MISIS
National University of
Science and Technology

ISMAN

THE SCIENTIFIC EDUCATIONAL CENTER OF SHS

2019

SHS CENTER – 30th ANNIVERSARY

The Scientific-Educational Center of SHS (SHS Center) of the National University of Science and Technology "MISIS" (MISIS) and the Merzhanov Institute of Structural Macrokinetics and Materials Science of the Russian Academy of Sciences (ISMAN) was established in USSR by the resolution № 744/119 of September 21, 1989 signed by the State Committee for Public Education and Presidium of the Academy of Sciences. The SHS Center was created in order to obtain the synergetic effect due to combining the effort and resources of the higher education and academic institutions in conducting basic research, developing technologies and educating specialists in various aspects of SHS.

An idea of creating the SHS Center belonged to academician A.G. Merzhanov, a pioneer of SHS and founder of ISMAN.

SHS Center has united the leading researchers of MISIS and ISMAN in the field of chemical physics, physics of combustion and explosion, physical chemistry, structural macrokinetics, physical materials science, powder metallurgy, metal treatment by pressure.

30 year history of the SHS Center is rich in scientific achievements that have reinforced the position over the world. Today, the SHS Center has authority for the development of various materials (ceramics and metal matrix composites, ultra-high-temperature materials, functional gradient materials, multicomponent and multilayer nanostructured films, hard tribological coatings, anticorrosion and heat-resistant coatings, biocompatible and bioactive coatings with anti-bacterial effect, self-lubricating coatings, nanoparticle dispersion-strengthened materials, et al.) for industrial technologies using SHS, powder metallurgy, magnetron sputtering, ion implantation assisted magnetron sputtering, pulsed electrospark deposition, as well as for certification and metrology of mechanical and tribological properties. More than 30 highly qualified researchers, including 5 doctors of science and professors, 16 PhD and associate professors, 6 engineers, 7 postgraduate students, and 7-12 master students are employed every year. The staff of SHS Center are the members of the Dissertation Boards at the MISIS and ISMAN, the members of editorial boards of the «Russian Journal of Non-Ferrous Metals», «Int. Journal of Self-Propagating High-Temperature Synthesis», "Ceramics Internationals", «Physical Surface Engineering», «Metal Science and Heat Treatment», "Materials", et al. Furthermore, they are the members of the scientific councils and committees, such as: the Scientific Council on Combustion and Explosion of the Russian Academy of Sciences; the Int. Committee on SHS and FGMs; the European Joint Committee on Plasma and Ion Surface Engineering; the Int. Committee of the Conferences and Symposiums on SHS, FGMs, Plasma Surface Engineering, CIMTEC, Metallurgical Coatings and Thin Films, et al.

The staff have published more than 1100 articles in the peer-reviewed journals, 100 patents, 16 books, including one of the latest – "Concise Encyclopedia of Combustion Synthesis: History, Theory, Technology, and Products", Elsevier, 2017, 466 p.

The education process is carried out in the SHS Center within the master's programs: "Powder and additive technologies of the functional materials and coatings synthesis», «Multicomponent nanostructured coatings. Nanofilms».

The SHS Center consists of the following subdivisions:

– Scientific-Industrial Plant of the SHS technologies;
– Sector of Mechanical Activation;
– Sector of Pulsed Electrospark Deposition (PED);
– Laboratory of Ion-Plasma Technologies;
– Laboratory of Functional Surfaces Characterization;
– Laboratory of Electronic Microscopy.

PERSONNEL

Levashov Evgeny Alexandrovich, Ph.D, Doctor of Science, Professor
Full Member of the Russian Academy of Natural Science,
Head of the Scientific-Educational Center of SHS,
Head of the Department of Powder Metallurgy and Functional Materials
Scientific area: SHS, powder metallurgy, high-temperature composites, hard materials, surface engineering, nanomaterials, multifunctional and biocompatible materials, additive manufacturing, characterization
Tel.: +7 (495) 638-45-00
Fax: +7 (499) 236-52-98
E-mail: levashov@shs.misis.ru

Shtansky Dmitry Vladimirovich, Ph.D, Doctor of Science
Principal Scientist of the Scientific-Educational Center of SHS,
Professor of the Department of Powder Metallurgy and Functional Coatings
Head of the Research Laboratory «Inorganic Nanomaterials»
Scientific area: Materials science of thin films and coatings, ion-plasma technologies, surface engineering, nanostructured and nanocomposite materials, biocompatible and bioactive materials, inorganic materials
Tel./Fax: +7 (499) 236-66-29
E-mail: shtansky@shs.misis.ru

Kurbatkina Viktoria Vladimirovna, Ph.D
Leading Research Scientist,
Scientific secretary of the Scientific-Educational Center of SHS,
Associate Professor of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Materials science, mechanical activation, SHS
Tel./Fax: +7 (499) 237-53-36
E-mail: vvkurb@mail.ru

Kiryukhantsev-Korneev Philipp Vladimirovich, Ph.D
Leading Research Scientist of the Scientific-Educational Center of SHS,
Associate Professor of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Nanostructured coatings, PVD-processes, GD optical emission spectroscopy
Tel.: +7 (495) 638-46-59
Fax: +7 (499) 237-53-36
E-mail: kiruhancev-korneev@yandex.ru

Kudryashov Alexandr Evgenevich, Ph.D
Leading Research Scientist of the Scientific-Educational Center of SHSScientific area: Surface engineering, pulsed electrospark deposition (PED), materials science, powder metallurgy.
Tel.: +7 (495) 955-00-26
Fax: +7 (499) 237-53-36
E-mail: aekudr@rambler.ru

Petrzhik Mikhail Ivanovich, Ph.D, Doctor of Science
Leading Research Scientist of the Scientific-Educational Center of SHS, Professor of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Materials science of amorphous, nanocrystalline and non-equilibrium alloys, coatings and composites, physical and mechanical properties
Tel.: +7 (499) 236-55-20
Fax: +7 (499) 237-53-36
E-mail: petrzhik@shs.misis.ru

Pogozhev Yury Sergeevich, Ph.D
Senior Research Scientist of the Scientific-Educational Center of SHS, Associate Professor of the Department of Powder Metallurgy and Functional Coatings
Scientific area: SHS, powder metallurgy, materials science, composite materials, surface engineering
Tel.: +7 (499) 236-32-91
Fax: +7 (499) 237-53-36
E-mail: yspogozhev@mail.ru

Zaitsev Alexandr Anatolievich, Ph.D
Senior Research Scientist of the Scientific-Educational Center of SHS, Associate Professor of the Department of Powder Metallurgy and Functional Coatings
Scientific area: nanostructured and nanocomposite materials, ultra-hard materials, diamond/BN tools, hard metals
Tel.: +7 (499) 236-32-91
Fax: +7 (499) 237-53-36
E-mail: aazaitsev@bk.ru

Novikov Aleksandr Valentinovich, Ph.D
Senior Research Scientist of the Scientific-Educational Center of SHS
Scientific area: SHS, materials science, composite materials
Tel.: +7 (499) 236-32-91
Fax: +7 (499) 237-53-36
E-mail: avnovikov@inbox.ru

Sheveyko Alexandr Nikolaevich
Research Scientist of the Scientific-Educational Center of SHS
Scientific area: Thin films, surface engineering, composite targets, pulsed electrospark deposition (PED)
Tel.: +7 (495) 638-46-59
Fax: +7 (499) 237-53-36
E-mail: sheveyko@mail.ru

Zamulaeva Evgenia Igorevna, Ph.D
Research Scientist of the Scientific-Educational Center of SHS
Scientific area: pulsed electrospark deposition (PED), surface engineering, powder metallurgy, hard metals
Tel.: +7 (495) 955-00-26
Fax: +7 (499) 237-53-36
E-mail: zamulaeva@gmail.com

Patsera Evgeny Ivanovich, Ph.D
Research Scientist of the Scientific-Educational Center of SHS,
Senior lecturer of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Materials science, mechanical activation, SHS, additive manufacturing
Tel./Fax: +7 (499) 237-53-36
E-mail: patsera_yevgeniy@mail.ru

Bychkova Marina Yakovlevna, Ph.D
Research Scientist of the Scientific-Educational Center of SHS,
Senior lecturer of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Materials science, composite materials, powder metallurgy, mechanical and tribological testing
Tel.: +7 (499) 236-55-20
Fax: +7 (499) 237-53-36
E-mail: bychkova@shs.misis.ru

Sidorenko Daria Andreevna, Ph.D
Research Scientist of the Scientific-Educational Center of SHS
Scientific area: Metal-matrix composites, nanomaterials, powder metallurgy, cutting tools, transmission electron microscopy (TEM)
Tel.: +7 (495) 638-44-42
Fax: +7 (499) 236-66-29
E-mail: dsidorenko@inbox.ru

Manakova Olga Sergeevna, Ph.D
Head of laboratory of the Scientific-Educational Center of SHS
Scientific area: Materials science, composite materials, nanomaterials, powder metallurgy, SHS, electrospark deposition, surface engineering
Tel.: +7 (495) 638-44-42
Fax: +7 (499) 236-66-29
E-mail: manakova_ol@mail.ru

Kuptsov Konstantin Alexandrovich, Ph.D
Research Scientist of the Scientific-Educational Center of SHS
Scientific area: Materials science, PVD, thermal stability, oxidation resistance
Tel.: +7 (495) 638-46-59
Fax: +7 (499) 237-53-36
E-mail: kuptsov.k@gmail.com

Loginov Pavel Alexandrovich, Ph.D
Research Scientist of the Scientific-Educational Center of SHS,
Senior lecturer of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Composite materials, cutting tools, mechanical alloying, nanoparticle reinforcement, transmission electron microscopy (TEM)
Tel./Fax: +7 (499) 237-53-36
E-mail: pavel.loginov.misis@list.ru

Potanin Artem Yurievich, Ph.D
Research Scientist of the Scientific-Educational Center of SHS
Scientific area: Materials science, SHS, powder metallurgy, electrode materials, ceramics for high-temperature applications
Tel.: +7 (499) 236-32-91
Fax: +7 (499) 237-53-36
E-mail: a.potanin@inbox.ru

Shvyndina Nataliya Vladimirovna
Leading Engineer of the Scientific-Educational Center of SHS
Scientific area: scanning electron microscopy (SEM), micro X-ray analysis (MXRA), transmission electron microscopy (TEM)
Tel.: +7 (495) 638-44-42
Fax: +7 (499) 236-66-29
E-mail: natali19-03@list.ru

Kaplansky Yuri Yurievich
Engineer, Ph.D Student of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Materials science, powder metallurgy, intermetallics, additive manufacturing, transmission electron microscopy (TEM)
Tel.: +7 (495) 955-00-26
Fax: +7 (499) 237-53-36
E-mail: ykaplanscky@mail.ru

Vorotilo Stepan

Engineer of the Scientific-Educational Center of SHS,
Ph.D Student of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Materials science, powder metallurgy, nanomaterials, structural ceramics, SHS, mechanochemistry, finite elements modelling
Tel.: +7 (495) 638-44-09
Fax: +7 (499) 237-53-36
E-mail: s.vorotilo@misis.ru

Avdeenko Evgeny Nikolaevich

Engineer of the Scientific-Educational Center of SHS,
Ph.D Student of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Materials science, powder metallurgy, hardmetals
Tel.: +7 (495) 955-00-26
Fax: +7 (499) 237-53-36
E-mail: avdeenko.misis@mail.ru

Lemesheva Margarita Vladimirovna

Engineer of the Scientific-Educational Center of SHS,
Ph.D Student of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Materials science, SHS, powder metallurgy, ceramic materials
Tel.: +7 (495) 955-00-26
Fax: +7 (499) 237-53-36
E-mail: lemescheva.margarita@yandex.ru

Ponomarev Victor Andreevich

Engineer of the Scientific-Educational Center of SHS,
Ph.D Student of the Department of Powder Metallurgy and Functional Coatings
Scientific area: Materials science, powder metallurgy, ceramic materials, PVD, nanostructured and nanocomposite materials, biocompatible and bioactive materials
Tel.: +7 (495) 638-46-59
Fax: +7 (499) 237-53-36
E-mail: ponomarev.viktor1993@yandex.ru

Mukanov Samat
Engineer, Ph.D Student of the Scientific-Educational Center of SHS
Scientific area: Materials science, surface engineering, mechanical and tribological properties, PED, additive manufacturing
Tel.: +7 (499) 236-55-20
Fax: +7 (499) 237-53-36
E-mail: sam-mukanov@mail.ru

RESEARCH AREAS

- Theory of SHS, structural macrokinetics, the mechanisms and kinetics of phase and structure transformation in combustion wave of heterogeneous chemical reactions. Mechanical activation of exothermic mixtures as an efficient method for controlling the process kinetics and product properties.
- Synthesis of new classes of advanced metallic and ceramic materials.
- Synthesis of electrodes and targets for PVD, pulsed electrospark deposition (PED), thermo-reactive electrospark surface strengthening (TRESS).
- Multifunctional and functionally graded materials (FGMs), including diamond-containing tools, and impact-resistant materials.
- Plasma physics, ion-plasma and ion-beam processes.
- PVD, PED, TRESS of the functional coatings (hard, tribological, heat- and corrosion resistant, optically transparent, biocompatible and bioactive with antibacterial effect).
- Powder metallurgy and materials science of hardmetals with hierarchical structure.
- Innovative powders for additive 3d-manufacturing, selective laser melting.
- Development of the metrological complex and normative-methodological base to ensure the uniformity of measurements of mechanical and tribological properties.

SCIENTIFIC RESULTS

Structural macrokinetics

The developed and refined theoretical models of combustion and structure formation processes include:

- The equation of transition from the diffusion combustion mode to the capillary spreading mode in its criterial form has been obtained for the solid–liquid systems (e.g., the ones based on titanium–carbon). Experimentally confirmed, this equation links the thermophysical, hydrodynamic, and diffusion parameters of the system with mixture composition and dispersity of the initial reagents.

- The competitive filling model for describing the macrokinetic characteristics of the combustion processes in capillary porous systems containing melts of the reagent and inert fill material.
The model of propagation of a thermal and chemical wave of gas-free combustion in multilayer systems.

- It was first ascertained via high-speed video imaging of a combustion wave that at the micro level the combustion zone is a combination of the explosion foci caused by the occurrence of a chemical reaction in separate unit cell, in which the reaction surface was formed.

- The mechanisms for structure formation of ceramic and metal-ceramic compositions in the combustion wave in various heterogeneous systems has been proposed.

- The research principles for controlling the SHS process (elemental synthesis in the solid–liquid systems and filtration synthesis in the solid–gas systems) by powerful ultrasonic fields have been designed. Ultrasound has been demonstrated to be an efficient tool for controlling the structure and properties of the synthesis products based on transition metal carbides, borides, and intermetallides.

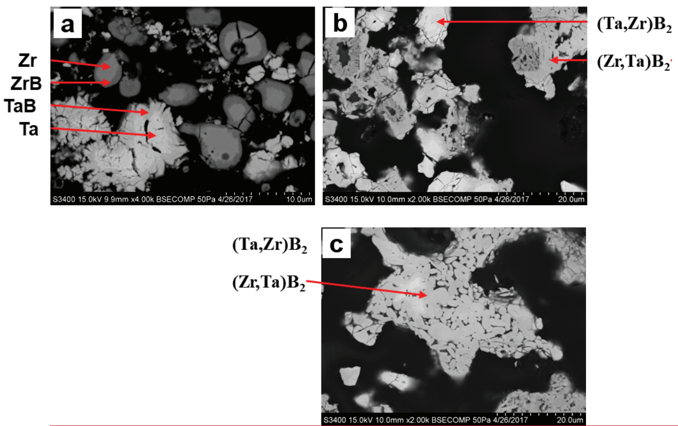
The macrokinetic features of combustion of the mixtures in the Ta-Zr-B and Ta-Hf-B systems were studied recently. Mechanisms of chemical conversions and phase formation of the synthesis products in the Ta-Zr-B and Ta-Hf-B systems were proposed. Primary layers of tantalum and zirconium borides or hafnium borides were detected in the preheating zone at temperatures below the melting point of the components. After zirconium/hafnium and boron have melted, temperature in the combustion zone reaches its maximum and main zirconium/hafnium diboride crystals are precipitated from the oversaturated melt. Combustion front in Zr-Ta-B and Hf–Ta-B systems propagates in the spin regime due to engagement of gas-phase transport mechanism. ZrB_2-based solid solution is formed as a result of the following reactions:

$$B_2O_{3\,(l)} + B \rightarrow 3/2 B_2O_{2\,(g)}$$

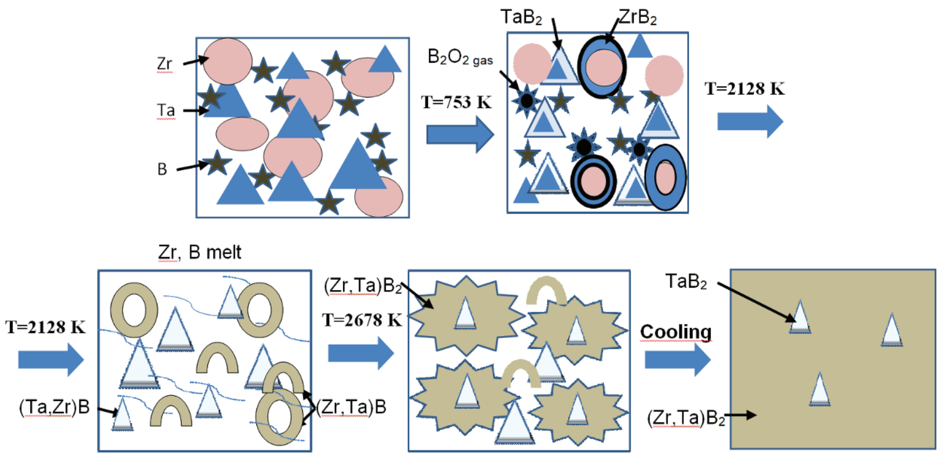
$$3\,Ta + 9\,B_2O_2 = 3\,TaB_2 + 6\,B_2O_3$$

$$2\,Zr + 6\,B_2O_2 = 2ZrB_2 + 4\,B_2O_3$$

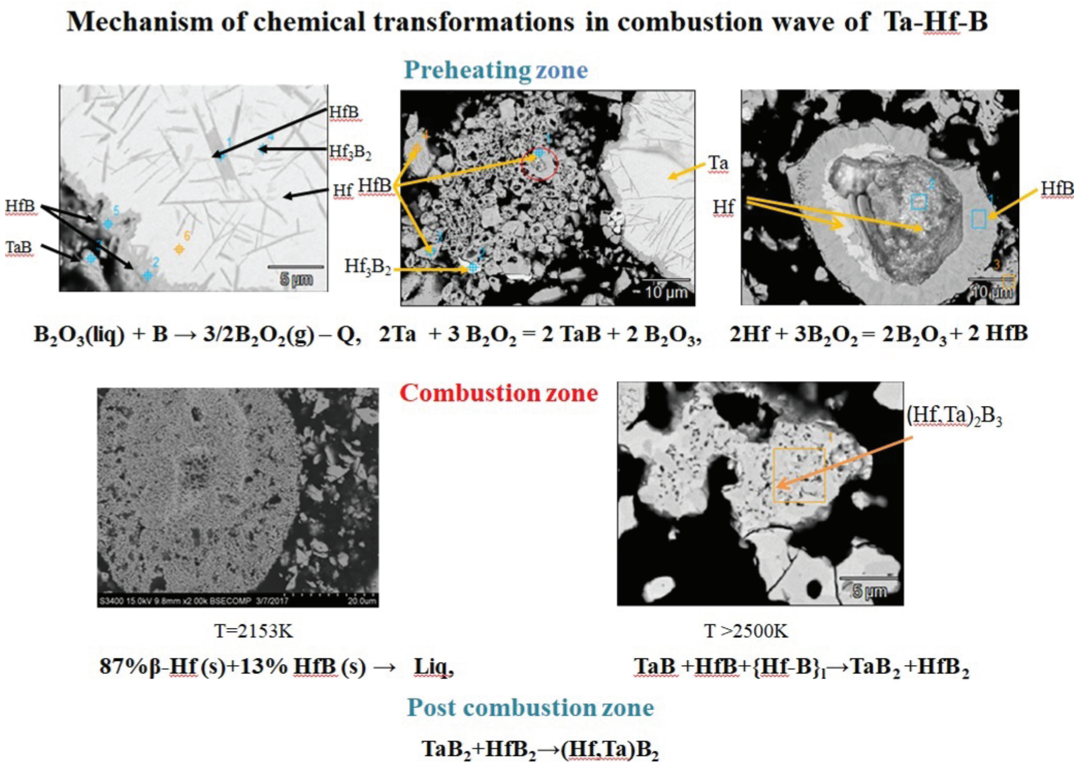
$$TaB_2 + ZrB_2 \rightarrow (Zr,Ta)B_2$$



The microstructure of the quenched combustion front for Zr-Ta-B and the phase composition of the structural components: a – preheating zone; b – combustion zone; c – post-combustion zone



Scheme of structure transformation in the combustion wave of Zr-Ta-B mixture



The synthesis products were processed into powders, and then consolidated using hot pressing (HP) or SPS. Properties (ρ-density, a-thermal diffusivity, C_p – thermal capacity, λ-coefficient of thermal conductivity, H-hardness, E-elastic modulus, R-elastic recovery) of the dense ceramics are presented in Table below.

Physical properties of the HP ceramics Zr-Ta-B and Hf–Ta-B

Composition	ρ, kg/m³	a, m²/s	Cp, J/kg·K	λ, W/m·K	H, GPa	E, GPa	R, %
(Zr,Ta)B_2	$7.35 \cdot 10^3$	$12.8 \cdot 10^{-6}$	444	42	70	594	96
(Zr,Ta)B_2 +TaB_2	$7.14 \cdot 10^3$	$12.1 \cdot 10^{-6}$	407	35	74	647	95
(Hf,Ta)B_2	$10.95 \cdot 10^3$	$14.6 \cdot 10^{-6}$	330	53	63	570	90
(Hf,Ta)B_2+TaB_2	$11.40 \cdot 10^3$	$8.8 \cdot 10^{-6}$	303	30	70	587	92

Mechanical activation (MA)

- The relationship between the structure and properties of the mechanically activated powder mixtures, as well as that between the physicochemical parameters of the combustion reactions and structure of the final products, has been established. MA enables carrying out SHS in low exothermic mixtures, including those strongly diluted with inert additives. MA results in an increase in the heat release rate and mixture reactivity due to particle disintegration, formation of the layered structure of grains, reduction of the coherent scattering regions, and an increase in density of structural defects and dislocations.

- The technological regimes of MA of the reaction mixtures for a number of compositions (Ti–Si, Mo–Si, Ti–Cr–C, Ti–B, Ti–BN, Ti–Si_3N_4, Ti–Cr–B, Cr–B, Mo–B, Ti–Ta–C, Ta-Zr-C, Ta-Hf-C, Ni–Al, Ti-Cr-Al-C, Ti-Si-C, Mo-Si-B, Cr-Al-Si-B, etc.) have been optimized. Previously unstudied ternary compounds (Ti_2CrB_2 and Cr_4Ti_9B) were identified among the synthesis products.

- It was ascertained that the adsorbed and dissolved oxygen in powder reagents of the Cr-B, Ti-Cr-B, Ta-Zr-B, Ta-Hf-B, Ta-Zr-C, Ta-Hf-C, and Ti-Ta-C systems plays an active role. It determines the mass transfer of boron and carbon to the reaction surface and reduces the effective activation energy of the combustion process. An increase in oxygen content in the reaction mixture leads to an increase in contribution of gas transfer.

Both Ta-Hf-C and Ta-Zr-C systems follow the well known gas-phase based mechanism of formation of metal carbides. The absorbed oxygen is released during the combustion and interacts with the solid carbon, resulting in the formation of gaseous CO. On the surface of the metallic particles, 2CO forms a CO_2 molecule and release an atom of carbon. This carbon reacts with metal with the formation of carbide. The CO_2 molecule then reacts with the solid C and forms 2CO again and the cycle repeats. Single-phase carbides (Ta,Zr)C and (Ta,Hf)C were synthesized by MA SHS at wide range of Hf/Zr concentrations (10-50%). Hot pressing and SPS yielded ceramics with relative densities up to 99% and high mechanical properties.

References

1. Kurbatkina, V.V., Patsera, E.I., Levashov, E.A. (2019). Combustion synthesis of ultra-high-temperature materials based on $(Hf,Ta)B_2$. Part 1: The mechanisms of combustion and structure formation. Ceramics International, 45(3), 4067-4075.

2. Kurbatkina, V.V., Patsera, E.I., Smirnov, D.V., Levashov, E.A., Vorotilo, S., Timofeev, A.N. (2019). Part 2. structure, mechanical and thermophysical properties of consolidated ceramics based on $(Hf,Ta)B_2$. Ceramics International, 45(3), 4076-4083.

3. Kurbatkina, V.V., Patsera, E.I., Levashov, E.A., Vorotilo, S. (2018). SHS processing and consolidation of Ta–Ti–C, Ta–Zr–C, and Ta–Hf–C carbides for ultra-high-temperatures application. Advanced Engineering Materials, 20(8), 1701075.

4. Kurbatkina, V.V., Patsera, E.I., Levashov, E.A., Timofeev, A.N. (2018). Self-propagating high-temperature synthesis of single-phase binary tantalum-hafnium carbide (Ta,Hf)C and its consolidation by hot pressing and spark plasma sintering. Ceramics International, 44(4), 4320-4329.

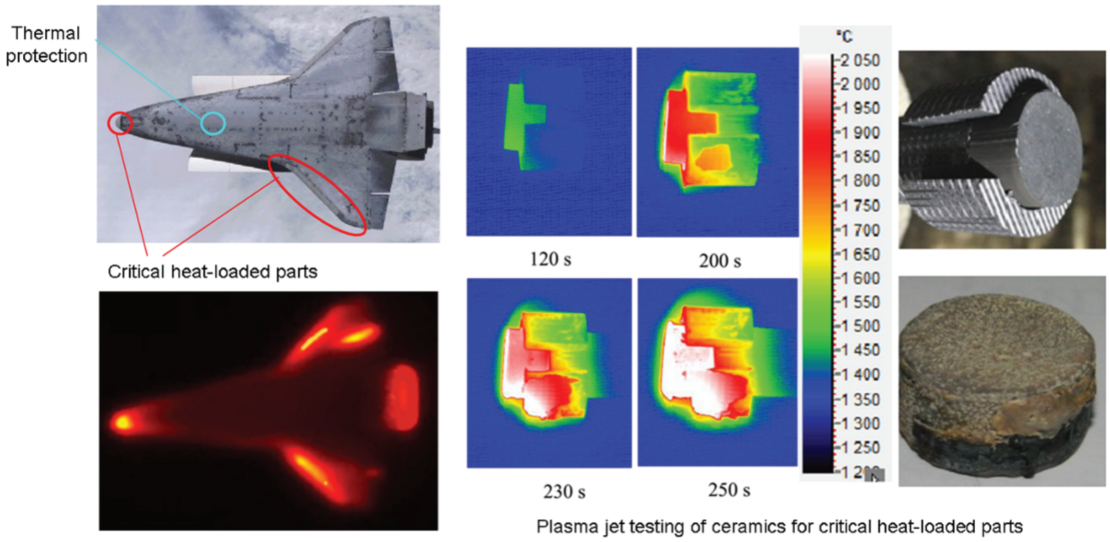
5. Kurbatkina, V.V., Patsera, E.I., Levashov, E.A., Timofeev, A.N. (2018). Self-propagating high-temperature synthesis of refractory boride ceramics $(Zr,Ta)B_2$ with superior properties. Journal of the European Ceramic Society, 38(4), 1118–1127.

6. Kurbatkina, V.V., Patsera, E.I., Vorotilo, S.A., Levashov, E.A., Timofeev, A.N. (2016). Conditions for fabricating single-phase (Ta,Zr)C carbide by SHS from mechanically activated reaction mixtures. Ceramics International, 42(15), 16491-16498.

7. Patsera, E.I., Levashov, E.A., Kurbatkina, V.V., Kovalev, D.Y. (2015). Production of ultra-high temperature carbide (Ta,Zr)C by self-propagating high-temperature synthesis of mechanically activated mixtures. Ceramics International, 41(7), 8885-8893.

Advanced ceramics

Ceramics are extensively applied in machining, aerospace industry, shipbuilding, medicine, and other industries, leading to a dramatic increase in performance, lifetime, and safety of engines and other critical elements. SHS Center is at the forefront of research in this vital area of materials science. The recent efforts were focused on the development of ceramic composites for machining, structural applications, and manufacturing of protective coatings for implementation in extreme environments.



Heating of critical parts during flight

Plasma jet testing of ceramics for critical heat-loaded parts

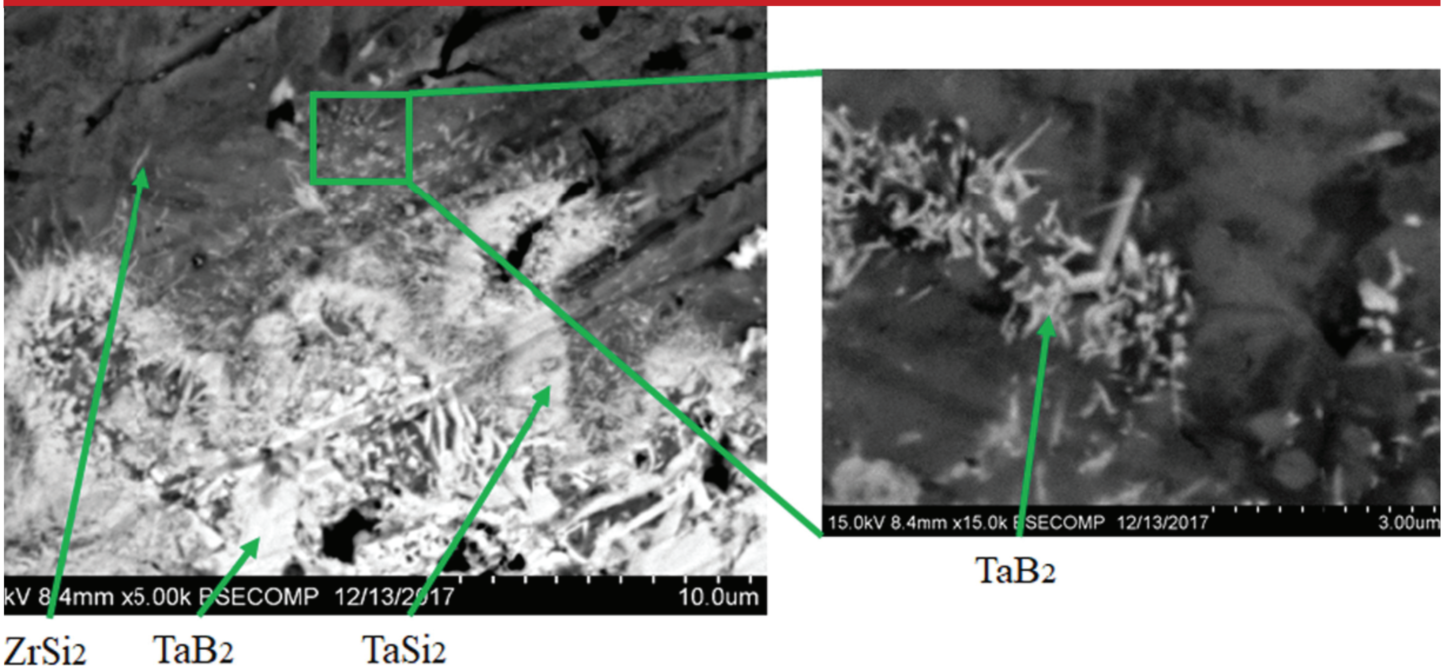
An array of new heat-resistant ceramics were developed in systems Mo–Si–B, Cr-Al-Si-B, Mo–Hf–Si–B, Zr–Ta–B, Zr–Ta–Si–B, Hf–Ta–B, Zr–Si–B, Zr–Si–Al–B, Zr–Si–B–C, Ta–Si–C. These systems were chosen as the proof-of-concept for the emerging approaches to the manufacturing of heat-resistant and mechanically advantageous ceramics, including the formation of hierarchical structures, microgradient structures, in-situ nanoparticles and nanofibers reinforcement. Dense ceramics Mo–Si–B, Zr–Si–B, Zr–Si–Al–B were produced by force SHS pressing, whereas in the systems Mo–Hf–Si–B, Zr–Ta–B, Zr–Ta–Si–B, Hf–Ta–B, Zr-Si-Mo-B, Zr–Si–B–C, Ta–Si–C the SHS was employed to produce micron-sized powders for consolidation by HP or SPS. Fine grade powders produced via different SHS routes were characterized by distinctly improved sinterability due to the high density of lattice defects and phase boundaries within individual particles.

SHS provides a particularly rapid and convenient synthesis route, while also offering some unique advantages related to the phase and structure formation mechanisms. Understanding and control of the combustion mechanisms allows fabricating the ceramics with multi-level structures and in-situ formed hardening precipitates (particles, needles, whiskers, wires, fibers).

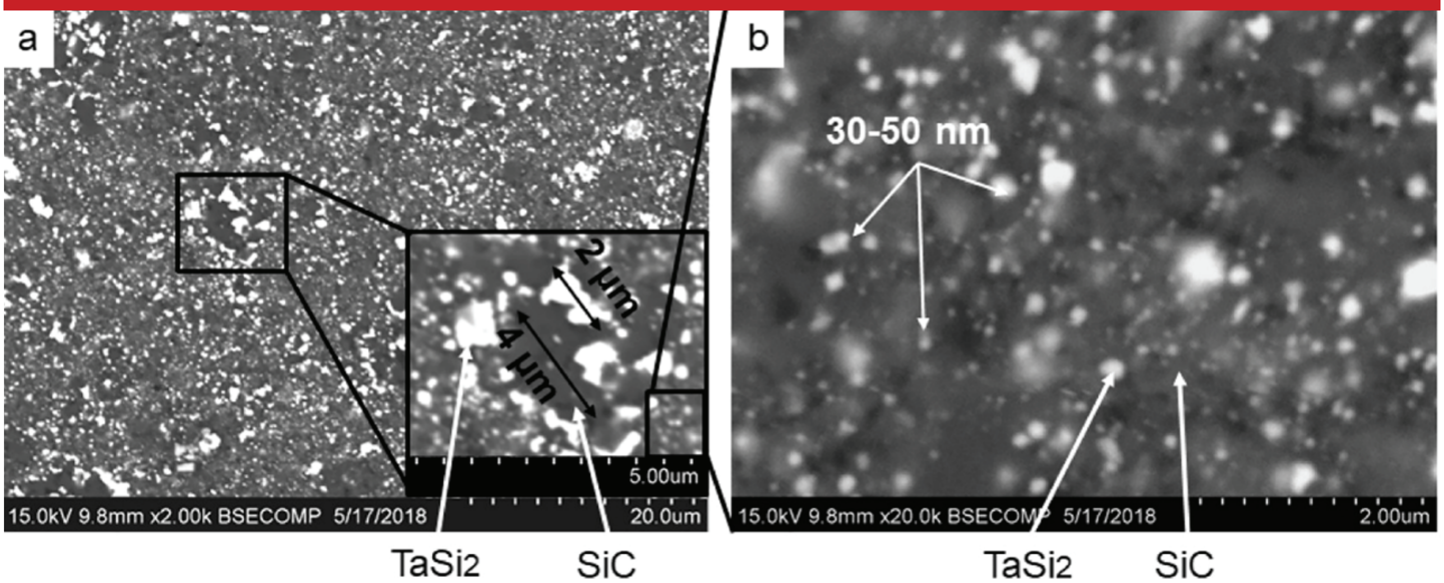
In particular, SHS in Ta-Si-C system yields the two-level structured composite, where the first- and second-order $TaSi_2$ and SiC particles are formed in different zones of combustion wave. Such microstructures provide increased fracture toughness due to the large grains size gradients. For these ceramics, outstanding mechanical and thermo-mechanical properties were attained, including super-hardness (up to 70 GPa), elastic recovery up to 96 %, Young's modulus up to 600 GPa, heat conductivity up to 82 Wt/(m×K).

The oxidation resistance of the developed ceramics was improved dramatically as compared to conventional counterparts due to the controlled formation of self-organized nanostructured multi-layer oxide films, which provides increased stability and protection even under the impact of high-velocity plasma jet (2500-3000 °C). The SHS-composites are now being tested for the application as high-temperature structural materials and as precursors for protective coatings.

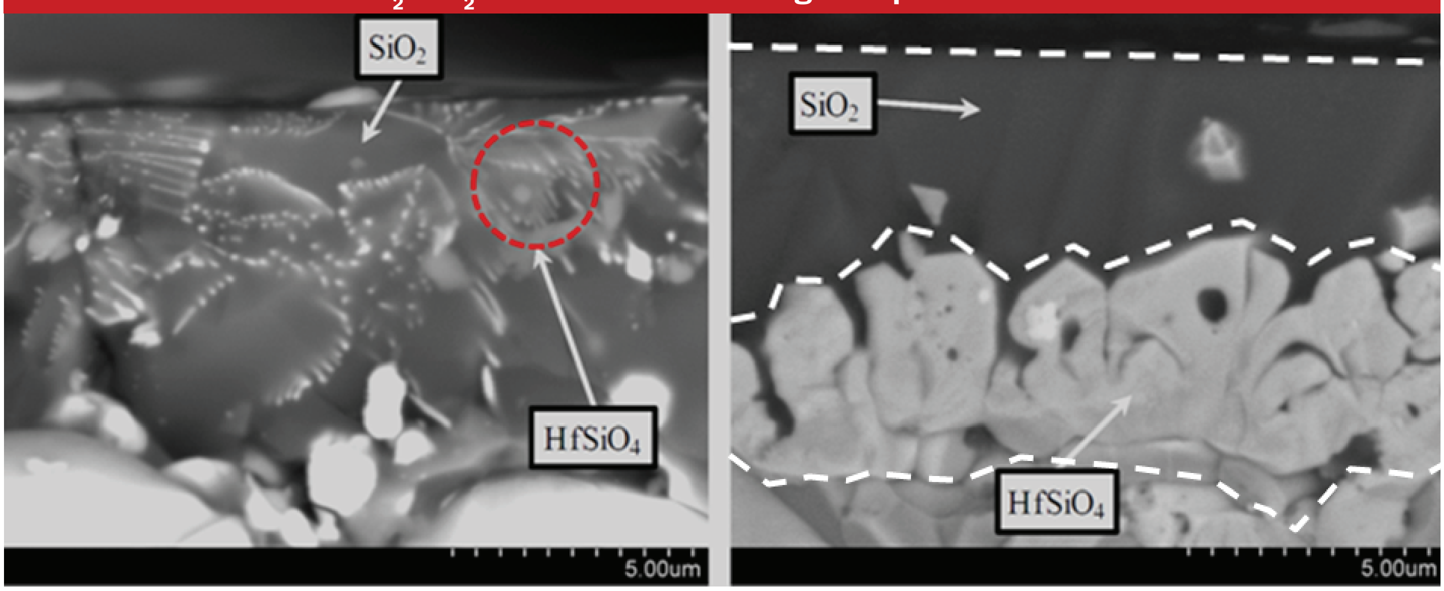
Formation of reinforcing TaB_2 needles in the combustion front of Zr-Ta-Si-B mixture



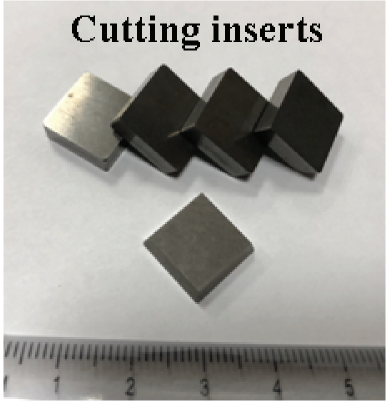
The two-level microstructure of $TaSi_2$-SiC composites

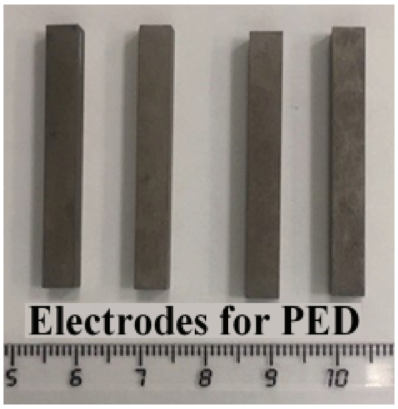


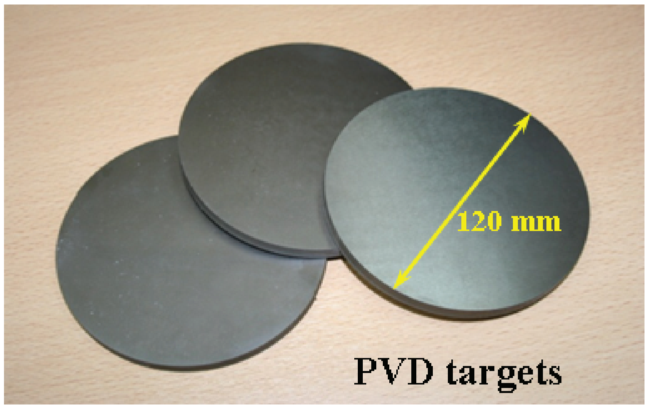
Self-organized nano-reinforced and two-layered oxide films on the surface of $MoSi_2$-HfB_2-MoB ceramics after high-temperature oxidation.

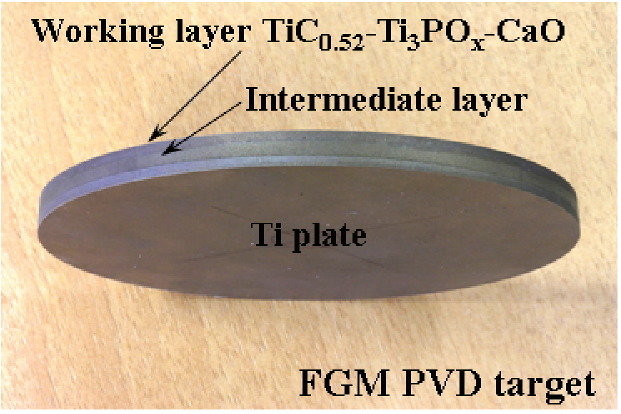


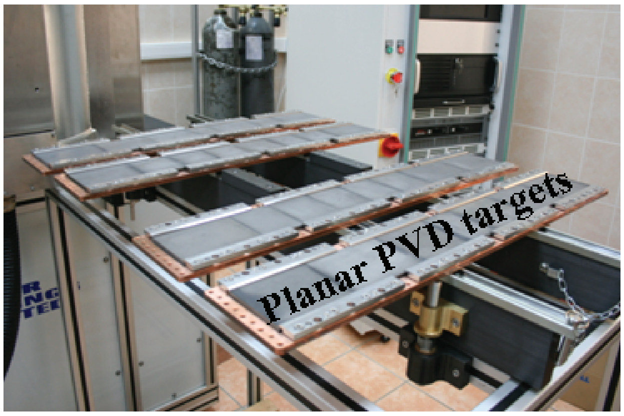
Ceramics for tool and PVD



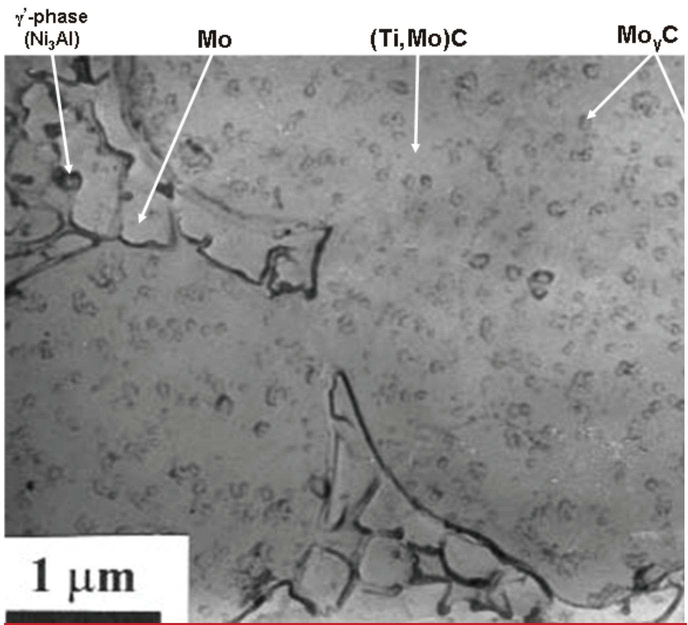








Two types of nanoparticles-strengthened alloys were developed for high-speed machining. The first type of alloys is based on the solid solution of refractory carbides and metallic matrix, which are strengthened by in-situ precipitated nanoparticles. For example, STIM-5 alloy is comprised of (Ti, Mo)C solid solution with Mo_yC precipitates and Mo matrix reinforced by Ni_3Al nanoparticles. Precipitation results from the decomposition of supersaturated solid solutions formed in combustion wave, allowing for a simultaneous increase of hardness, fracture toughness, ultimate strength, and impact resistance of these alloys. The second type of alloys is based on refractory compounds and metallic/intermetallic matrix, modified by the addition of refractory nanoparticles to the «green» reactive mixtures. STIM-40NA alloy is representative of this second type. It is based on TiC with NiAl matrix, modified by $NbC/ZrO_2/Al_2O_3$ nanoparticles. These nanoparticles alter the structure formation processes during SHS, resulting in an increase of strength, hardness, and fracture toughness of the alloys. Both types of alloys are currently being implemented in the machining industry and for manufacturing of protective coatings.



Microstructure of STIM-5 alloy with precipitation-strengthened carbide grains and Ni-Mo matrix.

The force SHS pressing was implemented at the manufacturing of PVD targets. One-step-processing yields ceramic/cermet/intermetallic/composite targets with various shapes, relative density up to 99.5 %, controlled homogeneous or gradient structures, high chemical purity and advanced mechanical properties, thermal and electrical conductivities.

Multicomponent targets in the systems TiB_2-Ti_5Si_3, TiC_xN_y-Ti_5Si_3-$TiAl_3$, CrB_x-Cr_5Si_3-Cr_4Al_{11}, $MoSi_2$-MoB, Mo_5SiB_2, ZrB_2-$ZrSi_2$, SiC-B_4C have been synthesized and implemented for magnetron sputtering of ultrahard, oxidation-resistant, optically transparent, tribological, corrosion resistant, bioactive with antibacterial effect coatings. For the biomedical application, an array of ceramic PVD targets and PED electrodes with the compositions $TiC_{0.5}$-CaO, TiC_xN_y-Si_3N_4-CaO, $TiC_{0.5}$-Ti_3PO_x-CaO, (Ti,Ta)C_x-Ti_3PO_x-CaO, TiC_x-TiCo-Ti_3PO_x-MgAg were developed for the deposition of multifunctional bioactive nanostructured coatings with antibacterial effect.

To prolong the working life of PVD targets, two approaches were used. First one is functional graded material (FGM) approach, comprised of working ceramic layer fastened to a load-bearing layer with a high thermal and electrical conductivity. The second one is the reinforcement of initial reactive pellets by continuous fibers or meshes made of refractory metals (Ta, W, Mo, etc.).

References

1. Vorotilo, S., Potanin, A.Y., Pogozhev, Y.S., Levashov, E.A., Kochetov, N.A., Kovalev, D.Y. (2019). Self-propagating high-temperature synthesis of advanced ceramics $MoSi_2$–HfB_2–MoB. Ceramics International, 45(1), 96-107.

2. Iatsyuk, I.V., Pogozhev, Y.S., Levashov, E.A., Novikov, A.V., Kochetov, N.A., Kovalev, D.Y. (2018). Combustion synthesis of high-temperature ZrB_2-SiC ceramics. Journal of the European Ceramic Society, 38(7), 2792-2801.

3. Vorotilo, S., Levashov, E.A., Kurbatkina, V.V., Kovalev, D.Y., Kochetov, N. A. (2018). Self-propagating high-temperature synthesis of nanocomposite ceramics $TaSi_2$-SiC with hierarchical structure and superior properties. Journal of the European Ceramic Society, 38(2), 433-443.

4. Litovchenko, N.V., Potanin, A.Y., Zamulaeva, E.I., Sukhorukova, I.V., Pogozhev, Y.S., Gloushankova, N.A., Ignatov, S.G., Levashov, E.A., Shtansky, D.V. (2017). Combustion synthesis of Ti-C-Co-$Ca_3(PO_4)_2$-Ag-Mg electrodes and their utilization for pulsed electrospark deposition of bioactive coatings having an antibacterial effect. Surface and Coatings Technology, 309, 75-85.

5. Potanin, A., Pogozhev, Y., Novikov, A., Levashov, E. (2017). Ceramic materials in a Ti-C-Co-$Ca_3(Po_4)_2$-Ag-Mg system obtained by MA SHS for the deposition of biomedical coatings. Metals, 7(9), 378.

Pulsed electrospark deposition (PED)

Equipment

The equipment line for PED includes both commercial devices of the «ALIER-METALL» brand and experimental installations with extended voltage ranges and controlled pulse parameters. For the formation of pulses modern high-power IGBT switches are used. Automatic installations allow increasing voltage and energy of a single pulse while maintaining its low duration and high frequency. Various modules are used for automatization: swinging assembly with a disc electrode, rotating axial electrode, multi-electrode systems, and robotic arm with a vibrating or rotating electrode assembly. For example, an multi-electrode system was tested for surfacing of the rolls with a deep profile; module with a rotating disc electrode was used to reinforce the diamond tube drills.

Low-voltage high-frequency equipment for PED

High-voltage pulse-generating unit for experimental installations

Multi-electrode system

Disc electrode machining

PED has been successfully used to surface reinforce or repair by varying the frequency–energy regimes and electrode composition (hard alloys, ceramics, intermetallic). SHS electrodes are selected on 5 groups depending on requirement to coatings properties.

Group 1 – STIM grade materials (synthetic hard instrumental materials) consisting of a hard phase and the metallic binder (20–60%). The following alloys are the examples of materials belonging to this group: STIM-20N (TiC-Ni), STIM-3B (TiC–Cr_3C_2–Ni), STIM-3V (TiC-Cr_3C_2-Fe), STIM 2/40NZh (TiC – nickel alloy CrNi70), STIM-40NA (TiC–NiAl), STIM-40TA (TiC–Ti_3AlC_2), STIM-9/20A (TiB_2 –TiAl), STIM-2/30NM, (TiC–Ni–Mo), STIM-60NT (TiC–TiNi), STIM 9/20NA (TiB_2–NiAl), and ZS-4 (Cr_2AlC), et al.

This group also comprises dispersion-hardened ceramics with the effect of simultaneous dispersion strengthening of carbide grains and the metal binding due to nanosized precipitations as a result of concentration separation of supersaturated solid solutions.

Depending on their composition, electrode materials are referred to as CNT– double titanium–niobium carbide (Ti,Nb)C), CZT – double titanium–zirconium carbide (Ti,Zr)C; and CTT – double titanium–tantalum carbide (Ti,Ta)C. Metal binder in amount 10-60 % of various compositions (Ni-Co-Al-Cr, Ni-Al, Ni) are added to the electrodes to improve the quality of the coatings being formed. Materials of Group 1 also include heat-resistant electrodes of compositions Cr-Al-B-Si, Cr-Al-B, Mo-Si-B, and Zr-B-Si. These materials are intended for coating operating at temperature around 1500 °C.

Furthermore, Group 1 includes the MAX-phases based materials with layered structure, low density, high thermal and electrical conduction, high strength, corrosion and heat resistance.

Group 2 – hard metals with nanosized additives: ZrO_2, Al_2O_3, NbC, Si_3N_4, W, WC, WC-Co, Mo-Al_2O_3, nanosized diamond. Nanosized component involved in exothermic mixture results in significant structure modification of final products (carbides, borides, silicides, intermetallides). The positive effect of electrode structure on the efficiency of PED process can be attributed to the increase in erosion capacity of the electrode. Discharge energy results in an increase in temperature on the electrode working tip up to the melting of the binder. Provided that the discharge energy remains constant, the intensity of electrode erosion increases with decreasing grain size. The erosion rate increases due to a stable flow of fine fragments, which are comparable with the grain size of the electrode material. The quality of the coating formed (density, thickness, uniformity) is improved, as well.

Group 3 – hard metal based on WC–Co fabricated with nanosized powder of WC. The average size of carbide phase in the electrode is 80 nm. The electrodes from Group 3 are referred to as SNM (sintered nanostructured material) or HPNM (hot-pressed nanostructured material).

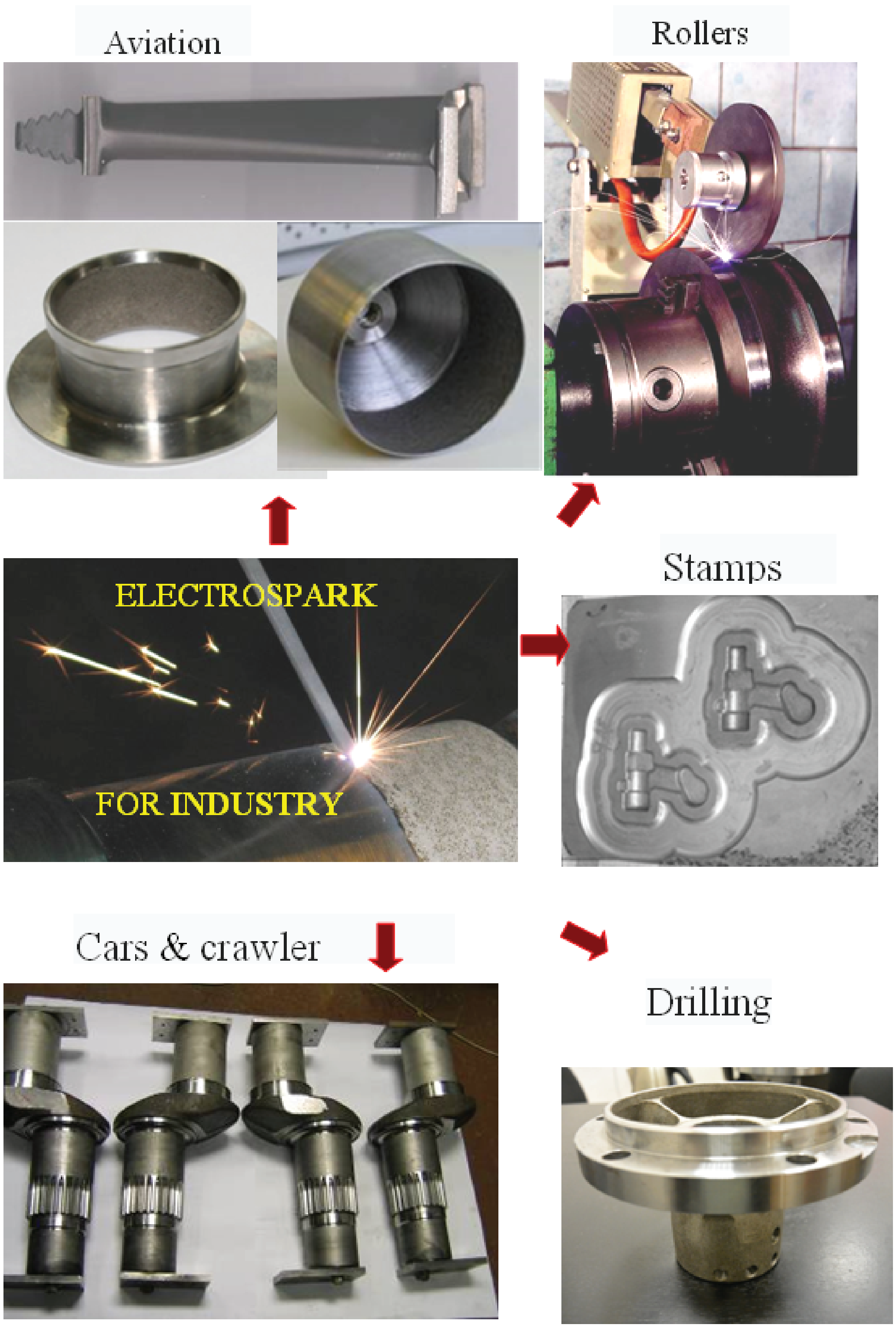
Group 4 – electrodes for TRESS. Such electrodes are comprised of thin-wall metallic tube filled with reactive powder mixture. On the one hand, the chemical reaction is maintained by discharge energy; on the other hand, heat release from the chemical reaction, which is comparable with the discharge energy, increases the total energy of the process. Additional heat evolution makes it possible to enhance the efficiency of deposition process.

Group 5 – near-eutectics alloys are used for two kinds of applications. Electrodes made of glass-forming metallic alloys are specifically prepared multi-element near-eutectic precursors of the amorphous phase (e.g., fast-quenched Fe–Mn–Ni–Si–C cast iron doped with boron in order to enhance its glass-forming ability). The use of melt quenched electrodes in PED results in the suppression of formation of refractory crystallites, reduction of the size of structural components and roughness due to lower melting point of the electrode. These electrodes with fine eutectics or amorphous structure have a high potential for applying nanostructured coatings.

A new direction in the application of near-eutectic electrodes is the surface treatment of products obtained by additive manufacturing (SLM) in order to eliminate surface defects and reduce roughness. A characteristic feature of such products is an increased surface roughness due to a formation of surface defects (pimples, cracks, pores). PED is successfully used for surface modification to restore damaged or worn surfaces and working edges of the used parts due to efficiency of the technology.

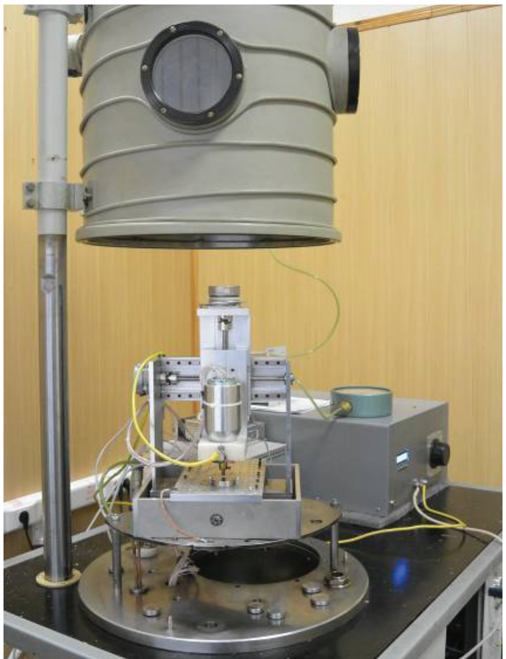
Advanced coatings for industry

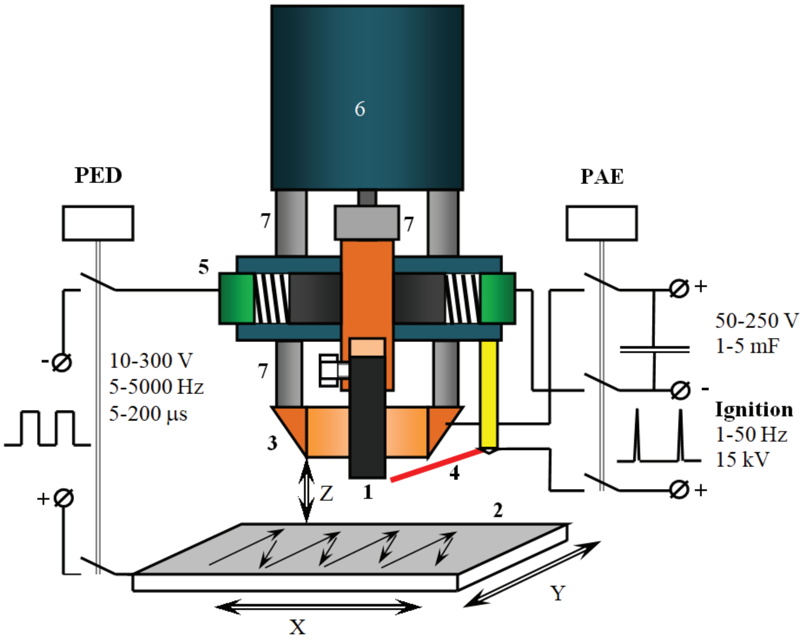
PED coatings are used to protect local areas of parts or tools from wear, corrosion or oxidation. Important feature of the machining process is a lack of heating of the part bulk and maintaining of mechanical properties. The depth of heating does not exceed the thickness of a coating. Enhanced adhesion of PED coatings is achieved by their layer-by-layer formation from local melting spots with a depth of less than 100 microns. A wide range of electrode compositions allows obtaining coatings with the necessary set of properties. For example, for dies and rolls hardening, compositions with a high content of hard phase and heat-resistant binder, such as STIM-40NAOKn (TiC - NiAl + ZrO_2nano) and STIM-11OKn (TiB_2 - NiAl + ZrO_2 nano) are used.
To protect titanium alloys used primarily in aviation, coatings with high hardness and low friction coefficient based on tungsten and titanium carbides are employed. For hardening nickel-alloy parts of aircraft engines, Cr-Al-Si-B, Mo-Si-B, Zr-Si-B materials are used due to combination of high hardness, wear and oxidation resistance.



New Technology Combining Pulsed Arc Evaporation (PAE) and PED

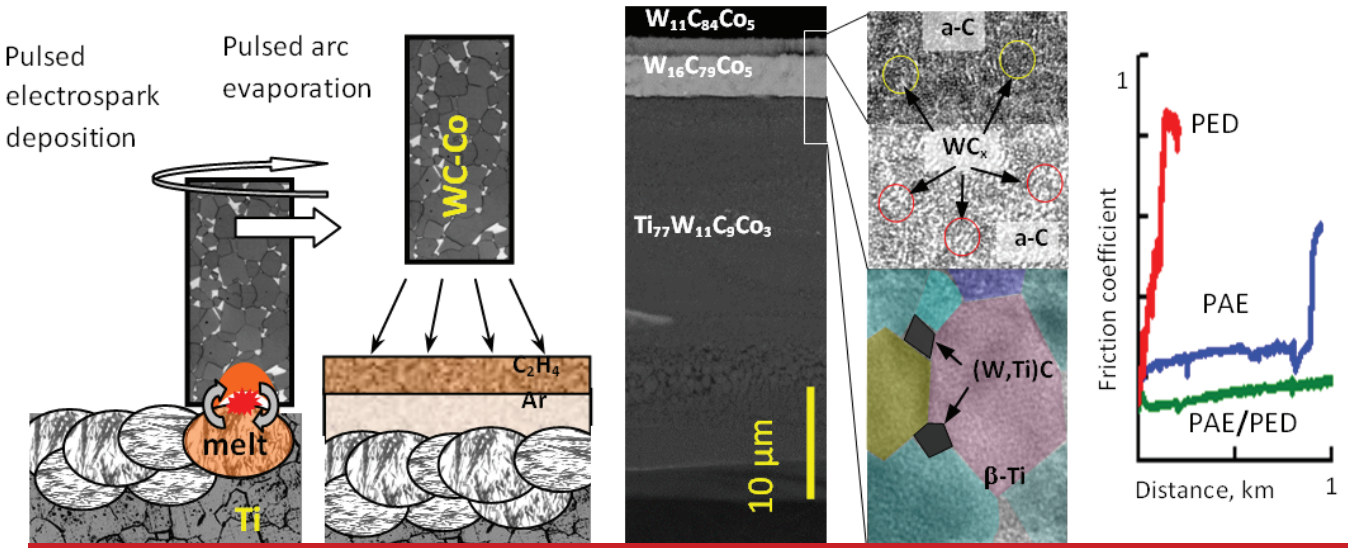
New technology combining PAE and PED in vacuum to fabricate two-layer coatings in a single technological run was developed.
The experimental setup consists of a three-axis computer numerical control (CNC) unit installed in a vacuum chamber. Iinstead of a machining spindle, the original rotating module with electrode was mounted into the CNC unit. This module consists of electric motor, isolated brush assembly for applying current to the rotating electrode, isolated circular anode and ignition electrode for implementation of the arc mode. The electrode assembly had an ability to move along the vertical (Z) axis. The substrate was mounted on an insulated programmable stage that could move along two horizontal axes (X and Y). In the PAE mode, it was possible to apply both positive and negative bias voltage to a substrate either for its heating by an electron current or for ion cleaning.





Scheme of the rotating deposition module mounted on 3-axis CNC machine: 1 – electrode, 2 – substrate, 3 – ring anode, 4 – ignition electrode, 5 – brush assembly, 6 – electric motor, 7 – insulating ceramics

The bottom layer, designed to achieve good adhesion to a substrate and provide high coating thickness and enhanced toughness, is produced by PED. Top layer providing high mechanical and tribological properties is deposited by PAE. The developed technology has been tested in various systems: TiNbC coatings on steels, TiC/C and WC/C on titanium alloys, and intermetallics TiNi and NiAl-based coatings on heat-resistant alloys were successfully obtained.
The cost-efficient technology combining PAE and PED in vacuum was developed as applied to deposition on Ti substrate with two-layer WC/a-C coating in a single technological run using the same WC-Co electrode. A superior tribological performance of the two-layer PAE/PED coatings was attributed to gradual changes in phase composition and grain size, as well as a combination of tailored mechanical properties. Hardness gradually increased from 3.6 GPa (Ti substrate) to 20 GPa (PAE layer), enhanced toughness and high thickness of the PED sublayer, which prevented the substrate from plastic deformation, and low friction coefficient of the top PAE layer due to its nearly amorphous WC/a-C structure with a large amount of a-C phase acting as a solid lubricant. In-situ mechanical TEM tests demonstrated superior adhesion strength of the PAE/PED interface able to withstand high stresses of 560 MPa. Utilization of two-step MS/PED technology permits to obtain bilayers coatings Ti-C-Ni-Al/Ti-C-Ni-Fe with improved crack-, wear- and oxidation resistance compared with single-layered Ti-C-Ni-Al counterparts deposited by MS, and with reduced friction coefficient and enhanced corrosion resistance compared with PED Ti-C-Ni-Fe coatings.



Schematic representation of the deposition process, structure and friction coefficients of two-layer PAE/PED coatings

References

1. Kuptsov, K.A., Sheveyko, A.N., Zamulaeva, E.I., Sidorenko, D.A., Shtansky, D.V. (2019). Two-layer nanocomposite WC/a-C coatings produced by a combination of pulsed arc evaporation and electro-spark deposition in vacuum. Materials and Design, 167, 107645.

2. Kiryukhantsev-Korneev, P., Sytchenko, A., Sheveyko, A., Vorotilo, S. (2018). Structure and properties of protective coatings deposited by pulsed cathodic arc evaporation in Ar, N_2, and C_2H_4 environments using the TiC-NiCr-Eu_2O_3 cathode. Coatings, 9(4), 230.

3. Kiryukhantsev-Korneev, P.V., Sheveyko, A.N., Shvindina, N.V., Levashov, E.A., Shtansky, D.V. (2018). Comparative study of Ti-C-Ni-Al, Ti-C-Ni-Fe, and Ti-C-Ni-Al/Ti-C-Ni-Fe coatings produced by magnetron sputtering, electro-spark deposition, and a combined two-step process. Ceramics International, 44(7), 7637-7646.

4. Kudryashov, A.E., Lebedev, D.N., Potanin, A.Y., Levashov, E.A. (2018). Structure and properties of coatings produced by pulsed electrospark deposition on nickel alloy using Mo-Si-B electrodes. Surface and Coatings Technology, 335, 104-117.

5. Kiryukhantsev-Korneev, P.V., Sytchenko, A.D., Kudryashov, A.E., Levashov, E.A. (2018). Protective coatings produced by electro-spark deposition with TiCNiCr-(Eu_2O_3) electrodes. CIS Iron and Steel Review, 16, 57-62.

6. Kiryukhantsev-Korneev, P.V., Kudryashov, A.E., Levashov, E.A. (2018). Recent achievements on oxidation-resistant Cr-(Al)-Si-B, Mo-(Al)-Si-B, Zr-(Al)-Si-B coatings obtained by magnetron sputtering and pulsed electrospark deposition (Part 1). Galvanotechnik, 109(4), 748-756.

7. Kiryukhantsev-Korneev, P.V., Kudryashov, A.E., Levashov, E.A. (2018). Recent achievements on oxidation-resistant Cr-(Al)-Si-B, Mo-(Al)-Si-B, Zr-(Al)-Si-B coatings obtained by magnetron sputtering and pulsed electrospark deposition (Part 2). Galvanotechnik, 109(5), 1044-1050.

8. Kudryashov, A.E., Eremeeva, Z.V., Levashov, E.A., Lopatin, V.Y., Sevost'yanova, A.V., Zamulaeva, E.I. (2018). On application of carbon-containing electrode materials in technology of electrospark alloying: Part 1. Peculiarities of coating formation using electrospark treatment of titanium alloy OT4-1. Surface Engineering and Applied Electrochemistry, 54(5), 437-445.

9. Kudryashov, A.E., Eremeeva, Z.V., Levashov, E.A., Lopatin, V.Y., Sevost'yanova, A.V., Zamulaeva, E.I. (2018). On the application of carbon-containing electrode materials in electrospark alloying technology. Part 2. Structure and properties of two-layer coatings. Surface Engineering and Applied Electrochemistry, 54(6), 535-545.

10. Petrzhik, M., Molokanov, V., Levashov, E. (2017). On conditions of bulk and surface glass formation of metallic alloys. Journal of Alloys and Compounds, 707, 68-72.

11. Kudryashov, A.E., Potanin, A.Y., Lebedev, D.N., Sukhorukova, I.V., Shtansky, D.V., Levashov, E.A. (2016). Structure and properties of Cr-Al-Si-B coatings produced by pulsed electrospark deposition on a nickel alloy. Surface and Coatings Technology, 285, 278-288.

SHS Materials for Coatings

The main long-term scientific achievements of the SHS Center scientific team in the field of advanced SHS materials and coatings are described in the recent review paper published in the International Materials Review.

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FULL CRITICAL REVIEW

Self-propagating high-temperature synthesis of advanced materials and coatings

E. A. Levashov[a], A. S. Mukasyan[a,b], A. S. Rogachev[a,c] and D. V. Shtansky[a]

[a]National University of Science and Technology 'MISIS', Department of Powder Metallurgy and Functional Coatings, Moscow, Russia; [b]Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, USA; [c]Institute of Structural Macrokinetics & Materials Science of Russian Academy of Science, Chernogolovka, Russia

ABSTRACT
Self-propagating high-temperature synthesis (SHS) or combustion synthesis (CS) is a rapidly developing research area. SHS materials are being used in various fields, including mechanical and chemical engineering, medical and bioscience, aerospace and nuclear industries. The goal of the present paper is to provide a comprehensive state-of-the-art review and to analyse a critical mass of knowledge in the field of SHS materials and coatings. We also briefly discuss the history and scientific foundations of SHS along with an overview of the technological aspects for synthesis of different materials, including powders, ceramics, metal-ceramics, intermetallides, and composite materials. Application of CS in the field of surface engineering is also discussed focusing on two main routes for applying SHS to coating deposition: (i) single-step formation of the desired coatings and (ii) use of SHS-derived powders, targets or electrodes in the coating deposition processes.

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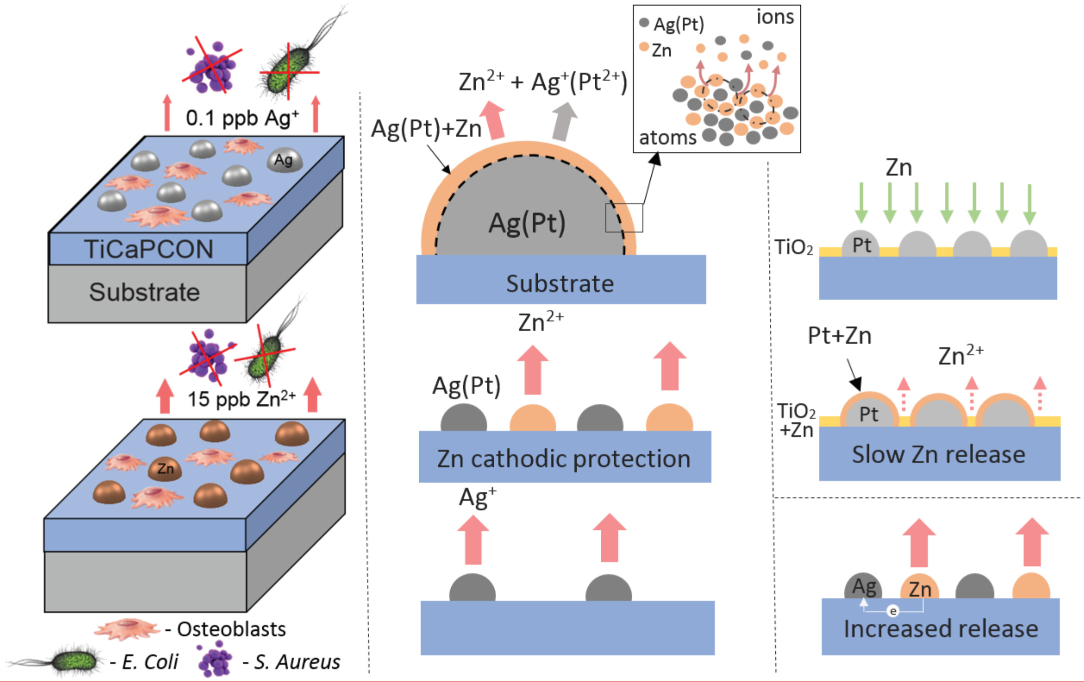
Self-propagating high-temperature synthesis; combustion synthesis; powders; ceramics; cermets; intermetallics; composites; porous materials; coatings

Biological Films for Medical Implants

The research team has extensive experience in obtaining new types of multicomponent bioactive nanostructured films by magnetron sputtering of composite SHS targets in combination with ion implantation. In recent years, the main efforts were aimed at obtaining bioactive yet bactericidal surfaces. To achieve the antibacterial characteristics, various approaches were considered: the introduction of bactericidal elements or antibiotics. The bioactive characteristics of TiCaPCO(N) films doped with Ag have been studied in vitro in simulated body fluid. It was shown that the concentration of the bactericidal component in biological environment can be controlled by the film surface roughness. The developed films have been successfully applied to modify the surfaces of metals, polymers, and de-immunized donor bones. A synergistic bactericidal effect from the simultaneous action of Ag ions and antibiotics has been demonstrated. The contribution of metal nanoparticles located on the surface of ceramic films in total material antibacterial activity was studied. The B-doped bactericidal TiCaPCON films were developed. Bactericidal surfaces with a controlled surface topography were obtained by photolithography method. The effect of surface topography (height of surface ledges and the distance between them) on the kinetics of the bactericidal ions release was studied. Multicomponent films with antibacterial effect were also developed and fabricated by PED. This method allows one to obtain relatively thick coatings (up to 100 μm) with controlled composition and roughness in a single (non-vacuum) technological cycle. New composite targets were developed for the deposition of coatings by the PED method. Developments in this area are protected by patents and «know-how». The invention «Multicomponent bioactive nanocomposite coatings with antibacterial effect» is included in the list of «100 best inventions of Russia» for 2015.



Schematic presentation of the ion release processes and its influence on the antibacterial activity

References

1. Ponomarev, V.A., Sheveyko, A.N., Sukhorukova, I.V., Shvindina, N.V., Manakhov, A.M., Zhitnyak, I.Y., Gloushankova, N.A., Fursova, N.K., Ignatov, S.G., Permyakova, E.S., Polčak, J., Shtansky, D.V. (2019). Microstructure, chemical and biological performance of boron-modified TiCaPCON films. Applied Surface Science, 465, 486-497.

2. Ponomarev, V.A., Shvindina, N.V., Permyakova, E.S., Slukin, P.V., Ignatov, S.G., Sirota, B., Voevodin, A.A., Shtansky, D.V. (2019). Structure and antibacterial properties of Ag-doped micropattern surfaces produced by photolithography method. Colloids and Surfaces B: Biointerfaces, 173, 719-724.

3. Sukhorukova, I.V., Sheveyko, A.N., Manakhov, A., Zhitnyak, I.Y., Gloushankova, N.A., Denisenko, E.A., Filippovich, S.Yu., Ignatov, S.G., Shtansky, D.V. (2018). Synergistic and long-lasting antibacterial effect of antibiotic-loaded TiCaPCON-Ag films against pathogenic bacteria and fungi. Materials Science and Engineering C, 90, 289-299.

4. Ponomarev, V.A., Sukhorukova, I.V., Sheveyko, A.N., Permyakova, E.S., Manakhov, A.M., Ignatov, S.G., Gloushankova, N.A., Zhitnyak, I.Y., Lebedev, O.I., Polčak, J., Kozmin, A.M., Shtansky, D.V. (2018). Antibacterial performance of TiCaPCON films incorporated with Ag, Pt, and Zn: Bactericidal ions versus surface microgalvanic interactions. ACS Applied Materials and Interfaces, 10(29), 24406-24420.

5. Zamulaeva, E.I., Sheveyko, A.N., Potanin, A.Y., Zhitnyak, I.Y., Gloushankova, N.A., Sukhorukova, I.V., Shvindina, N.V., Ignatov, S.G., Levashov, E.A., Shtansky, D.V. (2018). Comparative investigation of antibacterial yet biocompatible Ag-doped multicomponent coatings obtained by pulsed electrospark deposition and its combination with ion implantation. Ceramics International, 44(4), 3765-3774.

6. Sukhorukova, I.V., Sheveyko, A.N., Kiryukhantsev-Korneev, P.V., Levashov, E.A., Shtansky, D.V. (2017). In vitro bioactivity study of TiCaPCO(N) and Ag-doped TiCaPCO(N) films in simulated body fluid. Journal of Biomedical Materials Research - Part B Applied Biomaterials, 105(1), 193-203.

7. Sukhorukova, I.V., Sheveyko, A.N., Shvindina, N.V., Denisenko, E.A., Ignatov, S.G., Shtansky, D.V. (2017). Approaches for controlled Ag+ ion release: Influence of surface topography, roughness, and bactericide content. ACS Applied Materials and Interfaces, 9(4), 4259-4271.

8. Sukhorukova, I.V., Sheveyko, A.N., Firestein, K.L., Kiryukhantsev-Korneev, P.V., Golberg, D., Shtansky, D.V. (2017). Mechanical properties of decellularized extracellular matrix coated with TiCaPCON film. Biomedical Materials (Bristol), 12(3), 035014.

9. Shtansky, D.V., Levashov, E.A., Sukhorukova, I.V. (2015). Multifunctional bioactive nanostructured films. Hydroxyapatite (HAp) for biomedical applications (pp. 159-188).

10. Sukhorukova, I.V., Sheveyko, A.N., Kiryukhantsev-Korneev, P.V., Anisimova, N.Y., Gloushankova, N.A., Zhitnyak,I.Y., Benesova, J., Amler, E., Shtansky, D.V. (2015). Two approaches to form antibacterial surface: Doping with bactericidal element and drug loading. Applied Surface Science, 330, 339-350.

11. Sukhorukova, I.V., Sheveyko, A.N., Kiryukhantsev-Korneev, P.V., Zhitnyak, I.Y., Gloushankova, N.A., Denisenko, E.A., Filipovich, S.Yu., Ignatov, S.G., Shtansky, D.V. (2015). Toward bioactive yet antibacterial surfaces. Colloids and Surfaces B: Biointerfaces, 135, 158-165.

12. Shtansky, D.V., Levashov, E.A., Batenina, I.V. (2014). Multicomponent bioactive nanostructured films. Nanomaterials: Properties and Perspective Applications (pp. 355-383).

Plasma Modification of Biodegradable Polymers and Their Surface Functionalization

The research team has extensive experience in the deposition of plasma polymers by plasma polymerization, including on the surface of biodegradable nanofibers. A new strategy for the preparation of biodegradable polymer-based biomaterials for bone tissue engineering was developed. In vitro biological tests indicated that the osteoblasts adhesion and proliferation as well the alkaline phosphatase activity can be significantly improved by depositing the TiCaPCON film onto biodegradable polycaprolactone (PCL). It is shown that the modification of the PCL nanofibers with the COOH plasma polymers and the subsequent binding of NH_2 groups of protein molecules is a rather simple and technologically accessible procedure allowing the adhesion, early spreading, and growth of human fibroblasts to be boosted.

References

1. Manakhov, A., Permyakova, E.S., Ershov, S., Sheveyko, A., Kovalskii, A., Polčák, J., Zhitnyak, I.Y., Gloushankova, N.A., Zajíčková, L., Shtansky, D.V. (2019). Bioactive TiCaPCON-coated PCL nanofibers as a promising material for bone tissue engineering. Applied Surface Science, 479, 796-802.

2. Miroshnichenko, S., Timofeeva, V., Permykova, E., Ershov, S., Kiryukhantsev-Korneev, P., Dvořaková, E., Shtansky, D.V., Zajíčková, L., Solovieva, A., Manakhov, A. (2019). Plasma-coated polycaprolactone nanofibers with covalently bonded platelet-rich plasma enhance adhesion and growth of human fibroblasts. Nanomaterials, 9(4), 637.

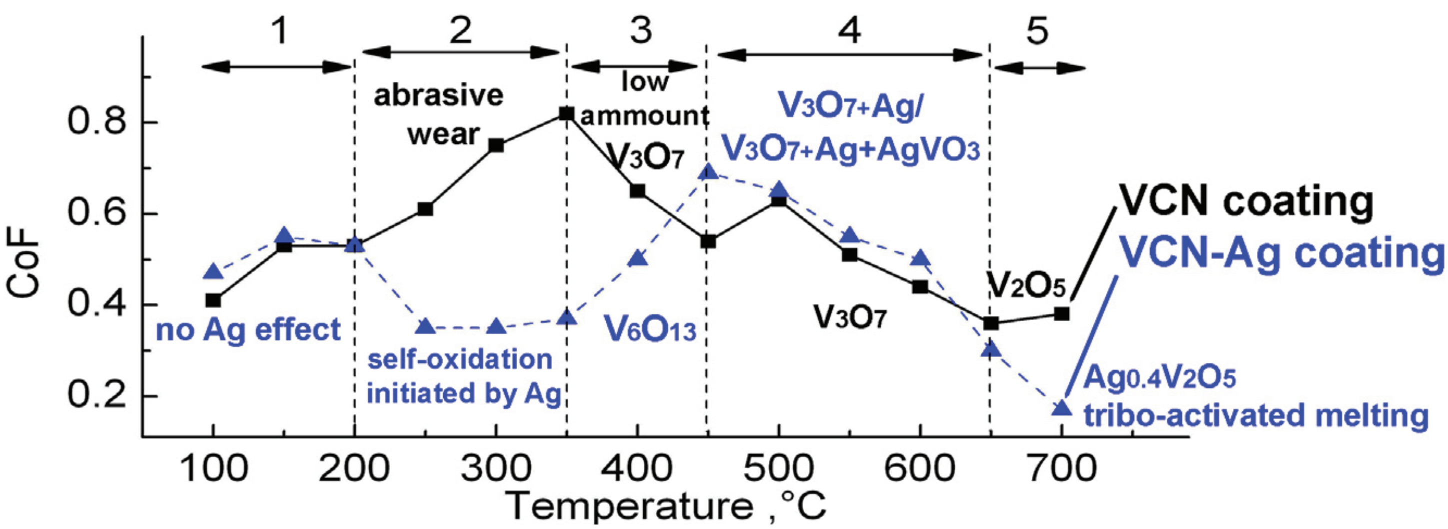
3. Manakhov, A., Kiryukhantsev-Korneev, P., Michlíček, M., Permyakova, E., Dvořáková, E., Polčák, J., Popov, Z., Visotin, M., Shtansky, D.V. (2018). Grafting of carboxyl groups using $CO_2/C_2H_4/Ar$ pulsed plasma: Theoretical modeling and XPS derivatization. Applied Surface Science, 435, 1220-1227.

4. Solovieva, A., Miroshnichenko, S., Kovalskii, A., Permyakova, E., Popov, Z., Dvořáková, E., Kiryukhantsev-Korneev, P., Obrosov, A., Polčak, J., Zajíčková, L., Shtansky, D.V., Manakhov, A. (2017). Immobilization of platelet-rich plasma onto COOH plasma-coated PCL nanofibers boost viability and proliferation of human mesenchymal stem cells. Polymers, 9(12), 736.

5. Manakhov, A., Kedroňová, E., Medalová, J., Černochová, P., Obrusník, A., Michlíček, M., Shtansky, D.V., Zajíčková, L. (2017). Carboxyl-anhydride and amine plasma coating of PCL nanofibers to improve their bioactivity. Materials and Design, 132, 257-265.

Surface Engineering to Reduce Friction and Wear

The research team conducts comprehensive research into the development of hard wear-resistant coatings with a low friction coefficient, including those designed to work in a wide temperature range. Si-Ta-C-(N), VCN-(Ag), MoCN-Ag, and TiNbCN-Ag systems were studied. The developed Si-Ta-C-(N) coatings are characterized by high thermal stability and oxidation resistance at temperatures up to 800°C. Tribological tests demonstrated the decrease of the coefficient of friction (CoF) of the coatings with increasing temperature: from 0.38 (25°C) to 0.28 (600°C) and 0.23 (800°C). The low wear rate and CoF of the Si-Ta-C-N coatings at elevated temperatures are explained by the formation of a thin (~100 nm) oxide layer and $TaSi_xO_y$ microfibers on the coating surfaces. A significant drop in the friction coefficient of the VCN-Ag coatings in comparison with their Ag-free counterparts was explained by (i) the surface self-oxidation initiated by Ag and the tribo-activated formation of $AgVO_3$ phase in the temperature range of 250–350°C and (ii) the formation of $Ag_{0.4}V_2O_5$ phase and its triboactivated melting above 650°C. We also demonstrated that simultaneous alloying with Nb and Ag permits to overcome the main drawbacks of TiCN coatings such as their relatively high values of friction coefficient at elevated temperatures and low oxidation resistance. It is shown that a relatively high amount of Ag (15 at.%) is required to provide enhanced tribological behavior in a wide temperature range of 25–700 °C. In addition, the prepared Ag-doped coatings demonstrated active oxidation protection and self-healing functionality due to the segregation of Ag metallic particles in damage areas such as cracks, pin-holes, or oxidation sites. The prospects of adding BN nanoparticles to liquid lubricants to reduce the friction coefficient and wear rate were also shown.



Schematic representation of phenomenological temperature-dependent friction model in the VCN-(Ag) coatings

References

1. Bondarev, A.V., Vorotilo, S., Shchetinin, I.V., Levashov, E.A., Shtansky, D.V. (2019). Fabrication of Ta-Si-C targets and their utilization for deposition of low friction wear resistant nanocomposite Si-Ta-C-(N) coatings intended for wide temperature range tribological applications. Surface and Coatings Technology, 359, 342-353.

2. Bondarev, A.V., Kvashnin, D.G., Shchetinin, I.V., Shtansky, D.V. (2018). Temperature-dependent structural transformation and friction behavior of nanocomposite VCN-(Ag) coatings. Materials and Design, 160, 964-973.

3. Bondarev, A.V., Kovalskii, A.M., Firestein, K.L., Loginov, P.A., Sidorenko, D.A., Shvindina, N.V., Sukhorukova, I.V., Shtansky, D.V. (2018). Hollow spherical and nanosheet-base BN nanoparticles as perspective additives to oil lubricants: Correlation between large-scale friction behavior and in situ TEM compression testing. Ceramics International, 44(6), 6801-6809.

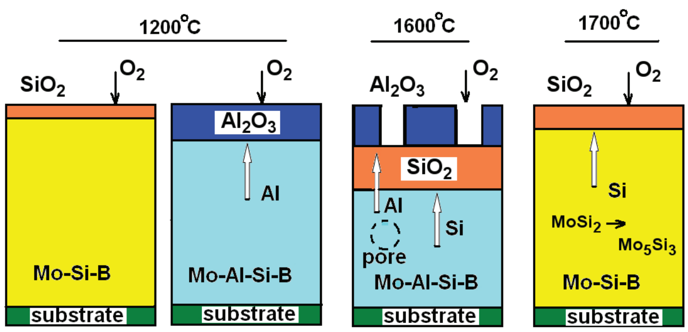
4. Bondarev, A.V., Golizadeh, M., Shvyndina, N.V., Shchetinin, I.V., Shtansky, D.V. (2017). Microstructure, mechanical, and tribological properties of Ag-free and Ag-doped VCN coatings. Surface and Coatings Technology, 331, 77-84.

5. Bondarev, A.V., Kiryukhantsev-Korneev, P.V., Levashov, E.A., Shtansky, D.V. (2017). Tribological behavior and self-healing functionality of TiNbCN-Ag coatings in wide temperature range. Applied Surface Science, 396, 110-120.

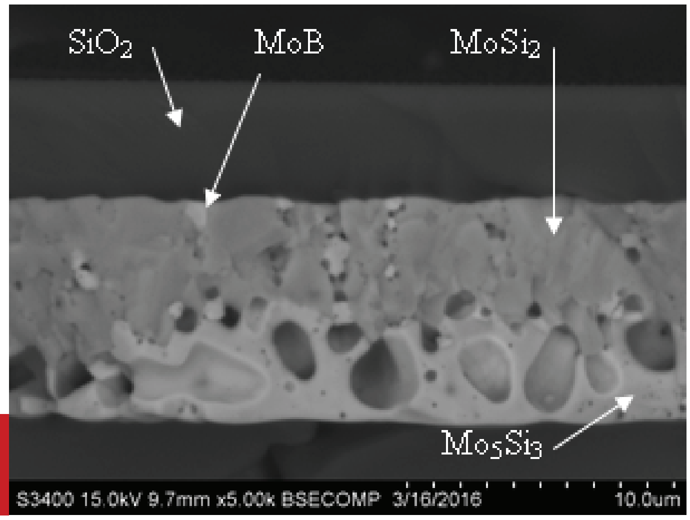
6. Bondarev, A.V., Kiryukhantsev-Korneev, P.V., Sidorenko, D.A., Shtansky, D.V. (2016). A new insight into hard low friction MoCN-Ag coatings intended for applications in wide temperature range. Materials and Design, 93, 63-72.

Oxidation Resistant Coatings

Mo-Si-B and Mo-Al-Si-B coatings were deposited by DC magnetron sputtering of MoSiB and MoAlSiB composite targets fabricated by the self-propagating high-temperature synthesis method. The Mo-Si-B coatings possess higher hardness, improved oxidation resistance and better thermal stability compared with their Mo-Al-Si-B counterparts. The 7-μm thick Mo-Si-B coatings were shown to successfully withstand oxidation during short-time exposure for 10 min at a temperature as high as 1700 °C due to the formation of protective silica scale. The oxidation of Mo-Al-Si-B coatings was accompanied by the diffusion of aluminum to the coating surfaces and the formation of a single Al_2O_3 layer at 1200–1300 °C and a double Al_2O_3-SiO_2 layer at 1500 °C, which were less protective against oxidation. The surface oxidation processes were also accompanied by phase transformations inside the oxygen-free part of both Mo-Si-B and Mo-Al-Si-B coatings with the formation of MoB and Mo_5Si_3 phases. Amorphous Cr-Al-Si-B coating demonstrated higher hardness up to 30 GPa and superior oxidation resistance up to 1300 °C, but high friction coefficient ~0.8. In contrast, the reactively deposited Cr-Al-Si-B-N coatings had lower hardness in a range of 18-20 GPa and oxidation resistance up to 1100 °C, but reduced friction coefficient ~0.4 and wear rate ~ $(2.0 \pm 0.1) \cdot 10^{-6}$ $mm^3N^{-1}m^{-1}$. The Cr-Al-Si-B coating demonstrated the lowest wear value among all tested coatings during impact tests. However it was the only coating to reveal any fracture. Reactively deposited coatings showed no failures but higher values of wear, which was associated with reduced hardness and lower brittleness compared to those of the Cr-Al-Si-B coating. The TiAlSiCN coatings with a «comb»-like nanocomposite structure were developed. The main cubic (Ti,Al)(C,N) phase was stable in a wide temperature range between 900 and 1600 °C, although its elemental composition was changed during heat treatments. The TiAlSiCN coatings were characterized by high hardness above 37 GPa in the temperature range 25–1300 °C. Oxidation resistance of TiAlSiCN coatings is limited by 1000 °C, but can be increased up to 1100 °C by additional Al-based layers.



Schematic representation of the oxidation mechanisms for Mo-Si-B and Mo-Al-Si-B coatings



References

1. Kiryukhantsev-Korneev, P.V., Iatsyuk, I.V., Shvindina, N.V., Levashov, E.A., Shtansky, D.V. (2017). Comparative investigation of structure, mechanical properties, and oxidation resistance of Mo-Si-B and Mo-Al-Si-B coatings. Corrosion Science, 123, 319-327.

2. Kuptsov, K.A., Kiryukhantsev-Korneev, P.V., Sheveyko, A.N., Shtansky, D.V. (2015). Structural transformations in TiAlSiCN coatings in the temperature range 900-1600 °c. Acta Materialia, 83, 408-418.

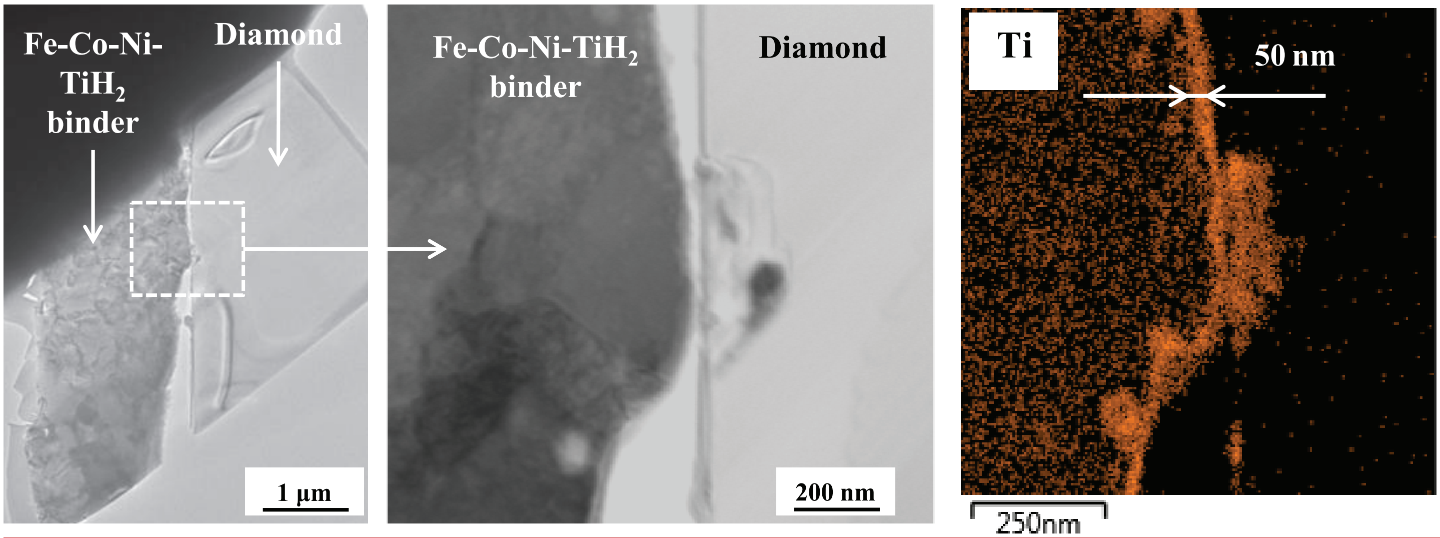
3. Kuptsov, K.A., Kiryukhantsev-Korneev, P.V., Sheveyko, A.N., Shtansky, D.V. (2015). Surface modification of TiAlSiCN coatings to improve oxidation protection. Applied Surface Science, 347, 713-718.

4. Kiryukhantsev-Korneev, P.V., Pierson, J.F., Kuptsov, K.A., Shtansky, D.V. (2014). Hard Cr-Al-Si-B-(N) coatings deposited by reactive and non-reactive magnetron sputtering of CrAlSiB target. Applied Surface Science, 314, 104-111.

Superhard materials with nanoparticle reinforced binder

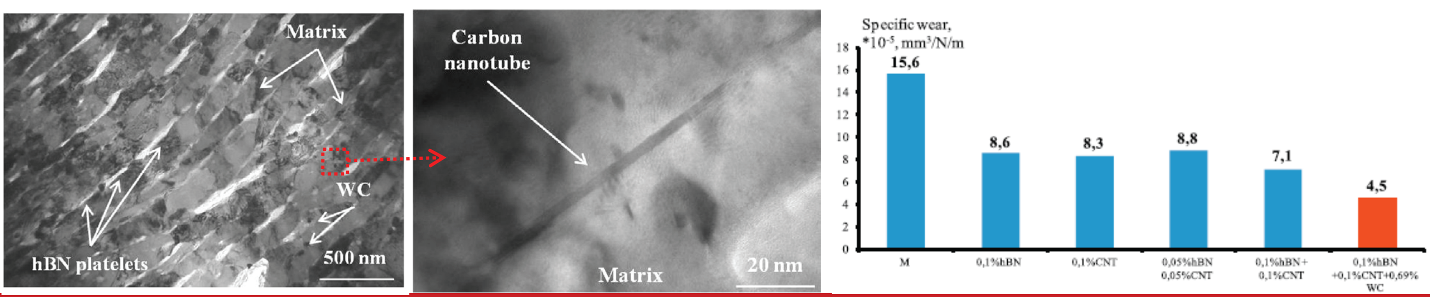
The conception consists in the development of novel compositions and production routes of multicomponent metallic binders for diamond cutting tool. It involves obtaining of nanostructure materials via mechanical alloying and hot pressing techniques, modification of the binders with nanoparticles of different refractory compounds, in-situ formation of protective tungsten carbide coatings on diamond single crystals and simultaneous using of different types of superhard materials (diamond and cubic boron nitride) for enhanced performance of the tool in particular operating conditions.

A group of authors for the first time showed the possibility of application of combined mechanical alloying and hot pressing techniques for production of binders with high strength and wear resistance (up to 20 times higher compared to commercially available analogues), which contributed much to the diamond tool cutting speed and service life. This method allowed obtaining nanostructure materials with low efforts, and achieving homogeneous distribution of all components in the binder despite their limited mutual solubility. One of the prime benefits of the developed method is a possibility of designing binders with unique adhesive properties through the dissolution of carbide forming dopant, such as titanium, chromium etc.



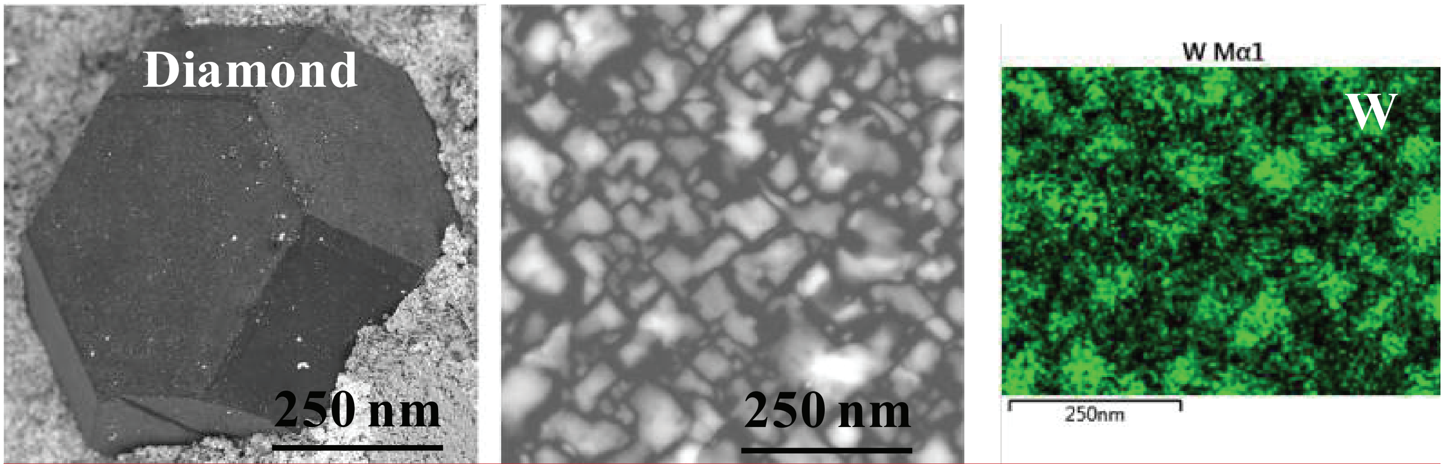
The interface of diamond and mechanically alloyed Fe-Co-Ni-TiH_2 binder and protective TiC interlayer on diamond surface

One of the novel approaches to enhance the binder properties is its hybrid nanomodification by nanoparticles with various crystalline structure and geometry. Hybrid metallic nanocomposites were demonstrated to have much higher mechanical properties than both nanoparticles-free metallic binder and nanocomposites reinforced with only one type of nanoparticles. Combining nanoreinforcements of different types and shapes particles (here, stiff and long carbon nanotubes, soft disc-shaped boron nitride hBN, and tungsten carbide WC) in the same metallic binder, one can synergistically improve mechanical properties, strength of the binder, and, ultimately, enhance wear resistance and reliability of machining tools.



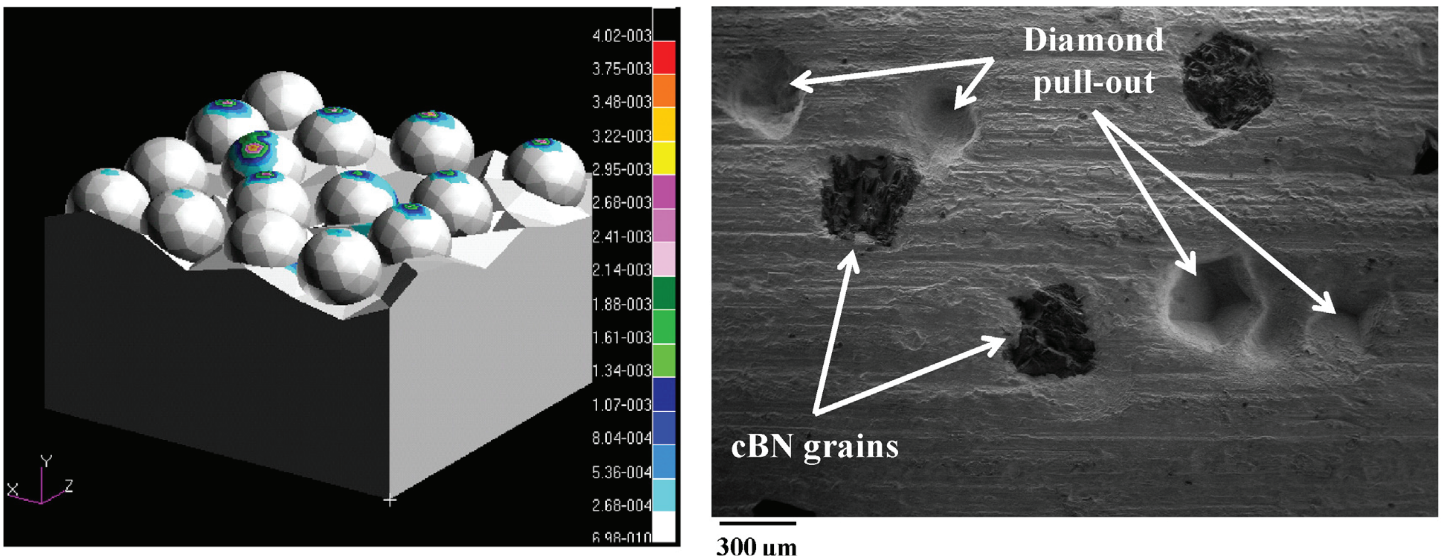
Structure of hybrid reinforced Fe-Ni-Mo binder and specific wear of initial and reinforced binder after tribological tests

The finding demonstrates the possibility of self-organized WC films formation on diamond single crystals in the presence of WC nanoparticles and catalysis metal in the binder (even if they do not contact with diamond). The coating is formed via the gas transport mechanism: mass transfer of gaseous WO_3 to the diamond surface, its chemisorption, reduction, and carbidization. Thermodynamic calculations and studies focused on chemical composition of the regions adjacent to the diamond–binder interface, where tungsten concentration on the diamond surface is higher than the average concentration in the material bulk, also confirmed that the gas transport mechanism is involved in the coating formation. This phenomenon could be a promising candidate for manufacturing of heat sink and heat spreader devices, as well as cutting tools.



Diamond grain covered by WC (a), crystal face (b) and W elemental map (c) after sintering with binder Cu+ Fe+WO_3

Both experimental and simulation studies were carried out to establish the optimal ratio of different types of superhard materials in diamond tool. The superhard tools with 25 % of diamond replaced by cubic boron nitride (cBN) grains demonstrate 20 % increased performance compared with pure diamond machining tools, and more than two times higher performance compared with pure cBN tools. Further, machining efficiency of the wheels modified by hBN particles was 80 % more than the efficient compared with conventional tool with the original binder. The developed diamond/cBN cutting tools find application in machining of steels, cast irons or low abrasive rocks (granites).



The simulation of working layer with diamond and CBN grains and surface of worn tool segment, demonstrating benefits of partial replacing of diamond to CBN

References

1. Loginov, P.A., Sidorenko, D.A., Shvyndina, N.V., Sviridova, T.A., Churyumov, A.Y., Levashov, E.A. (2019). Effect of Ti and TiH_2 doping on mechanical and adhesive properties of Fe-Co-Ni binder to diamond in cutting tools. International Journal of Refractory Metals and Hard Materials, 79, 69-78.

2. Vorotilo, S., Loginov, P., Mishnaevsky, L., Sidorenko, D., Levashov, E. (2019). Nanoengineering of metallic alloys for machining tools: Multiscale computational and in situ TEM investigation of mechanisms. Materials Science and Engineering A, 739, 480-490.

3. Loginov, P.A., Sidorenko, D.A., Bychkova, M.Y., Zaitsev, A.A., Levashov, E.A. (2019). Performance of diamond drill bits with hybrid nanoreinforced Fe-Ni-Mo binder. International Journal of Advanced Manufacturing Technology, 102(5-8), 2041-2047.

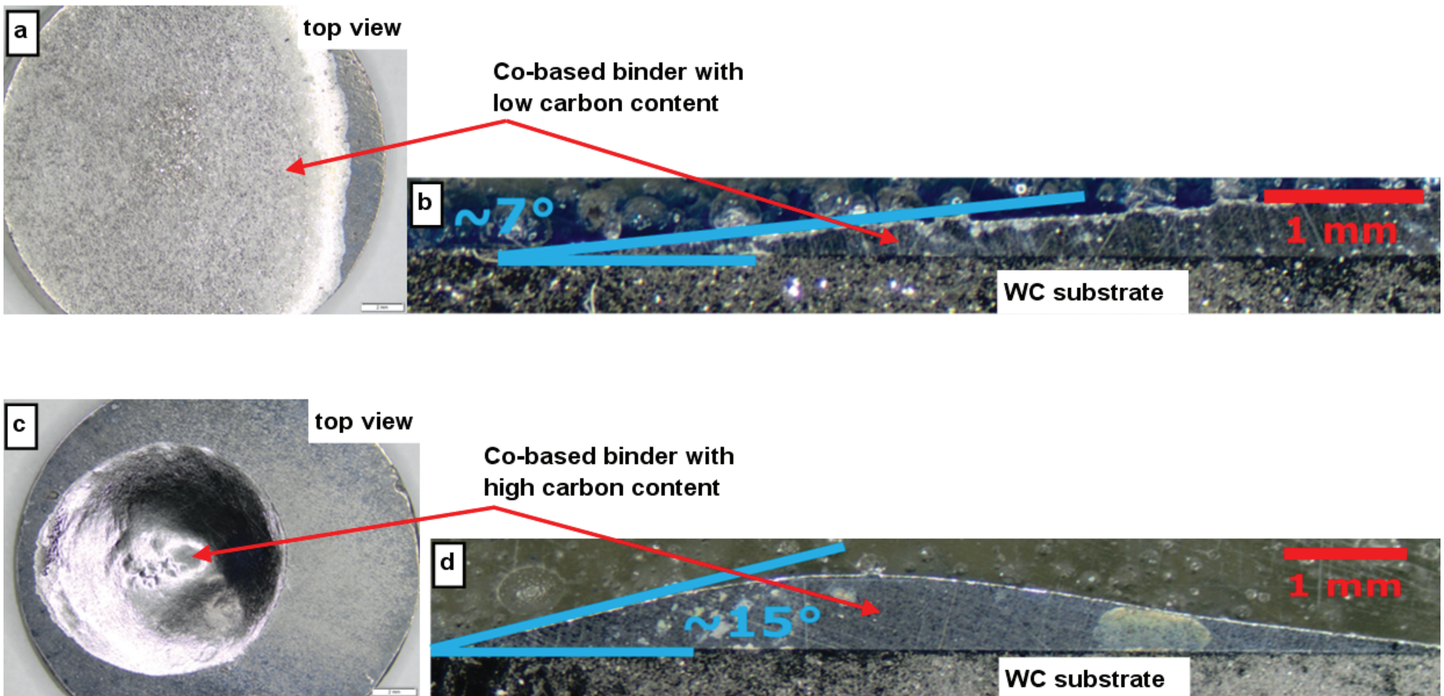
4. Loginov, P.A., Sidorenko, D.A., Levashov, E.A., Petrzhik, M.I., Bychkova, M.Y., Mishnaevsky, L., Jr. (2018). Hybrid metallic nanocomposites for extra wear-resistant diamond machining tools. International Journal of Refractory Metals and Hard Materials, 71, 36-44.

5. Sidorenko, D.A., Levashov, E.A., Kuptsov, K.A., Loginov, P.A., Shvyndina, N.V., Skryleva, E.A. (2017). Conditions for the in-situ formation of carbide coatings on diamond grains during their sintering with Cu-WC binders. International Journal of Refractory Metals and Hard Materials, 69, 273-282.
6. Loginov, P., Mishnaevsky, L., Jr., Levashov, E., Petrzhik, M. (2015). Diamond and cBN hybrid and nanomodified cutting tools with enhanced performance: Development, testing and modelling. Materials and Design, 88, 310-319.

Hard metals with hierarchical structure and superior properties

The wettability in the system W-C-Co with different carbon contents

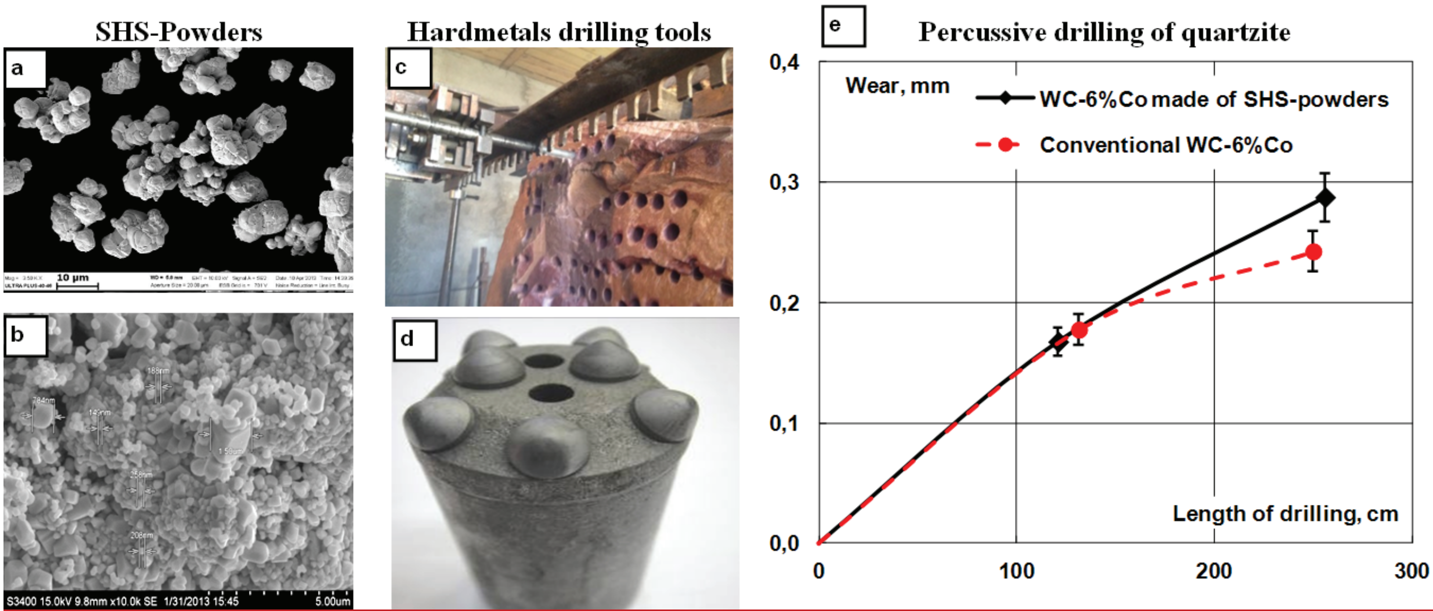
Traditionally, it is believed that the wettability of WC by liquid Co-based binders in WC-Co hard metals is complete. In the only two published works, in which the dihedral angle of liquid Co on WC was directly measured, just only pure Co was employed. Nevertheless, it is well known that the Co-based binders in real hard metals usually contain significant amounts of dissolved tungsten and carbon, the concentrations of which strongly depend on the total carbon content. On that ground the wettability of tungsten carbide by model alloys simulating real binders in WC-Co hard metals was examined by the research team depending on the carbon content varying from the very low carbon content corresponding to the η-phase formation to the very high carbon content corresponding to the free carbon formation. According to the experimental results, the wettability of tungsten carbide by liquid Co-based binders is complete at low carbon contents and becomes incomplete when increasing the carbon content. The wettability of WC by binder alloys saturated with carbon is relatively poor with the dihedral angle of nearly 15. The results obtained are of great fundamental importance because they make it possible to explain the well-known phenomenon of the Co migration in the functionally graded hard metals.



The top view and cross-section of the droplets of the binder model alloys after melting and spreading over the WC substrates: a, b – Co-based binder with a low carbon content (comprising some η-phase); c, d – Co-based binder with a high carbon content (comprising free carbon)

Near-nano and coarse-grained WC powders obtained by SHS

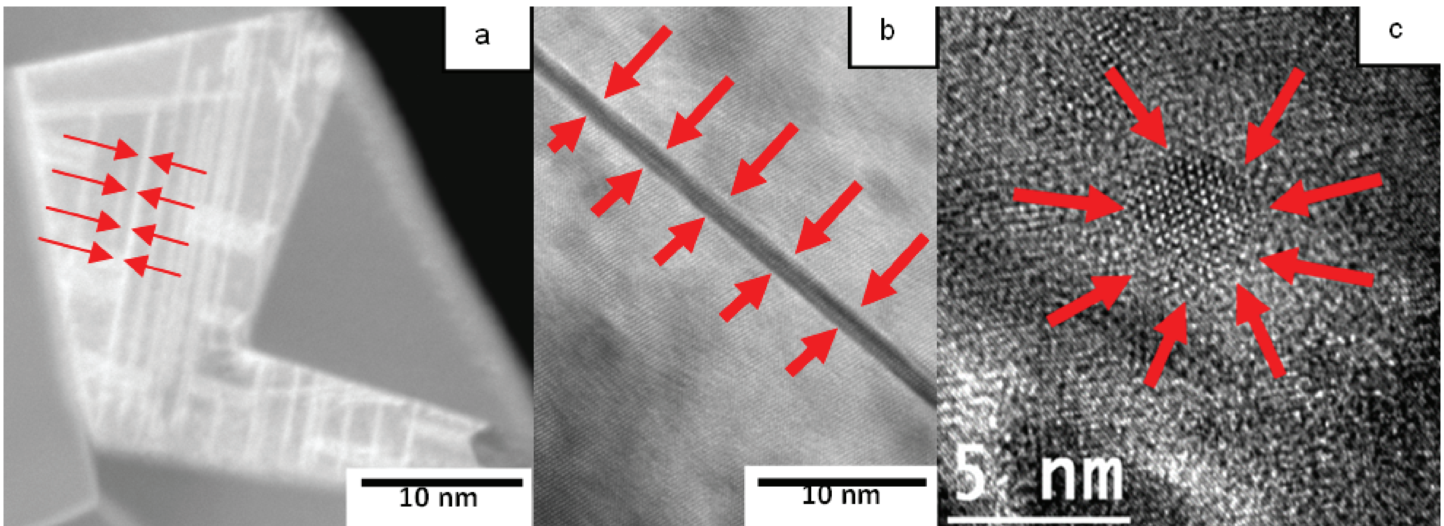
SHS as an alternative method of obtaining WC powders by magnesium reduction of WO_3 in the presence of carbon was proposed. With aid of the SHS method near-nano and coarse-grained WC powders were obtained with an average particle size of about 200 nm and 5 μm, respectively. The synthesized powders were fully carbidized and slightly oxidized (C_{total} = 6.13 %, O <0.077 %), which comply with the requirements of the hardmetal industry. Results of performance tests on percussive drilling of the coarse-grained 94 % WC-6%Co grades made from the SHS-powders and conventionally produced coarse-grained powders indicate that values of their wear-resistance are similar. Thus, it is established that high-quality WC-Co hard metals with different WC grain sizes varying from submicron to coarse-grained can be produced using the SHS-powders.



WC powders obtained by SHS (a, b); hard metals drilling tools (c, d); results of performance tests on percussive drilling of quartzite (e)

Coarse-grained hard metal

Comprehensive research on the development of hierarchical coarse-grained hard metals with an extremely homogeneous microstructure has been carried out. Compared with standard hardmetal grades the binder phase of hierarchical hard metals is strengthened by nanoparticles which appeared as a result of the concentration separation of a supersaturated solid solution of Ta and W in a Co matrix. The super-homogeneous microstructure is achieved through the use of narrow-fractional tungsten carbide powders and of functional additives that suppress the carbide grain growth.



STEM (a) and HRTEM (b, c) images of the binder phase in the hierarchical coarse-grained hard metals (nanosized precipitations highlighted by arrows)

The hierarchical coarse-grained hard metals with the extremely homogeneous microstructure have a unique combination of hardness, strength, toughness and wear-resistance according to the ASTM B611 test (11.7 GPa, 2600 MPa, 18.5 MPa·m$^{1/2}$ and 1.09×10^{-4} cm^3/rev) which considerably superior to the corresponding properties of conventional coarse-grained 94%WC-6%Co grades. The rock-cutting tools with the developed hierarchical hard metals are characterized by the tool life prolongation by up to 100% compared to conventional coarse-grained hard metals.

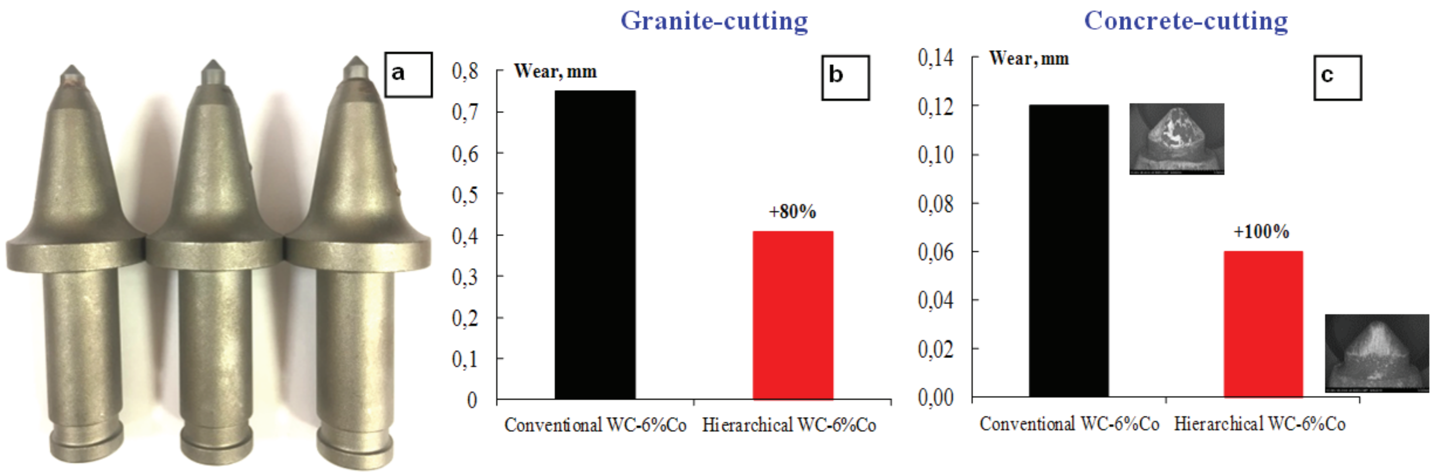


Figure 4. The rock cutting tools with hierarchical hard metals (a); wear of the tools made of hierarchical and conventional coarse-grained 94%WC-6%Co hard metals after granite (b) and concrete cutting (c)

References

1. Loginov, P., Zaitsev, A.A., Konyashin, I., Sidorenko, D., Avdeenko, E.N., Levashov, E.A. (2019). In-situ observation of hardmetal deformation processes by transmission electron microscopy. Part I: Deformation caused by bending loads. International Journal of Refractory Metals and Hard Materials, 84, 104997.

2. Loginov, P., Zaitsev, A.A., Orekhov, A., Sidorenko, D., Avdeenko, E.N., Levashov, E.A., Konyashin, I. (2019). In-situ observation of hardmetal deformation processes by transmission electron microscopy. Part II: Deformation caused by tensile loads. International Journal of Refractory Metals and Hard Materials, 84, 105017.

3. Konyashin, I., Zaitsev, A., Meledin, A., Mayer, J., Loginov, P., Levashov, E., Ries, B. (2018). Interfaces between model Co-W-C alloys with various carbon contents and tungsten carbide. Materials, 11(3), 404.

4. Konyashin, I., Zaitsev, A.A., Sidorenko, D., Levashov, E.A., Ries, B., Konischev, S.N., Sorokin, M., Mazilkin, A.A., Herrmann, M., Kaiser, A. (2017). Wettability of tungsten carbide by liquid binders in WC–Co cemented carbides: Is it complete for all carbon contents? International Journal of Refractory Metals and Hard Materials, 62, 134-148.

5. Zaitsev, A.A., Vershinnikov, V.I., Konyashin, I., Levashov, E.A., Borovinskaya, I.P., Ries, B. (2015). High-quality cemented carbides on the basis of near-nano and coarse-grain WC powders obtained by self-propagating high-temperature synthesis (SHS). International Journal of Self-Propagating High-Temperature Synthesis, 24(3), 152-160.

6. Zaitsev, A.A., Vershinnikov, V.I., Konyashin, I., Levashov, E.A., Borovinskaya, I.P., Ries, B. (2015). Cemented carbides from WC powders obtained by the SHS method. Materials Letters, 158, 329-332.

7. Zaytsev, A.A., Borovinskaya, I.P., Vershinnikov, V.I., Konyashin, I., Patsera, E.I., Levashov, E.A., Ries, B. (2015). Near-nano and coarse-grain WC powders obtained by the self-propagating high-temperature synthesis and cemented carbides on their basis. Part I: Structure, composition and properties of WC powders. International Journal of Refractory Metals and Hard Materials, 50, 146-151.

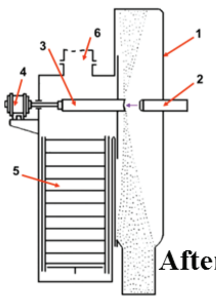
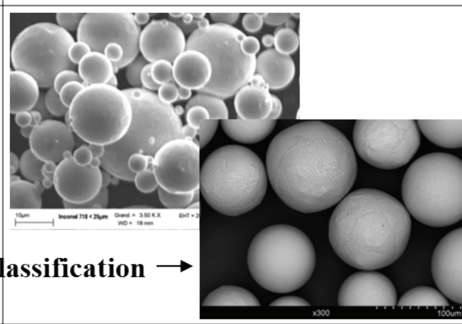
Innovative powders for additive manufacturing

Additive technologies (selective laser melting and selective electron beam melting) are widely developed for the manufacturing of items with complicated shape as applied to aerospace, shipbuilding, petrochemical, and medicine. Additive manufacturing use the spherical powders with a regulated particle size distribution without porosity or satellites.

Two technological approaches have been developed to produce innovative narrow-fraction spherical powders of heat-resistant intermetallic alloys based on NiAl, (Fe, Ni)Al and TiAl/Ti_3Al compounds.

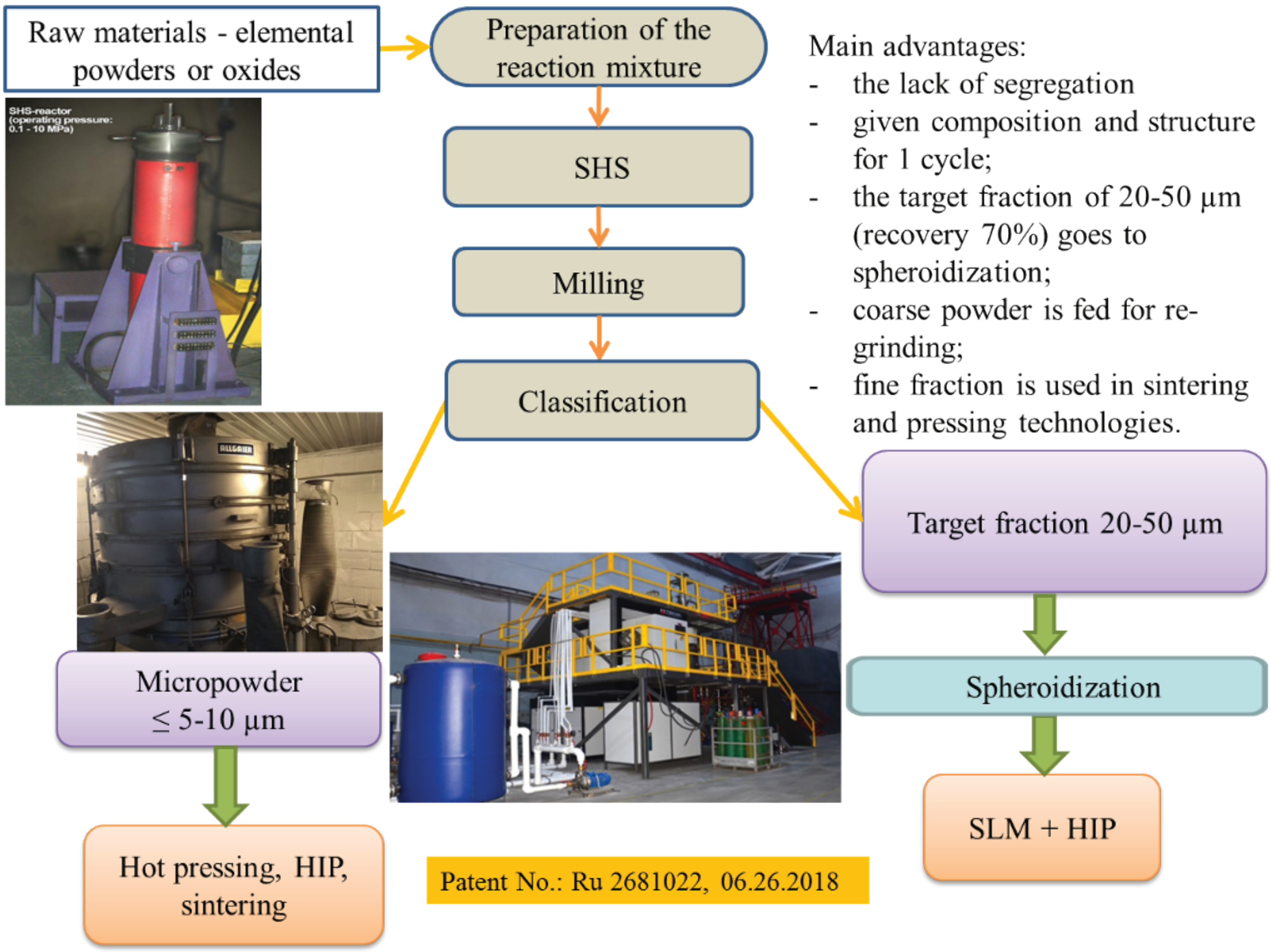
The 1st technology is based on: synthesis of required composition by the centrifugal SHS-casting; vacuum-induction melting of SHS- precursor and following by casting of long size electrodes in the steel shell; spherical powders spraying by plasma rotating electrode processing magnetic separation and powder classification.

The 1st technology. Production of spherical powders NUST "MISIS"-ISMAN-JSC "Kompozit"

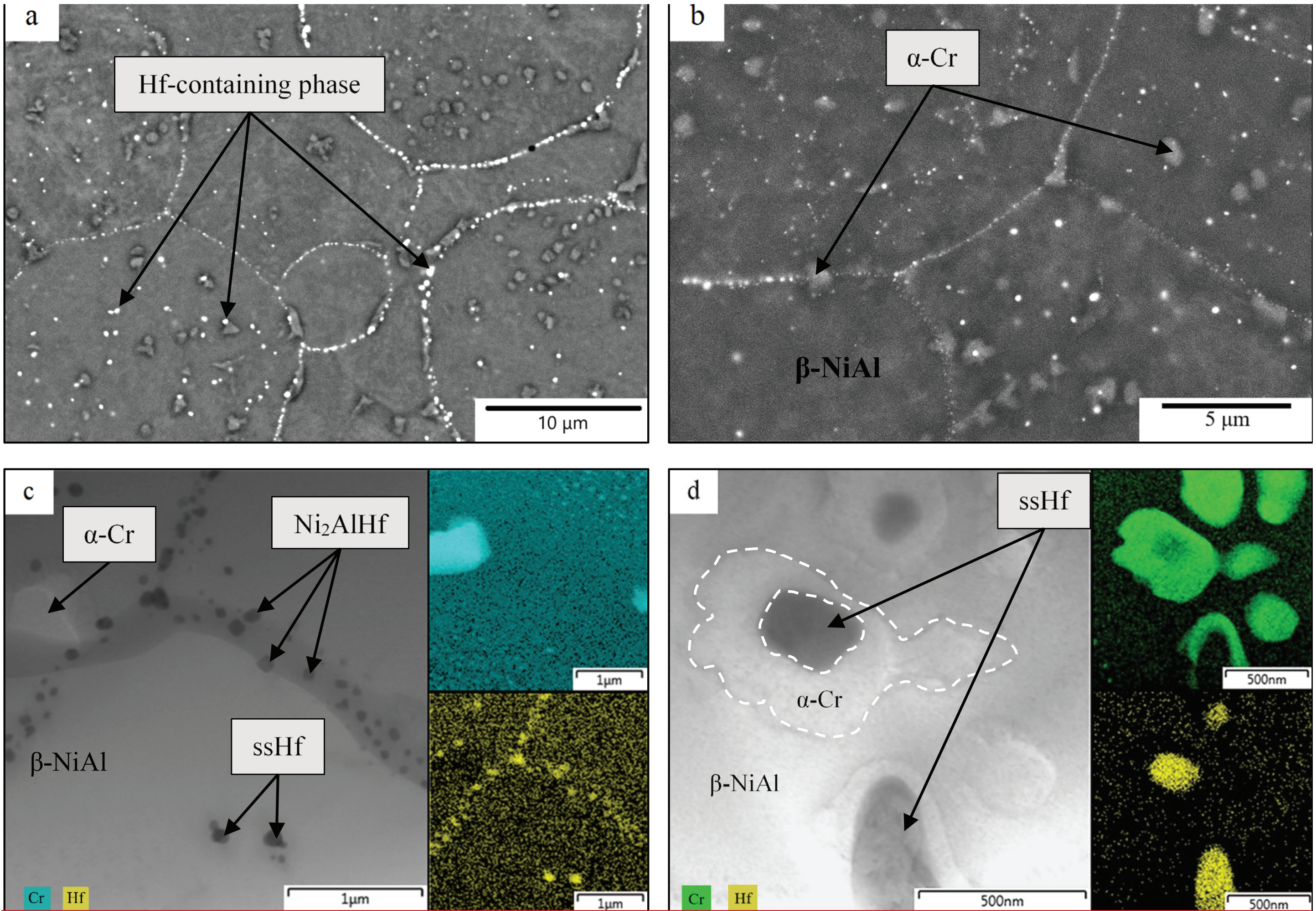
Technological operation	Equipment	Product
1. Centrifugal SHS-casting		
2. Vacuum-induction remelting and electrode casting	 	
3. Plasma rotating electrode processing	 	 After classification →

The 2nd technology is based on: SHS in elemental mixture; grinding the porous sinter; powders classification and their plasma spheroidization; ultrasonic treatment and powders classification.

The 2nd technology. Production of spherical micropowders
NUST "MISIS"-IMET RAS-JSC "Polema"

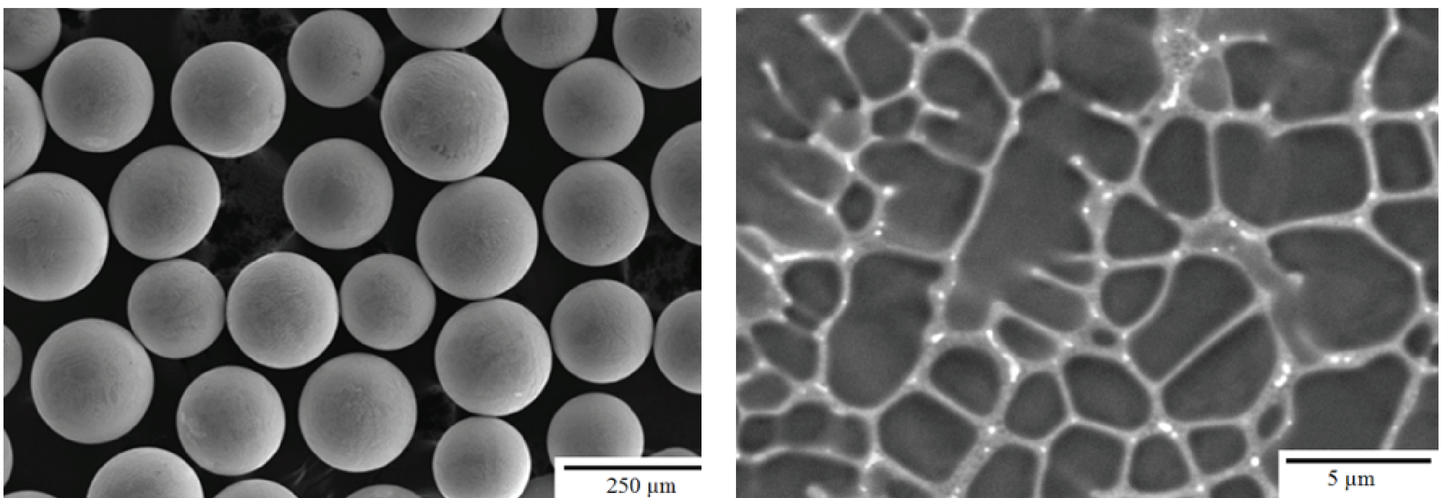


Optimization of the composition and combustion synthesis conditions made it possible to develop a number of new intermetallic alloys (NiAl-Cr-Co-Hf, NiAl-Fe-Cr-Co-Hf, et.al) with hierarchical structure and high strength at room and elevated temperatures.
Thus, the NiAl-Cr-Co-Hf alloy (CompoNiAl-M5-3) is characterized by three structural levels: 1st — NiAl based grains or dendrites, separated from each other by thin α-Cr interlayers (less than 1μm) with Hassler phase Ni_2AlHf nanoparticles distributed at the grain boundaries; 2nd — spherical α-Cr precipitates and Hf nanoparticles 50–100 nm inside NiAl grains; 3rd – α-Cr pre-precipitates 3-4 nm.



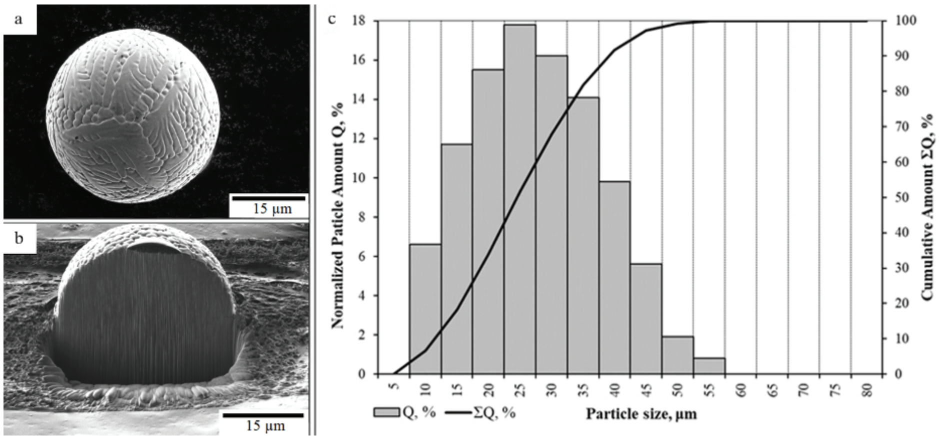
Microstructure of the $Ni_{41}Al_{41}Cr_{12}Co_6$ alloy HIP: (a, b) – SEM image; (c, d) STEM image with EDXS maps of the same area

According to the 1st technology, two types of spherical powders (100-160 µm) were obtained in one cycle: intermetallic CompoNiAl-M5-3 and composite Fe-NiAl-Cr-Co-Hf.



The morphology and microstructure of CompoNiAl-M5-3 spherical powders

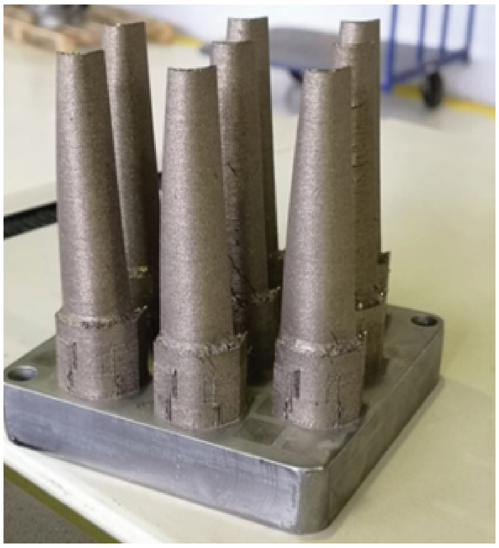
The 2nd technology provided the production of spherical powders (20-45 µm). The particle size was in the 10–55 µm range at D50 = 26 µm. The degree of plasma spheroidization is 98 %, satellites were absent. The powder is characterized by density and flow properties – 3.75 g/cm^3 and 20 s, respectively.



The SEM with layer-by-layer etching of a spherical particle by Ga ions (a, b) and the granulometric composition of spheroidized CompoNiAl-M5-3 micropowders (c)

The SLM parameters were optimized in order to build a turbine rotor blade models.

Turbine rotor blades



At room temperature, the CompoNiAl-M5-3 alloy in the as- HIP has a follow properties under conditions of compressive stress: Young's modulus (E) = 180 GPa, ultimate strength (σ_b) = 2870 MPa; conditional yield strength ($\sigma_{0.2}$) = 1130 MPa at the plastic deformation degree (ε) = 17 %. At 850 °C and a strain rate $0{,}01^{s-1}$, the E и $\sigma_{0.2}$ are equal 138 GPa и 455 MPa.

References

1. Kaplanskii, Y.Y., Sentyurina, Z.A., Loginov, P.A., Levashov, E.A., Korotitskiy, A.V., Travyanov, A.Y., Petrovskii, P.V. (2019). Microstructure and mechanical properties of the (Fe,Ni)Al-based alloy produced by SLM and HIP of spherical composite powder. Materials Science and Engineering A, 743, 567-580.

2. Kaplanskii, Y.Y., Zaitsev, A.A., Levashov, E.A., Loginov, P.A., Sentyurina, Z.A. (2018). NiAl based alloy produced by HIP and SLM of pre-alloyed spherical powders. evolution of the structure and mechanical behavior at high temperatures. Materials Science and Engineering A, 717, 48-59.

3. Kaplanskii, Y.Y., Korotitskiy, A.V., Levashov, E.A., Sentyurina, Z.A., Loginov, P.A., Samokhin, A.V., Logachev, I.A. (2018). Microstructure and thermomechanical behavior of Heusler phase Ni_2AlHf-strengthened NiAl-Cr(Co) alloy produced by HIP of plasma-spheroidized powder. Materials Science and Engineering A, 729, 398-410.

4. Kaplanskii, Y.Y., Zaitsev, A.A., Sentyurina, Z.A., Levashov, E.A., Pogozhev, Y.S., Loginov, P.A., Logachev, I.A. (2018). The structure and properties of pre-alloyed NiAl-Cr(Co,Hf) spherical powders produced by plasma rotating electrode processing for additive manufacturing. Journal of Materials Research and Technology, 7(4), 461-468.

5. Zaitsev, A.A., Sentyurina, Z.A., Levashov, E.A., Pogozhev, Y.S., Sanin, V.N., Loginov, P.A., Petrzhik, M.I. (2017). Structure and properties of NiAl-Cr(Co,Hf) alloys prepared by centrifugal SHS casting. Part 1 – room temperature investigations. Materials Science and Engineering A, 690, 463-472.

6. Zaitsev, A.A., Sentyurina, Z.A., Levashov, E.A., Pogozhev, Y.S., Sanin, V.N., Sidorenko, D.A. (2017). Structure and properties of NiAl-Cr(Co,Hf) alloys prepared by centrifugal SHS casting followed by vacuum induction remelting. Part 2–Evolution of the structure and mechanical behavior at high temperature. Materials Science and Engineering A, 690, 473-481.

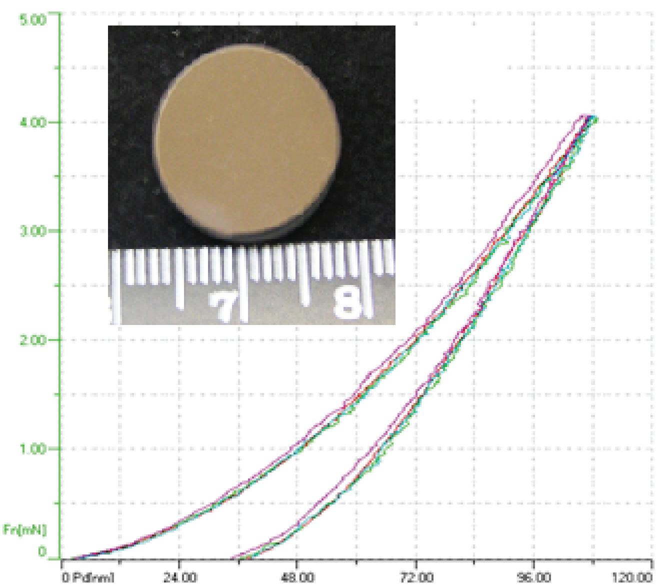
Ensuring the uniformity of measurements of functional properties of nanomaterials

Ensuring the uniformity of measurements of functional properties of nanomaterials such as hardness, modulus of elasticity, adhesion strength, friction coefficient, wear rate and surface roughness is a key question of positive development and commercialization in nanoindustry. To achieve this purpose, the metrological complex based on modern equipment such as nano-hardness tester, scratch tester, tribometer, atomic force microscope, optical and mechanical profilers, impact tester has been created and implemented into the Testing Laboratory of Functional Surfaces (accredited by Association of Analytical Centers «ANALITICA»).

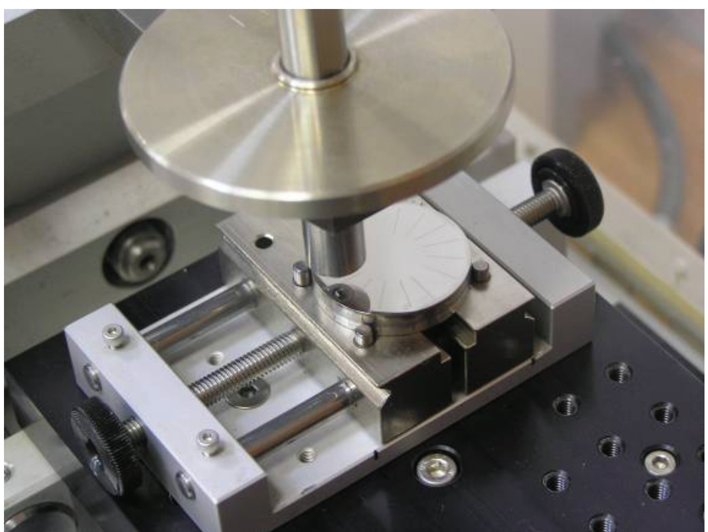
Using these measuring instruments a wide range of experimental research has been carried out to create good practice for attestation of nanostructured materials. Main metrological characteristics of instrumental indentation (ISO 14577), sliding (ASTM G99-05) and scratching (ASTM C1624-05) methods were experimentally revealed and more than 9 procedures for measuring surface roughness, mechanical and tribological characteristics of nanomaterials and calibrating the corresponding measuring instruments have been developed and certified.

It was established using certified measuring procedures that for developed in SHS center biocompatible TiCCaPON coatings there was a range of indenter penetration depths in which the measured Young's modulus had a constant value regardless of the substrate material, but the value of this range for certain «coating-substrate» systems differed. The widest interval was observed for the coating on fused quartz. This experimental result was used to create **State reference material of modulus of elasticity** (No.9451-2009) with an increased value (E=202 GPa) comparing to that one for polished fused quartz (E=72 GPa). Several samples of **State reference material of modulus of elasticity** were purchased by «Nienschanz-Scientific» – the exclusive distributor of high-precision analytical equipment produced by CSM Instruments (Switzerland) – to complete the Nano-Hardness Testers with calibration samples with enhanced modulus of elasticity.

Selected tribological pairs «TiCCaPON coating on a titanium substrate – alumina ball» and «TiCrBN coating on a titanium substrate – hard metal ball», showing stable friction coefficient values less than 0.2 and higher than 0.6, respectively, were used to create **State reference materials of friction coefficient** No.9651-2010 and No. № 9652-2010.



Appearance (in insert) and four experimental mean indentation curves performed at different areas of SRM of Young modulus.



SRM of friction coefficient of nanocrystalline material with the established value f = 0.194 and the extended uncertainty of 8 % installed at the stage of tribological testing for metrological certification

So, three State Reference Materials (SRM) ensuring adequate equipment calibration and traceability of measuring mechanical and tribological properties of nanostructured surfaces have been created and certified. According to the results of two subsequent metrological certifications of the SRMs the frequency of monitoring was increased up to 3 years because of their high temporal stability, and the validity of normative-technical documentation and type approval certificates was extended until 2020.

All developed and certified measuring instrument type descriptions, measurement procedures and SRMs were included into Federal Information Fund for Ensuring the Uniformity of Measurements (**fundmetrology.ru**).

References

1. Petrzhik, M.I. (2017). Doctoral thesis «Methods of nanostructuring and certification of mechanical and tribological properties of functional alloys and coatings based on Ti, Zr, Fe, Co and Ni» (defended in May 2017, NUST MISIS).

2. Levashov, E.A., Shtansky, D.V., Kiryukhantsev-Korneev, P.V., Petrzhik, M.I., Tyurina, M.Y., Sheveiko, A.N. (2010). Multifunctional nanostructured coatings: Formation, structure, and the uniformity of measuring their mechanical and tribological properties. Russian Metallurgy (Metally), 2010(10), 917-935.

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Accreditation certificate

№ AAC.A.00060

Valid to
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Accreditation Body AAC "Analitica" certifies that
The Testing Laboratory for Functional Surfaces
of the Federal State Autonomous Educational Institution of Higher Professional Education "National University of Science and Technology "MISiS"
4, Leninsky pr., tw. Moscow, 119049
is accredited in accordance with the recognized International Standard ISO/IEC 17025:2005 (GOST ISO/IEC 17025 - 2009). This accreditation demonstrates technical competence for a defined scope and the operation of a laboratory quality management system (refer Joint ISO-ILAC-IAF Communiqué dated January 2009).

The scope of laboratory (center) accreditation is described in the Appendix.

Head of
Accreditation body **I. Boldyrev**

23 December 2013

Apt 1320, 1, Leninskyi pr., Moscow, 119991, Russia, Tel/fax 959-93-43, 959-93-33
http://aac-analitica.ru e-mail: info@analitica.org.ru

LIST OF THE RECENT INTERNATIONAL PATENTS

- Levashov E.A., Azarova E.V., Ralchenko V.G., Bol'shakov A., Ashkinazi E.E., Ishizuka Hiroshi, Hosomi Satoru. Substrate for CVD deposition of diamond and method for the preparation thereof. Patent of the USA № 9663851 of 30.05.2017.
- Levashov E.A., Azarova E.V., Ralchenko V.G., Bol'shakov A., Ashkinazi E.E., Ishizuka Hiroshi, Hosomi Satoru. Substrate for CVD diamond deposition and method for forming deposition surface. Patent of Japan № 5919343 of 18.05.2016.
- Levashov E.A., Andreev V.A., Kurbatkina V.V., Zaitsev A.A., Sidorenko D.A., Rupasov S.I. Copper based binder for the fabrication of diamond tools. Patent of the USA № 9156137 of 13.10.2015.
- Levashov E.A., Andreev V.A., Kurbatkina V.V., Zaitsev A.A., Sidorenko D.A., Rupasov S.I. Copper based binder for the fabrication of diamond tools. Patent of China № ZL 201180011937.3 of 15.10.2014.
- Levashov E.A., Andreev V.A., Kurbatkina V.V., Zaitsev A.A., Sidorenko D.A., Rupasov S.I. Cooper Based Binder for the Fabrication of Diamond Tools. Patent of Korea № 10-1426184 of 28.07.2014.
- Levashov E.A., Kurbatkina V.V., Shtansky D.V., Sanz A. Method of Fabricating a Target. European Patent № 1957687 of 17.04.2013. Bulletin 2013/16. Application 06829045.1 of 14.11.2006.
- Levashov E.A., Shtansky D.V., Glushankova N.A., Reshetov I.V. Biocompatible Multicomponent Nanostructured Coatings for Medical Applications. Patent of the USA No. 8075682 of 13.12. 2011.
- Levashov E.A., Shtansky D.V., Glushankova N.A., Reshetov I.V. Biocompatible Multicomponent Nanostructured Coatings for Medical Applications. European Patent No. 1912685 of 10.12.2014, Bulletin 2014/50, Application No. 05825079.6 of 29.01.2008.

LIST OF THE AWARDS RECEIVED AT PRESTIGIOUS FORUMS AND INTELLECTUAL PROPERTY EXHIBITIONS (2013-2019)

- Special award of Taiwan Invention Association for the invention «Method for obtaining electrodes from alloys based on nickel aluminide», presented at Seoul International Invention Fair (SIIF-2018), 2018, Seoul, Korea. Authors: Levashov Evgeny, Pogozhev Yuri, Sentyurina Zhanna, Zaitsev Alexander, Sanin Vladimir, Yukhvid Vladimir, Andreev Dmitry, Ikornikov Denis
- Outstanding innovation prize of Association of Thai Innovation and Invention Promotion for the invention «Method for deposition of bioactive coating with antibacterial effect», presented at Inno Design Tech Expo, 2018, Hong Kong, China. Authors: Levashov E.A., Kudryashov A.E., Zamulaeva E.I., Shtansky D.V., Pogozhev Y.S., Potanin A.Y., Shvindina N.V.
- Silver medal in 2018 Hong Kong International and Design Competition (IIDC) for the invention «Method for deposition of bioactive coating with antibacterial effect», presented at Inno Design Tech Expo, 2018, Hong Kong, China. Authors: Levashov E.A., Kudryashov A.E., Zamulaeva E.I., Shtansky D.V., Pogozhev Y.S., Potanin A.Y., Shvindina N.V.
- Silver prize for the invention «Method for obtaining electrodes from alloys based on nickel aluminide», presented at Seoul International Invention Fair (SIIF-2018), 2018, Seoul, Korea. Authors: Levashov Evgeny, Pogozhev Yuri, Sentyurina Zhanna, Zaitsev Alexander, Sanin Vladimir, Yukhvid Vladimir, Andreev Dmitry, Ikornikov Denis.

- Honor award and certificate of Association of Portuguese inventor’s, innovator’s and creatives (APIICIS) for the excellent invention «Method for obtaining electrodes from alloys based on nickel aluminide», presented at International Trade Fair «Ideas – Inventions – New Products» (iENA-2018), 2018, Nuremberg, Germany. Authors: Levashov Evgeny, Pogozhev Yuri, Sentyurina Zhanna, Zaitsev Alexander, Sanin Vladimir, Yukhvid Vladimir, Andreev Dmitry, Ikornikov Denis.

- Honored diploma and gold medal for the invention «A method for obtaining electrodes from alloys based on nickel aluminide», presented at International Trade Fair «Ideas – Inventions – New Products» (iENA-2018), 2018, Nuremberg, Germany. Authors: Levashov Evgeny, Pogozhev Yuri, Sentyurina Zhanna, Zaitsev Alexander, Sanin Vladimir, Yukhvid Vladimir, Andreev Dmitry, Ikornikov Denis.

- Academician Kurdyumov honorary medal to Levashov Evgeny Alexandrovich for outstanding achievements in the field of physical metallurgy, 2018, Moscow, Russia.

- Honored diploma and gold medal with Nicola Tesla image for the invention «Method for deposition of bioactive coating with antibacterial effect», presented at 35th International Exhibition of Inventions, New Technologies and Industrial Design «INVENTIONS-BELGRADE 2018», 2018, Belgrade Serbia. Authors: Levashov E.A., Kudryashov A.E., Zamulaeva E.I., Shtansky D.V., Pogozhev Y.S., Potanin A.Y., Shvindina N.V.

- Honored diploma and gold medal for the invention «Method for obtaining electrodes from alloys based on nickel aluminide», presented at the XXI Moscow International Salon of Inventions and Innovative Technologies «Archimedes-2018», 2018, Moscow, Russia. Authors: Levashov E.A., Zaitsev A.A., Sanin V.V., Pogozhev Yu.S., Kaplanskii Yu.Yu., Sanin V.N., Yukhvid V.I., Sentyurina Zh.A.

- Moscow Government Prize to young scientists in the field of advanced industrial technologies for the invention «Development of a new generation of cutting diamond tool with nanomodified binder and a hybrid working layer», 2017, Moscow, Russia. Authors: Sidorenko D.A., Loginov P.A.

- Honored diploma and gold medal for the invention «Method for producing of bioactive coating with antibacterial effect», presented at the XVIII Moscow International Salon of Inventions and Innovative Technologies «Archimedes-2015», 2015, Moscow, Russia. Authors: Levashov E., Kudryashov A., Zamulaeva E., Shtansky D., Pogozhev Yu., Potanin A., Shvindina N.

- Grand Prix in nomination «The Best Inventor of Moscow» to Prof. Evgeny Levashov in frame of the XVIII Moscow International Salon of Inventions and Innovative Technologies «Archimedes-2015», 2015, Moscow, Russia.

- Honored diploma to Sukhorukova I.V. for the best report at the youth section, presented at the VI International conference «Crystal physics and deformation behavior of advanced materials», 2015, Moscow, Russia.

- Honored diploma to Loginov P.A. for the best report at the youth section, presented at the VI International conference «Crystal physics and deformation behavior of advanced materials», 2015, Moscow, Russia.

- Bronze Prize for the invention «Method of producing the bioactive coating with antibacterial effect», presented at the Seoul International Invention Fair 2015 (SIIF-2015), 2015, Seoul, Korea. Authors: Levashov Evgeny, Kudryashov Aleksander, Zamulaeva Evgeniya, Shtansky Dmitry, Pogozhev Yury, Potanin Artem, Shvindina Nataliya.

- Thailand Award for the best international invention «Method of producing the bioactive coating with antibacterial effect», presented at the Seoul International Invention Fair 2015 (SIIF-2015), 2015, Seoul, Korea. Authors: Levashov Evgeny, Kudryashov Aleksander, Zamulaeva Evgeniya, Shtansky Dmitry, Pogozhev Yury, Potanin Artem, Shvindina Nataliya.

- Honored diploma and silver medal of Eureka! Competition for the innovation «Method of producing the bioactive coating with antibacterial effect», presented at the World Exhibition of Inventions, Research and New Technologies 2015 (INNOVA 2015), 2015, Brussels, Belgium. Authors: Levashov Evgeny, Kudryashov Aleksander, Zamulaeva Evgeniya, Shtansky Dmitry, Pogozhev Yury, Potanin Artem, Shvindina Nataliya.

- Honored diploma of Federal Service for Intellectual Property of Russian Federation for the invention «Method of producing the bioactive coating with antibacterial effect», presented at the World Exhibition of Inventions, Research and New Technologies 2015 (INNOVA 2015), 2015, Brussels, Belgium. Authors: Levashov Evgeny, Kudryashov Aleksander, Zamulaeva Evgeniya, Shtansky Dmitry, Pogozhev Yury, Potanin Artem, Shvindina Nataliya.

- Honored diploma of The French Federation of Inventors (FFI) and Europe France Inventors (EFI) for the invention «Method of producing the bioactive coating with antibacterial effect», presented at the World Exhibition of Inventions, Research and New Technologies 2015 (INNOVA 2015), 2015, Brussels, Belgium. Authors: Levashov Evgeny, Kudryashov Aleksander, Zamulaeva Evgeniya, Shtansky Dmitry, Pogozhev Yury, Potanin Artem, Shvindina Nataliya.

- Certificate of participation and gold medal for the invention «Method of producing the bioactive coating with antibacterial effect», presented at the 26-th International Invention, Innovation & Technology Exhibition 2015 (ITEX 2015), 2015, Kuala Lumpur, Malaysia. Authors: Levashov Evgeny, Kudryashov Aleksander, Zamulaeva Evgeniya, Shtansky Dmitry, Pogozhev Yury, Potanin Artem, Shvindina Nataliya.

- Honored award of World Invention Intellectual Property Associations (WIIPA) for the invention «Method of producing the bioactive coating with antibacterial effect», presented at the 26-th International Invention, Innovation & Technology Exhibition 2015 (ITEX 2015), 2015, Kuala Lumpur, Malaysia. Authors: Levashov Evgeny, Kudryashov Aleksander, Zamulaeva Evgeniya, Shtansky Dmitry, Pogozhev Yury, Potanin Artem, Shvindina Nataliya.

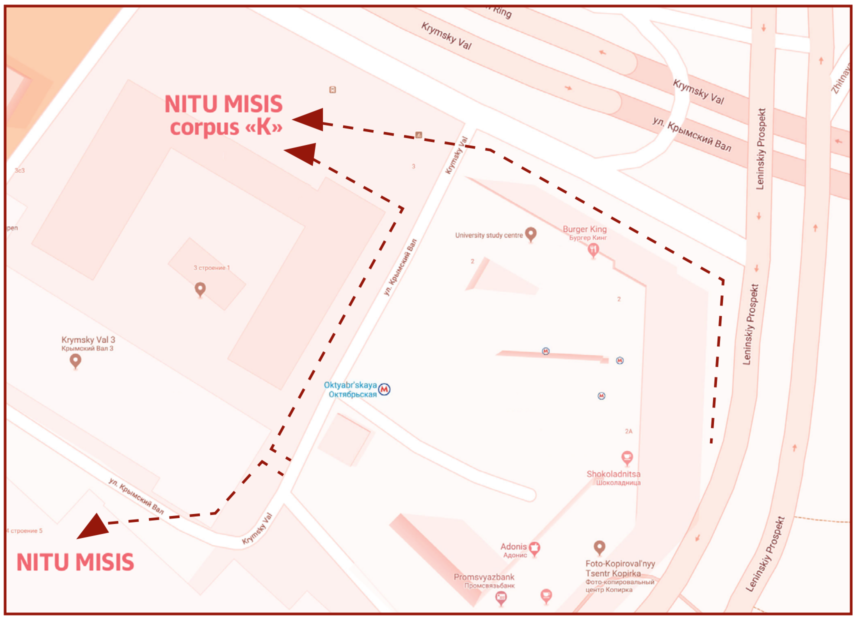
- Honorary title «Honorary inventor of Moscow», given to Prof. Levashov Evgeny Alexandrovich by Moscow Government, 2014, Moscow, Russia.

The main building of NUST MISIS

Leninskiy prospect, 4
119049, Moscow, Russia

The building of NUST MISIS on Krymsky val

Krymsky val, 3
119049, Moscow, Russia



Address for correspondence

Leninskiy prospekt, 4, 164
119049, Moscow, Russia

shs.misis.ru

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