}$ ,  $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-Al-Si}$  systems are studied depending on composition of the initial charge, the ratio and sizes of initial components, density and diameter of initial samples, the presence of activators in the initial charge, etc. Primary attention is given to determining conditions for obtaining cast ferrochromes, as well as on combustion limits.

To select proper reducers and optimum conditions of the process realization preliminary thermodynamic calculations for the systems considered were performed.

In experiments powdered chromium oxide  $\text{Cr}_2\text{O}_3$ , iron oxide  $\text{Fe}_2\text{O}_3$ , aluminum and silicon with particle size less than 50  $\mu\text{m}$  were used. Cylindrical pellets 20-50 mm in diameter and 75-80 mm height were prepared from the initial mixtures and were ignited in the silica sand medium at atmospheric pressure. Relative density of these samples averages between 0.1 and 0.25 corresponding to that of for the loosen sample. Microthermocouple technique is used for measuring combustion parameters ( $T_c$  and  $U_c$ ) by application of tungsten-rhenium thermocouples 0.2 mm in diameter. Controlling the experiments and recording the signals from the thermocouple is performed by a PC linked to the setup. Burned down samples were examined by XRD and chemical analyses (to determine contents of the iron and free silicon). Scanning electron microscopy (BS-300) is used for studying the microstructure of samples.

Main features of combustion synthesis of ferrochrome alloys with various compositions, as well as factors influencing on combustion characteristics, completeness of phase separation, density, microstructure and the composition of the product are revealed. It is shown that composition and the yield of ferrochrome alloys may be regulated by changing the ratio of oxides and type of the reducer in the initial charge.

Optimum conditions for realization of the process with different ratios of iron and chromium oxides are determined. The results on combustion of model systems  $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-Al(Si)}$  and  $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-Al-Si}$  are of practical interest in respect to obtaining ferrochromes from  $\text{Cr}_2\text{O}_3$ -lean ores.

## Combustion Synthesis of the MoSi<sub>2</sub>-SiC Composite: Role of the Activator

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In the work a problem was set to investigate the possibility of synthesizing molybdenum disilicide-silicon carbide composite under the activated combustion mode. Besides, the requirements for the product were that it be obtained with variable ratio of components, required microstructure and particle size.

It is established that without an activator the combustion synthesized composite may contain silicon carbide less than 10 wt.%, while using Teflon as activator allows to expand combustion limits and to obtain composite with high content of silicon carbide [1]. As shown in [1] combustion in the initial Mo-Si-C-(C<sub>2</sub>F<sub>4</sub>)<sub>n</sub> mixture may be initiated in the nitrogen environment (at pressures more than 30 atm) at the presence of small amounts of Teflon (<5 wt.%). However XRD and chemical analyses have indicated that in this case the formed molybdenum disilicide is partly nitrated yielding Mo<sub>5</sub>Si<sub>3</sub> and Si<sub>3</sub>N<sub>4</sub>. For this reason further investigations were carried out in argon atmosphere. As the data obtained have illustrated, two combustion regimes are realized depending on gas pressure. The first is low-temperature one, when P<sub>Ar</sub><5 atm, and the combustion temperature is lower than 1000°C. The high temperature regime corresponds to: P<sub>Ar</sub>>7 atm, and combustion temperature ~1800°C. It is established that low temperature regime corresponds to fluorination of silicon. During this stage MoSi<sub>2</sub> and SiC are not formed. They appear only at high-temperature regime (proved by XRD analysis).

Microstructural analyses have shown that products with fine particles (<5 μm) are obtained in nitrogen atmosphere or from mixtures containing high amounts of Teflon. However, these composites contain significant amount of silicon nitride and Mo<sub>5</sub>Si<sub>3</sub>. Products obtained in argon medium have relatively large grains (from 5 to 15 μm).

Thus, changing the combustion conditions and the type of an activator one can obtain MoSi<sub>2</sub>-SiC composite with wide range of components (10-90%), as well as *in situ* regulate the microstructure of products.

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## **SHS-Metallothermy: Cast Ferromolybdenum Synthesis from Roasted Molybdenum Concentrate**

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Currently the greater part of molybdenum produced in the world is consumed for alloying steels. It is well known that adding 2-5 % molybdenum to steels leads to improving their mechanical, corrosion, thermal and other properties. To achieve the best homogeneity of the molybdenum distribution in steels it is usually introduced as an ferromolybdenum alloy.

This research is devoted to producing ferromolybdenum alloys by a directed combustion mode using as a raw material the molybdenum oxide concentrate (with the content of molybdenum about 57-58 wt.%) from the “Zangezour Copper Molybdenum Combine” CJSC (Armenia). The reduction of the concentrate mentioned was performed by application of ferrosilicide mixtures containing different amounts of silicon (45 and 75%). Application of these latter has allowed to regulate the content of molybdenum and iron in the products, chemical and phase composition of cast alloys and their microstructure. As a result of investigations optimum conditions for synthesizing ferromolybdenum alloys with iron content of 55-70 wt.% have been determined. Besides, based on some technological features of the SHS, it became possible to regulate purposefully the reduction of molybdenum oxide, avoiding explosions, which may accompany the ferromolybdenum production in the conventional approach.

## **A New SHS Method for Special Ferroalloys Production**

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Common ferromanganese alloys produced by the Self-Propagating High-temperature Synthesis (SHS) are not competitive with regard industrial grades produced by other technologies. It is convenient to apply the SHS technology for producing special ferroalloys which is problematic and even impossible via other methods. The present study deals with the SHS-production of carbon-free ferromanganese.

Recently metallic manganese is used for alloying high-quality, low-carbon steels and for special carbon-free alloys. In this work a low-cost, high-quality carbon-free ferromanganese, produced via SHS, is proposed for the same purpose instead of metallic manganese. The proposed technology considerably reduces the cost of the end-product and increases its quality. The technology is simple and environmentally safe.

For production of carbon-free ferromanganese a new deoxidizer was used which is obtained from industrial waste of aluminum and manganese. This allowed to reduce the aluminum powder waste by 95%. During the synthesis in high-pressure reactor, the rate of extraction of manganese from the ore concentrate is increased by 7-9% (83-85% instead of 74-76%) in contrast to the aluminothermic technology.

## **Ferrochrome Obtaining from Chromite Deposits by Aluminothermic Reduction**

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Nitrogen and chromium containing steels – being a need for the development of our industry – possess outstanding mechanical (durability, wear-resistant) and chemical (corrosion-resistant) properties. Nitrated ferrochrome is considered as the best dopant for these steels. Conventionally obtained ferrochrome is burdensome, energy-consuming and environmentally hazardous technology.

Aluminothermic method of obtaining nitrated ferrochrome from local chromite ores has many advantages as compared with the conventional technology. During the synthesis, high-temperature aluminothermic self-propagating reduction of ferrous chromite is employed at 3000K, where no external heat source is needed. The synthesis could be carried out without the use of furnace or kiln, which can be considered as one of the main advantages over the currently used technology.

Chromite concentrate (with 53% of  $\text{Cr}_2\text{O}_3$ ), utilizing the described technology, is obtained by simple gravitation enrichment method. The concentrate could serve as raw material for the obtainment of nitrated ferrochrome as our preliminary investigations showed.

Experiments were carried out in a crucible. The feed (charge) was prepared from chromite concentrate, aluminum powder, CaO and  $\text{SiO}_2$  with the addition of  $\text{CrO}_3$  and  $\text{KNO}_3$  to keep the reaction going (to increase the heat balance).  $\text{KNO}_3$  also is an important additive for the synthesis of nitrated ferrochrome.  $\text{Fe}_3\text{O}_4$ -Ti-C mixture was used as an initiator (fuse) in the top and bottom of the charge. Optimization of charge composition as depended upon particle size, reaction temperature, etc. is performed. The obtained metallic phase investigated by the X-Ray, spectral and chemical analysis methods is nitrated ferrochrome, where 66–70% chromium and 1% of nitrogen was present. The tailings (with 5% content of  $\text{Cr}_2\text{O}_3$ ) could go as ingredient for producing refractory materials.

In conclusion it could be said that a new method of obtaining ferrochrome is proposed from local chromite-containing ores by the aluminothermic reduction without the use of any furnace. This method could also be practiced for other non-ferrous and ferrous technology end-users.

## Reduction of Copper Concentrate by Aluminothermic Method

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Wasteless, complex and environmentally friendly technology development for the processing of non-ferrous ores of Armenia is a pressing issue for the country. In this regard, it is important to extract iron, zinc, lead from copper-containing ores along with copper. By the way, the copper concentrate obtained from copper-containing deposit of Shahumyan, contains 19.3% Cu, 2.4% Zn, 1.03% Pb and 29.89% Fe. Complex processing of this concentrate allows to obtain Fe-based alloys containing Zn, Pb, Cu as a dopant.

The conventional method of processing of sulphide ores demands oxidizing roasting accompanied by evolving SO<sub>2</sub> which is troublesome to handle. In this regard, in this work we propose a wasteless technology without use of furnaces. The technology is based on aluminothermic reduction of sulphide ores.

Preliminary calculations show the thermodynamic possibility of aluminothermic reduction of Cu, Fe, Zn, and Pb. Gibbs free energy values of these reactions are in the region from -200 to -400 kJ Mole<sup>-1</sup>.

Primarily, as before the aluminothermic reduction, the mixture was activated mechanically (fine grinding) to decrease the sulphur content in the alloy. Grinding of the sulphides was carried out both in air and by the wet method. After this main fraction of the powder (about 87%) has particle sizes less than 40 µm. X-Ray data show that sulfates and oxides, along with an amorphous mass were obtained after mechanical activation. These results also were confirmed by chemical analysis methods.

The activated concentrate was later reduced aluminothermically in the presence of KNO<sub>3</sub>, CaO and SiO<sub>2</sub>. During the self-propagating high-temperature synthesis, the temperature elevates up to 3000<sup>0</sup>C. This temperature is enough to obtain the alloy and to separate the tailings and the metallic phases. The metallic phase was investigated by X-Ray method which confirmed that Fe-based Zn, Pb, Cu containing alloy was obtained with small inclusion of sulphur.

Thus, the bases of a new technology for processing the sulphide ores are laid. The elaborated technology is wasteless, energy-efficient allowing to extract many metals in the form of dopant.

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